

1. INTRODUCTION

1.1. Nature of air ions

Air ions are a traditional research subject of the science of atmospheric electricity, since ions determine the conductivity of atmospheric air and therefore affect the processes of the global atmospheric electric circuit [Hoppel, et al., 1986]. In atmospheric electricity the term "air ion" signifies all airborne particles that are electrically charged and serve as a basis of air conductivity. Hence "air ions" comprise a large variety of charged particles of different chemical composition, mass and size, from molecular clusters up to large aerosol particles [Dolezalek et al., 1985; Tammiet, 1998a].

The air in the planetary boundary layer is weakly ionized, the relative concentration of ions is about 10^{-16} . Ionization is produced mainly by cosmic rays and decay of radioactive substances in the ground and in the air. Initially formed primary ion pairs (single-charged positive ion and free electron) are converted into "cluster ions" within the first microsecond. During their lifetime (about 100 s), cluster ions undergo series of transformations by ion-molecule reactions, continuously changing their chemical identity before reaching the state of "terminal ions". The result is a composition of cluster ions which strongly depends on the age of ions and on the concentration of trace species in the air [Mohnen, 1977; Keesee and Castleman, 1985; Viggiano, 1993].

The formation of cluster ions is also dependent on the thermodynamical properties of the clusters and the environment [Castleman et al., 1978]. If the cluster ions grow to a critical size, about 1–2 nm, then spontaneous nucleation is followed [Bricard et al., 1972; Raes and Janssens, 1985; Yu and Turco, 2000]. The cluster ions behave like kernels of condensation of nucleating vapors, converting them from the gas phase into aerosol phase. Two concurrent processes, ion-induced nucleation [Yu and Turco, 2000] and homogeneous nucleation [Kulmala et al., 2000], are considered as possible ultrafine aerosol formation routes in atmospheric air.

The cluster ions are removed from atmosphere either by random attachment to the aerosol particles, resulting in formation of "aerosol ions", by ion-ion recombination or other loss mechanisms, or they are transformed via ion-induced nucleation from cluster ion class to the class of charged nanometer particles. Subsequent growth of the "new particles" by condensation and coagulation towards large sizes follows after nucleation bursts (e.g. Weber et al., 1997; Mäkelä et al., 1997; Birmili et al., 2000). The aerosol ions just like ordinary aerosol particles above 1.6 nm experience all the processes known from aerosol physics: growth by vapor condensation, coagulation, wet and dry removal (deposition), and propagation in the atmosphere [Hidy, 1984; Hoppel et al., 1990; Seinfeld, 1998].

1.2. Characterization of air ions

The principal quantitative characteristic of air ion is its "electrical mobility". The electrical mobility of an ion is defined as the coefficient of proportionality between the drift velocity v and the applied electric field strength E by the formula $K = v E^{-1}$. In the case of weak fields and low concentration of ions the electrical mobility is related to the diffusion coefficient of ions by the simple Einstein equation $D = k T K q^{-1}$, where q is the ion charge, k is the Boltzmann constant and T is the absolute temperature [Israël, 1970; Mason and McDaniel, 1988]. According to their mobility the air ions are classified into small or cluster ions if the mobility $K > 0.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, intermediate ions, and large ions if the mobility $K < 0.03 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ [Tammiet, 1998a].

Mobility depends on both the properties of an ion (size, mass, charge and structure) and of the environment in which the ion moves. The determination of parameters of ions (mass, size) from the mobility measurements is the problem of air ion and aerosol particle spectrometry [Eiceman and Karpas, 1994; Ramamurthi et al., 1993; Mäkelä et al., 1996b]. There is no valid general law relating mobility of ion to ion size or mass. Various gas kinetic theories (e.g. Mason and McDaniel, 1988) have been applied to molecular ions and cluster ions. The Stokes-Millikan empirical equation is used when the particle size is comparable to or larger than the mean free path of the gas molecules (about 60 nm in air at STP) [Fuchs, 1955; Israël, 1970; Seinfeld, 1998].

A universal semiempirical model which approaches the Chapman-Enskog equation in the free molecule limit and the Stokes-Millikan equation in the macroscopic limit was proposed by Tammiet [1995, 1998b]. The electrical mobility of a single-charged particle of a radius r_m and mass m_p among gas molecules of mass m_g is given by

$$K = f \frac{e}{6\pi\eta\delta} \sqrt{1 + \frac{m_g}{m_p}} \left\{ 1 + \frac{l}{\delta} \left[a + b \exp\left(-c \frac{\delta}{l}\right) \right] \right\}, \quad (1)$$

where $\delta = r_m + h + r_g(T_{eff})$ is the collision distance between the particle and a gas molecule with collision radius r_g at temperature T_{eff} , and h is the difference between the collision radius and the mass radius of the particle (about 0.12 nm). The constant e is the elementary charge, η is the gas viscosity and l is the mean free path of the gas molecules. The constants a , b and c are the slip factor coefficients, $a = 1.2$, $b = 0.5$ and $c = 1$. The factor f takes into account the inelastic collisions and the polarization interaction (substantial below 2 nm).

A simple approximation formula for the small ion mass-mobility correlation in standard conditions is given by Tammiet [1998b]: $K \approx (1200 \text{ u} / m_p)^{1/3} - 0.2$, where K is in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$, and the mass is in the range of 30–2100 u. The regression model is based on the experimental data by Kilpatrick [1971].

