

NOTES AND CORRESPONDENCE

Direct Measurement of Contained Silver Iodide Aerosol Decay by Atomic Absorption Spectrophotometry

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1. Introduction

The nucleation effectiveness of a contained silver iodide aerosol tends to decrease with time presumably due primarily to particle agglomeration and deposition. It can be argued that the overall rate of change in the number of ice nuclei with time, \dot{n} , can be expressed by a differential equation involving the sum of two terms (Davies, 1966) of the form

$$\dot{n} = -k_1 n - k_2 n^2. \quad (1)$$

This equation involves the assumptions that the rate of deposition is first-order with respect to n and that the rate of agglomeration is second-order with respect to n . A further assumption is that the rate constants k_1 and k_2 are independent of n . The above model for AgI-aerosol decay has been neither confirmed nor rejected on the basis of reported experiments due to the previous difficulty of separating the two effects rigorously using cloud chamber data alone.

Reported in this note is a method for observing directly the concentration of silver iodide in an AgI-aerosol. The method is based on the application of atomic absorption spectrophotometry (AAS) to the direct determination of silver in air. A feature of the analytical method is that AAS is sensitive only to the concentration of silver, and thus the effect of agglomeration, e.g., an increase with time of the average mass per particle, has no effect upon the macroscopic concentration of silver iodide in the air sample. The time-rate-of-change in silver concentration is therefore a direct measure of the rate of deposition of AgI-aerosol particles upon the container walls. To demonstrate the application of AAS to the measurement of airborne silver in

the concentration range typical of certain weather modification activities, the rate of disappearance of silver iodide from AgI-aerosols contained in balloons of three different volumes was measured by AAS.

2. Experimental procedure

Since the analytical potential of AAS as recognized by Walsh (1955), the technique has received widespread application in analytical chemistry. In a report on the current status of AAS as a major analytical method, Lewis (1968) points out that more than 60 elements are being determined routinely in solution with approximately 3000 AAS instruments in the United States. However, the application of AAS to the direct determination of metal fumes in air, i.e., methods which do not employ an extraction step prior to analysis, has been made for only a few elements (White, 1967; Thilliez, 1967). The instrument used for this study is the Perkin-Elmer 303 atomic absorption spectrophotometer which is described by Kahn and Slavin (1963). The use of this instrument for the determination of airborne silver is described in the three paragraphs that follow.

Sampling technique. The three, approximately spherical, rubber weather balloons employed in this study were filled from the air-diluted effluent of a conventional ground-type silver iodide generator. A 10-liter syringe was used to fill the balloons to the rated capacities of 10, 20 and 40 liters, respectively. The measured initial ice-nucleation activity of the AgI-containing air samples was approximately 10^7 liter⁻¹ at -20°C , time being measured with reference to the time of filling. The

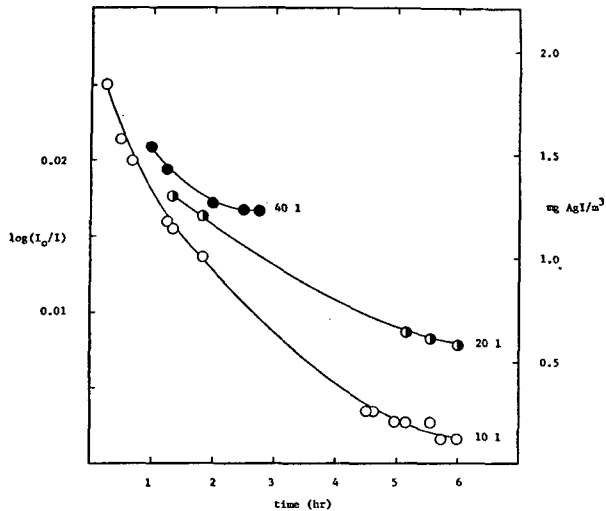


FIG. 1. Variation of AgI-aerosol concentration with time and container volume.

AgI-containing air was introduced into the spectrophotometer burner through the liquid nebulizer port at the rate of $0.24 \text{ liter min}^{-1}$ by means of a hypodermic-like needle piercing a rubber tube connected to the sample balloon. The connecting tube was fitted with a pinch-clamp to interrupt flow to the burner when desired. The balloons were clamped in place for spectrophotometric measurements to prevent false readings due to dislodgment of deposited AgI particles.

Spectrophotometer operation. Manufacturer's recommendations were followed regarding operation of the spectrophotometer for atomic absorption analysis of silver using the standard air-acetylene burner. The instrumental settings were the following: wavelength, 3280.7 \AA ; silver lamp current, 12 mA; air pressure, 28 psi; acetylene pressure, 8 psi; slit width, 0.3 mm; scale amplification not required. A potentiometric recorder was used to monitor the output of the instrument. A relatively short sampling period ($\sim 5 \text{ sec}$) was used for each data point to minimize the change in total balloon volume due to air withdrawal.

