# The real part of the mean complex refractive index and the mean density of samples of atmospheric aerosol particles

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#### ABSTRACT

The computation and the physical explanation of the spectral extinction of light in the atmosphere are mainly influenced by some specific prerequisites such as the number and the size of the atmospheric aerosol particles as well as their complex refractive index. Both size and complex refractive index are functions of the relative humidity. During the last years quite a number of investigations into the size distribution of the atmospheric aerosol particles have been carried out. Their refractive index, however is hardly known. An attempt has been made to overcome this deficiency with a new quantitative method for the simultaneous measurement of the real part of the mean complex refractive index and the mean density of samples of atmospheric aerosol particles. This measuring method and the first preliminary results of measurements are presented in this paper. The arithmetical means of nine measurements are 1.57 for the real part of the mean complex refractive index and 2.7 g cm<sup>-3</sup> for the mean density. Both these values are valid for a relative humidity of  $0.40 \pm 0.05$ . These measurements have been used for computing the dependency of both these quantities on the relative humidity. Formulae for these computations are deduced and the computational results for two samples of aerosol particles are presented: While the relative humidity varied between 0 and 1, for both samples the real part of the complex refractive index varied between 1.33 and about 1.7 and the mean density between 1 g cm<sup>-3</sup> and about 4 g cm<sup>-3</sup>.

## Introduction

The spectral extinction of solar radiation in the visible is caused by gas molecules and aerosol particles. It effects the sky radiation and its phenomena. The computation of the spectral extinction of radiation in the atmosphere and the distribution of the spectral radiance of the sky are based upon Rayleigh's law of the extinction of light by gas molecules and on the Mie theory of the extinction of light by spherical particles. The Mie theory applies to spheres whose radii are comparable with the wavelength of the incident light. If this theory is applied to the atmospheric aerosol particles it is necessary to know not only their number and size but also their complex refractive index.

This paper is a preparatory study. It deals with the preliminary results of measurements of the real part of the mean complex refractive index and the mean density of samples of

aerosol particles and with computations of the functional variation of both these variables with the relative humidity.

The simultaneous measurement of the real part of the mean refractive index and the mean density of samples of aerosol particles

#### A. THEORY

The principle of measurements of the real part of the mean refractive index and the mean density of samples of atmospheric aerosol particles is described in this section. The only presumption for these measurements is the validity of the empirical rule for the real part of the complex refractive index by Arago and Biot [1]:

$$V_{12}n_{12} = V_1n_1 + V_2n_2. \tag{1a}$$

V is the volume and n is the real part of the refractive index. The subscripts "12", "1" and

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"2" denote the mixture and both its constituents. The mixture rule (1a) applies very well to mixtures, solutions and dispersions, if the following prerequisites are fulfilled:

- No chemical reactions between the constituents should start.
- 2.  $V_1$  must be very large compared with  $V_2$ , i.e. there should be a distinct predominance of one of the constituents [5, 6].
- 3. In case of colloidal dispersions  $n_1$  must be almost equal to  $n_2$ . If this is not true, the spatial dimensions of the particles should not be greater than about 0.5  $\mu$  [10].

For the simultaneous measurements of the real part of the mean refractive index and the mean density of samples of aerosol particles it is necessary to apply the formula (1a) to systems of samples of aerosol particles in liquids. However, this is not readily admissible since the samples of aerosol particles are constituted of various homogeneous substances with the volumes  $V_i$  and the real parts of the refractive indices  $n_i$ . Rather, the second term  $V_2 \cdot n_2$  in the formula (1a) must be substituted by a sum as follows:

$$V_{12}n_{12} = V_1n_1 + \sum_i V_i n_i.$$
 (1b)

In order to give a uniform shape to both the equations (1a) and (1b), it is suitable to define

$$V \cdot n = \sum_{i} V_{i} n_{i}, \qquad (2)$$

where V is the volume and n the real part of the mean refractive index of the sample of aerosol particles. The quantity n is to be interpreted as the real part of the refractive index of a hypothetic homogeneous substance which has the volume V and can take the place of the aerosol particles in the system aerosol particles-liquid.

