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# Determination of aerosol extinction coefficient and mass extinction efficiency by DOAS with a flashlight source*

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With the method of differential optical absorption spectroscopy (DOAS), average concentrations of aerosol particles along light path were measured with a flashlight source in Chiba area during the period of one month. The optical thickness at 550 nm is compared with the concentration of ground-measured suspended particulate matter (SPM). Good correlations are found between the DOAS and SPM data, leading to the determination of the aerosol mass extinction efficiency (MEE) to be possible in the lower troposphere. The average MEE value is about $7.6 m^2 \cdot g^{-1}$, and the parameter exhibits a good correlation with the particle size as determined from the wavelength dependence of the DOAS signal intensity.

**Keywords:** aerosol extinction coefficient, differential absorption optical spectroscopy, mass extinction efficiency, size distribution

**PACC:** 8670G

## 1. Introduction

The technique of differential optical absorption spectroscopy (DOAS) is based on differential absorption, i.e., the difference of maximum and minimum absorption of the probed gas species spectrum.[1] Recently, there has been growing interest in advanced techniques to monitor air pollution in city areas, particularly in Asian countries. Potentially, DOAS enables simultaneous monitoring of a variety of pollutants found in the atmosphere.[2−4]

In the DOAS method, light generally from a broadband xenon high-pressure lamp is transmitted a distance up to several kilometers in atmosphere. In the previous papers, we have demonstrated how to use an aviation obstruction light (white flashlight) in DOAS to monitor air pollution.[5,6] The optical thickness of $NO_2$ molecules and aerosol can be retrieved by detecting the transmitted light intensity from flash light source by using a simple telescope and a commercially available CCD spectrometer.

The study of urban aerosols is important for radiation budget and air pollution.[7] Aerosols are small airborne particles present in the troposphere and stratosphere in liquid or solid state, or as liquid droplets containing a solid nucleus. New aerosol droplets are produced by means of two different mechanisms. The first is the heterogeneous nucleation on solid materials (e.g. mineral dust, sea salt spray, soot in the troposphere or volcanic ash and soot, micrometeorites, aluminium oxide) in the troposphere and stratosphere,[8,9] and the second one is the homogeneous condensation of supersaturated gases.[10,11] These vapours can also arise from atmospheric gases by chemical reactions (e.g. sulfuric acid vapour from sulfur dioxide).

The purpose of the present paper is to report the aerosol information obtained from the flash-light DOAS measurements in Chiba, about 30km south-

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east of Tokyo along the east coast of Tokyo Bay. The aerosol optical thickness is measured in the wavelength range of 300–800 nm using a compact charge-coupled-device (CCD) spectrometer. The optical thickness at 550 nm is compared with the suspended particulate matter (SPM) concentration measured at a ground station. A good correlation of DOAS optical thickness with the ground SPM data is obtained. The DOAS signal in the wavelength range of 500–550 nm is employed to obtain the wavelength dependence of the optical thickness, usually expressed in the Angstrom parameter. And the mass extinction efficiency (MEE), defined as the ratio of the optical parameter (extinction coefficient) to the mass parameter (mass concentration), is given as well.[12–14]

## 2. Method of MEE measurement and aerosol retrieved

The DOAS technique is originally developed to investigate spectral signatures of trace species in the atmosphere, but the structureless extinction (i.e. the sum of scattering and absorption) of aerosol particles can also be retrieved from the measurement if the robust alignment of the system is reasonably maintained.[15] Because the intensity fluctuation due to the atmospheric turbulence is averaged afterwards, the resulting variation in the DOAS intensity is mainly due to the aerosol extinction. Since the length of the optical path is known, it is straightforward to convert the aerosol optical thickness to the average value of the aerosol extinction coefficient $\alpha_{\rm a}$ (in units of $\rm m^{-1}$). On the other hand, the aerosol (or SPM in the air-pollution studies) amount in optical path can be measured with conventional sampling methods such as the $\beta$-ray absorption method. This quantity is normally expressed in units of $\rm g{\cdot}m^{-3}$. The MEE parameter is obtained by the ratio of $\alpha_{\rm a}$ to the SPM concentration, and expressed in units of $\rm m^2{\cdot}g^{-1}$. The MEE is an essential parameter linking the mass concentration with the light scattering.

