

AIR IONS AND ELECTRICAL AEROSOL ANALYSIS

TARTU 1992

E. Tamm, A. Mirne and Ü. Kikas

Introduction

The generation of aerosol particles in corona discharges has been known for a long time [1,2], but their size spectrum and physical-chemical nature have not been thoroughly studied. The reason is a low development of methods and equipment for the measurement of particle spectra at the beginning of the nanometer size range (particle diameter $D \approx 1-20$ nm) which includes particles generated in corona discharge. The aim of the present paper is the study of the regularities of the evolution of the spectrum of these particles. The paper also has an applied aim - to study the possibility to use "corona" aerosols as calibration aerosols in the above size range where to date such aerosols do not practically exist.

Design of the experiment

The experimental set-up is shown in Fig. 1.

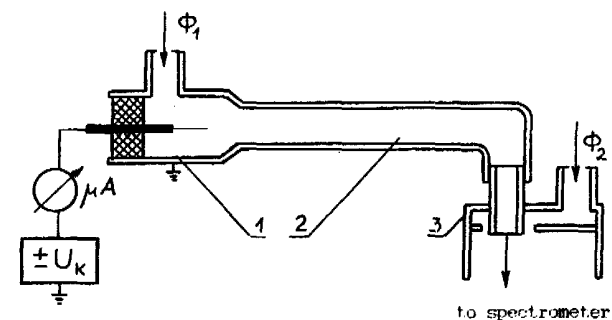


Fig. 1. Diagram of the experimental set-up.

An unipolar corona discharge is produced in the charger 1 in the point-to-cylinder discharge gap. In the present investigation Sn rod was used, but analogous results have been obtained with Pt and Fe rods. The corona current was varied in the limits 1-40 μA by the selection of voltage U_k , the

current was controlled with a micro-ammeter.

The air (air flow Φ_1) filtered with a high efficiency fibre filter was blown through the charger. The air with the corona products was directed into a cylindrical relaxation chamber 2. Chambers of two different shapes were used (Table 1), the relaxation time was controlled by changing the air flow Φ_1 .

Table 1

Configuration	Material of chamber walls	Diameter cm	Length cm	Volume cm ³
I	Al	2.4	80	280
II	PCV	0.6	200	60

Before injection into the spectrometer the aerosol was mixed with filtered air (air flow Φ_2) in the mixer 3, this was done to avoid further changes in the particle spectrum and to bring the general air flow rate to the value required by the spectrometer.

The measurement of the particle spectrum

To measure the nanometer-range spectrum of aerosol particles we used an electric aerosol spectrometer (EAS) of Tartu University [3]. EAS nominal measurement range (particle diameter 10 nm-10 μ m) turned out to be unsuitable and the spectrometer had to be modified. We used only one measuring capacitor (with a diffusion charger). The measurement limits (2.4-17.8 nm and 0.7-5.6 nm) were achieved by decreasing the voltage on the acceleration electrode. In the EAS the aerosol particles were charged in the corona charger with small air ions. As the ions of the EAS charger fell into the first part of the range (0.7-5.6 nm), the real lower limit of the measurement was 1.8 nm. At this limit an empirical correction had to be introduced to eliminate the distorting influence of the ions.

The particle spectrum was computed using the least squares method [4]. The apparatus matrix was computed theoretically by the formula presented in [5]. The technical parameters of the EAS were considered to be known, the size and the electrical mobility of the particles were linked with Milliken's formula. It was assumed that in the EAS charger, the

particles obtain maximally one elementary charge, the probability of particle charging has been computed by M. Noppel on the basis of the theory by Fuchs [6] taking into account the equation of Salm [7] and using the ion parameters presented in [8].

The influence of the space charge of the ions of the charger was taken into account by the correction of the EAS technical parameters on the basis of an extension of the recording of charger ions in comparison with the recording of low concentration air ions injected from the outside in the case of a switched off charger. Diffusional particle losses on the walls of the inlet device of the spectrometer were not taken into account, as they only have a value of about 20% for the lower limit of the range, and quickly decrease with the growth of particle size.

