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# AIR IONS AND ELECTRICAL AEROSOL ANALYSIS

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## SPECTRA OF NEAR-GROUND ATMOSPHERIC AEROSOLS

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### Introduction

Aerosol particles cover a wide size range from a couple of nanometers to some tens of micrometers. Their size distribution is one of the most important characteristics of atmospheric aerosols. The spectra of number, surface or mass concentrations contribute significant information about the character of processes in the aerosol.

Various shapes of particle number distributions are encountered in measurements. A monomodal spectrum is characteristic of stratospheric aerosol but it has also frequently been measured in near-ground unpolluted air [1, 2, 3]. Since Whitby [4] many authors support the multimodal model of number distribution of atmospheric aerosols. According to Jaenicke [5] a multimodal distribution is typical of both countryside aerosol and tropospheric background aerosol. The measurements of Hoppel [3] in the central part of the Atlantic Ocean showed clearly bimodal distribution functions of marine aerosol. A dropping spectrum with monotonously descending number concentrations towards larger particles is mainly described for urban areas [6].

The identification of different types of spectra in natural measurements is connected with the variety and peculiarities of atmospheric processes during measurement. Partially, as suggested by M. Noppel [7], it may be conditioned by the use of different equipment and methods by different authors.

The present paper gives a survey of atmospheric aerosol spectra measured at different locations of Baltic region in different conditions, but with the same equipment. The paper focuses on the density functions of the distribution of the number concentration.

### Models of atmospheric aerosol spectra

Classically, the number distribution of over 0.1 μm dia particles is described by Junge's formula

$$N(r) \sim r^{-b}. \qquad (1)$$

Most measurement results in the atmosphere have agreed with the formula satisfactorily, whereas the power $b$ is about 4 .

V.I. Smirnov [8] has specified the distribution function of the particles of 0.1-20 μm radius. As a result of an analytical solution of the coagulation problem he has obtained a distribution function which can be presented by two power functions.

$$f(r)=\begin{cases} f_B(r) = C_B r^{-2.5}, & r_o \le r \le r^* \\ f_M(r) = C_M r^{-4.5}, & r^* \le r \le r_{max} \end{cases} \qquad (2)$$

where $r^*$ is the transition radius between two functions. For normal atmospheric conditions $r^* \approx 1.01$ μm . Unfortunately, relevant literature does not contain data on the comparison of measurement data with formula (2).

The picture of the distribution of particle sizes below 0.1 μm is considerably less clear. Junge's and Smirnov's formulas are not suitable for the description of the spectrum in the region below 0.1 μm. They yield an unlimited growth of the number of particles when the sizes of the particles decrease. The measurements, however, show a decrease or only a slight increase of the number concentration towards finer particles.

Several empirical distribution functions have been proposed for the description of the spectrum of the number concentration in a wide size range from 0.01 to 20 μm. A good survey of the models can be found in H. Tammet [9] who also proposes a new 4-parameter KL model distribution:

$$n_1(r) = \frac{A}{(r/r_x)^K + (r_x/r)^L}, \qquad (3)$$

where $n_1(r) = dN(r)/d(\ln r)$. One of advantages of this distribution is a good physical interpretability of the parameters: $K$ and $L$, respectively, are the slopes of the right and the left asymptotes of the distribution, whereas $r_x$ and $A$ are the coordinates of the intersection of the asymptotes. Depending on whether $L < 0$ or $L > 0$, the KL formula describes a monomodal or a dropping spectrum.

The multimodal spectrum is usually described by means of the sum of the log-normal distributions.



**The measurement conditions**

The analysed spectra have been obtained as a result of 4 measurement series carried out in the Baltic region. The measurement locations are: the city of Tartu, Estonia (July 1987 and January 1989 - Tartu.JU, Tartu.JA), the clean air field station at Voore in Estonian inland (August 1987), the coastal field station of Preila on the Kura Peninsula, Lithuania (August 1989). The measurements were carried out round the clock with intervals 5 min (15 min at Preila). Most of the spectra are those of a fair weather; rain, thunderstorm, fog, haze or snow were observed in about 20% of the measurement time. The height of the measurement place from the ground varied between 3 m and 6 m. The length of a series of measurements did not exceed 11 days, thus the seasonal changes are not represented in the data. Total of about 5400 spectra has been analysed.

