A LIMITATION ON ELECTRICAL MEASURES OF AEROSOLS*

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INTRODUCTION

All aerosol measurement methods which use aerosols' electrical charging in the presence of free ions, but in the absence of a strong external electric field, are what I am referring to as "electrical measures of aerosols".

There are numerous such methods which have been used in the past and which are currently employed. Based upon the assumption that there is a constant, natural, background ion source, atmospheric conductivity has been used as a measure of the presence of aerosol particles because such particles remove the effective charge carriers from the atmosphere. Another variety of electrical measure is the total charge acquired by the aerosol under either natural or artificial charging conditions. Currently, the most widely cited electrical method for aerosol size distribution analysis is the "diffusion charging mobility analysis method" in which the electrical current due to the controlled unipolar charging of the aerosol is measured while increasing mobility fractions of that aerosol are removed. The hypothesis is that by monitoring the diminution of aerosol current as a function of the known particle electrical mobilities removed, a measure of the aerosol size distribution is derived.

Fundamental to all such measures of aerosol size is the assumption that any aerosol can be put in a well-defined charge state. This note presents an examination of that assumption. From this examination, a rigorous condition for the applicability of diffusion charging measures of aerosol size will follow.

AEROSOL CHARGE ACQUISITION

In the atmosphere there are numerous natural and artificial sources of available charge. Ionization by cosmic rays and radioactive decay products from
the earth supply a continuous source of bipolar (both positive and negative) background ions while concentrated radioactive sources, corona discharges, combustion, and thermionic emission in various arrangements provide bipolar or unipolar (only a single polarity) ions. It is known that such free ions only survive for less than ten microseconds under atmospheric conditions before they begin participating in clustering reactions with atmospheric trace gases. (3) The evolution a single ion undergoes once it starts clustering is dependent in detail upon the varieties and concentrations of such molecules as \( \text{SO}_2 \), \( \text{NH}_3 \), \( \text{H}_2\text{O} \), \( \text{NO}_x \), numerous organic species, and others present. (4) As a result, its physical properties such as mass and mobility are also sensitive to the atmospheric trace gases. Whatever the fate of an individual ion, a spectrum of ions of differing chemical and physical properties will be in evidence whenever a number of ions are simultaneously present. Consequently, there is no intrinsic meaning to the citation of a single ion species (or a physical property such as mobility) as characterizing the small ions under a particular set of conditions in the atmosphere.

The motion of an ion in the vicinity of an aerosol particle depends upon the physical characteristics of both the ion and the particle. For the sake of mathematical tractability, the particle is usually approximated as a sphere, an approximation which is well justified in many atmospheric circumstances. Two limiting, conceptually straightforward cases are relevant in treating aerosol charge acquisition. One is the macroscopic or collision-dominated case wherein the ion mean free path, with respect to collision with the neutral gaseous molecules, is very small in comparison to the particle radius. Under such conditions, particle charge acquisition should be capable of accurate
description in macroscopic terms since the variables determining charging are accessible to macroscopic control. The other case is the free-molecular approximation wherein the ion mean free path is considerably larger than the particle radius. When the ion mean free path is of the same order of magnitude as the particle radius, the ion is in the transition regime of kinetic theory.\(^{(5)}\)

The equations for bipolar polydisperse aerosol charging by polydisperse ions can be written as

\[
\frac{d}{dt}(p^P_{jn}) = p^P_{jn-1} \sum_i p^D_{jn-1i} U^P_{jn-1i} I^P_i - p^D_{jn} \sum_i p^P_{jn} U^P_{jn} I^P_i + p^D_{jn+1} \sum_i B^{-p}_{jn+1i} I^{-p}_i - p^P_{jn} \sum_i B^{-p}_{jn} I^{-p}_i
\]

+ ion equations

\[p^P_{jn} = \text{number density of particles in size-class } j, \text{ carrying } n \text{ charges of sign } p\]

\[i^P_i = \text{number density of small ion species } i \text{ which is of polarity } p\]

\[U^P_{jni} = \text{volumetric acquisition rate of ion specie } (i, p) \text{ by a } j\text{-sized, }n\text{-charged particle of polarity } p\]

\[B^P_{jni} = \text{volumetric acquisition rate of ion specie } (i, p) \text{ by a } j\text{-sized, }n\text{-charged particle of polarity } -p.\]