A very strong dependence of particle mobility on their diameter in this size range made it possible to use a spectrometer with heightened resolution power. The above real measurement range was split into eight fractions uniformly in a logarithmic scale. The limits of the fractions were (in nm) 1.8; 2.4; 3.2; 4.2; 5.6; 7.5; 10; 13; 18.

The possible particle generation in the corona charger of the EAS was specially investigated. At the injection of filtered air to the inlet of the spectrometer, the numerical fraction concentrations in the calculated spectrum (100-200 cm⁻³) were found to be in the limits of measurement interference. Only in the first fraction (1.8-2.4 nm dia) a heightened particle concentration was observed. This could be caused by shift in the regime of the charger (the absence of precipitation of ions to particles), or it could be a trace of very "young" particles of the charger.

Results

The aerosol generated by the system of discharge gap and chamber turned out to be monodisperse with a geometric standard deviation $\sigma_g \approx 1.2...1.3$. The other two parameters of the spectrum - the average diameter and the numeric particle concentration - are clearly dependent on the regime parameters of the system. Most illustrative was the presentation of the results as a dependence of the average diameter and the productivity (the total number of particles generated per second) on the corona current and relaxation

time (Table 2). The productivity was computed as a product of the sum of the measured fraction concentrations on the total air flow rate ($\Phi_1 + \Phi_2$).

Table 2

The dependence of the productivity N and the particle diameter D on the time of relaxation T (air flow rate Φ_1) and the corona current I

A. Negative corona, configuration I

$\Phi_1: \text{cm}^3 \cdot \text{s}^{-1}$	44		22		11	
$T: \text{s}$	8,3		12,5		25	
$I: \mu\text{A}$	$N \cdot 10^{-7}$ s^{-1}	D nm	$N \cdot 10^{-7}$ s^{-1}	D nm	$N \cdot 10^{-7}$ s^{-1}	D nm
2	-	-	3,7	2,0	3,2	3,7
4	-	1,8	7,4	2,9	7,2	5,7
10	22	2,4	-	-	-	-
13	31	2,8	-	-	25	9,0
24	45	3,6	-	-	32	14,5
36	64	4,2	46	7,5	46	18,0

B. Negative corona, configuration II

$\Phi_1 = 44 \text{ cm}^3 \cdot \text{s}^{-1} \quad T = 1.35 \text{ s}$			$\Phi_1 = 11 \text{ cm}^3 \cdot \text{s}^{-1} \quad T = 5.4 \text{ s}$		
$I: \mu\text{A}$	$N \cdot 10^{-7}: \text{s}^{-1}$	$D: \text{nm}$	$I: \mu\text{A}$	$N \cdot 10^{-7}: \text{s}^{-1}$	$D: \text{nm}$
19	-	2	1	-	2
			2	1.7	3.5
30	19	3.0	4	5.6	4.9
			9	22	9.0
36	28	3.5	14	36	10.0
			25	46	11.0
41	36	3.9	30	46	12.5
			39	56	14.5

C. Positive corona, configuration II

$\Phi_1 = 11 \text{ cm}^3 \cdot \text{s}^{-1} \quad T = 5.4 \text{ s}$		
$I: \mu\text{A}$	$N \cdot 10^{-2}: \text{s}^{-1}$	$D: \text{nm}$
4	1.0	2.9
9	6.1	4.1
14	18.4	8.5
19	36.0	10.0
24	52.0	13.0

The analysis of the data presented in Table 2 shows that in the case of a negative corona the productivity N is linearly dependent on the current I of the corona and nearly independent of the relaxation time:

$$N \sim I \quad (1)$$

Deviations from the law (1) are well explicable by diffusion losses on the walls of the chamber. The dependence of the particle diameter D on the regime parameters has a more complex character and is in good conformity with the law

$$D \sim T \sqrt{I} \quad (2)$$

where T is the average relaxation time. It appears that the coefficient of proportionality in (2) depends on the configuration of the chamber. In the present case for configurations I and II (Table 1) the difference is about fourfold.