The diversity of the measurement conditions makes it possible to conjecture that the analysis gives a picture of the aerosol spectra occurring in the Baltic region.

In all series a Tartu University electrical aerosol spectrometer *EAS* was used. The spectrometer gives a 12-fraction representation of the spectrum in the region 0.01-10 μm.

**The frequency of occurrence of different types of spectra**

All three above-mentioned shapes of spectra were present in the analysed spectra. Fig. 1 presents examples of types of spectra.

The frequencies of occurrence of spectra of different shapes are presented in Table 1. Those differ strongly at different locations.

Table 1

Frequencies of occurrence of different types of spectra in %

| Location | No. of spectra | dropping | monomodal | bimodal |
|---|---|---|---|---|
| Voore | 1612 | 7.8 | 85.9 | 6.3 |
| Preila | 861 | 6.7 | 49.6 | 43.8 |
| Tartu.JU | 1695 | 38.5 | 61.4 | 0.1 |
| Tartu.JA | 1228 | 12.8 | 86.7 | 0.5 |

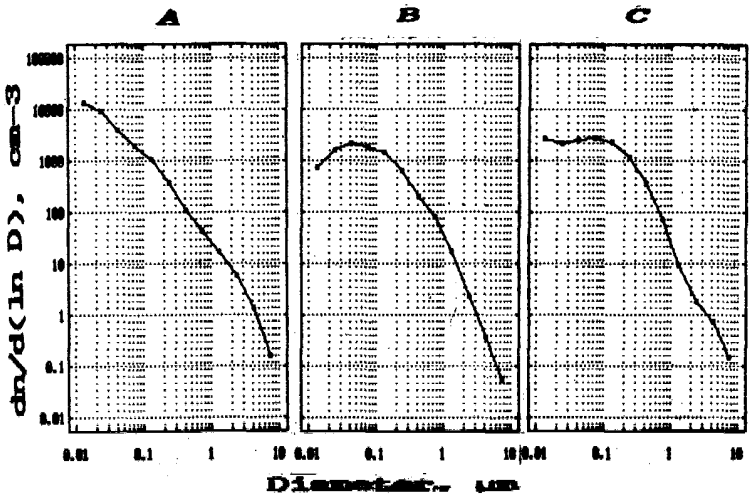


Fig. 1. a - dropping spectrum (Tartu, July 10, 8:30-9:30 (the mean of 12 spectra)
b - monomodal spectrum (Voore, August, average of nighttime (603 spectra)
c - bimodal spectrum (Preila, August 20-21, 23:00-16:00 (the mean of 64 spectra).

It can be seen that the dominant spectrum is monomodal one at all the measurement locations. It is explained by the case when the generation of small particles from the gaseous state does not fully compensate their transformation into larger fractions.

Numerous bimodal spectra were observed only at Preila. It may be a general property of the coastal aerosol, or a peculiarity of the weather during the measurement period. The data do not enable to unambiguously decide for either of the explanations. At Preila, the occurrence of the bimodal spectra was connected with haze (Fig. 2). On four days when the hollow spectrum occurred almost throughout the whole sunny period, haze or low fog clouds were observed. On the other hand, only few bimodal spectra occurred in clear sunny days when the UV-radiation of the sun contained a high proportion of shortwave radiation. The clear peak of bimodal spectra was present in fractions 3, 4, or 5, i.e. in the diameter range 0.03-0.2 µm and the fine particles peak below 0.01 µm.



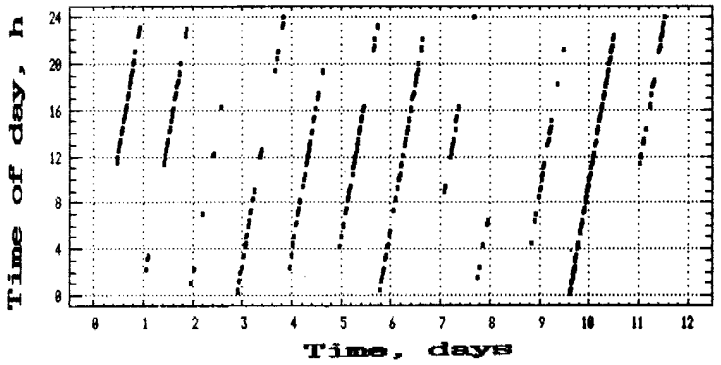


Fig. 2. The time of day of the occurrence of the bimodal spectra at Preila.

