ULTRAFINE PARTICLES IN ATMOSPHERIC ELECTRICITY

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The ultrafine particles are called air ions in atmospheric electricity. The paper deals with traditional and new classification of air ions in atmospheric electricity and tools of ion-particle parameter conversion. The problem of cluster-particle discrimination is examined. A brief overview of the atmospheric electrical particle measurement techniques is presented. Some results of atmospheric electrical measurements of particle size distribution and the role of ultrafine particles in the atmospheric electricity are discussed.

INTRODUCTION

The mechanism of electrical conductivity of air is a classic research subject in atmospheric electricity (Israel, 1970). The carriers of electrical current in air are charged airborne particles of size of 0.5-200 nm and their evolution is influenced by neutral airborne particles. The cooperation of aerosol and atmospheric electricity research is providing both sides with some extra knowledge.

The first measurements of air ion mobility were made by J.J. Thomson and Rutherford (1896) in a laboratory experiment. According to the contemporary interpretation, they have studied charged clusters of diameter of 0.6-0.7 nm. The air ions of low mobility and large size were measured by Townsend (1898) and Lenard (1900) in laboratory experiments and by Langevin (1905) in natural atmospheric air. The diameter of air ions measured by Langevin was about 90 nm and they are often called the Langevin ions today. First measurements of intermediate air ions (diameter about 10 nm) were published by Pollock (1915).

An overview of ultrafine particle related concepts and methods of ground-level atmospheric electricity research and a digest of measurement results obtained in Tartu University is presented in the paper.

AIR IONS AND AEROSOL PARTICLES

Classification of air ions

Carriers of conductive current in the air are called the atmospheric ions or the air ions independent of their physical nature. They can be molecular ions, charged clusters, solid or liquid airborne particles of any size. The parameter of an air ion that can be reliably measured using standard techniques of atmospheric electricity is the electrical mobility $K = v/e$, where v is the drift velocity of the air ion and E is the intensity of the electric field.

Traditionally, the air ions are classified according to their electrical mobility:

fast or small or light ions with mobility $K > 0.5\ \mathrm{cm^2/(V{\cdot}s)}$,
intermediate ions, and
slow or large or heavy ions with mobility $K < 0.01\ \mathrm{cm^2/(V{\cdot}s)}$.

The boundary between small and intermediate ions has a physical background but the boundary between intermediate and large ions is a convention.

The alternate classification is based on the physical nature of air ions:

cluster ions are charged clusters,

aerosol ions are charged ultrafine and fine particles.

The problem of discriminating between clusters and ultrafine particles will be discussed later.

In a primary act of ionization a free electron and a positive molecular ion are created. The lifetime of free electrons and molecular ions in natural air is very short and their role in the ground-level atmospheric electricity is negligible. The average lifetime of a cluster ion is one minute. About 3% of them will recombine with cluster ions of another polarity and 97% will attach to aerosol particles. Resulting aerosol ions are called the secondary aerosol ions. The primary aerosol ions are the particles with inherent electric charge that are formed as a result of ion-induced nucleation. The secondary aerosol ions are dominating among all aerosol ions.

The aerosol ions could be classified as ultrafine and fine aerosol ions according to the particle size.

Size-charge relation for particles

The cluster ions are never considered in uncharged state. A particle of the diameter of less than 30 nm in the bipolar ionic atmosphere is neutral or charged by one elementary charge. There is no reliable empirical data available about size-charge relation for nanometric particles. Well-founded theoretical calculations of ion-particle attachment coefficients are published by Hoppel and Frick (1990). The coefficients have been essentially depending on the mass of cluster ions. Probably, Hoppel and Frick have slightly overestimated the mass of positive ions and underestimated the mass of negative ions for average atmospheric conditions. When the average over both polarities is used, a simple approximation for the particles of the diameter of less than 30 nm can be derived and recommended as a tool for practical calculations:

$$p = 0.0065 d_{nm} + 0.024/(d_{nm}+0.3) - 0.018,$$

where d_{nm} is the numerical value of the diameter expressed in nanometers and p is the probability of carrying an elementary charge of one polarity. The probability of being neutral is $1 - 2p$. The relative error of the approximation is less than 6% for the particles of the diameter of less than 20 nm.

