THEORETICAL AND OPTICAL STUDIES OF HUMIDITY EFFECTS ON THE SIZE DISTRIBUTION OF A HYGROSCOPIC AEROSOL (*)

by

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RÉSUMÉ

L'effet de l'humidité sur le coefficient de diffusion de la lumière et l'effet correspondant sur la taille d'un aérosol de NaCl a été calculé et observé. Le rayon de l'aérosol a été calculé comme étant une fonction de l'humidité relative utilisant une équation d'adsorption physique pour les particules solides de NaCl et une combinaison de la loi de Raoult et de l'équation de Kelvin pour les gouttelettes de solution liquide. L'équation de Rayleigh a été utilisée pour calculer la proportion du coefficient de diffusion à une certaine humidité par rapport au coefficient de diffusion à une humidité nulle. L'augmentation prévue dans la proportion des coefficients de diffusion est entre un et deux ordres de grandeur pour la phase de transition d'une particule solide de sel à une gouttelette de solution saturée, qui concorde favorablement avec la proportion mesurée optiquement avec un néphélomètre intégrateur.

ABSTRACT

The effect of humidity upon the light scattering coefficient, and correspondingly the size, of a NaCl aerosol was calculated and observed. The aerosol radius was calculated as a function of relative humidity using a physical adsorption equation for the solid NaCl particles and a combination of Raoult's law and the Kelvin equation for the liquid solution droplets. The Rayleigh equation was used to calculate the ratio of the scattering coefficient at some humidity to the scattering coefficient at zero humidity. The predicted increase in the ratio of scattering coefficients is between one and two orders of magnitude for the phase transition of a solid salt particle to a saturated solution droplet, which agrees favorably with the ratio optically measured with an integrating nephelometer.

I. — INTRODUCTION.

The visibility of both natural and man-made atmospheres (such as stack plumes) is significantly dependent upon humidity. The increase in the size of a hygroscopic particle due to the sorption of water results in a substantial increase in the light scat-

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tering coefficient (especially in the Rayleigh scattering range) and hence a reduction in visibility. The effects of humidity upon aerosols are being studied optically and theoretically to : (a) relate visual range to humidity, (b) understand the processes causing visible steam plumes from stacks, and (c) gain information concerning the basic sorption processes on aerosol surfaces. A sodium chloride aerosol was used in the initial phase of this continuing study because of the previous investigations of this aerosol [1], [2].

II. — Theory.

The light scattering coefficients per particle were calculated as a function of original particle size (at zero relative humidity) and relative humidity. For the adsorption of water vapor onto a solid NaCl aerosol particle the following physical adsorption equation [3] was used to calculate the NaCl-H_2O particle radius :

$$r = \left[r_0^3 + \frac{[(r_0 + \Delta r_m)^3 - r_0^3]\, R_T\, e^{(E_1 - E_L)/RT}}{(1 - R_T)[1 - R_T + R_T\, e^{(E_1 - E_L)/RT}]} \right]^{1/3}$$

R_T is the percent relative humidity divided by 100. The other terms are defined at the end of this paper. For the absorption of water vapor by a salt solution droplet a combination of Raoult's law and the Kelvin equation was used to calculate the droplet radius as a function of relative humidity and original salt particle radius as presented below :

$$R_T = \left\{ 1 - i \left[\frac{\frac{1}{M_w}}{\frac{1}{M_s} - \frac{1}{M_w} + \frac{\rho_d\, r_d^3}{\rho_s\, r_p^3}} \right] \right\} e^{\frac{2\, M_w\, \gamma_d}{RT\, \rho_d\, r_d}}$$

The effects of humidity on the optical properties of an aerosol arises from changes in the size, refractive index, and possibly shape of the particles. For aerosol particles small in size compared to the wavelength ($r < 0.05\ \lambda$) the Rayleigh scattering equation can be used to calculate the light scattering coefficient as a function of particle size, refractive index, and wavelength of light. In this range the light scattering coefficient is proportional to the sixth power of the aerosol radius which thus provides a very sensitive measure of changes in the aerosol size. The Rayleigh scattering equation is valid for $2\ \pi r/\lambda$ less than 0.3. For calculating the scattering coefficients of the salt solution droplets the following equation, which is an extension to the Rayleigh scattering equation [4] and is valid to $2\ \pi r/\lambda = 0.8$, was used.

$$S = \frac{128\ \pi^5\ r^6}{3\ \lambda^4} \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \left[1 + \frac{12\ \pi\ r}{5\ \lambda} \left(\frac{m^2 - 2}{m^2 + 2}\right)\right]$$

III. — Experimental system.

Light scattering measurements were obtained using a system in which a sodium chloride aerosol was generated with a modified Dautrebande nebulizer, exposed to a controlled humidity, passed through a light scattering instrument, and then through a humidity measuring instrument. A schematic of the aerosol generating system is shown in Figure 1.