Dropping spectra were in significant amounts observed only in urban air in summer. The formation conditions of this kind of spectrum are an intense generation of fine particles on the one hand, and their relatively slow passage into the larger fractions on the other hand. The results of Tartu.JU confirm the hypothesis that the intensity of particle generation is determined by the amount of polluting gases and by the photochemical processes in these gases: the frequency of occurrence of dropping spectra (Fig. 3.1) corresponds to the daily variations of solar irradiation (Moscow time two hours ahead the local time is used) and to the life rhythm of city.

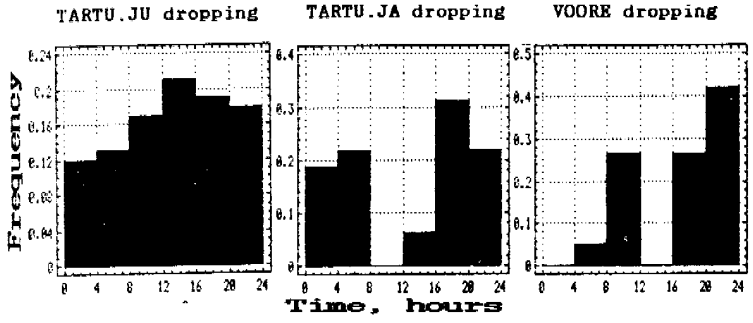


Fig. 3. Daily frequencies of occurrence of dropping spectrum: 1. Tartu, July; 2. Tartu, January; 3. Voore, August.

Somewhat unexpectedly, in winter Tartu.JA series, there are few dropping spectra and their daily frequency variation (Fig. 3.2.) does not correspond to the variation of solar irradiation. Rather, it is similar to the frequency distribution at Voore (Fig. 3.3) where dropping spectra occur mainly in the evening or at night. In most cases their appearance is connected with increased air humidity. The high concentration level on the one hand and the dominance of the monomodal spectra shape on the other hand can be explained by the intensive precipitation of fine particles to submicron and coarse particles which occur more often in the winter spectrum (Table 2).

The average spectra, total number, and mass concentration are presented in Table 2.

The dominance of monomodal spectra at Voore can be expected. At a location investigated with an aim of setting up a regional background station we really observed a low intensity of the generation of new particles, the monomodal shape of the spectrum and generally low particle concentration.

Table 2

Average number concentration spectra

| Frac. No. | Limits μm | Tartu.JU $cm^{-3}$ | Tartu.JA $cm^{-3}$ | Voore $cm^{-3}$ | Preila $cm^{-3}$ |
|---|---|---|---|---|---|
| 1 | .010-.018 | 3688 | 2685 | 625 | 1520 |
| 2 | .018-.032 | 3584 | 3852 | 1144 | 1420 |
| 3 | .032-.056 | 2074 | 2405 | 1191 | 1321 |
| 4 | .056-.10 | 1210 | 1345 | 985 | 1229 |
| 5 | .10-.18 | 600 | 731 | 783 | 1028 |
| 6 | .18-.32 | 217 | 295 | 327 | 552 |
| 7 | .32-.56 | 62 | 112 | 102 | 194 |
| 8 | .56-1.0 | 23 | 40 | 35 | 46 |
| 9 | 1.0-1.8 | 9.6 | 13 | 8.7 | 6.8 |
| 10 | 1.8-3.2 | 2.7 | 3.1 | 1.4 | 1.1 |
| 11 | 3.2-5.6 | .55 | .61 | .27 | .35 |
| 12 | 5.6-10.0 | 0.5 | .06 | .03 | .08 |
| Total number $cm^{-3}$ | | 11600 | 11500 | 5207 | 7318 |
| Total mass $\mu g \cdot cm^{-3}$. | | 67 | 87 | 48 | 63 |



The mean spectra are not in all locations of the monomodal type: in summer in Tartu, July and at Preila they are dropping. At Preila this effect is created by the simultaneous influence of the dropping and bimodal spectra, in Tartu, July the reason is the influence of relatively few spectra with very high concentrations of fine particles.