Traditionally, the measured mobilities of small air ions are given in literature as reduced to the standard condition using the Langevin rule

$$K_0 = K \frac{273.15K}{T} \frac{p}{101325Pa}, \quad (2)$$

were p is the gas pressure and T is the absolute temperature. This procedure merely provides a standardization with respect to the gas number density, but not with respect to gas temperature [Mason and McDaniel, 1988]. The Langevin rule is correct only in the limit of zero-size molecular ions, and considerable errors are possible when the rule is applied to cluster ions. In the reduction procedure given by Tammet [1998b, 1995], the pressure dependence of the natural mobility of small air ions is the same as predicted by Langevin rule, but the temperature dependence (in the range $\pm 50^\circ\text{C}$) is essentially different. In the mobility range of $0.5\text{--}3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, the temperature power varies from about 0.4 to 0.9, increasing with ion mobility.

An experimental study of the temperature variation of cluster ion mobility is complicated, because the possible temperature effect on the composition and size of clusters could obscure the physical effect (e.g. Thuillard, 1995). The mobilities of large air ions are given in literature as measured, and the question of possible reduction to standard conditions has not been raised.

1.3. The balance of ions in the atmosphere

The balance of ions in the atmosphere comprises three main problems: first, the balance between small (cluster) ions and aerosol particles (the effect of aerosol particles on ion depletion); second, the balance between neutral and charged fractions of aerosol particles (charging state of aerosol particles); and third, the imbalance of polar ions caused by the Earth's electric field (electrode effect) [Tverskoy, 1949; Israël, 1970; Chalmers, 1967; Hoppel et al., 1986].

The small positive and negative ions are generated primarily by ionizing radiation in equal quantities. Two concurrent processes, ion-ion recombination and adsorption of small ions by aerosol particles, are responsible for the sink of small ions in atmospheric air. The simplified balance equation of small ions in a bipolar environment, considering equal numbers of positive and negative small ions and symmetrical charging of aerosol particles, can be written as [Israël, 1970; Hoppel and Frick, 1986]

$$\frac{dn}{dt} = q - \alpha n^2 - \beta_{\text{eff}} Z_{\text{tot}} n, \quad (3)$$

where q is the ionization rate, α is the recombination coefficient, n is the concentration of small ions, Z_{tot} is the total number concentration of aerosol particles, and β_{eff} is the effective ion-aerosol attachment coefficient for

polydisperse aerosol particles (approximately proportional to the mean diameter of aerosol particles). This simplified balance equation does not take into account the variability of small ion concentration due to advection and turbulent diffusion, loss by ion-induced nucleation and drift in the Earth's electric field.

The electrode effect causes an imbalance of small ion concentration close to the ground, in conditions of low turbulence below a few meters; the turbulent mixing could considerably increase the thickness of the electrode layer by dispersing the positive "fair-weather" space charge to upper levels [Hoppel et al., 1986; Knudsen and Israelsson, 1994].

The simplified balance equation of small ions has an analytical steady state solution [Israël, 1970]:

$$n = \frac{2q}{\beta_{\text{eff}} Z_{\text{tot}} + \sqrt{\beta_{\text{eff}}^2 Z_{\text{tot}}^2 + 4\alpha q}}. \quad (4)$$

It can be also presented in the form: $n = q\tau$, where the parameter τ has the dimension of time and therefore can be interpreted as the "mean lifetime" of small ions in steady state conditions [Israël, 1970]. The time constant of the transfer to steady state condition ($dn/dt=0$) is about 1 minute in the continental boundary layer air.

The independent parameters of the balance equation have the following average values often cited in publications. The recombination coefficient α , which depends on the nature of small ions and the properties of environment [Israël, 1970; Hoppel and Frick, 1986], has an average value about $1.5 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$. In continental areas the parameter β_{eff} varies in the range of $1\text{--}2 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$, depending on the size distribution of aerosol particles [Hoppel, 1985]. The value of $1.6 \cdot 10^{-6} \text{ cm}^3 \text{ s}^{-1}$ is commonly used for rough estimates. The average ionization rate, caused by radioactive substances in the ground and in the air and by cosmic radiation, about $10 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$, is considered as a standard for continental areas. The ionization rate decreases with altitude near the ground and increases at higher altitudes up to 15 km (maximum about $50 \text{ ion pairs cm}^{-3} \text{ s}^{-1}$) [Hoppel et al., 1986; Rosen et al., 1985].

At a rural site, where typically $Z_{\text{tot}} = 10^4 \text{ cm}^{-3}$, $n = 590 \text{ cm}^{-3}$ and $\tau = 60 \text{ s}$, the recombination term in Eq. 4 is responsible for about 5% of the losses of small ions. Assuming very clean conditions when $Z_{\text{tot}} = 200 \text{ cm}^{-3}$ (in polluted urban air $Z_{\text{tot}} = 10^5 \text{ cm}^{-3}$), the estimated concentration of small ions is about 2500 cm^{-3} (60 cm^{-3}) and the mean life-time is about 250 s (6 s).

