

Chemical composition and size distribution of atmospheric aerosols over the Deccan Plateau, India

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(Manuscript received May 27, 1980; in final form June 16, 1981)

ABSTRACT

Measurements on atmospheric total aerosol were made at Poona during the summer and winter seasons of 1978–79. An Andersen particle sampler Model 20-810, Mark II (Andersen 2000 Inc. U.S.A.) which samples atmospheric particles with diameters ranging between 0.4 and 10.0 μm was used for the measurement. The mass distribution of the total aerosol, and separately for the chloride, sodium, ammonium, sulphate and nitrate components were obtained.

The mass distribution of the aerosols exhibited a bimodal distribution in the size ranges 0.4–0.6 μm and 5–6 μm . The chloride and sodium components exhibited by and large a unimodal distribution. The ammonium and sulphate components exhibited a bimodal distribution during the monsoon and a unimodal distribution during the winter. The nitrate component exhibited a bimodal distribution during the monsoon and winter. The molecular form of this component appears to be ammonium nitrate in the sub-micron range and sodium nitrate in the higher size range (1–10 μm).

1. Introduction

Observations on the size distributions of atmospheric aerosols and their chemical components would be valuable for the understanding of the mechanisms of atmospheric aerosols and their role in the formation and growth of cloud drops. The size distribution of atmospheric aerosols have been studied by several investigators and the results reviewed (Twomey, 1977; Butler, 1979; and Penkett et al., 1979). However, information on the chemical composition of atmospheric aerosols is meagre, possibly due to the difficulties in fractionating and collecting sufficient materials for chemical analysis (Kadowaki, 1976). Such observations on the Indian sub-continent have been few, and hence measurements were undertaken during the summer and winter seasons of 1978–79 at Poona (18°32' N, 73°51' E, 559 m above m.s.l.) located in the Deccan Plateau in Maharashtra State. An Andersen particle sampler which samples atmospheric particles with diameters ranging between 0.4

and 10.0 μm was used for the measurements. The mass distribution of the total aerosol, and separately for the chloride, sodium, ammonium, sulphate and nitrate components were obtained. The relation between the size distribution of the aerosols and their chemical composition was studied as a function of maritime and continental air masses and the possible mechanisms for the formation of the atmospheric aerosols were studied. The results of the study are presented below.

2. Sampling and site

An Andersen particle sampler, Model 20-810, Mark II (Andersen 2000 Inc. U.S.A.) was used to sample the atmospheric total aerosol. The details of the sampler have been described by Andersen (1966). The sampler was operated at a constant flow rate of 28.3 l·min⁻¹. The sampler was installed on the terrace of the Institute's building at a height of about 12 m above ground level. The

atmospheric aerosol samples obtained from the above location are representative of the natural conditions since the observational site is free from obstructions and sources of local pollution. For the collection of sufficient material for chemical analysis, the sampling cycle of each observation was about 4–5 days. The sampler was also protected from rain by a suitable elevated shelter without disturbing the airflow.

3. Meteorological conditions

Poona is about 100 km away from the west coast. The airflow in the lower troposphere is predominantly westerly during the summer monsoon (June–September). A large influx of moisture is brought inland from the Arabian sea. The wind in the lower troposphere reverses with the withdrawal of the monsoon and an easterly flow sets in from October and continental air masses, rich in nuclei of continental origin, pass over the region. The characteristics of the monsoon circulation and rainfall have been reviewed by Ananthkrishnan (1977).

4. Analysis

Aerosols were collected on the stainless steel plates at different stages of the Andersen sampler. The deposits on each plate were scraped and transferred into glass beakers by washing with 50 ml doubly distilled water. The suspensions of each sample were heated and filtered after cooling. The filtrates were concentrated using infra-red lamps until the volume was reduced to 20 ml. The back-up filters containing the aerosols were cut into pieces and treated in the same way. The extracts obtained from the impactor plates and the back-up filters

were then analysed for chloride, sulphate, ammonium, nitrate and sodium. The chloride and sulphate ion concentrations were determined colorimetrically by using the mercuric thiocyanate method (Florence and Farrar, 1971) and the barium iodate method (Klockow and Ronicke, 1973) respectively. The ammonium and nitrate ion concentrations were determined colorimetrically by using the Berthelot colour reaction procedure (Weatherburn, 1967) and the brucine method (Jenkins and Medsken, 1964) respectively. The sodium ion concentration was determined by using the flame photometric method. The calibration curves for different chemical constituents were obtained by preparing standard solutions using analar grade chemicals. These calibrations were periodically repeated to obtain accurate results. The concentrations of different chemical constituents were obtained with reference to the blank solutions, and standard deviations were calculated. These results and the detection limits for various chemical constituents are given in Table 1.