An approximation for larger particles based on the tables by Hoppel and Frick has been published in (Tammet, 1991).

Mobility-mass conversion tools for clusters

The mobility and mass of cluster ions can be measured simultaneously in laboratory experiments. A data set for ion mass from 35.5 up to 2122 u published by Kilpatrick (1971) is used by various authors. The data can be fitted by formulas:

$$K_{cm} = (850/m_u)^{1/3} - 0.3, \qquad m_u = 850/(K_{cm} + 0.3)^3,$$

where K_{cm} and m_u are the numerical values of mobility and mass expressed in $cm^2/(V\cdot s)$ and u. The mean-square relative fitting error is 3.2%.

Size-mobility conversion tools for particles and clusters

The Millikan equation is an excellent approximation of the size-mobility relation for fine particles. It can be modified to cover the whole range of fine particles, ultrafine particles and clusters (Tammet, 1992). In case of normal air pressure and room temperature the following algorithm can be used:

$$F = 0.5\cdot\exp\left(-\left(\frac{d_{nm}}{1.32}\right)^6\right), \qquad G = \sqrt{\left(1 + \left(\frac{0.4}{d_{nm}}\right)^3 / \left(1 + \left(\frac{0.7}{d_{nm}+0.73}\right)^4\right)\right)},$$

$$K_{cm} = \frac{0.00943}{d_{nm}+0.73}\left(1 + \frac{129}{d_{nm}+0.73}\left(1.4 + 0.35\cdot\exp\left(-\frac{d_{nm}+0.73}{144}\right) + F\right)\right)G.$$

The correction G is essential only when $d < 1$ nm and the correction F when $d < 1.7$ nm. In case of larger particles the above algorithm is the same as the ordinary Millikan formula where the diameter is replaced by $d + 0.73$ nm considering the size of air molecules and Van der Waals forces. The algorithm

$$a = 4 + \exp(-3/(\sqrt{(1 + 93000K_{cm})} - 1)),$$

$$d_{nm} = 90a\ /\ (\sqrt{(1 + 19060aK_{cm})} - 1) - 0.73$$

is inverting the above algorithm with relative error less than 0.15% for all diameters over 1.8 nm.

In the size range of 1.7-260 nm the above $K = K(d)$ algorithm is approximated by simple formulas with error of K_{cm} less than 0.32% and of d_{nm} less than 0.2%:

$$K_{cm} = \left(\frac{2}{1 + d_{nm}/0.73} + 0.0023\right)^2,$$

$$d_{nm} = 0.73\left(\frac{2}{\sqrt{K_{cm}} - 0.0023} - 1\right).$$

Distinction between clusters and particles

The clusters and fine particles can be discriminated considering the applicability of various models of their internal physical structure. An external distinction is that the particles can be characterized by the internal temperature and they can absorb the energy of colliding air molecules but molecules and clusters cannot. The result is that the air molecules are thermally accommodated when colliding with particles and elastically scattered by clusters. It follows that a factor in the drag equation derived according to the Chapman-Enskog kinetic theory is different for clusters and particles. The fitting of the data presented by Kilpatrick (Tammet, 1992) was successful when the collisions were considered in case of $d < 1$ nm as elastic-specular and in case of $d > 1.7$ nm as accompanied by thermal accommodation. The critical diameter of 1.32 nm was found as a boundary separating clusters and ultrafine particles. The corresponding mass is 1300 u and mobility 0.5 $cm^2/(V\cdot s)$.

MEASUREMENT TECHNIQUES

Drift tube and aspiration condenser

Drift tubes are the most popular instruments for measuring cluster ion mobilities in laboratory experiments. They have been used for measuring of ultrafine particles of size of up to 3 nm (B.A. Thomson and Iribarne, 1977). Too high driving voltage would be required for measuring larger particles. A drift tube can provide excellent mobility resolution if the cluster ions are generated inside the instrument and measured in the first milliseconds of their life. If the natural ions are studied, the resolving power is limited by the ratio of the full volume of the tube and the volume of the sample air where the ions are initially located. If the sample air volume in a large drift tube is about 1 liter and the ion fraction concentration is about 10 cm^{-3}, the full charge of about 1 fC is near the noise level of a typical amplifier. Therefore, the drift tubes are not effective when the natural ions are measured.