Attachment of small ions to aerosol particles gives rise to a size dependent statistical charge distribution on the aerosol particles: some are positively and some negatively charged while others are neutral. To treat the problem in its complexity, we require the solution of a system of balance equations for small ions of negative and positive polarity and particles with various numbers of elementary charges [Israël, 1970; Hoppel and Frick, 1986]. The problem is

more complicated in the real atmosphere because of the variable nature of small ions, their mean mobility, mass and concentration, which determine the microphysical process of ion-aerosol attachment [Fuchs, 1955; Hoppel and Frick, 1986; Yair and Levin, 1989; Reischl et al., 1996].

According to laboratory experiments and theoretical considerations, the steady state charge distribution on large aerosol particles determined by the diffusion of small ions to particles is close to the Boltzmann distribution. Corrections have been found to be necessary in the case of ultrafine particles below 100 nm [Hoppel and Frick, 1986; Tamm et al., 1991; Reischl et al., 1996].

The time in which the aerosol particle population approaches charge equilibrium depends on the rate at which small ions collide with aerosol particles. If the concentration of aerosol particles is high compared to that of small ions, then the time required to reach equilibrium charge distribution of initially uncharged particles is typically in the range of about 0.5–1 hour [Hoppel, 1985]. Considering a polluted urban environment, where the concentration of particles is large and variable, it is unlikely that the charge equilibrium is ever attained. For rural areas, away from direct sources of aerosol particles, the assumption of charge equilibrium is believed to be fairly good [Israël; 1970; Hoppel, 1985]. However, the charge equilibrium during events of new particle formation by nucleation needs further study.

1.4. Environmental importance of air ions

The problem of environmental importance of air ions involves two subjects: air ions as an environmental factor and as an environmental indicator.

Air ions play an important role in several atmospheric processes such as electrical processes and aerosol particle formation. An investigation of ion chemistry and the properties of cluster ions (mass, mobility) is essential for understanding the factors that affect air conductivity and aerosol formation.

Air ions as charge carriers determine the conductivity of air and thereby they also influence other parameters of the global atmospheric electric circuit: conduction current from the ionosphere to the ground and the potential gradient of the atmospheric electric field or space charge density [Ogawa, 1985; Hoppel et al., 1986; Rycroft et al., 2000]. The transfer of space charge by convection and turbulent eddies ("convection currents") has a direct impact on the electrical structure of the boundary layer [Israël, 1973]. The atmospheric conductivity is mainly determined by mobile small ions according to the equation: $\lambda_{\pm} = e K_{\pm} n_{\pm}$, where n_{\pm} is the average concentration and K_{\pm} is the mean mobility of small ions.

Air ions are involved in formation of secondary aerosol particles by ion-induced nucleation and are responsible for the establishment of charge distribution on initially neutral aerosol particles. The route of ultrafine aerosol particle production via ion-induced or homogeneous nucleation, as well as the microphysical process of their future evolution to become cloud condensation

nuclei (CCN), is currently a point of issue [Raes and Van Dingenen, 1992; Raes, et al., 2000; Kulmala et al., 2000; Yu and Turco, 2001]. In principle, a charge on a particle is a factor that could favor particle growth by condensation and coagulation.

Atmospheric aerosols are known to affect the Earth's radiation balance directly by reflecting and absorbing radiation and indirectly by serving as CCN that in turn influence the optical properties (albedo and optical thickness) of clouds [Hoppel et al., 1990; Shine and Forster, 1999]. The same effect can be attributed to the large air ions, since more than 40% of aerosol particles above the diameter of 60 nm are charged in bipolar atmosphere assuming steady state charge distribution [Hoppel and Frick, 1986, Reischl et al., 1996]. At present the aerosols are the most uncertain factor of radiative forcing [IPCC, 1996].

Speaking of recent investigations, the role of ions in atmospheric processes could be underestimated. The correlation between the intensity of galactic cosmic rays (modulated by solar activity) and total cloud cover reported by Svensmark and Friis-Christensen [1997] might be explained by the role of atmospheric ionization in aerosol particle production and/or growth. The hypothesis of "cosmic ray-cloud link" is currently a point at issue (e.g. Marsh and Svensmark, 2000; Harrison, 2000; Kirkby and Laaksonen, 2000).

The large concentration of massive ions (>450 u) measured in the exhaust plume of jet aircraft supports the theory of chemiions growing into an aerosol mode via ion-induced nucleation [Yu and Turco, 1998; Arnold et al., 1999].

The electric deposition of airborne particles (small ions, unattached radon daughter clusters and charged aerosol particles below 200 nm) by the atmospheric electric field was proposed as a factor of enhanced pollution damage of trees [Tamm et al., 1998; Tamm et al., 2001]. The electric deposition is enhanced under thunderclouds and high voltage power lines due to the increased electric field.

Widespread belief of the direct biological effects of air ions on live organisms deserved critical comments by Dolezalek, et al. [1985]. The physical and chemical side-effects associated with ion generation (by natural or artificial ionization) are probably the main cause of observed biological relevance. The large air ions just like aerosol particles in ambient air can affect human health due to their depositing in the respiratory tract [McClellan and Miller, 1997].

The mobility spectrum of natural air ions is known to respond to many processes of local and regional scale: air pollution, environmental radioactivity, boundary layer turbulence and meteorology.

The electrical conductivity of atmosphere, which is inversely proportional to the aerosol particle content in the air, has been used as an indicator of particulate pollution. The conductivity measurements, dated back to the beginning of the 20th century, represent a valuable information about regional changes in the atmospheric aerosol loading (e.g. Manes, 1977; Sheftel et al.,

1994; Klimin and Shvarts, 1996). Measurements above the oceans have been carried out to estimate global changes (e.g. Cobb and Wells, 1970; Misaki et al., 1972b; Kamra and Deshpande, 1995). Unfortunately, the use of conductivity measurements for the assessment of particulate pollution is complicated due to their sensitivity to the ionization rate.