Further considerations also require us to know the mean density  $\varrho$  of the sample of aerosol particles which is defined as

$$\varrho = \left(\sum_{i} m_{i}\right) / V, \tag{3}$$

where the masses  $m_i$  are related to the volumes  $V_i$ .

If volume additivity is assumed for the system of a sample of aerosol particles in a liquid, the volume of the system is equal to

the sum of the volumes of the liquid and of the sample of aerosol particles:

$$V_{12} = V_1 + V. (4)$$

 $m = \sum_i m_i$  is the total mass of the sample of aerosol particles. Then  $V = m/\varrho$ , and by making use of the equations (2) and (4) the equation (1b) can be rewritten as

$$-m \cdot n + V_1(n_{12} - n_1)\varrho = -m \cdot n_{12}. \tag{5}$$

Equation (5) is linear with respect to n and  $\varrho$ . These quantities are unknown for samples of aerosol particles. All the other quantities in equation (5) can be obtained by direct measurements: The mass m of the sample of aerosol particles by weighing, the volume  $V_1$  of the liquid by pipetting and the real parts of the refractive indices of the system  $n_{12}$  and the liquid  $n_1$  by means of an ABBE refractometer. If such measurements are accomplished for two physically different systems which contain aerosol particles of the same sample, the following two linear equations in n and  $\varrho$  are obtained:

$$-m \cdot n + V_{1}(n_{12} - n_{1}) \varrho = -m \cdot n_{12}$$
 (6)

and 
$$-m' \cdot n + V_1'(n_{12}' - n_1')\rho = -m' \cdot n_{12}'$$
. (7)

This system of equations can be solved for n and  $\varrho$  without difficulty. This is the description in principle of the method for measuring the real part n of the mean complex refractive index and the mean density  $\varrho$  of samples of atmospheric aerosol particles.

#### B. Performance of the measurements

#### (a) Collecting the samples

The samples of aerosol particles have been collected in an automatic jet impactor on the roof of the Meteorological-Geophysical Institute of Mainz University. The uniform reciprocation of a small glass plate under the jet inside of the impactor effects a regular deposition of aerosol particles on this glass plate.

The distance between the end of the jet and the glass plate is 0.6 mm. At its end, the jet has a slot 15 mm in length and 0.6 mm in width. About 4 m<sup>3</sup> per hour of ambient air are taken in by the jet.

For computing the dimensions of the smallest particles which are caught by the impactor, the following assumptions1 have been made for simplification:

- 1. All aerosol particles have the density 2 g cm<sup>-3</sup>.
- volume.
- 3. Stokes's law is valid for the movement of the aerosol particles in the space between the end of the jet and the surface of the glass plate.
- 4. The aerosol particles have the same surface characteristics as polystyrol latex spheres.

Under these assumptions, the impactor calibrations by Stern et al. [12] can be applied to the automatic jet impactor. Hence, theoretically, the automatic jet impactor catches all aerosol particles whose equivalent radii are greater than 0.15  $\mu$ . (The equivalent radius is the radius of a sphere having the same volume as the aerosol particle.)

### (b) Preparing the physically different systems of aerosol particles in liquids

It has been explained in the theoretical section that the measurement of the real part of the mean refractive index and the mean density of samples of aerosol particles requires two physically different systems of aerosol particles in liquids.

These systems must be so conditioned, that the equations (6) and (7) are linear independent from each other. Systems which meet this condition can be prepared in two ways:

- 1. By changing the concentration if the same liquid is used, i.e.  $V_1 \neq V_1'$  when  $n_1 = n_1'$ .
- 2. By using different liquids with different real parts of the refractive indices, i.e.  $n_1 \neq n_1$ .

Measurements and model computations have shown that only the second way is practicable. Therefore this way has been followed for all the measurements.