Properly speaking, \(P\) and \(I\) should be considered as random variables\(^{(6)}\) with mean values as measured in the laboratory. In that case, the charging equations become stochastic differential equations reflecting the nonuniformity of the ion-aerosol mixture. The substantial and possibly important additional complications such a treatment would entail have not yet been addressed. Therefore, the above equations will be considered as deterministic which means that their solution is unique for a given set of initial conditions.
For the sake of clarity, only unipolar, monodisperse aerosol charging will be considered below which is expressed by setting $i^{-p} = 0$ and dropping the $j$ and $p$ indices. Nonetheless, the following arguments apply equally well to the bipolar case. Their consequences for polydisperse aerosol charging will be discussed below. The unipolar charging equations can therefore be written

$$\frac{dP_i}{dt} = \sum_{n} \left( U_n I_i - P_n \sum_{n} U_{ni} I_i \right).$$

In the collision-dominated case,

$$U_{ni} = U^c_{ni} = \mu_i \nu_i,$$

where $\mu_i$ is the electric mobility of ion species $i$. This gives

$$\frac{dP_i}{dt} = \left( \sum_{n} \left( P_{n-1} f^c_n - P_n f^c_n \right) \nu_i \right) I_i.$$

Since $\sum_{i} \nu_i I_i$ is the ionic conductivity of the atmospheric segment under consideration and is a macroscopic quantity which can be controlled to compensate for external conditions, a well-defined charge state can be achieved for the aerosol.

By similar considerations for the free molecular case,

$$\frac{dP_i}{dt} = \left( \sum_{n} \left( P_{n-1} f_{n-1}^{f.m.} - P_n f_{n}^{f.m.} \right) \nu_i \right) I_i,$$

where $f_{n-1}^{f.m.}$ is again a factor dependent solely upon particle characteristics and $\nu_i$ is the mean ionic speed. This time $\sum_{i} \nu_i I_i$ is not an obvious macroscopic variable which implies that aerosol charging in the free molecular regime is governed by a quantity which is poorly defined in macroscopic terms.
If $R$ is the particle radius and $\lambda_i$ the ion mean free path, the transition regime is usually delimited as $0.25 < Kn_i < 10$ where $Kn_i = \lambda_i / R$. To understand the difficulty of bringing an aerosol in this size range to a well-defined charge state, it is useful to express the general volumetric charge acquisition rate as

$$U_{ni} = f_n R X \nu_i.$$ 

In the collision-dominated regime we can then show that $f_n = f_n^c \frac{e}{4kt}$ ($e$ = elementary unit of charge, $k$ = Boltzmann's constant, $T$ = temperature) and $X = \lambda_i$ while in the free molecular regime $f_n = f_n^{f.m.}$ $R$ and $X = 1$. This demonstrates that in the transition regime $X$ is explicitly a function of ion properties and at least implicitly a function of $R$ while $f_n = f_n^{tr}$ remains a function of particle properties alone. Then $X = X(R, \lambda_i, ...)$ and the charging equations are

$$\frac{dP_n}{dt} = (P_n - f_n^{tr} - P_{n-1} f_{n-1}^{tr}) R X(R, \lambda_i, ...) I_i.$$ 

Since $X(R, \lambda_i, ...)$ is a function about which very little is known either experimentally or theoretically, aerosol charging in this regime is equally poorly defined.

While polydisperse aerosol charging for particles which are all in either the collision-dominated or free molecular regimes may still be treated experimentally by starting with some calibration procedure wherein an ad hoc determination of the charging variables are made, this procedure cannot be extended to apply to an aerosol in which the transition and either of the other kinetic theory regimes is included. The fundamental physical obstacle is that charging
depends upon differing parameters and the careful control of one, such as conductivity, does not guarantee that another, such as $\sum \bar{v}_i I_i$, will have any clearly defined value. This difficulty is compounded by the fact that even the mathematical form of $X(R, \lambda_i, ...)$ for the transition regime is not known.

**AEROSOL MEASUREMENT**

If the atmospheric cluster ion spectrum were unique or at least clearly defined, some calibration procedure which related the peculiarities of that spectrum to the charging of each of a variety of sizes of monodisperse aerosols could be devised. As has been discussed, this is not the case. This means that measurements dependent upon diffusion charging made in one set of atmospheric conditions will most likely have little quantitative relationship to those taken at either another time or place unless the ionic conductivity was controlled and comparisons were made only for particles in the collision-dominated regime.

In terms relevant to measurements made in the lower troposphere, the free molecular regime corresponds to particles somewhat below $0.01\mu m$ radius while particles in the collision-dominated regime are generally on the order of $0.1\mu m$ radius or larger.

**ILLUSTRATIVE EXAMPLE**

The operational consequences of the foregoing discussion can be very well illustrated by a brief discussion of the performance of the Electrical Aerosol Analyzer or "EAA" (Thermo-Systems, Inc., St. Paul, Minnesota). This is the field instrument based upon the original Whitby Aerosol Analyzer that first used the "diffusion charging mobility analysis hypothesis" for aerosol size distri-
bution measurements.