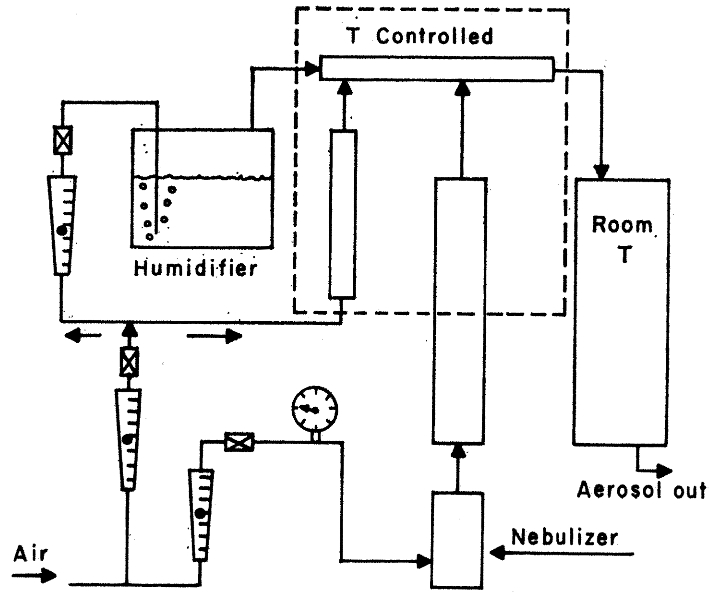

FIG. 1. — Aerosol Generating Flow System.

Solutions of from 0.01 to 0.3 % NaCl by weight were nebulized, passed into a heated chamber (T = 50° C), and mixed with a stream of moist air and a stream of dry air. The humidity of the aerosol was varied by changing the individual flow rates of the moist and dry air streams, yet maintaining the net diluent air flow constant so as to avoid changes in the aerosol concentration.

Two different instruments were used for measuring the light scattering coefficient of the NaCl aerosol, an aerosol photometer and an integrating nephelometer. The aerosol photometer, constructed for use in studies relating air pollution to visibility [5], [6], is of a standard two beam design, has a path length of 183 cm. and a sensitivity to about 0.03 % extinction. Some difficulties have been encountered due to minute deposits of NaCl aerosol on the photometer windows. These salt deposits tend to mask the effect of humidity upon the aerosol within the sample cell, probably due to capillary condensation upon the windows. The integrating nephelometer was designed with a minimum of windows to avoid this problem. This instrument, of which the original was devised about 1943 [7], measures the amount of light scattered. The main components of this device are a light source (xenon flash tube with an opal glass to act as a cosine diffuser) and a light detector (10 stage RCA 5891 photomultiplier tube). A schematic of the integrating nephelometer is shown in Figure 2.

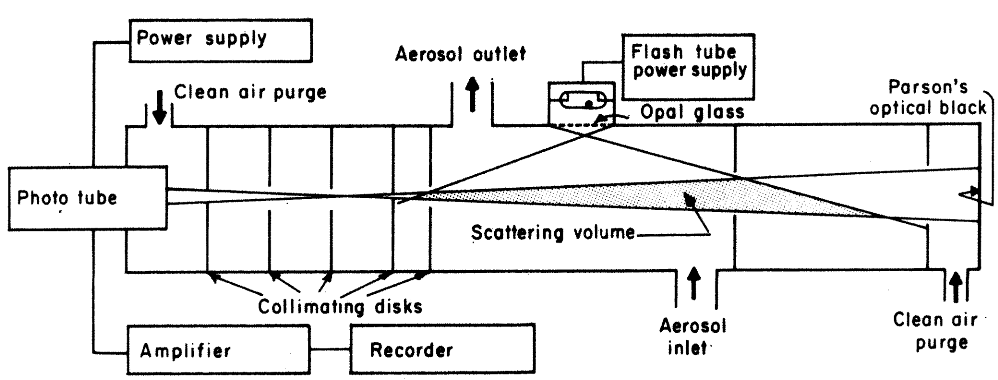

FIG. 2. — Integrating Nephelometer.