The systems of aerosol particles of the same sample in different liquids have been prepared in such a way that

$$\frac{m}{V} = \frac{m'}{V'},\tag{8}$$

 $n = n_1 + (n_1' - n_1) \frac{(n_{12} - n_1)}{(n_{12} - n_1) - (n_{12}' - n_1')}$ 2. The aerosol particles have the same aerodynamic behaviour as spheres of the same

and 
$$\varrho = \frac{m}{V} \frac{(n'_{12} - n_{12})}{(n_{12} - n_{1}) - (n'_{12} - n'_{1})}.$$
 (10)

i.e. both these systems had the same concentra-

tion. Then, very simple equations for n and  $\varrho$ 

can be derived from the equations (6) and (7):

The masses m and m' have been weighed with a microscale with an accuracy of about 1-5 % and the volumes  $V_1$  and  $V_1'$  have been measured with micropipettes with an accuracy of about 1-3 %. The masses have always been greater than 1 mg and the volumes have always been greater than 0.1 cm<sup>3</sup>. The weighing and pipetting has been carried out indoors at relative humidities of  $f_0 = 0.4 \pm 0.05$ . In the same room and at the same relative humidity, the aerosol particles have been carefully mixed with the liquids in vials. Then, the vials have been closed with a cut stopper and left alone for some hours. After this, the aerosol particles in the liquids have been dispersed. The volume concentrations of the dispersions have always been about 10<sup>-2</sup>.

The liquids have been water, immersion oil, bromic benzol and monobromic naphtalene. Adverse chemical reactions between the aerosol particles and these liquids are not to be expected. The systems of aerosol particles and these liquids are volume additive except for about  $5 \cdot 10^{-2}$  %.

## (c) Measurements with the ABBE refractometer

The real parts of the refractive indices of the systems  $n_{12}$  and  $n'_{12}$  and for the mere liquids  $n_1$  and  $n'_1$  have been measured with an ABBE refractometer with monochromatic light of  $0.589 \mu$  wavelength at a temperature of 23°C.

It is feasible to reach a measuring accuracy of 1·10-4 for the real part of the refractive index with the ABBE refractometer. In order to guarantee this measuring accuracy, variations of the measuring temperature of only up to 0.1°C were admissible because of the great thermal dispersion of the refractive indices of the organic liquids which were used. This requirement has been fulfilled at all the measurements.

#### C. Results of the measurements

In Table 1 the results of nine measurements of the real part of the mean refractive index

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<sup>&</sup>lt;sup>1</sup> Presently these assumptions are under investigation.

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Table 1. Real part n of mean refractive index and mean density $\varrho$ of samples of atmospheric aerosol-
particles at relative humidity $f_0 = 0.4 \pm 0.05$ , temperature 23°C and monochromatic light of
wavelength $0.589~\mu$

No. of sample	Calendar date	Sampling- time, h	n	(g em <sup>-3</sup> )
	1966			
1	18-22 Jan.	94	$\boldsymbol{1.58 \pm 0.02}$	$3.4 \pm 1.0$
2	3-12 May	219	$1.54 \pm 0.015$	$\boldsymbol{2.2 \pm 0.3}$
3	12-17 May	115	$1.50 \pm 0.015$	$1.8 \pm 0.4$
4	17-20 and 23-24 May	95	$\boldsymbol{1.63 \pm 0.03}$	$2.8\pm0.7$
5	6–10 June	97	$1.62\pm0.035$	$3.3 \pm 0.8$
6	30  June-5 July	115	$\boldsymbol{1.63 \pm 0.02}$	$3.4 \pm 0.7$
7	27 Aug2 Sept.	95	$1.54 \pm 0.015$	$\boldsymbol{2.0 \pm 0.4}$
8	8-9 Sept.	31	$1.54 \pm 0.03$	$2.5 \pm 0.9$
9	9-14 Sept.	112	$1.55 \pm 0.015$	$2.4 \pm 0.4$

and the mean density of samples of aerosol particles are summarized. The arithmetic means of these measurements are 1.57 for the real part of the mean refractive index and 2.7 g cm<sup>-3</sup> for the mean density. The measuring errors are 1–2% for the real part of the mean refractive index and 15–30% for the mean density. Thus, this measuring method is more qualified for measuring the real part of the mean refractive index than the mean density.

It has been estimated that the systematic errors can reach the magnitude of the measuring errors.