Owing to its sensitivity to the environmental radioactivity, conductivity is used in environmental monitoring stations as an indicator of radioactive pollution by nuclear tests and accidents (e.g. Israël, 1973; Israelsson and Knudsen, 1986; Retalis and Pitta, 1989).

Since conductivity measurements do not have an unambiguous interpretation, many researchers have been looking for other electrical methods and factors to determine particulate pollution of air (see Smirnov, 1983; Flagan, 1998). The concepts of "electrical factor of air pureness" by Allik [Tverskoy, 1949] and "aerosol electrical density" [Tammets, 1991] are based on the measuring of depletion rate of small ions by aerosol particles. The parameter deduced from these measurements is a diameter concentration of aerosol particles. The mobility spectrum of large ions, if it is in balance with aerosol particle size spectra, is a proper measure of atmospheric aerosol pollution. Its practical use is confined to the size range of ultrafine particles, since most of the large ion mobility spectrometers have a lower limit at about $2 \cdot 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ (diameter 120 nm) due to technical complications and uncertainties in size-spectra calculation [Misaki et al., 1972a, 1975; Dhanorkar and Kamra, 1993a].

The simultaneous measurements of small ions and large ion mobility spectra over a wide range, applying the balance equation of small ions together with an appropriate model of ion-aerosol attachment and size-mobility correlation (e.g. Hoppel and Frick, 1986; Tammets, 1995), enable to estimate the ionization rate of air [Dhanorkar and Kamra, 1994; Hörrak et al., 1998d]. In continental areas, the ionization rate is an indicator of environmental radioactivity; its variation is weakly influenced by cosmic rays. The ionization rate can be used as an indicator of stability of boundary layer just like the concentration of radon [Porstendörfer, 1994; Kataoka et al., 1998].

The atmospheric-electric fog effect, the decrease of air conductivity in fog and its increase at the termination of the fog event that may precede actual appearance and dissipation of the fog, respectively, can be used in weather forecasting [Hoppel et al. 1986].

The dependence of ion chemistry on trace constituents in air has been used to detect some trace species, important in the atmospheric aerosol formation (NH_3 , HNO_3 , H_2SO_4 , OH), by mass spectrometric technique (e.g. Tanner and Eisele, 1991; Eisele and Tanner, 1991, 1993; Ziereis and Arnold, 1986; Mount et al, 1997). The small ion mobility spectrometry (IMS, drift tube technique) is widely used to detect some trace species in air (e.g. Carr, 1984; Eiceman and Karpas, 1994). The major environmental and industrial applications of IMS include monitoring of toxic chemicals, stack gases, and chemicals that are

considered hazardous to man and environment (e.g. military gases, explosives, drugs). The mean mobility of small ions (measured by aspiration technique) also showed response to air pollution [Hoppel, 1970; Parts and Salm, 1992].

1.5. Earlier research

The measuring of air ions has a long history beginning with studies of atmospheric electricity around 1900. The apparatus and measurement theory are reviewed in detail in [Israël, 1970; Tammets, 1970; Flagan, 1998].

The general shape of the atmospheric ion mobility spectrum has been known since the discovery of three major ion groups: small, large and intermediate ions [Elster and Geitel, 1899; Langevin, 1905; Pollock, 1915]. The basic principles of the mechanism of electrical conductivity in gases were formulated earlier by J. J. Thomson in 1898 (see Thomson and Thomson, 1928).

Zeleny [1900] and Erikson [1921] introduced mobility spectrometers (first and second order differential, respectively) to study the mobility spectra of ions in laboratory experiments with artificial ionization. The exploitation of spectrometers for measurements in atmospheric air was complicated mainly due to low sensitivity of electrometric amplifiers. Thus, for many years up to about 1950's the "ion spectrum" was characterized mainly in terms of broad mobility classes based upon the measurements by means of Gerdien and Ebert type aspiration condensers. According to Israël's proposal [Israël and Schulz, 1933] the ion spectrum was divided arbitrarily into five conventional groups.

Until 1950's the measurements of atmospheric ion spectra were rare and only a few examples could be found (e.g. Nolan and de Sachy, 1927; Israël and Schulz, 1933; Hogg, 1939; Yunker, 1940a; Misaki, 1950; Sikсна, 1950). Commonly Zeleny's divided electrode method or Israël's double condenser method was used [Israël, 1931]. A single spectrum presented by Yunker [1940a] (measured by Erikson's method) is unique in that it clearly shows a minimum between small and intermediate ions at about $0.5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. Hogg [1939] and earlier Nolan and de Sachy [1927] have found that in the range of intermediate and large ions a spectrum contains a number of ion groups.

Israël [1970], summarizing the early measurements, concluded that the atmospheric "ion spectrum" contains two main ion classes: small ions with a maximum at about $1.6 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and large ions at about $3 \cdot 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, continuously distributed with respect to mobility. The spectral region in-between is sparsely and variably populated by intermediate ions. Examples of the mobility spectra of atmospheric ions obtained by various authors and of methods used up to 1964 are given in [Eichmeier, 1972], and similar data about artificially produced small ions in [Eichmeier and Herden, 1968].