In the EAA, the aerosol stream is first passed through a charger whose design is intended to maintain a constant number density of ions. The most closely related parameter which can be controlled is the ion current and this is what is actually regulated in this device. Since the ion current is directly proportional to the ionic conductivity, the EAA does produce a well-defined charge distribution upon the largest particles of the aerosol which are in the collision-dominated regime. Because of this, general agreement has been found between the EAA and optical particle counters when both devices have been properly calibrated.

Similarly, in a study to determine the role of cluster ion variability on the performance of the EAA, a statistical analysis of data showed narrow confidence intervals for parameters related to charging of particles in or near the collision dominated regime. Conversely, that same study showed that at a 90% confidence interval the particle current due to the transition regime particles were broad and could vary over almost an order of magnitude.

A mathematical model for the ideal EAA has been constructed and computed. This model includes six sizes of particles and six species of cluster ions and incorporates the essential features of constancy of total small ion conductivity in the charger and classification of particles according to their electrical mobility. Variability of the cluster ion spectrum produced in the charger corona is included by weighting the ion distribution among the species represented in differing ways. Ion removal is accomplished either by collision with an aerosol particle or by removal due to the constant ion current. The following table gives the calculational inputs and results. N(R) is the number density of sampled particles of R micrometers and the headings "Successive Numerical Flux Differences" give the differences in fluxes of charges carried by particles be-
<table>
<thead>
<tr>
<th>TABLE</th>
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<tbody>
<tr>
<td>NUMERICAL RESULTS OF MATHEMATICAL MODEL OF EAA PERFORMANCE</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>ION INDEX</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>MASS (AMU)</td>
<td>69</td>
<td>73</td>
<td>88</td>
<td>109</td>
<td>148</td>
<td>279</td>
</tr>
<tr>
<td>MOBILITY (cm$^2$/V-sec)</td>
<td>2.2</td>
<td>2.1</td>
<td>2.0</td>
<td>1.8</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>MEAN FREE PATH (um.)</td>
<td>0.022</td>
<td>0.020</td>
<td>0.018</td>
<td>0.015</td>
<td>0.011</td>
<td>0.0056</td>
</tr>
</tbody>
</table>

**CASE 1**

| IONIC FRACTION FROM CORONA | 0.10 | 0.10 | 0.10 | 0.10 | 0.20 | 0.40 |
| IONIC FRACTION IN CHARGING REGION | 0.062 | 0.065 | 0.068 | 0.076 | 0.18 | 0.55 |

**SUCCESSIVE NUMERICAL FLUX DIFFERENCES**

| 0.0 | $1.0 \times 10^5$ | $1.4 \times 10^5$ | $2.4 \times 10^4$ |

**CASE 2**

| IONIC FRACTION FROM CORONA | 0.40 | 0.20 | 0.10 | 0.10 | 0.10 | 0.10 |
| IONIC FRACTION IN CHARGING REGION | 0.33 | 0.17 | 0.091 | 0.10 | 0.12 | 0.18 |

**SUCCESSIVE NUMERICAL FLUX DIFFERENCES**

| 0.0 | $1.7 \times 10^5$ | $2.3 \times 10^5$ | $2.4 \times 10^4$ |
between successive total flux measurements according to the EAA's operational parameters. The first is zero because of the omission of particles under 0.005μm from the model and the fourth and higher differences are each equal in the two cases presented here because the corresponding particles were computed as if they were all in the collision dominated regime due to the inavailability of any reasonably accurate expression for \( U^{tr}_{n1} \) that included the image force for particles of 0.05μm radius. The ionic fractions from the corona were chosen as being representative of plausible real variations in the ion spectrum that can occur in the presence of differing fractions of atmospheric trace gases that may occur under field conditions. As a result, a 70% discrepancy in the flux differences corresponding to the transition regime charged particle flux is computed whereas the "diffusion charging mobility analysis hypothesis" says the numbers should be equal.

CONCLUSIONS

The foregoing discussion, which will be elaborated in a series of papers now in preparation, indicates that due to the physics of the process of charge acquisition by an aerosol particle, a rigorous condition exists for giving any aerosol a well-defined charge distribution if the particles can all be assumed to have similar physical properties. That condition is that all the particles be in the collision-dominated region \( \lambda_i/R < 0.25 \) and that the cluster ion conductivity be held constant.

For smaller particles, no such conditions are possible nor is any laboratory calibration of the process meaningful due to the variable and indeterminate nature of the cluster ions which are central to the charging process.
The meaning of these results for current instrumentation is that quantitative comparison among, or averaging of, data acquired at different times of places is not possible. The methods likely do have meaning as relative measures of size distribution in one location and over a time span during which the atmospheric trace gases may be considered to be constant.
REFERENCES

1. Israel, H., Atmospheric Electricity, Volume I (translated by D. Ben Yaakov and Baruch Benny), Israel Program for Scientific Translations Ltd. (1971), NTIS TT67-51394/1.