Recently, Lagrosas *et al*[16] pointed out that there exists a close relationship between the MEE parameter and the aerosol size parameter defined as $x{=}2\pi\lambda/r$ ($\lambda$ is the wavelength used in measurement and $r$ the radius of the aerosol particle). The size parameter dependences of MEE and the extinction efficiency $Q_{\rm ext}$,[16–20] are shown in Lagrosas's paper, from which an inverse correlation is evident between the size parameter $x$ and MEE, the so-called "size effect".[16] The dependence of MEE on $x$ is more or less similar among various types of aerosol particles. The decrease in MEE with the increase of $x$ is ascribable to the decrease in the light-scattering efficiency for larger particles.

With a continuously operated single-wavelength (532nm) lidar system, Lagrosas *et al*[16] studied the relationship of the SPM concentration with the aerosol extinction measured and the influences of size, rapid growth[20] and informed the mixture of aerosol particles[21] on MEE. In the present paper, DOAS is exploited to study MEE. Since the optical measurement is carried out in quite a wide range of wavelength, it is expected that the variation of MEE with the size parameter can be directly investigated. And the change of rapid growth effect with wavelength can be studied, too. It is possible to show that the effect manifests itself only in some range of wavelengths. Another important advantage of the DOAS measurement is that by using the wavelength range of 710–740 nm, for instance, the amount of water vapour along the optical path can be directly retrieved. This information will be of importance for the interpretation of the temporal variation of MEE.

The aerosol optical thickness $\tau_{\rm a}$ can be defined as

$$\tau_{\rm a} = \alpha_{\rm a} L = \ln k I_0(\lambda) - \ln I(\lambda) - \tau_{\rm Rayleigh}(\lambda) - \tau_{\rm gas}(\lambda). \quad (1)$$

Here $\alpha_{\rm a}$ is the extinction coefficient, $L$ is distance, $I_0(\lambda)$ is the spectrum of the light source observed at a location close to the light source. And $I$, the observed light intensity, and $\tau_{\rm gas}$, the gas absorption, can be obtained from the analysis of DOAS signals. The Rayleigh scattering, $\tau_{\rm Rayleigh}$, can be calculated from

$$\tau_{\rm Rayleigh}(\lambda) = 8\pi^3 (n-1)^2 / (3\lambda^4 N), \quad (2)$$

where $N$ is the air density and $n$ is the refractive index of air. After removing the contributions of the gas absorption and Rayleigh scattering, we can determine the aerosol optical thickness if the correlation factor $k$ is known. The visibility at 550 nm, $V$, can be calculated from Mie extinction coefficient using the well-known Koschmeider relationship:

$$V = 3.912/\alpha_{\rm a}. \quad (3)$$

In the general case the visibility of $V{=}$50km represents a typical condition for a relatively clear atmosphere. Since in Chiba, the distance of the DOAS measurement is 5.5km, $V{=}$50km leads to the aerosol optical

thickness of $\tau_a$=0.43. This value is used to empirically determine the system constant $k$. It is noted that when $V$ is changed by $\pm 10\%$, for instance, the value of $k$ changes only $\pm 2\%$.

The basic principle of the aerosol retrieval has been described in our previous paper,[5] the dependence of aerosol optical thickness $\tau_a(\lambda)$ on the wavelength $\lambda$ is assumed as follows:

$$\tau_a(\lambda) = B\left(\frac{\lambda}{550}\right)^A. \quad (4)$$

Here, constants $A$ (Angstrom exponent) and $B$ (turbidity constant, i.e. the aerosol extinction coefficient corresponding to the wavelength of 550 nm) are to be determined by fitting this expression to the optical thickness derived from the DOAS spectra. The aerosol extinction coefficient at 550nm is calculated by using the relationship of $\alpha_a$ (550) $=B/L$, and the mass extinction efficiency (MEE) is thus obtained by

$$\mathrm{MEE} = \alpha_a(550)/\rho, \quad (5)$$

where $\rho$ is the SPM concentration measured by ground sampling (with a $\beta$-ray detector).