The early devices (their sensitivity and resolving power) and techniques of spectra measurements were understandably unsatisfactory in many cases (see

Israël, 1970; *Tammet*, 1970) and only few of the data obtained up to 1950's are now other than of historical interest. Since 1950's, many years after the pioneering work of *Israël* [1931], several improvements of aspiration technique have been made to achieve precise mobility spectrometry of high resolution (e.g. *Misaki*, 1950, 1961a, *Whipple*, 1960; *Hoegl*, 1963; *Tammet*, 1970). The novel techniques became possible after the introduction of modern electronic devices, especially for measuring weak currents.

Probably beginning from *Junge* [1955], interest in atmospheric ion mobility spectra measurements started to grow. Aerosol classification by electrical mobility was the only method applicable for assessment of particle size distribution below about 0.2 μm . Owing to Junge's model of charges on particles, the complete size distribution of atmospheric aerosols (0.01–40 μm) was obtained for the first time. Junge's approach to ultrafine aerosol characterization was used later by *Misaki et al.* [1972a, 1975] and *Sekigawa et al.* [1981]. The aspiration condenser measurements of atmospheric ion spectra dominated prior to the late 1970's, then commercial aerosol instruments (including particle chargers) became more widely available [*Whitby and Clark*, 1966; *Liu and Pui*, 1975; *Knutson and Whitby*, 1975]. Afterwards, research activity in the field of atmospheric large ions gradually diminished, while aerosol measurements became common [*Flagan*, 1998; *McMurry*, 2000].

The discussion below is mainly confined to the recent measurements (after *Israël*, 1970) of natural air ion mobility spectra and to various classes of air ions in the atmosphere. Measurements of the mobility spectra of natural air ions could be most generally characterized by the mobility range and resolution and by the frequency and duration of recordings. In various studies, these characteristics have varied to a large extent, depending on the particular goals and technical resources of the researchers. Measurements of detailed mobility spectra over a wide range were carried out episodically, and the duration of measurement periods was limited.

The spectrometers of small, intermediate and large ions designed by *Misaki* [1961a] have a high resolution of eight logarithmically divided fractions per decade of mobility. At first the spectra of small ions ($0.2\text{--}3\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) were measured at two locations in Japan [*Misaki*, 1961b] and those of large ions ($4.2\cdot 10^{-5}\text{--}10^{-2}\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) in the New Mexico semidesert [*Misaki*, 1964]. Thereafter measurements over a wide range of $10^{-4}\text{--}3.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ were carried out at three sites in Japan [*Misaki et al.*, 1972]. The total duration of measurements made in the course of 3–15 day campaigns during 1960–1971 was roughly 3–4 months. Some features of the dynamic spectrum of atmospheric small and large ions (diurnal variations, correlation between small and large ions, evolution of spectra and changes due to atmospheric pollution) were discussed. Changes in the size distribution of aerosol particles following the dispersion of particles from land to ocean were studied by *Misaki et al.* [1975].

Eichmeier and Braun [1972] used a second order differential scanning type mobility spectrometer. The measuring of the mobility spectra of natural ions over a range of $0.01\text{--}2.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ took some hours. Spectra measured at two sites in Southern Bavaria showed maxima of positive and negative small ions at 1.46 (1.36) and 1.83 (1.75) $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. With decreasing mobility the concentration goes through a minimum and rises in the range of intermediate ions. The concentration of small ions decreases with increasing air pollution, fog and rain.

Sekigawa et al. [1982a, 1983] developed a second order differential mobility analyzer to scan the mobility range of $0.05\text{--}0.0003\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The mobility spectra were converted into size spectra of 8–80 nm. In some cases a bipolar charger was added to the system [*Nakatani et al.*, 1982]. Some examples of the evolution of aerosol particle size spectra recorded during a year of regular measurements in Tokyo area, Japan, were presented. The diurnal variation and variability of spectra were considered in their dependence on the characteristics of air masses [*Sekigawa et al.* 1981, 1982b].

Drozdowicz et al. [1982] measured the mobility spectra of natural air ions ($0.03\text{--}6\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) with a second order differential scanning type spectrometer in Cracow, Poland. Occasional measurements over a few days at chosen places which differed in air pollution showed a response of mobility spectra to air pollution levels. They concluded that the shape of the spectra may be a qualitative indicator of atmospheric air pollution by ultrafine particles.

Dhanorkar and Kamra [1991, 1993a] designed and built a mobility spectrometer with three Gerdien condensers which covers a range of $0.00023\text{--}3.4\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. They recorded 28 spectra (6 spectra per day) at Pune, India, in 1991. The concentrations of small, intermediate, and large ions were recorded at the same place during a one-year period in 1990–1991 [*Dhanorkar and Kamra*, 1993b]. The average diurnal variations of spectral classes (through four seasons) and contribution to air conductivity were studied, and mechanisms leading to such variations were discussed.

In addition to the measurements over a wide mobility range listed above, measurements of various air ion categories of small, intermediate or large ions, sometimes limited to one group only, can be found in literature.

