B-8.3 Studies on Chemical Composition and Optical Character for Aerosol Particles in Troposphere.

Contact person Hidenori Yoshiyama
Air Quality Measurement Div., Atmospheric Environmental Protection Dept.,
National Institute for Resources and Environment
16-3 Onogawa,Tsukuba,Ibaraki 305, Japan
Tel/Fax:0298-58-8283 E-mail:yoshiyama@nies.go.jp

Total Budget for FY1996-1998 ; 24,000,000 Yen (FY1998 ; 7,911,000 Yen)

Abstract

It was confirmed to be able to detect with real-time measurement at lowest concentration 1.2ppb of SO_2 gas. And, it could not to detected the nitrogen monoxide of 20.8ppb and the ammonia of 2.02ppm as the interfering substance. As the ammonium sulfate aerosol was measured, the reaults of this analyzer shown good agreement with an Electrostatic Aerosol Analysis. This results will be present the atmospheric environmental journal.

For the derivation of the optical characteristic of PSL particles, we developed the equipment which measure the scattering pattern. And, the size of PSL particles were derived by the regression analysis between the theory and the measurement data about extreme angles. The size and the refractive index about the smoke particle of mosquito coil were presumed within the range of 1.55-1.56 for real part.

In full consideration of the composition and number concentration of the troposphere aerosol, numerical analysis regarding the radiation budget of global scale for various physical factors was carried out, and it is found that the scattering effect of the interrupt of direct radiation influences stronger than the green house effect produced by troposphere aerosol.

Key Wards Aerosol, Composition analysis, Optical charactor, Temperature change,

1. Introduction

As the estimation about the equilibrium of the atmospheric radiation of the gloval scale, we cannot disregards the aerosol particles in the atmospheric with the cloud. Newly generated fine particles by photochemical reaction of gases such as SO_2 or NO_2 and the particles blown up from the volcanos were suspended in the stratosphere up to about 20km alutitude. However, although the whole nmber of stratospheric particles are a little, the concentration distribution extends global scale because of the residenca time is long remarkably. As the results, if the aerosol concentration and complex refractive index in the stratosphere had changed, the illuminance of the surface of all over the earth will changes, the temperature of the surface becomes change with the global scale too.

On the other hand, the distribution of particle concentration in the stratosphereare

limited as the time or space because of the particles are suspending a shot residence time such as a few week. But, the amount of particles are very much compare with tropospheric particles. As the particles are genetated continuously and global scale, and/or the radiative equilibrium of the global scale will become one of big problems, if the particles will be generates continuously for a long time.

For the measures of green house effects, it is importants that the compound of particles, the concentration and the optical characters are very useful to the simulation of claimate change. Those particles interrupts the light from the sun, and the temperature of surface of ground are decleased by the particles. It is concidered that the origins are the complex refractive index of particles as the factors.

2. Reseach Objective

From this views, the research objective are establishment of the real time measurement techniques for the sulfur compounds in the particles. For example, the particle containing the sulfuric acid which are concidered one of the most main compositions.

And we aims the establishment of the method of presuming an optical characteristic of complex refractive index.

Moreover, we will simulates the temperature change of the global scale base on the data base of actual particles under the assumed concentration and optical characters.

3. Research method and result

A. Chemical analysis of particles

① Analyzer of sulfite compound

The analysis of the Sulfuric acid mist based on chemiluminescence method was developed for composition analysis. The sample atmosphere is sucked with 200ml/min by the suction pump, and provides with the reactor which converts SO_2 into SO in first steps. The sulfur compound is converted SO_2 in this reactor, and SO_2 is transformed to reduce to SO by additional hydrogen gas of excessive. The SO is led to the chemiluminescence cell. The SO is reacted with O_3 in second step by next reaction.

$$SO + O_3 \rightarrow SO_2 + O_2$$

The ultraviolet light by chemiluminescence is detected by photomultiplier tube.

② Caliburation

The caliburation and sensitivity of equipment was made by SO_2 standard gas. The concentration of SO_2 and the output had a liner relation, and the max concentration is 95 ppb, minimum is 1.6 ppb. The calibration curve that maximum concentration 95 ppb and lowest concentration 1.6ppb were detected since the sulfur dioxide was diluted by standard air. The linearity was obtained as the noise is considered. It has been understood to be able to measure even 1.2ppb. Moreover, the result of repeat are shown the good and the steady from the same output in three time

measurements.

③ Ammonium sulfate

The ammonium sulfate aerosol by the spray drying method was generated, the concentration of the elemental sulfur by this device is measured and the result of compare with the Electrostatic Aerosol Analyzer (EAA) which measures the particle size distribution of the aerosol particle is discussed, and the number concentration of the elemental sulfur for each unit volume is shown. It is understood that there is a good correlation in this device and EAA. The case of ammonium nitrate aerosol was not detected because of which did not contain the elemental sulfur in the molecule.