## 3. Experiment

Figure 1 shows the schematic of experimental setup.[5] An astronomical telescope (Meade, DS-115) with an aperture diameter of 115mm images a point light source located at a far distance. The image goes into the entrance slit (5$\mu$m wide) of a CCD spectrometer (Ocean Optics, USB2000). This spectrometer (89mm wide$\times$63mm long $\times$34mm high) has a mechanically stable, crossed Czerny–Turner design with a fixed grating. The CCD array consists of 2048 elements and is very sensitive in the wavelength range of 200–800nm. The resulting resolution is 0.3nm per pixel. The CCD gate duration is set at 300ms in the experiment. Between successive gate periods, there exists a time lag of 7ms, in which each spectral data is sent to a personal computer (PC) through the universal serial bus. Data acquisition can be attained successfully even when no trigger (synchronous with the flashlight) is applied to the CCD spectrometer, though this relatively long gate time, as compared with the flashlight duration (about 0.5ms), causes somewhat increasing amount of the background skylight.

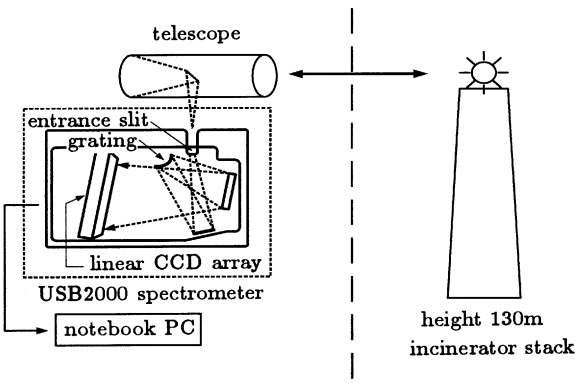



**Fig.1.** Experimental setup for measuring SPM.

In Chiba region, a xenon strobe (Sanken, FX-7) installed at the top of an incinerator stack (130m) is employed as the light source. Four lamps are mounted at the same height, each covering a horizontal range of 120° with the intensity of approximately 300W/sr. The distance from the source to the DOAS system is about 5.5km. The aviation-obstruction lamps flash for approximately 0.5ms every 1.5s. The light intensity is diminished at dusk and dawn, and during the nighttime blinking red lights replace the flashlights. Thus, the DOAS measurement is limited in daytime.

## 4. Results and discussion

In the aerosol retrieval from the DOAS data, we let the system constant $k$ be the value from the clear-day data. In Chiba dataset, we assume the data measured at 10:00 on 10 September 2004 to be the clear case, leading to a system constant $k$=9.0$\pm$0.2.

Figure 2(a) shows the correlation between the SPM concentration and aerosol optical thickness at 550nm and Fig.2(b) the correlation between the SPM concentration and aerosol extinction coefficient observed during the daytime on 11 September 2004. For both cases, good correlations are evident, and the MEE value is calculated to be about 5.6m$^2\cdot$g$^{-1}$.