## Approximation of atmospheric aerosol spectra with model spectra

An aerosol spectrum obtained with an electrical spectrometer is actually a 13-parameter model of the real spectrum, whereas the spectrum is described as a superposition of 13 triangular elementary spectra. In many cases the description of the spectrum in such detail is not necessary and a model with a smaller number of parameters may be used. To study the use of model spectra, the average spectra of measurement series have been compared with above described models.

Table 3 presents the powers of the power function approxi-

Table 3

Approximation parameters of average spectra for a power function or the KL-function

| Approx. func. | $rf(r)=r^{b_i}$ | | | $rf(r) = \frac{A}{(r/r_m)^K + (r_m/r)^L}$ |
|---|---|---|---|---|
| Approx.limits:μm | .1-10 | .1-1 | 1-10 | .01 - 10 |
| Parameter / Location | $b_1$ | $b_2$ | $b_3$ | $K$ |
| Voore | -2.5 | -1.8 | -3.2 | 2.2 |
| Tartu. JU | -2.2 | -1.9 | -3.0 | 2.0 |
| Tartu. JA | -2.2 | -1.7 | -3.1 | 1.7 |
| Preila | -2.5 | -1.8 | -2.5 | 3.2 |
| Junge (1) | -3* | - | - | -3 |
| Smirnov (2) | | -1.5* | -3.5* | |

* The powers in formulae (1,2) and in the Table 5 are different by 1 because different representations are used.

mations of average spectra and $K$-parameter of the KL-approximation, comparing them to the parameters of the respective Junge's (1) or Smirnov's (2) formulas. It can be seen that in the region 0.1-10 μm the approximation of the spectrum with two power functions according to (2) is fully justified. Selecting $r^{*} \approx 1$ μm we obtain a good agreement with the parameters of Smirnov's formula.

An exception among the agreeing parameters $b_2$ and $b_3$ is $b_3$ at Preila. Also correlation analysis for Preila showed that the range of particles over 1 μm behaved practically independently of the rest of the spectrum. Supposedly an independent source of large particles formed by seaspray was active there. As can be seen in Table 3, Junge's two-parameter model does not make it possible to identify such peculiarity in the spectrum.

In Table 3 the parameter $K$ of the KL-model fluctuates more than Junge's or Smirnov's parameters. This is caused by the dependence of $K$ on the position of the maximum of the spectrum. Thus, the KL-approximation is not useful when only description of the spectra of large particles is needed.

The KL-model makes it possible to approximate monomodal and dropping spectra in a wide size range. Thus, bimodal spectra (in the present case about 13% of all spectra) were left out of the description. Table 4 presents the parameters of the KL-model of the average spectra of the measurement locations. An original computer program compiled by H. Tammet was used for the approximation.

Table 4

Parameters of the KL-approximation of average spectra

| Parameter / Location | $A$ | $r_x$ | $K$ | $L$ |
|---|---|---|---|---|
| Voore | 4068 | 47 | 2.2 | 0.6 |
| Tartu. JU | 9394 | 19 | 2.0 | -0.2 |
| Tartu. JA | 12259 | 17 | 1.7 | 0.8 |
| Preila | 1935 | 134 | 3.2 | -0.1 |

Generally, the KL-parameters describe spectra in correspondence with the 13-parameter model. To demonstrate that,



the pairwise comparison of the daily variations of the parameters of two models was done. Some more pronounced examples are presented in Fig. 4.