According to Table 1 it takes about 1–9 days until a quantity of 10–20 mg aerosol particles is collected which is required for the meaurements. Due to these long collection times it is not possible to give a meteorological explanation of the results. Furthermore, the number of measurements is too limited for making general statements on the real part of the mean complex refractive index and the mean density of samples of aerosol particles at Mainz.

# Volume V, real part n of the mean complex refractive index and density $\varrho$ of samples of aerosol particles as functions of the relative humidity

Atmospheric aerosol particles partly consist of hygroscopic material. Therefore, they absorb moisture from the air in case of increasing relative humidity and they dispose of moisture in case of decreasing relative humidity. Hence, changes in the relative humidity result in changes

of the chemical constitution of the aerosol particles. Therefore their mass, their volume, the real part of their mean refractive index and their mean density change with relative humidity.

A. A FORMULA FOR THE MASS OF A SAMPLE OF AEROSOL PARTICLES AS A FUNCTION OF THE RELATIVE HUMIDITY

According to McDonald [9], a modification of Raoult's law can be given for electrolytical solutions in the following form:

$$1-f=1\left/\left(1+\frac{M_s}{i\cdot M_w}\frac{m_w}{m_s}\right),\right.$$

where f is the equilibrium relative humidity over the electrolytical solution,  $M_s$  is the molecular weight of the salt,  $M_w$  is the molecular weight of the water,  $m_s$  is the mass of the solute salt,  $m_w$  is the mass of the water and iis van't Hoff's factor. Generally, i is known to be a function of the solute concentration, however, it also can be determined as a function of the relative humidity because  $m_{in}/m_{e}$  and f are unequivocally linked to each other. According to the interpretation of Raoult's law, i can be conceived as the quotient of the number of the seeming solute ions in the solution to the number of solute salt molecules; it must be determined by individual measurements for each salt or combination of salts resp.

For simplifying the modification of Raoult's law a coefficient of mass increase is defined by

$$\mu_s(f)=i\frac{M_w}{M_s}.$$

After a slight rearrangement, the law then reads:

$$\frac{m_w}{m_s} = \mu_s(f) \frac{f}{1 - f}.$$
 (11)

It can be assumed that the major part of the dry hygroscopic matter of the samples of aerosol particles consists of salts [7]. Therefore, it appears appropriate to define a function for the mass of water taken up by a sample of aerosol particles, which has the same form as the equation (11):

$$\frac{m_w(f)}{m_h} = \mu_h(f) \frac{f}{1-f},\tag{12}$$

where  $m_w(f)$  is the mass of the water taken up by the sample of the aerosol particles at the relative humidity f,  $m_h$  is the mass of the hygroscopic matter in dry state and  $\mu_h(f)$  is called the coefficient of mass increase of the hygroscopic matter. In most cases, the mass  $m_h$  of the dry hygroscopic matter of a sample of aerosol particles is unknown and the mass  $m_0$  of the dry sample of aerosol particles is known. Therefore, it is efficient to multiply the equation (12) with  $m_h$  and to divide it by  $m_0$ . Hence

$$\frac{m_w(f)}{m_0} = \mu_h(f) \frac{m_h}{m_0} \frac{f}{1 - f}.$$
 (13)

By defining  $\mu(f) = \mu_h(f) \frac{m_h}{m_h}$  (14)

the equation (13) is transformed into

$$\frac{m_w(f)}{m_0} = \mu(f) \frac{f}{1-f}.$$
 (15)

 $m_{w}(f)/m_{0}$  is the relative mass increase of a sample of aerosol particles referred to the dry mass  $m_{0}$ ;  $\mu(f)$  is the coefficient of mass increase of this sample.