There are less data from the experiments with positive corona (Table 2C), but even these are sufficient to show that here the dependencies are somewhat different:

$$N \sim I^2 \quad (3)$$

and

$$D \sim T \cdot I \quad (4)$$

In all the cases the percentage of charged particles turned out to be small and comparable with the percentage of charged particles at bipolar equilibrium charging.

A threshold of particle generation by the corona current was not detected. If the current was decreased, the average

particle size gradually faded out of the measurement range. No sharp changes were observed.

It is interesting to consider the results of the study of laboratory air. A minimum in the particle spectrum was observed near 5 nm (fraction concentrations of the order of 500 cm^{-3}). Large temporal aerosol concentration changes were observed, especially in the range of smallest sizes. These changes can probably be explained by fluctuational processes of the generation and coagulation particle growth.

The results of our experiments (in the limits of measurement error) confirmed the lack in the air of ions with mobilities higher than $2 \text{ cm}^2/(\text{V}\cdot\text{s})$, though it is likely that there are neutral particles of equivalent sizes. This demonstrates a radical limitation of the electrical method of aerosol particle size measurement which presupposes an obligatory joining of a small ion to a particle. The resulting particle cannot be "smaller" than a small ion.

Discussion

We designed a model of the process on the basis of the established regularities (1), (2), (3) and (4).

The independence of the productivity on the relaxation time points to the condensation mechanism of particle growth. Also, a small width of the particle spectrum ($\sigma_g \approx 1.2$) is characteristic of a condensation aerosol.

Coagulation as the main mechanism of particle growth is rejected by the fact that this growth is not accompanied by a sharp decrease of the number of particles. Furthermore, small width of spectra is not characteristic of strongly coagulated aerosols.

It is known that the change of the diameter of particles at the condensation of vapour on them takes place according to the proportionality

$$\frac{dD}{dt} \sim \frac{A(t)}{D} \quad (5)$$

Here it has been assumed that the pressure of the saturating vapour at the surface of a particle is zero, and that the pressure in the distance is proportional to the concentration of the vapour A . Let us assume that this concentration decreases according to the equation:

$$A(t) = A_0 \exp(-t/\tau), \quad (6)$$

where τ is an equivalent time constant. Let the corona discharge produce B molecules of vapour in a unit of time, then $A_0 = B/\Phi_1$, where Φ_1 is the air flow rate, and

$$\frac{dD}{dt} \sim \frac{1}{D} \frac{B}{\Phi_1} \exp(-t/\tau). \quad (7)$$

After integration and square rooting we obtain:

$$D(t) = \sqrt{K \frac{B}{\Phi_1} \tau [1 - \exp(-t/\tau)]}. \quad (8)$$

Here it is assumed that $D(0) = 0$, and the coefficient of proportionality has been expressed through K . In the experiment the particle size was determined through the relaxation time T which is connected with Φ_1 by the relaxation volume V (see Table 1):

$$\Phi_1 = V/T.$$

We get:

$$D = \sqrt{K \frac{B}{V} \frac{\tau}{T} [1 - \exp(-T/\tau)]} \cdot T. \quad (9)$$

For low T/τ the expression (9) can be written as:

$$D = \sqrt{K \frac{B}{V}} \cdot T. \quad (10)$$

If to assume that the number of the nuclei of future particles and the mass of vapour produced in a unit of time are both proportional to the corona current, i.e.

$$N \sim I \quad \text{and} \quad B \sim I, \quad (11)$$

then formula (10) agrees with the experimental relations (1) and (2) for negative corona. If to assume that

$$N \sim I^2 \quad \text{and} \quad B \sim I^2, \quad (12)$$

then the case of positive corona is described (experimental formulas (3), (4)).