④ Influence by pressure

It is concidered that an influence by the pressure of the cell when the sulfur monoxide is reacted with ozone in the chemiluminescence analysis by this device. The SO_2 gas of a constant concentration was reacted with ozone, and the emission intensity of chemiluminascence was measured by changing the pressure of cell using the control valve installed at the suction pump. As the pressure in the luminescence cell low, the sensitivity rised.

⑤ Interfering substance

The obstruction by the nitrogen monoxide and ammonia gases was examined. But, those gases were not detected at the concentration 20.8ppb of the nitrogen monoxide and 2.02ppm of the ammonia.

B. Optical Character for Aerosol Particles

A light-scattering instrument for rapid, single-particle sizing was developed. The light scattered by a single particle of PSL is measured with a photodiode array and the PSL particle diameter is estimated from Mie theory.

① Introduction

The particle size and refractive index are therefore the most important characteristics of standard particles used for calibrating optical instruments. Polystyrene Latex (PSL) particles are commonly used for calibration purposes. The nominal diameter of PSL particles quoted by manufacturers is determined by electron microscopy. Typically the particle size is determined by measuring the particle shape on the photograph, which leads to measurement error.

② Instrument

A continuous argon ion laser is used as the light source and is linearly polarized by a glan laser prism. The laser beam is focused by a convex lens of focal distance of 30 mm. A pump is used to draw particles into the sub-chamber. The pump is stopped, and the particles are drawn with a sub-pump from the pre-chamber to the scattering volume. A single particle is moved to the focal point of the laser beam through the upper flow nozzle, and is irradiated by the laser beam inside the small space of the

scattering volume. The scattered light from the single particle is detected with two linear photodiode array placed near the scattering volume and parallel to the light axis. Each photodiode array were placed the arrangement of vertical each other, and has 512 photodiodes, each 25 ㎛ wide and 2.5 mm high. The range of the scattering angle is from 53 to 127 degrees. The entire detector is controlled by a data acquisition control system, and 40 milliseconds and 1 kBytes of computer memory are required for each single scan.

③ Measurement of angular scattering pattern and estimation of size

a. PSL particles

The standard PSL particles of 1.696 were measured as a sample. Particles in the this size range have scattering patterns with few extrema, so the particle size was derived from the scattering patterns using Mie theory. The angular scattering pattern of light polarized perpendicular to the polarization plane, we investigated the estimation of particle size for light polarized parallel to the polarization plane. The theoretical intensities were computed using Mie theory with the refractive index of real part 1.5945 and imaginary part 0. The position of the extrema for the measured and theoretical intensities of a given particle size are not in good agreement. The difference of the theoretical maxima and minima is less than the difference of the corresponding measured maxima and minima. It is indicated that this particles were actually not 1.696 μ m in diameter. To determine the actual size of this particles, we calculated the scattering intensity for particles ranging in size from 1.645 to 1.665 μ m, at a size increment of 0.005 μ m

b. Smoke particles

From the refractive index and the size parameter which is most closely scattering pattern, the angle showing extrema and measurement data were compared each other.

As the results, the size parameter is 7.7 and the refractive index is 1.55 is the best fitted value. This value are good agree with a Okada's data. It is concidered that this method is correct. The calculated scattering pattern using the this factor estimated the scattered pattern in the parallel to the polarization of the laser light which is measured at the same time. It is found that the particle size and the refractive index estimated by this method were correct.

C. Numerical Simulation for the Global Climate Change

① Introduction

It is very difficult to determine whether aerosol particles have positive or negative GWP in stratosphere and troposphere. The tendency of aerosol on global warming is dependent on the environmental parameters and conditions, and it should be make clear numerically and experimentally. In this work, numerical simulation of the radiation budget regarding several kinds of qualitative and quantitative changes of cloud and aerosol was performed to obtain feasible prediction on the global climate change caused by so called greenhouse gases. Besides the numerical simulation, the models on aerosol

and cloud in numerical code were checked experimentally, and some modifications were proposed on the cloud model for Cirrus, because there has been a few reports on the feasibility of such models.

② Method

Numerical analysis was carried out with Lowtran7 regarding the radiation budget in global scale for various physical factors: the number concentration, composition and optical properties of atmospheric aerosols. Resulting effects of aerosol particles in a stratosphere and a troposphere were discussed with respect to the global temperature change for the variety of those physical factors of particles. Most numerical simulations were performed with LOWTRAN7 for the cases summarized in Table 1, and some were calculated with MODTRAN3.7. The differences between LOWTRAN7 and MODTRAN3.7 were also checked for several cases. Qualitative and quantitative changes of aerosol particles were taken place by changing the data on the extinction coefficients and the optical thickness in LOWTRAN7.