The equation (14), which defines the coefficient of mass increase, shows that the amount of water taken in by the sample of aerosol particles depends on the chemical structure of the hygroscopic matter, and furthermore, that it is directly proportional to the mass ratio

of the dry hygroscopic matter to the total dry matter. Moreover, the equation (14) shows that the physical properties of the hygroscopic matter which are characterized by  $\mu_h(f)$ , are also included in  $\mu(f)$ , because  $m_h/m_0$  is a specific constant for each individual sample of aerosol particles. Unfortunately,  $\mu_h(f)$  and thus also  $\mu(t)$  include the capillary influences occurring in the space between the solid constituents of the sample of the aerosol particles except for very high relative humidities. These influences always effect an increase in the mass of the water taken up by the sample. The amount of this increase cannot be determined exactly, in case of decreasing relative humidity it might be different from that in case of increasing relative humidity. Due to the well known supersaturation effects in saltwater [8, 11] it is to be expected that below a specific threshold value of relative humidity which depends on the chemical composition of the hygroscopic substance,  $\mu(f)$  is greater in case of decreasing than of increasing relative humidity. Winkler [13] found in his measurements that  $\mu(f)$  was greater in case of decreasing than of increasing relative humidity; however, the amounts were different in the individual samples of aerosol particles.

The total mass of a moist sample of aerosol particles is

$$m(f) = m_w(f) + m_0. (16)$$

Hence, the relative mass of a sample of aerosol particles referring to  $m_0$  is expressed as

$$\frac{m(f)}{m_0} = 1 + \mu(f) \frac{f}{1 - f}.$$
 (17)

B. Formulae for the volume v, the real part n of the mean complex refractive index and the mean density  $\varrho$  of a sample of aerosol particles as functions of the relative humidity

The derivation of the functions V = V(f), n = n(f) and  $\varrho = \varrho(f)$  is based upon the assumption that volume additivity of samples of atmospheric aerosol particles is fulfilled at all relative humidities. Hence

$$V = \sum_{i} V_{i}. \tag{18}$$

According to the present knowledge of the behavior of the salts in samples of aerosol

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particles this prerequisite is fulfilled for V except for 1-2 %.

The volume V = V(f)

The equation (15) which has been given for the relative mass increase can be transferred into a formula for the relative volume increase, which reads

$$\frac{V_w(f)}{V_0} = \mu(f) \frac{\varrho_0}{\varrho_w} \frac{f}{1 - f}.$$
 (19)

 $V_w(f) = m_w(f)/\varrho_w$  is the volume of water condensed on the sample and  $V_0 = m_0/\varrho_0$  is the volume of the dry matter of the sample of aerosol particles.

For simplifying the equation (19), the coefficient of volume increase is defined as

$$\varphi(f) = \mu(f) \frac{\varrho_0}{\rho_m}. \tag{20}$$

Since  $\varrho_0/\varrho_w$  is a constant for each sample, the reflections which have been made on  $\mu(f)$  also hold for  $\varphi(f)$ . Because it is assumed that the prerequisite of volume additivity is fulfilled, the volume of the moist sample of aerosol particles is expressed as

$$V(f) = V_{10}(f) + V_0. (21)$$

Then the formula for the relative volume of the sample of aerosol particles referring to  $V_0$  is obtained as a function of the relative humidity.

$$\frac{V(f)}{V_0} = 1 + \varphi(f) \frac{f}{1 - f}.$$
 (22)

The real part n = n(f) of the mean complex refractive index

The following derivation is based upon the formula (2). Due to the volume additivity of the sample of aerosol particles the sum on the right side of this equation can be converted into a sum of two terms for simplification. The first term covers the water suspended in the sample, the second term covers the dry matter of the aerosol particles. We then obtain

$$\sum_{i} V_{i} n_{i} = V_{w} n_{w} + V_{0} n_{0}.$$
 (23)

 $n_w = 1.33$  (in light of the wavelength 0.589  $\mu$ ) is the real part of the refractive index for water and  $n_0$  is the real part of the mean refractive index of the dry matter of the sample of aerosol

particles. Using the equations (21) and (23) the equation (2) is transformed into

$$n(f) = n_w + (n_0 - n_w) \frac{V_0}{V(f)}.$$
 (24)

By substitution with the help of the equation (22) the formula for the real part of the mean complex refractive index is obtained as a function of the realtive humidity.

$$n(f) = n_w + \frac{n_0 - n_w}{1 + \varphi(f)f/1 - f}.$$
 (25)

The mean density  $\varrho = \varrho(f)$ 

The mean density of a sample of aerosol particles is defined by

$$\varrho(f) = m(f)/V(f) = \varrho_0 \frac{m(f)/m_0}{V(f)/V_0}.$$
 (26)