Calibration and data presentation. According to the Beer-Lambert relation, absorbance, $\ln(I_0/I)$, is directly proportional to the concentration of absorbing species in the optical path. Calibration was accomplished by measuring absorbance as a function of AgI concentration for a series 1 gm liter^{-1} KI in acetone solutions containing varying amounts of AgI. The relationship between $\ln(I_0/I)$ and the concentration of Ag [μg] was found to be linear over the concentration range $0.02\text{--}0.7 \mu\text{g Ag ml}^{-1}$. The concentration of silver in air was then calculated by equating, for a given absorbance, the mass-flow-rate of silver from solution, $\dot{m}_{\text{Ag}}(\text{soln})$, to the mass-flow-rate of silver from air,

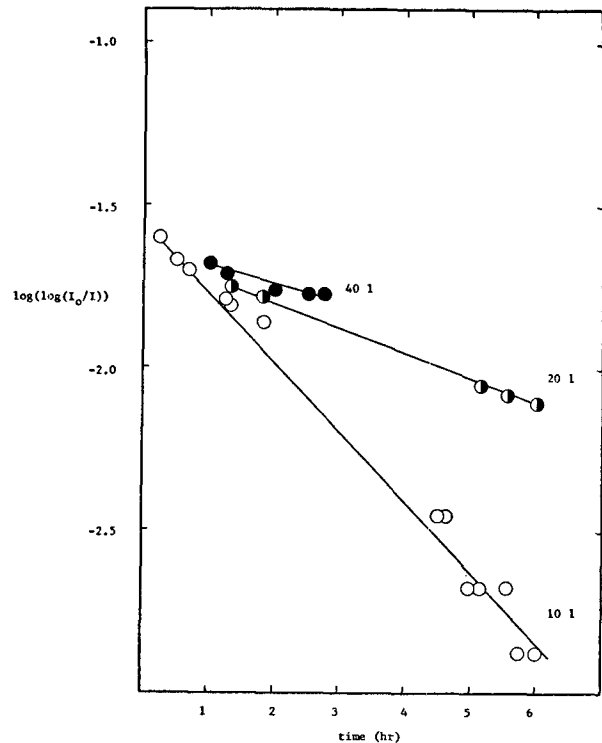


FIG. 2. Effect of container volume on AgI-aerosol first-order concentration decay.

$\dot{m}_{\text{Ag}}(\text{air})$. Thus,

$$\dot{m}_{\text{Ag}}(\text{air}) = \dot{m}_{\text{Ag}}(\text{soln}),$$

where $\dot{m}_{\text{Ag}} = c_{\text{Ag}}\dot{V}$, c_{Ag} is the concentration of silver [$\mu\text{g ml}^{-1}$], and \dot{V} the volume flow rate [ml min^{-1}]. Then

$$c_{\text{Ag}}(\text{air})\dot{V}(\text{air}) = c_{\text{Ag}}(\text{soln})\dot{V}(\text{soln}),$$

and

$$c_{\text{Ag}}(\text{air}) = c_{\text{Ag}}(\text{soln})\dot{V}(\text{soln})/\dot{V}(\text{air}). \quad (2)$$

Subsequent work,¹ in which calibration was accomplished by an air filtration technique, shows that the assumptions involved in (2) lead to a consistently high value for $c_{\text{Ag}}(\text{air})$. The data in Fig. 1, a plot of $\ln(I_0/I)$ vs time for each of the three balloons, are therefore corrected for the above error.

3. Discussion

Fig. 1 shows that the rate of contained AgI-aerosol concentration decay is apparently dependent upon container volume. Fig. 2 reveals, within experimental error, that the decay processes are first-order with respect to silver iodide concentration. Additionally, the

¹ Edwards, H. W., 1968: Direct determination of silver in air by atomic absorption spectrometry. Paper presented at Southwest Regional Meeting, Amer. Chem. Soc., Austin, Tex. Abstract in *Southwest Report*, 21, No. 4, p. 39A.

observed first-order decay constants increase in order of decreasing container volume as follows:

$$k_1(40 \text{ liters}) : k_1(20 \text{ liters}) : k_1(10 \text{ liters}) = 1.0 : 1.5 : 4.0$$

If it is assumed that the first-order decay process is due to wall deposition of silver iodide particles, it can be argued that the rate constant would be directly proportional to the surface area of the container and inversely proportional to the volume of the container. Assuming spherical geometry for the containers of this study, k_1 would then be expected to vary as $1/r$, where r is the radius of the balloon. Using this relationship to predict a semi-quantitative relationship among the rate constants for the three balloons, the following is obtained:

$$k_1(40 \text{ liters}) : k_1(20 \text{ liters}) : k_1(10 \text{ liters}) = 1.0 : 1.3 : 1.6$$

Although the simple area/volume model for the volume-dependence of the first-order rate constant can be used to predict the direction of the dependence, the simple model clearly fails to account for the observed semi-quantitative relationship among the rate constants. The basis for the discrepancy between the predicted and observed rate-constant correlations, however, is not immediately apparent from the data reported herein.

In addition to demonstrating that AAS can be used for the direct measurement of airborne particulates, in

this case silver iodide in finely divided form, this work suggests that atomic absorption data could be used effectively in conjunction with cloud chamber data to obtain an analytical expression for the overall time-rate-of-change in nucleation effectiveness for a contained silver iodide aerosol. Additionally, AAS provides a method for rigorously obtaining the economically significant correlation between mass and particle efficiencies for a silver iodide aerosol.

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