The sample air is continuously sucked through an aspiration condenser that enables to collect the ions from a large air volume and keep the sensitivity of the instrument high enough to measure natural air ions. The aspiration condenser is an efficient instrument in the mobility range of 0.0003-3 $cm^2/(V\cdot s)$.

The integral and differential aspiration condensers

The simplest air ion meter known as Gerdien instrument is equipped with a cylindrical aspiration condenser, where the sample air is filling a full cross-section of the condenser and the current is measured from the full area of the collector electrode. The undivided aspiration condenser is called the integral condenser. It provides the best concentration sensitivity and the poorest mobility resolution. When the driving voltage is low, the collected current is proportional to the air conductivity. If the driving voltage is high and only small ions are present, the collected current is saturated and ion concentration is measured. The average mobility can be found as the ratio of air conductivity and ion concentration. The sophisticated analysis of the volt-ampere characteristic allows to calculate the mobility distribution of ions (Israel, 1970; Tammet, 1970). However, an enormous effect of "error amplification" prevents the real resolution of ions with the mobility ratio less than two.

The physical differentiation of the volt-ampere characteristic can be carried out dividing the air intake into a narrow layer of sample air and a wide layer of deionized air, and/or dividing the collector electrode and measuring the current only from a narrow section of the electrode. The corresponding versions of an aspiration condenser are called:

the first-order differential condenser with the divided air flow,
the first-order differential condenser with the divided electrode,
the second-order differential condenser.

The best mobility resolution is provided by the second-order differential aspiration condenser. Usually, the record of the volt-ampere characteristic of a second-order differential condenser is directly interpreted as a diagram of mobility distribution of the air ions. The differential condensers of first order were rarely used considering their simplified design.