Since the investigation is restricted to samples which fulfill the prerequisite of volume additivity, the equations (17), (20) and (22) together can be used for substitution in this definition. Then the formula for the mean density of samples of atmospheric aerosol particles is immediately obtained as a function of the relative humidity.

$$\varrho(f) = \left(\varrho_0 + \varrho_w \varphi(f) \frac{f}{1 - f}\right) \left(1 + \varphi(f) \frac{f}{1 - f}\right)^{-1}. \quad (27)$$

The equations (22), (25) and (27) are the new formulae for the volume, the real part of the mean complex refractive index and the mean density of samples of aerosol particles as functions of the relative humidity. The unknown quantities in these formulae are only the coefficient of volume increase together with the volume, the real part of the mean refractive index or the mean density resp. of the dry matter. Each of these three formulae can be transformed easily into a more general form with the volume, the real part of the mean refractive index or the mean density resp. at any relative humidity.

# C. Computations for the samples of aerosol particles No. 5 and No. 6 of Table 1

The following computations of the functions  $V(f)/V_0$ , n(f) and  $\varrho(f)$  are based upon measurements of the relative mass increase  $m_w(f)/m_0$ 

by Winkler, [13], the measurements of  $n(f_0)$  and  $\varrho(f_0)$  by the author and the formulae derived in the two previous sections. Winkler's measurements are summarized in Table 2. The relative mass increases which are given in this table for the samples No. 5 and No. 6 are arithmetic means of 5 or 3 measurements each. These measurements have been taken while the sample No. 5 and No. 6 were being collected. The values given in the table are valid for increasing relative humidity. The measurements taken for decreasing relative humidity have not been evaluated since they were too sparse.

According to the formula (15) the relative mass increase and the relative humidity are correlated by the coefficient of mass increase alone. Therefore, coefficients of mass increase have been computed for the samples No. 5 and No. 6. They are listed together with measuring errors in Table 3. Their values vary between 0.126 and 0.149 together with those of their errors between 6 % and 15 %. Thus, the numerical values of  $m_w/m_0$  as functions of f are known for these two samples with errors ranging between 6 % and 15 %.

Apparently, for both these samples the coefficients of mass increase are constant within the range of measuring accuracy. But the evaluation of some more measurements has proved that this is not a general conclusion. However, it can be seen from computations that in case of small values of  $\mu$  it may be assumed  $\mu = \mu(f = 0.9) = \text{const.}$  without causing great errors in  $m(f)/m_0$  (not in  $m_w/m_0$ ).

For computing  $V(f)/V_0$ , n(f) and  $\varrho(f)$  from the measurements, the equations (22), (25) and (27) are transformed with the help of the equations

Table 2. Relative mass increase  $m_w/m_0$  for different relative humidities at room temperatures

	$m_w/m_0$		
f	Sample No. 5	Sample No. 6	
$0.925 \pm 0.01$	1.66 +1%	$1.77 \pm 1 \%$	
$0.90 \pm 0.01$	$1.29 \pm 1$	$1.29 \pm 1$	
$0.85 \pm 0.01$	$0.842 \pm 1$	$0.738 \pm 2$	
$0.80 \pm 0.01$	$\boldsymbol{0.566 \pm 1}$	$\boldsymbol{0.524 \pm 2}$	
$0.75 \pm 0.01$	$0.438 \pm 1$	$0.394 \pm 2$	
$0.70 \pm 0.01$	$0.348 \pm 1$	$0.306 \pm 3$	
$0.65 \pm 0.01$	$0.258 \pm 2$	$0.244 \pm 4$	
$0.60 \pm 0.01$	$0.202 \pm 3$	$0.200 \pm 5$	
$0.40 \pm 0.01$	$0.084 \pm 3$	$0.087 \pm 6$	

Table 3. Coefficient of mass increase  $\mu$  as a function of relative humidity f

f	$\mu$		
	Sample No. 5	Sample No. 6	
0.925	0.134 + 15%	0.143 + 15 %	
0.90	0.143 + 12	0.144 + 12	
0.85	0.148 + 9	0.130 + 10	
0.80	0.141 + 7	0.131 + 8	
0.75	0.146 + 6	0.131 + 7	
0.70	$0.149 \pm 6$	0.131 + 8	
0.65	0.139 + 6	0.132 + 8	
0.60	0.135 + 7	0.133 + 9	
0.40	0.125 + 7	0.130 + 10	