The size distribution of the total aerosol was obtained from the manufacturer's calibration of the Andersen sampler. The effective cut-off diameters (ecd) for different stages of the sampler are given in Table 3. The mass of the aerosols collected on different stages of the sampler was obtained using an analytical microbalance. The cumulative mass percentages in different size ranges are obtained by dividing the amount of mass collected on each stage by the total amount of mass collected on all the stages. The details of obtaining the size and mass distributions of the aerosols were described by Andersen (1966). The ecd's of different stages of the sampler given in Table 3 were specified by the manufacturer for spherical particles of unit density. Ambient aerosols do not have such unique characteristics and thus leads to uncertainty in the size fraction actually collected (Butler, 1979). The

Table 1. Average concentration of different chemical components, and those of the blank along with the detection limit

	Cl ⁻	Na ⁺	NH ₄ ⁺	SO ₄ ⁻	NO ₃ ⁻
Average concentration ($\mu\text{g m}^{-3}$)	2.96	2.13	0.71	1.74	1.37
Concentration of blank ($\mu\text{g ml}^{-1}$)	0.55	0.35	0.03	0.15	0.15
	(0.05)	(0.05)	(0.01)	(0.04)	(0.02)
Detection limit ($\mu\text{g ml}^{-1}$)	0.15	0.05	0.01	0.10	0.10

Figures in brackets indicate standard deviations.

Table 2. Average concentrations and mass median diameters (mmd) of different components in the monsoon and winter seasons

Season	No. of samples	Total Aerosol		Chloride		Sodium		Ammonium		Sulphate		Nitrate		Cl/Na
		$\mu\text{g m}^{-3}$	mmd	$\mu\text{g m}^{-3}$	mmd	$\mu\text{g m}^{-3}$	mmd	$\mu\text{g m}^{-3}$	mmd	$\mu\text{g m}^{-3}$	mmd	$\mu\text{g m}^{-3}$	mmd	
Monsoon	12	73.5 (20.39)	1.40 (0.34)	4.30 (0.95)	2.40 (0.29)	3.31 (1.25)	2.40 (0.31)	0.74 (0.24)	1.50 (0.68)	2.00 (1.17)	1.50 (0.37)	1.32 (0.38)	2.30 (0.63)	1.3 (0.59)
Winter	18	125.6 (31.07)	1.20 (0.50)	1.62 (0.42)	2.10 (0.74)	0.95 (0.25)	2.20 (0.73)	0.68 (0.23)	0.60 (0.12)	1.48 (0.50)	0.90 (0.36)	1.41 (0.61)	1.50 (0.55)	1.7 (0.20)

Figures in brackets indicate standard deviations.

effect of the wind speed and the density of the aerosol particles on the particle collection efficiency were discussed by Butler (1979).

5. Results

5.1 Atmospheric total aerosol

The average mass of the atmospheric total aerosol during the monsoon and winter seasons was found to be $73.5 \mu\text{g m}^{-3}$ and $125.6 \mu\text{g m}^{-3}$ respectively. The average mass median diameter (mmd) in the monsoon and the winter was $1.4 \mu\text{m}$ and $1.2 \mu\text{m}$ (Table 2) respectively.

A typical example showing the cumulative mass size distribution for 27 July–4 August 1978 is shown in Fig. 1. From hereon, the mass size distributions are referred to as size distributions. The size indicates diameter of the particle.

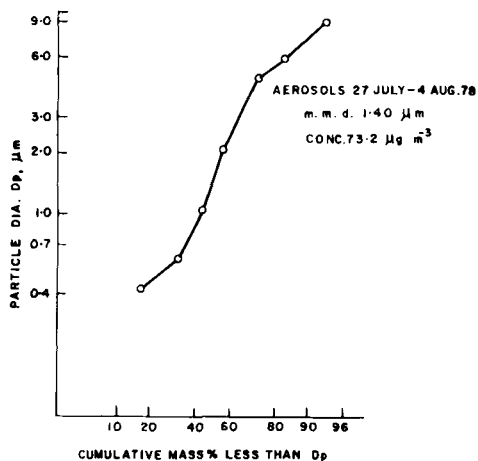


Fig. 1. Cumulative size distribution curve for total aerosol during the monsoon.

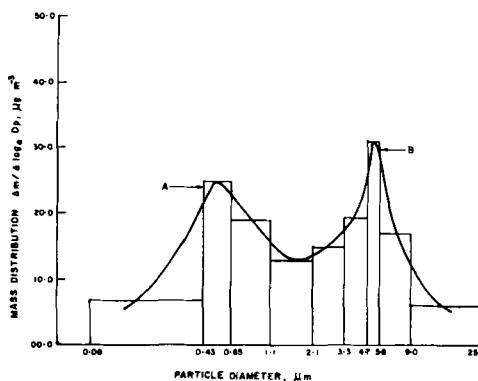


Fig. 2. Typical example of the histogram and size distribution for total aerosol (27 July–4 August 1978).