The very high sensitivity of the integrating nephelometer has been demonstrated by its ability to measure the difference in the scattering coefficient between particle free air and carbon dioxide at atmospheric pressure and 20° C. Although the nephelometer depends on the constant intensity of flashes from the xenon tube (which exhibits a variation of about 3%), the sensitivity and stability of the instrument are sufficient to observe the main features of the optical effects of humidity on a NaCl aerosol.

A liquid film hygrometer [8] was used for measuring the partial pressure of water (and hence the relative humidity at a constant temperature) of the aerosol system. This instrument depends upon the reversible sorption of water by a liquid (polyethylene glycol) contained in the dielectric of a capacitor. Careful operation and calibration permits measurement of the relative humidity at 20° C to about $\pm$ 1 %. The hygrometer is insensitive to the aerosol. A schematic of the hygrometer detector is shown in Figure 3.

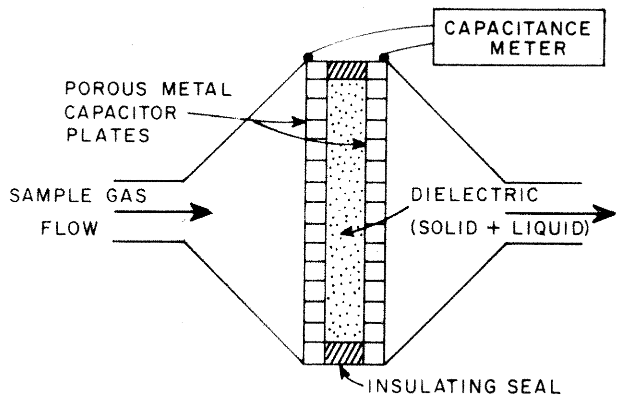

Fig. 3. — Liquid Film Hygrometer Detector.

IV. — Results.

The dependence of the radius of a NaCl aerosol particle upon relative humidity as calculated by a physical adsorption equation (solid-liquid particle) and as calculated by the Raoult and Kelvin equations (salt solution droplets) are shown in Figure 4.

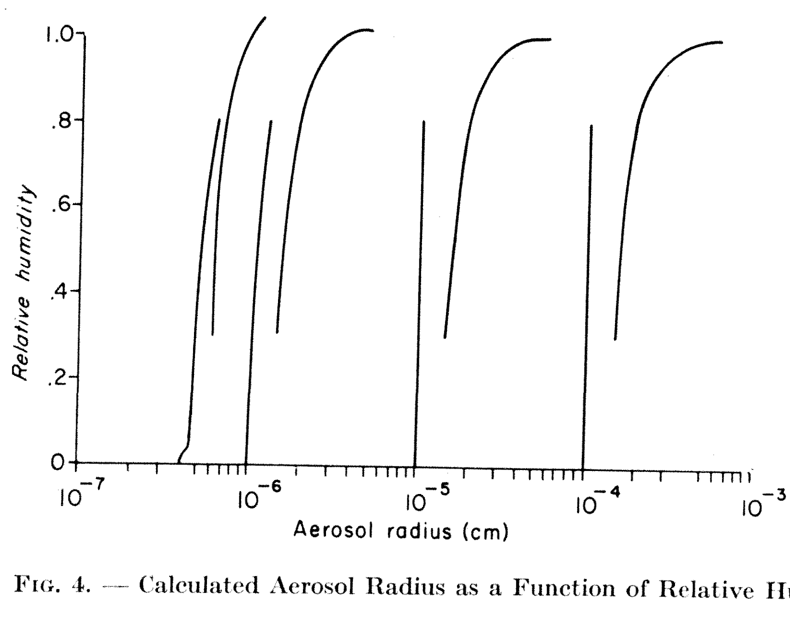

Fig. 4. — Calculated Aerosol Radius as a Function of Relative Humidity.