(15) and (20) in such a way that they comprise only measured quantities:

$$\frac{V(f)}{V_0} = 1 + \frac{m_w(f)/m_0}{\frac{\rho_w}{\rho(f_0)} \left[1 + \frac{m_w(f_0)}{m_0}\right] - \frac{m_w(f_0)}{m_0}}, \quad (28)$$

$$n(f) = n_w + \frac{n(f_0) - n_w}{1 + \frac{\varrho(f_0)}{\varrho_w} \left[1 + \frac{m_w(f_0)}{m_0}\right]^{-1} \left[\frac{m_w(f)}{m_0} - \frac{m_w(f_0)}{m_0}\right],$$
(29)

$$\varrho(f) = \frac{1 + m_w(f)/m_0}{\frac{1}{\varrho(f_0)} \left[1 + \frac{m_w(f_0)}{m_0}\right] + \frac{1}{\varrho_w} \left[\frac{m_w(f)}{m_0} - \frac{m_w(f_0)}{m_0}\right]}.$$
(30)

The computational results are presented in the Figs. 1, 2 and 3. They show:

- At f = 0.9, the volumes of both the samples are about 6.5 times those of the dry constituents.
- 2. Both the samples prove that the real part of the mean refractive index as well as the mean density are nearly linear functions of the relative humidity, the former ranging between 1.33 and about 1.7 and the latter between 1 g cm<sup>-3</sup> and about 4 g cm<sup>-3</sup>.

The numerical value n=1.5 of the real part of the mean refractive index upon which Bullrich [2] based his computations becomes fact by both the samples of aerosol particles at relative humidities between 0.65 and 0.75. The measured results of  $n \approx 1.5$  for relative humidities between 0.5 and 0.6 and  $n \approx 1.44$  for relative humidities between 0.8 and 0.9 which Eiden [4] found for the real parts of the

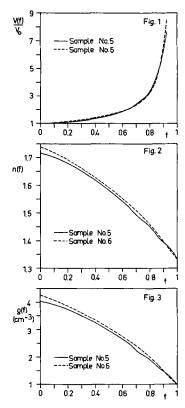


Fig. 1. Relative volume  $V(f)/V_0$  as function of relative humidity f (eq. (28)).

Fig. 2. Real part n(f) of the mean refractive index as function of relative humidity f (eq. (29)).

Fig. 3. Mean density  $\varrho(f)$  as function of relative humidity f (eq. (30)).

mean refractive indices are in good agreement with the computations presented in this paper. Eiden based on measurements of the elliptic polarization of light scattered by aerosol particles in a volume of atmospheric air. These measurements have been taken in weather situations which were characterized by high concentrations of aerosol particles. It must be emphasized that neither the above computational results nor Eiden's measured results can be accepted generally because the chemical composition of the aerosol particles varies with time and space. They can be taken only as a hint for the range which might be expected for the variation of the real part of the mean refractive index and the mean density as functions of the relative humidity. Up to now, any estimate of this range was mere speculation.

#### Outlook

The future planning includes the improvement of the collection method to reduce the sampling time and the accomplishment of serial investigation at Mainz and other locations. These serial measurements should be carried out at different wavelengths of light and different size groups of the aerosol particles.

Eiden [4] has not only measured the real part of the mean refractive index but also its imaginary part, i.e. the mean absorptive index. He found a decrease in the mean absorptive index with increasing relative humidity. It is easy to derive a formula for the mean absorptive index of samples of aerosol particles as a function of the relative humidity, because the optics of absorbing media can be derived from the optics of transmissive media by substituting the real refractive index by the complex refractive index  $n_c = n - ik$ . Then the formula for k = k(f) is analogous to that for n = n(f), namely

$$k(f) = k_w + (k_0 - k_w) \left(1 + \varphi(f) \frac{f}{1 - f}\right)^{-1}$$
. (31)

k(f) and  $k_0$  are the mean absorptive indices of the moist and the dry sample of aerosol particles resp.,  $k_w$  is the absorptive index of water. Since in most cases  $k_w$  is negligible in the visible, the formula (31) indicates that considerable variation of the absorptive index of a sample of aerosol particles with the relative humidity can be expected. It appears worth while studying this phenomenon more thoroughly in view of the computation of the spectral extinction of the solar radiation in the atmosphere as well as the physical explanation of its measurements in order to solve some problems related with it [3].