The feasibility of the cloud and aerosol models in MODTRAN3.7 was evaluated by comparing with measured irradiances. In the measurement, the total irradiance and visibility were obtained with two pyrheliometers and telephotometer set at Tanabe Campus of Doshisha University in Japan (34.6 ° N, 135.5 ° E) for more than 10 months. Both data were essential for the evaluation of adaptability of the code for the research on the global radiation. Meanwhile total irradiance and visibility, temperature, relative humidity, kinds of cloud, and cloudiness were also recorded simultaneously. The measured total irradiances were compared with the values by MODTRAN3.7, which were calculated with the same physical and environmental conditions. Sensitivity analysis of Modtran3.7 was also carried out for the parameters on the surface albedo, the cloud model and the visibility.

③ Results and discussions

Global increase of number concentration of atmospheric aerosols in stratosphere results in the decrease of surface temperature of earth due to the attenuation of solar irradiance by aerosols in atmosphere. The variation of refractive index and number concentration of aerosols in troposphere were also effective on the global temperature change; especially the particles having large extinction efficiency showed strong negative GWP as shown in Table 2 (a–c).

Seasonal change and daily variation of the irradiance between the measured and calculated ones fit well within the difference of 15% for all the cases. From the sensitivity analysis, the visibility and the surface albedo were not so important for the variation of irradiance. Averaged values of the calculated irradiance for the daytime agreed quite well with that of the measured one in low cloudiness, but not so well at the situation of higher cloudiness when the standard cirrus model was used. Most cloud models except cirrus model intercept the direct solar irradiance, however, the cirrus model lets through the direct solar irradiance considerably. In our experiment, the ratio

of direct solar irradiance was not so large even in the case of cirrus. The discrepancy between measured and calculated one was decreased satisfactory both for the seasonal and the daytime when the modified cirrus model, which model changed the thickness from 1.0 to 1.7km and altitude from 10 to 4.7km, was employed instead of the original one.

The large discrepancy in winter season was mainly due to the fundamental problem originating in the mechanism of bimetal used in the pyrheliometer. The reflectivity of white side of bimetal increases according to the decrease of incident angle of light, and the total difference of strain of the bimetal increases when the zenith angle becomes larger than 60 degrees.

④ Conclusion

It becomes clear that the enlargement of number concentration of atmospheric aerosols acts to the negative side in the global warming, and the GWP of atmospheric aerosols both in troposphere and stratosphere is negative in contrast to the several greenhouse gases. Thought a slight discrepancy still remained in the case of large zenith angles due to the structure of a pyrheliometer, the MODTRAN3.7 code would be feasible for the research on the global radiation budget. Still the special notice on the kind of cloud was kept in mind.

Table 1 Aerosol data for the simulation

	Case 1	Case 2	Case3
Stayed Position	Troposphere (Altitude 3 ~ 10km)	Troposphere (Altitude 3 ~ 10km)	Troposphere (Altitude 3 ~ 10km)
Stayed condition	Uniform in all the world	Uniform in all the world	Uniform in all the world
Chemical composition	Carbon aerosol	aerosol for Standard-1 MODEL	Carbon aerosol
Particle Density	Standard-1 MODEL×2	Standard-1 MODEL×2	Standard-1 MODEL
Stayed term	12 months	12 months	12 months

Table 2(a) Irradiance and the change of surface temperature of Earth by Case 1

Season	Irradiance [Wm^{-2}]	
	Standard-1	Case 1
Spring	542	507
Summer	523	490
Autumn	515	497
Winter	543	507
E	531	500
ΔT [K]	-11.5	

Table 2(b) Irradiance and the change of surface temperature of Earth
by Standard-1 and Case 2, Case1 and Case 3

Season	Irradiance [Wm^{-2}]			
	Standard-1	Case 2	Case 1	Case 3
Spring	542	534	507	529
Summer	523	518	490	513
Autumn	515	511	497	505
Winter	543	536	507	530
E	531	525	500	519
ΔT [K]	-2.2		-7.0	

Table 2(c) Irradiance and the change of surface temperature of Earth
by Standard-1 and Case 2, Case1 and Case 3

Season	Irradiance [Wm^{-2}]			
	Standard-1	Case 3	Case 1	Case 2
Spring	542	529	507	534
Summer	523	513	490	518
Autumn	515	505	497	511
Winter	543	530	507	536
E	531	519	500	525
ΔT [K]	-4.4		-9.3	