The dependence of the shapes of the functions $N = N(I)$ and $B = B(I)$ on the polarity of the corona can be explained by the difference of the physical nature of the discharge for

different polarities. Negative corona has pulse character with a nearly constant amplitude and duration of current pulse. An increase of the average value of the current is achieved by a proportional increase of the frequency of pulses. This explains the proportionality of the vapour production rate to the average current. Positive corona has a continuous character. A detailed explanation of the shape of function (12), as well as of the dependence of the production of vapour on the pulse amplitude at negative corona, are out of the scope of the present investigation.

Comparing Table 2B with Table 2C at the same air velocity it can be seen that a relation between the productivity and the diameter is evident. This is possible if $N \sim B$, i.e. the sign of the corona does not influence the proportionality between the number of nuclei and the amount of vapour. This indicates that the nuclei are formed together with the vapour generated by the corona discharge.

Now we will consider the influence of the shape of the relaxation chamber on the proportionality coefficient in formula (2) for average particle diameter. Formula (10) shows that the relation of the values of this coefficient for two shapes is to be equal to the square root of the relaxation volumes. From Table 1 we obtain: $\sqrt{V_I/V_{II}} = 2.18$. The difference between the obtained estimate of the relation of coefficients and the experimental value cannot be explained by experimental errors. Also it was not possible to get the estimate of τ which would have made it possible to estimate the diffusion coefficient of the particles of the postulated vapours and thus to decide about its nature. The above facts point to the necessity of further development of the model and of further experimental investigations.

Conclusions

The proposed model of the generation of aerosol particles in the corona discharge adequately describes the experimentally established general properties of the phenomenon. A number of details require further investigation.

Simple adjustment of the average size and good replicability of the particle spectrum makes it possible to use the corona discharge as a generator of a nanometer range calibration aerosol.

References

1. Nolan, P.J., O'Toole, C.P.J. The condensation nuclei produced by point discharge // *Geofisica pura e applicata*. - 1959. - Vol. 42. - Pp. 117-126.
2. Загайнов В.А. и др. Исследование образования высокодисперсных аэрозольных частиц в коронном разряде // *Тез. докл. V всесоюз. конф. "Аэрозоли и их применение в народном хозяйстве"*. - М., 1987. - Т. I. - С. 37.
3. Мирме А.А., Тамм Э.И., Таммет Х.Ф. Электрогранулометр аэрозольных частиц с широким пределом измерения // *Уч. зап. Тарт. ун-та*. - 1981. - Вып. 566. - С. 84-82.
4. Таммет Х.Ф., Мирме А.А., Тамм Э.И. К проблеме электрического анализа аэрозолей // *Труды ИЭМ*. - М., 1983. - Вып. 30 (104). - С. 122-136.
5. Таммет Х.Ф. Об электрической гранулометрии аэрозолей // *Уч. зап. Тарт. ун-та*. - 1975. - Вып. 348. - С. 30-33.
6. Фукс Н.А. О стационарном распределении зарядов аэрозольных частиц в биполярно ионизированной атмосфере // *Изв. АН СССР. Сер. геофиз.* - 1984. - Но. 4. - С. 579-586.
7. Сальм Я.Я. Об униполярной зарядке первоначально заряженного аэрозоля // *Уч. зап. Тарт. ун-та*. - 1977. - Вып. 443. - С. 57-61. (See this volume pp. 68-71).
8. Hussin, A. et al. Bipolar diffusion charging of aerosol particles. I: Experimental results within the diameter range 4-30 nm // *J. Aerosol Sci.* - 1983. - Vol. 14, N 5. - Pp. 671-677.

Translated from:

Тамм Э.И., Мирме А.А., Кикас Ю.Э. Коронный разряд как генератор монодисперсного аэрозоля нанометрового диапазона // *Уч. зап. Тарт. ун-та*. - 1986. - Вып. 824. - С. 123-131.