The point at which the solid to liquid transition occurs is not shown, however, it is known to be size dependent. Because the NaCl aerosol used in the experiments was not monodisperse, it is more significant to compare the calculated and measured light scattering coefficients. The ratio of the aerosol scattering coefficient at a certain relative humidity to the scattering coefficient at zero relative humidity is graphically presented as a function of relative humidity in Figure 5.

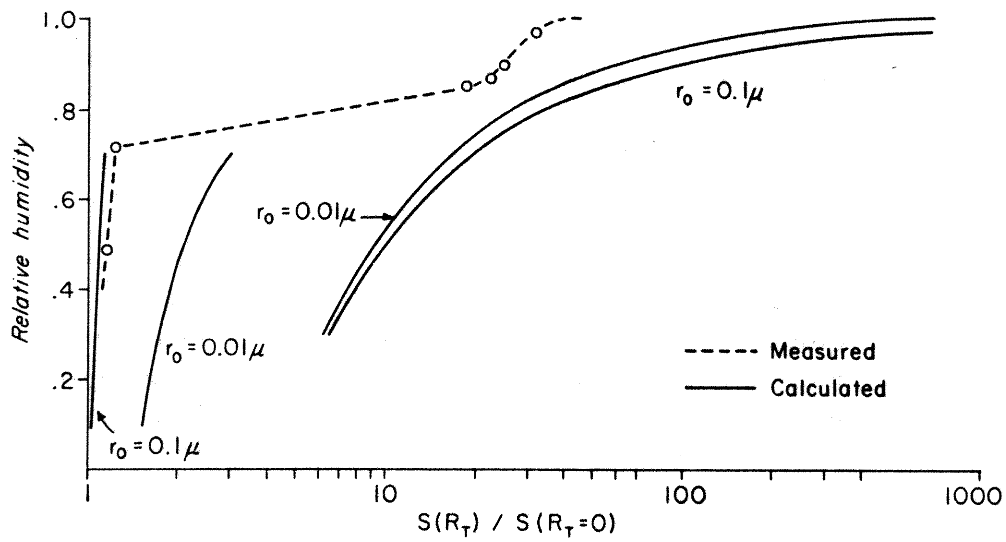

FIG. 5. — Ratio of Scattering Coefficients of Wet Aerosol to Dry Aerosol as a Function of Relative Humidity.

The calculated ratio of scattering coefficients shown in Figure 5 is approximately proportional (except for the change in refractive index) to the 6th power of the ratio of wet to dry aerosol radii.

At low humidity (solid particle region) some changes in the observed scattering coefficients were observed, however, the results were inconclusive and more measurements are to be made. At the high humidities (solution droplet region) the observed ratio of scattering coefficients was somewhat less than that calculated. This was the result of the NaCl aerosol size distribution extending beyond the range of applicability of Rayleigh scattering. At larger aerosol sizes ($2\pi r / \lambda > 0.5$) the scattering coefficient is proportional to the radius to a power less than 6 and thus the observed ratio of r_{wet}/r_{dry} would corresponding be less than $(r_{wet}/r_{dry})^6$.

Qualitatively the measured ratio of light scattering coefficients agreed favorably with those predicted by the sorption equations and the Rayleigh scattering equations. In particular, the transition from solid to liquid is easily detected. Thus it appears that this straightforward approach for describing the effect of humidity on the scattering coefficients (and correspondingly the aerosol size) of a hygroscopic aerosol is appropriate for this case of the Rayleigh scattering region.

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NOMENCLATURE

E_1	heat of adsorption of monolayer.
E_L	heat of liquefaction of adsorbing gas.
i	van't Hoff Factor.
m	refractive index.
M_s	molecular weight of salt.
M_w	molecular weight of water.
r	particle radius.
r_o	radius of dry particle.
r_d	radius of solution droplet.
Δr_m	thickness of monolayer of adsorbed gas.
R	universal gas constant
R_T	percent relative humidity /100.
S	light scattering coefficient.
$S(R_T)/S(R_T = o)$	ratio of scattering coefficient of wet particle to scattering coefficient of dry particle.
T	absolute temperature.
Greek Symbols.	
ρ_d	density of solution droplet.
ρ_s	density of salt.
λ	wavelength of light.
γ_d	surface tension of solution.

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