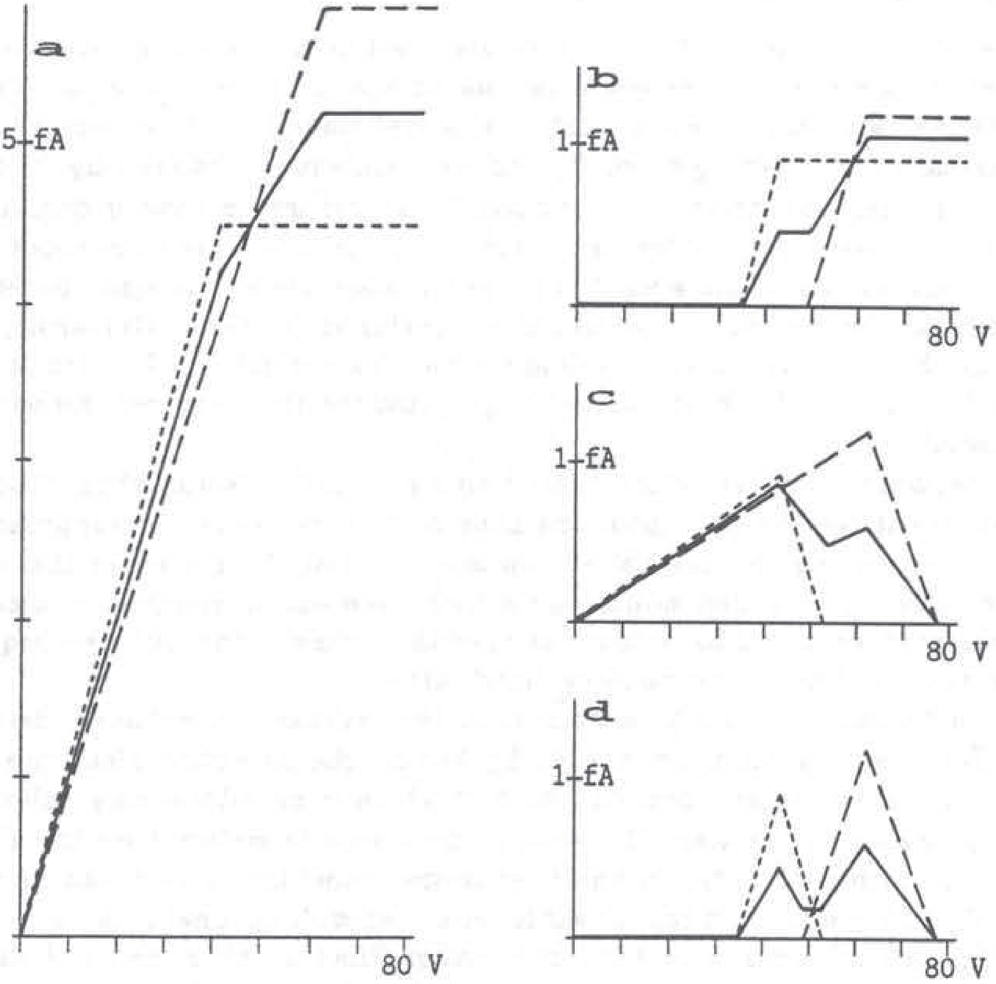

Fig. 1. The ideal volt-ampere characteristics: a - the integral aspiration condenser, b - the first-order differential condenser with divided air flow, c - the first-order differential condenser with divided electrode, d - the second-order differential condenser. The total air flow is assumed to be 1000 cm^3/s, and the total active capacitance of the collecting electrode 50 pF. The dividing proportions are assumed to be 20% + 80% for air flow as well for the electrode capacitance. The three diagrams are corresponding to:

dotted - 1000 cm^{-3} of $d = 6.5$ nm particles,
dashed - 1000 cm^{-3} of $d = 8.0$ nm particles,
continuous - 500 cm^{-3} of $d = 6.5$ nm and
500 cm^{-3} of $d = 8.0$ nm particles.

The ideal volt-ampere characteristics of various aspirations condensers are given in Fig. 1. Real volt-ampere characteristics are slightly smoothed by diffusion of the air ions and other disturbing factors (Tammet, 1970), and disfigured by the measurement noise. Therefore, the correct estimating of the mobility distribution is a complicated mathematical procedure even in case of the second-order differential condenser.

Scanning and multichannel techniques

Two alternate techniques of the mobility distribution measurement are used in the atmospheric electricity research. In case of scanning technique the aspiration condenser with one collector electrode is used and the volt-ampere characteristic is measured step by step. The driving voltage is changed by discrete steps in some instruments and continuously in the others. In case of continuous change a compensating capacitor and a bridge circuit are used to suppress the induction current that could exceed the measurement current in many orders of magnitude. In the scanning spectrometers designed in Tartu University the continuous change of the driving voltage is carried out using a RC-circuit with time constant of 10-30 s that automatically provides the required logarithmic scale of mobility.

The measurement time is considered as an essential factor when choosing the measurement technique. About one hour or more is needed to suppress the noise when measuring the natural air ion mobility distribution using the scanning technique. The parallel multichannel technique was introduced to accelerate the measurements and to reduce the specific errors rising with the sequential measurement of changing mobility distribution.

A multichannel instrument differs from the ordinary one-channel second-order differential aspiration condenser by having the collecting electrode that has been divided into many sections each of which is simultaneously collecting the ions of various mobilities. The measurement time is reduced by the factor equal to the number of sections. The first multichannel instrument was built by Yunker (1940). However, the real advantages of the multichannel technique were not realized before creating an advanced mathematical model of the multichannel mobility spectrometer and computerization of the measurement process. Several multichannel instruments with up to 50 parallel channels have been designed in Tartu University (Matisen et al., 1992).

MEASUREMENTS OF ULTRAFINE PARTICLES IN ATMOSPHERIC ELECTRICITY

Cluster ions

During its lifetime a cluster ion collides with nearly 10^{12} molecules. Thus the cluster ions can concentrate trace gases of very low concentration if they have an extra high electron or proton affinity. For example, Eisele (1986) demonstrated that a considerable fraction of cluster ions in the unpolluted atmosphere probably consists of a molecule derived from pyridine. Therefore, the chemical composition and the size of cluster ions are depending on the spectrum of the trace gases in the air and can vary in various locations and conditions.