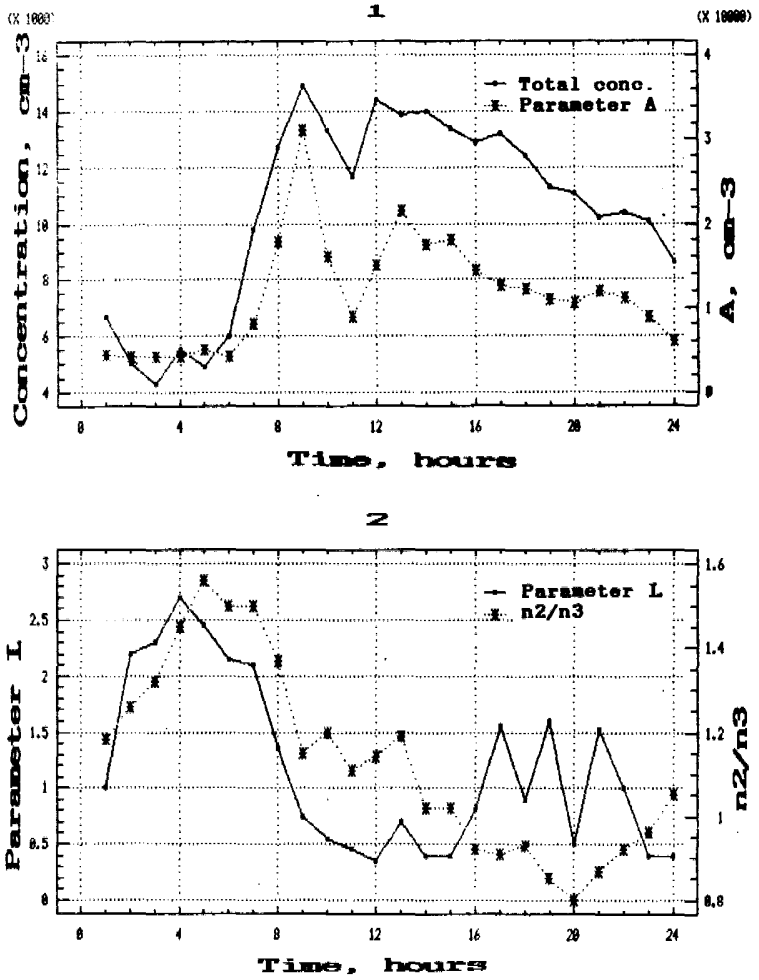


Fig. 4. Daily variations of the KL-model and the measured spectrum parameters: 1. KL-parameter $A$ and the total particle concentration $S$, 2. KL-parameter $L$ and the ratio of fine particle fraction concentrations $N_3/N_2$, Voore.

It can be seen that the average daily variations of KL-parameter $A$ and of the total particle concentration $N$ (Fig. 4.1) have quite similar walks.

The parameter $L$ and the ratio of fraction concentrations $N_3/N_2$ describe the slope of the left wing of spectra and characterize the rate of particle generation: the higher $L$ and $N_3/N_2$ the smaller the generation rate of fine particles. The average daily walks ( Fig. 4.2) of the above parameters are similar before 16.00. The oscillation of the parameter $L$ in the evening-time can be explained by its dependence on the spectral mode, which changes together with relative humidity of air.

**Conclusions**

Analysing the number concentration spectra of atmospheric aerosol measured during about 900 hrs at different times and at different locations, we met spectra of three different shapes: dropping (16.4% of the cases), monomodal (71.1%), and bimodal (12.7%). The frequency of occurrence of different types was significantly dependent on the measurement location.

The appearance of the spectrum of a certain type was not connected with quick fluctuations of the aerosol. Once arisen, a spectral type was usually maintained over several hours. The monomodal spectrum was more likely in regions with cleaner air, at night and in winter. The dropping spectrum was more likely in polluted air, in daytime and in summer. The bimodal spectra were frequent among the spectra of coastal aerosol on days with haze.

In the approximation of the coarse part ($d > 0.1$ μm) of the average spectra in representation $rf(r)$ with power functions we obtained Junge's constant between -2.2 and 2.5, Smirnov's formula (3) constants between 1.7 and 1.9; -2.5 and -3.2, respectively. For the description of spectra the use of the Smirnov's formula is preferable, especially, when the independent coarse particle sources are acting.

The fitting of atmospheric aerosol spectra by KL-model gives a good agreement with 13-parameter model for the dropping and monomodal spectra types.



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