Hoppel and Kraakevik [1965] recorded the tropospheric small ion mobility spectrum in the range of $0.2\text{--}4\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ above the exchange layer (32 spectra). The average mobility reduced to STP of about $1.2\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the negative-to-positive ratio 1.1 were nearly constant at altitudes from 3 to 5 km. In laboratory experiments [*Hoppel*, 1970] the mobility spectrum of positive air ions was quite stable with an average mobility of about $1.35\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (at STP). Addition of water vapor to dry filtered clean air led to a definite change in the negative ion spectrum only: a decrease of the mean mobility from 2.1 to $1.7\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Appearance of ions of mobilities $0.2\text{--}1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was recorded after the filtered air system was disturbed and additional polluted laboratory air

flowed into the system.

Suzuki et al. [1982] measured the mobility distribution of small ions by a multi-electrode Gerdien condenser which remarkably reduced the measuring time compared with the usual two-electrode type condenser. One-day measurements (17 spectra) lead to the average spectra of positive and negative ions with average mobilities of 1.15 and 1.21 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively.

Cabane and Milani [1983] presented the results of one-night measurements of small ions of 0.5–3 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ in a well-ventilated room in the center of Paris. The spectra were measured by an integral Gerdien condenser by switching the voltage in 30 steps. These spectra have some specific character, with two spectral classes, the first one corresponding to mobilities above 1.4 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and the second to mobilities 0.5–1.4 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. The existence of low mobility ions was explained in terms of air pollution involving nucleation.

Kojima [1984] measured air ion mobility spectra over the range of 0.0085–0.24 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. Five series (7–10 days) of measurements were carried out at the campus of the Science University of Tokyo in Noda during three seasons from summer 1983 to spring 1984. The main contributors to the variation of intermediate ion concentration were solar radiation and relative humidity.

Tammet et al. [1987a, b] carried out measurements of mobility spectra of small and intermediate ions (0.32–3.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) at Tahkuse during one-year, in 1985–1986. A second order differential spectrometer with 6 collector electrodes enabled measurement of spectra in every 5 minutes. Statistical results of these measurements (average spectra, dependence of spectra and mean mobility on wind and air temperature, diurnal and annual variations of mean mobility, as well as the concentration of small and intermediate ions) can be found in [*Tammet et al.*, 1992; *Salm et al.*, 1992; *Hörrak et al.*, 1988a, b, 1994].

Retalis and Retalis [1998] studied the effects of air pollution and wind on large-ion concentration (critical mobility 0.00025 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) in the air above Athens in 1969–1980. Almost always they found a significant correlation of large ions with other pollutants (NO_2 , O_3 , SO_2 , smoke) and wind speed.

Kitagawa et al. [1981, 1983] conducted measurements of spatio-temporal representativeness of air ions. Simultaneous measurements of the concentration of small ions, Aitken and Mie particles were made at 5 stations situated within a circle of 20 km around Tokyo regularly for 3 years during 1976–1979. The correlation coefficient between small ions at different stations was on the average 70%, for Aitken and Mie particles about 50%.

Reiter [1984] studied the dependence of air conductivity on the concentration of Aitken nuclei, fine aerosol particles (0.3–0.8 μm), and atmospheric visibility, over the period 1973–1983. It was shown that these particulate air pollution parameters could not be simply derived from the total conductivity. Additional measurements of meteorological parameters (especially fog) were found to be necessary. Small ion concentration measurements during 1973–1978 showed an influence of meteorological

conditions [*Reiter*, 1985]. This dependence on weather was due to the atmospheric content and size of aerosol particles.

Annual and diurnal variations of different air ion categories have engaged the interest of many researchers. Diurnal variations are discussed in [*Weiss and Steinmaurer*, 1937; *Hogg*, 1939; *Yunker*, 1940b; *Norinder and Siksna*, 1952, *Misaki and Kanazawa*, 1969; *Arold and Matisen*, 1992; *Israelsson and Tammet*, 2001], diurnal and annual variations in the course of routine measurements in [*Wait and Torreson*, 1934; *Reinet*, 1958; *Prüller*, 1970; *Manes*, 1977; *Tuomi*, 1989; *Retalis et al.*, 1991; *Dhanorkar and Kamra*, 1993b]. The integral Gerdien condensers were widely applied in these measurements. In some cases the mobility boundaries used were too wide and therefore the variation of ion populations of the different types present within the mobility range was less obvious. In general, the annual and diurnal variations exhibited some peculiarities depending upon the prevailing meteorological conditions and local air pollution, which affect the aerosol particle concentration and ionization rate close to the ground.

Information about chemical composition of the cluster ions of tropospheric interest has been obtained mainly from the mass spectrometric measurements beginning with *Eisele* [1983] and *Arnold et al.* [1984]. Some positive and negative ions (mostly cores of ions below 230 u) were mass-identified (e.g. *Eisele*, 1989a, b; *Eisele and Tanner*, 1990; *Tanner and Eisele*, 1991). Routes of atmospheric ion evolution have been proposed [*Keese and Castleman*, 1985; *Viggiano*, 1993]. In this connection, valuable information is obtained from model studies based on formal chemical kinetics [*Huertas and Fontan*, 1977; *Luts*, 1995, 1998; *Beig and Brasseur*, 2000].

Measurements of artificially generated small ion mobility spectra by means of a drift tube give essential information about the processes of air ion transformations which involve changes in their structure and chemical composition.