The one-year continuous measurements of natural cluster ion mobilities were carried out at a sparsely populated village Tahkuse, Estonia (Salm et al., 1990). The average distributions presented in Fig. 2 are probably typical for the rural regions.

Fine aerosol ions

Air ions of the diameter of over 10 nm are usually secondary aerosol ions. The results of early measurements are summarized by Israel (1970). Salm (1988) has calculated the mobility distribution corresponding the average of particle size distributions, measured during last decades by various scientists. The result is presented in wide bars in Fig. 3. The four-month averages of directly measured aerosol ion distribution (Salm et al., 1990) are presented in pin bars in the same figure. The accordance of the diagrams is confirming the applicability of the theoretical model used by Salm.

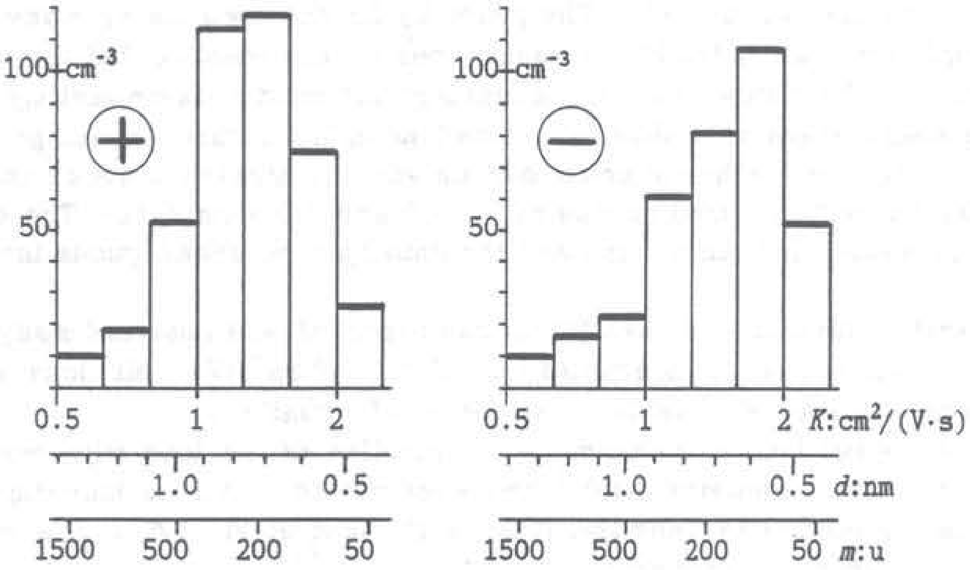

Fig. 2. Annual average mobility, mass and size distribution of natural cluster ions in village Tahkuse, Estonia.

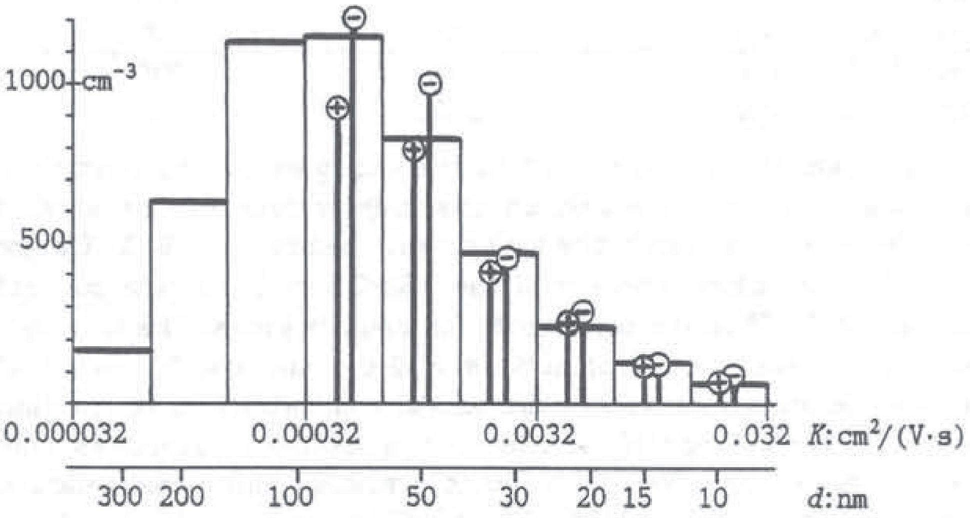

Fig. 3. Distribution of aerosol ions. The wide bars mark the fraction concentrations of elementary charges carried by particles according to the calculations by Salm (1988). The pin bars with heads + and − mark average values of fraction concentrations for positive and negative aerosol ions measured in village Tahkuse, Estonia.