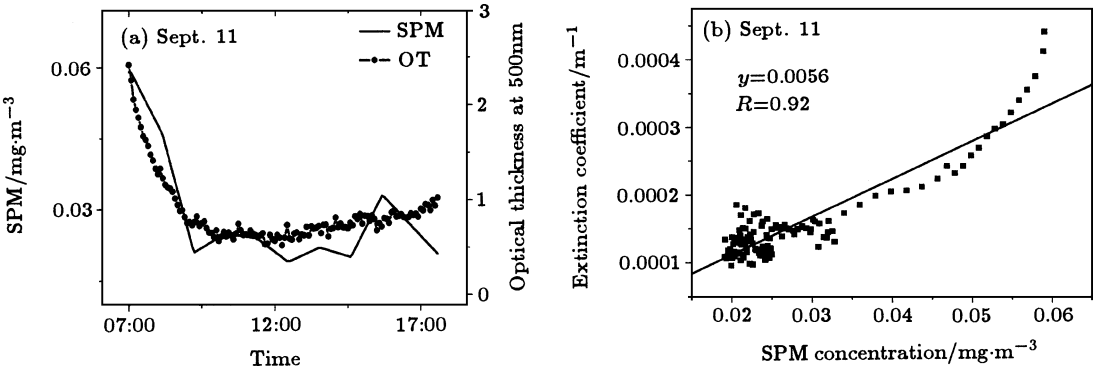



**Fig.2.** (a) Optical thickness data at 550nm and SPM data on 11 September 2004, and (b) the correlation plot to derive the MEE value (5.6m$^2$·g$^{-1}$).

The variations of MEE and the Angstrom exponent during a period of one month are shown in Fig.3, in which each data point represents an average of the diurnal data. Also a good correlation can be found between the two parameters. The Angstrom exponent is a good measure of the particle size, high and low values indicating the dominance of fine and coarse particles, respectively. The result in Fig.3 shows clearly that the particle size is influential to the value of MEE, as recently proposed as "size effect" on the MEE value.[16]

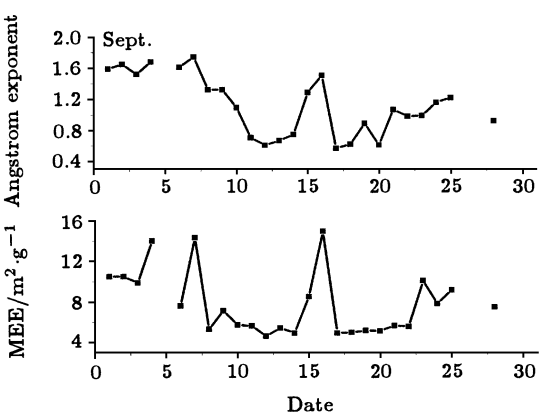



**Fig.3.** One-month variation of the MEE and Angstrom exponent in September 2004, leading to a correlation coefficient of about 0.83. The average value for the MEE data is about 7.6m$^2$·g$^{-1}$ and that for the Angstrom exponent is 1.1.

In DOAS system, we have measured the absolute humidity (AH) by using the wavelength range of 710–740nm, then RH can be obtained at a known temperature.

In Fig.4, one hour average values for MEE and RH are shown, and good correlation can be found between them. So, we can see that high RH is due to high MEE value, this has good fit to the "rapid growth" theory.

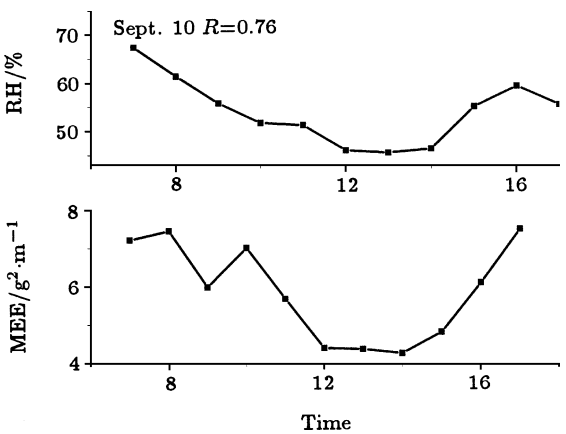



**Fig.4.** One-day variation of the MEE and RH in Sept. 10, leading to a correlation coefficient $R$ of about 0.76.

## 5. Conclusion

We have applied the pulsed DOAS technique to the measurement of tropospheric aerosols. Through a one-month campaign, for aerosol retrieval, the optical thickness at 550nm was compared with the concentration of SPM. A good correlation has been found between the DOAS and SPM data. This correlation makes it possible to analyse the MEE of aerosol particles in the lower troposphere. It is found that in September 2004, the monthly average value of MEE in Chiba is about 7.6m$^2$·g$^{-1}$. This relatively high value of MEE suggests the dominance of fine aerosols, though additional effect of the humidity should also be considered.

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