Two classes of small ions have been found in the laboratory experiments studying the evolution of mobility spectra in connection with particle formation by radiolytic processes [*Bricard et al.*, 1972, *Cabane et al.*, 1976, 1977]. The first class consisted of ions of discrete mobilities above 1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ whose amplitudes varied with ion age. The second class of ions (0.1–1 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) formed a continuous group whose mean mobility decreased continuously as the ions aged. The first class probably corresponded to the group of thermodynamically stable clusters, while the second class to the ions above the critical size for nucleation.

Nagato and Ogawa [1998] showed that during aging the peak in the positive ion spectrum gradually shifted towards lower mobility: from about 1.8 to 1.0 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ with increase of ion age from 0.03 to 5 s. The relative intensity of the dominant peaks of negative ions at 1.7 and 1.9 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ varied with ion age. Ions of higher mobility became dominant at about 1 s. Subsequent

evolution of the spectral peak of negative ions toward lower mobilities was expected from a comparison with the mobility spectra of natural air ions that showed maxima between 1.3 and 1.7 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. At an age of about 1–3 s ions form an almost continuous spectrum without separated spectral lines. *Nagato et al.* [1999] made the first attempt to combine air ion mobility and mass spectrometric measurements in field experiments. Positive ions (age about 0.1 s) with mobilities less than 1.5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ became dominant with increasing air temperature. Correspondingly, the ion fraction with high masses of 200–450 u increased in comparison with the fraction below 200 u. The observed temperature dependence was expected to be related to changes in the chemical composition of neutral gaseous species in air.

Laboratory experiments have revealed that ion clusters could be largely involved in the nanometer aerosol production in $\text{SO}_2/\text{NH}_3/\text{H}_2\text{O}/\text{Air}$ mixtures irradiated by ionizing radiation [*Ramamurthi et al.*, 1993; *Mäkelä et al.*, 1995; *Kim et al.*, 1997, 1998]. The mean mobility of cluster ions, which depends on the thermodynamical properties of the cluster and the environment, showed a decrease at higher saturation of condensable vapor in air [*Mäkelä et al.*, 1996a].

As already mentioned by *Israël* [1970], there are only a few studies on the size distribution of aerosol ions (intermediate and large ions) in the atmosphere. So far as we know, publications containing results of systematic measurement are still lacking. The charge distribution on aerosol particles in atmospheric air suffers insufficient experimental proof. Insofar as we know, only few attempts have been made in this field (e.g. *Israël*, 1970; *Hörrak et al.*, 1998a, c; *Mäkelä et al.*, 2001). Also, the mean mobility of small ions and its annual and diurnal variations have been only briefly discussed in [*Tammet et al.*, 1992; *Salm et al.*, 1992; *Hörrak et al.*, 1994, 1998b]. A short summary of mobility spectra of natural small ions and their mean mobilities is given in [*Mohnen*, 1977].

Air ion measurements in the Air Electricity Laboratory (AEL, founded in 1964) of the University of Tartu are summarized below. AEL has a long experience in investigations of air ion and charged particle mobility spectra [*Salm*, 1986, *Matisen et al.*, 1992; *Langus and Tammet*, 1992]. The basic principles of mobility spectrometry have been published in the papers [*Tammet*, 1970, 1975b, 1992a] and [*Tammet et al.*, 1983].

Atmospheric electric measurements at the University of Tartu can be traced back to 1930's when Prof. Johan Vilip acquired a Gerdien condenser for measuring air conductivity. In 1937 Anatoli Mitt carried out measurements of small air ion concentration during the whole year in Tartu [*Mitt*, 1946]. Later Jaan Reinet developed original air ion counters and with Hugo Marran studied the variation of small, intermediate and large ion concentrations during the year 1951 in Tartu [*Reinet*, 1958; *Marran*, 1958]. In 1960–1963 Paul Prüller carried out regular measurements of various categories of small, intermediate and large

air ions over a wide mobility range down to $0.00025 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with improved instrumentation [*Prüller and Reinet*, 1966; *Prüller*, 1970].

In these measurements the relationships between air ion classes in urban atmosphere, their diurnal and annual variations, as well as correlation with meteorological factors, dependence on weather types and air pollution, were investigated. The relation between the ion concentration and meteorological factors was found to be largely indirect, caused by the variation of ionization rate and aerosol particle content in air. The different behavior of cluster ions above $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ (called molions) and the total concentration of small ions above $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was noticed [*Reinet*, 1958]. The limiting mobility of $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ was proposed as conventional boundary between small and large air ions [*Prüller*, 1970].

In 1974 H. Tammet succeeded in establishing the dependence of small ion mobility spectra on the trace gaseous admixtures in air [*Tammet*, 1975a]. For this purpose a special air ion spectrometer had been designed [*Tammet et al.*, 1977]. Small ions were generated by corona discharge (or radioactive source) in the inlet of an aspiration spectrometer and measured in the mobility range of $0.6\text{--}2.4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ after aging about 1 s. The mobility spectrum was sensitive to the content of many trace species (gases, vapors at concentrations below $1 \mu\text{g m}^{-3}$) in air giving rise to certain specific ion families with characteristic mobilities [*Iher and Salm*, 1982; *Iher et al.*, 1983]. The phenomenon has been increasingly studied up to the present time [*Parts and Salm*, 1992; *Parts*, 1997; *Parts and Luts*, 2000]. *Iher and Salm* [1981] studied the dependence of the spectra of small air ions on the age of ions.