Ultrafine aerosol ions

The concentration of secondary aerosol ions of the diameter of few nanometers in the natural air is very low and these ions are not available for measurement using ordinary instruments. The enlarged concentration of ultrafine aerosols can be expected in extra situations when primary aerosol ions are intensively generated as a result of ion-induced nucleation. Therefore, the measurement of air ions in the mobility range of 0.1–0.5 $cm^2/(V\cdot s)$ can be considered as a method to obtain information about the role of ion-induced nucleation in the real atmosphere.

The first message about the ions of the 10 nm diameter by Pollock (1915) cannot be qualified as authentic. The paper by Pollock does not give any information confirming the reliability of measurements. It is possible that the conclusion made by Pollock was a result of misinterpretation of measurement errors.

The measurement data about ultrafine ions in the natural air are poor. The reasons for this are technical complications and the disadvantageous tradition to classify the air ions into groups of 0.1–1.0 and 1.0–∞ $cm^2/(V\cdot s)$. The cluster ions are presented in both groups and the data have no unambiguous interpretation.

In Tartu University, Reinet (1958) has observed and analyzed many extra situations with enhanced concentration of 0.1–1.0 $cm^2/(V\cdot s)$ air ions during annual continuous measurements in the center of a small town.

Several situations of enhanced concentration of air ions with mobilities 0.32–0.5 $cm^2/(V\cdot s)$ (diameter 1.4–1.9 nm) were recorded during long-time continuous measurements in Tahkuse, Estonia (Tammet et al., 1992). The extreme examples of hourly averages are:

			Concentration of ions with mobility	
Date	Hour	Polarity	0.32–0.5 $cm^2/(V\cdot s)$	0.5–2.5 $cm^2/(V\cdot s)$
13 June 1985	3 a.m.	+	390	610
13 June 1985	3 a.m.	-	15	300
5 Sep 1985	5 p.m.	+	39	390
5 Sep 1985	5 p.m.	-	510	700

The well-developed charge asymmetry in the examples can be considered as a symptom of ion-induced nucleation on the cluster ions of one sign. Similar effects were measured in laboratory experiments before (e.g. B. A. Thomson and Iribarne, 1977). The annual average of the 0.32–0.5 $cm^2/(V\cdot s)$ ion concentration in Tahkuse was 24 cm^{-3} as for positive as for negative ions. The time variations of partial concentrations of subfractions 0.32–0.4 and 0.4–0.5 $cm^2/(V\cdot s)$ were intercorrelated positively as well as the partial concentrations of fractions with mobilities both over 0.5 $cm^2/(V\cdot s)$. The concentrations of fractions one below and another over 0.5 $cm^2/(V\cdot s)$ were not correlated. This observation is confirming the thesis that the mobility 0.5 $cm^2/(V\cdot s)$ and diameter 1.3–1.4 nm can be considered as a border discriminating ultrafine particles from clusters.

The source of ions with mobilities 0.32–0.5 $cm^2/(V\cdot s)$ in Tahkuse was not identified. The instrumentation was situated near a small farm where local sources of organic vapors were not controlled. The three-week measurements near the coastline in the area of Matsalu nature preserve in 1992 have shown, that the concentration of ultrafine aerosol ions with mobility 0.1–0.5 $cm^2/(V\cdot s)$

typically does not exceed few ions per cm^3 when local agricultural and biological sources of organic vapors are excluded. Probably, the ion-induced nucleation in the ground-level atmospheric air should be considered as essentially depending on the trace gases of biological and anthropogenic origin.

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