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#### REFERENCES

- Arago, D. F. J. & Biot, I. B. 1806. e.g. Mém. acad. France 7.
- Bullrich, K. 1964. Scattered radiation in the atmosphere and the natural aerosol. Advances in Geophysics 10, 99-200.
- Danzer, K. H. & Bullrich, K. 1965. The influence of absorption on the extinction of solar and sky radiation. *Applied Optics* 4, 1500-1503.
- Eiden, R. 1966. The elliptical polarization of light scattered by a volume of atmospheric air. Applied Optics 5, 569-575.
- Heller, W. 1945. The determination of refractive indices of colloidal particles by means of a new mixture rule or from measurements of light scattering. *Physical Review* 68, No. 1, 5-10.
- Heller, W. 1965. Remarks on refractive index mixture rules. Journal of Physical Chemistry 69, No. 4, 1123-1129.
- Junge, C. E. 1963. Air Chemistry and Radioactivity.

- New York and London, Academic Press, pp. 111-208.
- Junge, C. 1952. Die Konstitution des atmosphärischen Aerosols. Annalen der Meteorologie, No. 5, Supplement.
- McDonald, J. E. 1952. Erroneous cloud-physics applications of Raoult's law. Journal of Meteorology 10, 68-70.
- Nakagaki, M. & Heller, W. 1956. Effect of light scattering upon the refractive index of dispersed colloidal spheres. *Journal of Applied Physics* 27, No. 9, 975-979.
- Orr, C., Hurd, F. K., Hendrix, W. P. & Junge. C. E. 1958. The behavior of condensation nuclei under changing humidities. *Journal of Meteorology* 15, No. 2, 240-242.
- Stern, S. C., Zeller, H. W. & Schekman, A. I. 1962.
  Collection efficiency of jet impactors at reduced pressures. I & EC Fundamentals 1, 273-277.
  Winkler, P. 1967. Diplomarbeit. Mainz.

# ВЕЩЕСТВЕННАЯ ЧАСТЬ СРЕДНЕГО КОМПЛЕКСНОГО ПОКАЗАТЕЛЯ ПРЕЛОМЛЕНИЯ И СРЕДНЯЯ ПЛОТНОСТЬ ПРОБ АТМОСФЕРНОГО АЭРОЗОЛЯ

Такие специфические параметры, как число и размеры аэрозольных частиц, а также их показатель преломления, оказывают существенное влияние на расчет и физическую интерпретацию спектрального ослабления света в атмосфере. Как размеры, так и показатель преломления являются функциями относительной влажности. В течение последних лет было выполнено довольно большое число работ по исследованию спектра размеров частиц атмосферного аэрозоля, тогда как и показатель преломления изучен значительно меньше.

Была предпринята попытка устранить это несоответствие с помощью нового количественного метода одновременного измерения действительной части среднего комплексного показателя преломления и средней плотности частиц атмосферного аэрозоля. Этот

экспериментальный метод, а также первые предварительные результаты измерений изложены в настоящей статье. Среднее арифметическое из девяти измерений действительной части показателя преломления равно 1,57, для средней плотности 2,7 г/см3. Обе эти величины имеют место для относительной влажности  $0.40 \pm 0.05$ . Измерения были использованы для расчета зависимости обеих величин от относительной влажности. Выведены формулы для расчетов и представлены результаты вычислений для двух проб атмосферного аэрозоля: в то время, как относительная влажность изменялась от 0 до 1, в обоих случаях действительная часть показателя преломления менялась в пределах от 1,33 до 1,7, а средняя плотность — от 1г/см<sup>2</sup> до 4г/шм³.