Measurements of small ions of age about 1 s generated in ambient air were made in summer 1984 [*Tammet et al.*, 1985; *Hörrak et al.*, 1994]. The mobility spectra of negative and positive ions in urban air (in Tartu) were unimodal with peaks at about 1.8 and $1.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively. In the rural air (at Tahkuse) the spectrum of positive ions acquired another dominant peak at $1.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. A laboratory experiment established that the addition of (di)amines (typical trace gases in rural air) into the air generated positive ions with higher mobilities [*Parts*, 1992].

Small ions of age 1 s were measured in fresh ventilated laboratory room air during 1986–1996 [*Parts*, 1995, 1999a, b]. The mean mobility of negative and positive ions varied in the range of $1.6\text{--}1.7 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and $1.13\text{--}1.23 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively; the ratio of polar mobilities was about 1.3–1.5. In general, the spectra negative ions of age 1 s extended from 0.95 to $2.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and that of positive ions from 0.75 to $1.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. However, a considerable number of ions down to $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ are present in the spectrum of natural air ions.

The mobility spectrum of large air ions of $0.0005\text{--}0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and the concentration of small ions were measured in ordinary room air with a 10-channel spectrometer over a period of 6 months during 1981–1982 [*Salm*, 1981;

Salm and Reinart, 1992]. The measurements showed that the maximum of the spectral function of conductivity lay at mobility $0.001 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, while in the mobility range of $0.05\text{--}0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ air ions were practically missing.

During summers since 1976, observations of atmospheric electricity were arranged in several areas of the Soviet Union in order to initiate regular measurements at environmental monitoring stations [*Arold and Matisen*, 1979, 1992]. In 1978–1984 the measurements were carried out on the island of Vilsandi, Estonia [*Arold et al.*, 1981; *Ruhnke, et al.*, 1983; *Hõrrak*, 1987].

The first measurements of natural small ions at Tahkuse Observatory were carried out during 1985–1986 [*Tammet et al.*, 1992]. An original spectrometer covering mobility range of $0.32\text{--}3.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ had been designed and built for these measurements [*Tammet et al.*, 1987a]. The mobility of $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ appeared as a lower boundary of small ions. The fraction of $0.32\text{--}0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ had a behavior quite different from that of small ions as regards spectra evolution and annual and diurnal variations [*Tammet et al.*, 1988, 1992; *Hõrrak et al.*, 1988b]. A special study showed that the average mobilities of both negative and positive small ions reduced to the standard conditions (1.36 and $1.56 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, respectively) decreased about 20% if the air temperature increased from $-5 \text{ }^\circ\text{C}$ to $25 \text{ }^\circ\text{C}$ [*Salm et al.*, 1992]. The dependence of small ion spectra on average wind direction showed a decrease in the mean mobility when the wind turned from south to north [*Hõrrak et al.*, 1988a]. In both cases the variation of the mean mobility of negative ions was in accordance with the relative intensity of peaks at 1.1 and $1.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The internal structure of small positive ion spectra remained unresolved.

The observed regularities of the intermediate ion concentration and the mean mobility of small ions have been explained by the presence of some trace species (gases or vapors) in the air that led to the growth of cluster ions.

A complex of air ion spectrometers covering the mobility range of $0.00032\text{--}3.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ has been operating at Tahkuse Observatory since 1988 [*Tammet*, 1990; *Hõrrak et al.*, 1990, 1994, 2000].

1.6. Main objectives of the present study

So far as we know, publications dealing with the results of systematic measurement of atmospheric ion mobility spectra in a wide mobility range are still lacking. Due to the complexity and large-scale variability of atmospheric processes, episodic measurements are insufficient to characterize the regularities of the mobility spectra of natural air ions. Long-term measurements of air ions in a wide range of mobility are necessary to draw statistically founded conclusions about the shape and variations of the mobility spectra. The present thesis wishes to partially fill this gap.

This first problem involves periodical maintenance of the measuring system, updating of software and hardware, verification of the data to obtain a reliable database extending over many years.

The other objectives are the following:

- verification of the anthropogenic atmospheric pollution level at Tahkuse to comply with a standard for the background monitoring stations of atmospheric electric measurements;
- statistical characterization of the air ion mobility spectrum, variability of the concentrations of spectral classes, the average diurnal and annual variations;
- specification of the classification of air ions by mobilities based on statistical data analysis;
- characterization of the bursts of intermediate ions in atmospheric air, the conditions of their occurrence and possible mechanisms of generation;
- detection of the main regularities in the variation of mean mobility of small ions: annual and diurnal variations, the correlation with air ion classes and meteorological parameters;
- contribution of small, intermediate and large ions to the electrical conductivity of air, the effect of mean mobility of small ions;
- study of covariation of ultrafine aerosol particle size spectra and air ion mobility spectra. Test of the procedures of conversion between mobility spectrum and size spectrum in atmospheric conditions. Assessment of atmospheric electric measurements as a source of information about atmospheric aerosols.

The problem of classification of air ions is essential because the mobility boundaries defined in textbooks of atmospheric electricity are rather speculative conventions. Regularities in the concentration of intermediate and large ions contain essential information about the charged fraction of ultrafine aerosol particles and could contribute to the field of atmospheric aerosol research. The formation of nanometer aerosol particles (intermediate ions) is still topical. The variation in the mean mobility of small ions, as well as the variability of air conductivity caused by changes in the mean mobility has been poorly studied.

This thesis mainly deal with the period from September 1, 1993 to October 27, 1994.