There were no significant variations in the distributions during the observation period. A typical example of a distribution based on the data sample obtained between 27 July and 4 August 1978 is shown in Fig. 2. The computations of the size distributions shown in Fig. 2 were based on the method of Kadowaki (1976) and the details are given in Table 3. The size distribution exhibited two modes which were, by and large, log-normal. The diameters of the particles in the first (A) and second (B) modes were $0.4\text{--}0.6 \mu\text{m}$ and $5.0\text{--}6.0 \mu\text{m}$ respectively. The mean distributions suggested that the total aerosol particles were predominant in mode A during the winter, and in mode B during the monsoon.

5.2. Chloride and sodium

The average concentrations of chloride and sodium were significantly higher during the monsoon than during the winter. There is no significant change in the mmd's of chloride and sodium between the monsoon and the winter (Table 2). The value of the ratio Cl/Na was 1.3 during the

Table 3. Determination of histogram and size distribution curves of total aerosol

Impactor stage no.	50% e.c.d. (μm)	Concentration of total aerosol Δm ($\mu\text{g m}^{-3}$)	$\Delta \log_e D_p^*$	$\Delta m / \Delta \log_e D_p$ ($\mu\text{g m}^{-3}$)
0	9 (<25)	6.1	1.0	6.1
1	5.8	7.4	0.439	16.7
2	4.7	6.4	0.210	30.6
3	3.3	7.1	0.350	20.3
4	2.1	6.7	0.451	14.9
5	1.1	8.6	0.646	13.3
6	0.65	10.1	0.525	19.3
7	0.43	10.4	0.412	25.3
Back-up filter	(0.08)	12.6	1.68	7.5

* $\Delta \log_e D_p = \log_e D_{p_{n+1}} - \log_e D_{p_n}$, D_{p_n} = value of 50% e.c.d. of nth stage.

Table 4. Mole ratios and percentage contributions by different constituents of the fine (>0.1–<2 μm) and coarse (>2–<10 μm) size aerosols during the monsoon and the winter seasons

Season	Mole ratio Cl/Na		Percentage contribution				Mole ratio NH_4/SO_4		Percentage contribution			
	Fine	Coarse	Fine		Coarse		Fine	Coarse	Fine		Coarse	
			Cl	Na	Cl	Na			NH_4	SO_4	NH_4	SO_4
Monsoon	1.08	1.05	45	45	55	55	2.03	1.80	56	55	44	45
Winter	1.10	1.08	53	51	47	49	2.60	1.82	81	71	19	29

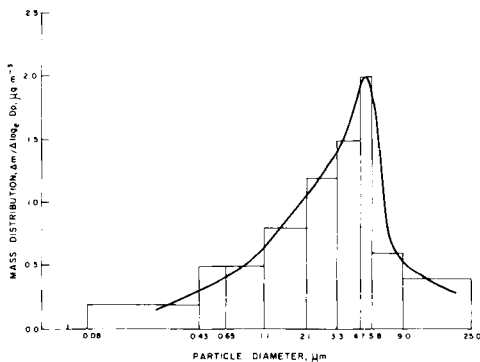


Fig. 3. Histogram and size distribution for chloride (28 August—2 September 1978).

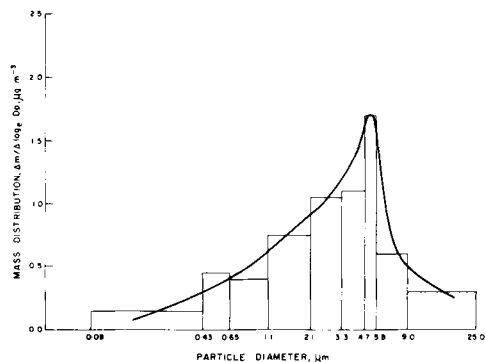


Fig. 4. Histogram and size distribution for sodium (28 August—2 September 1978).

monsoon and 1.7 during the winter. The mole ratio of Cl/Na in the sub-micron and coarse aerosols during the monsoon and the winter seasons was around one (Table 4). Figs. 3 and 4 show the distribution curves for chloride and sodium respectively. The distributions were approximately log-normal and showed a unimodal distribution which

was in good agreement with mode B of the size distribution curve for the total aerosol (Fig. 2). The cumulative mass distributions of sodium and chloride during the monsoon are shown in Fig. 5. There is close agreement between the two distributions. The concentrations of chloride and sodium at Poona are markedly larger than those reported

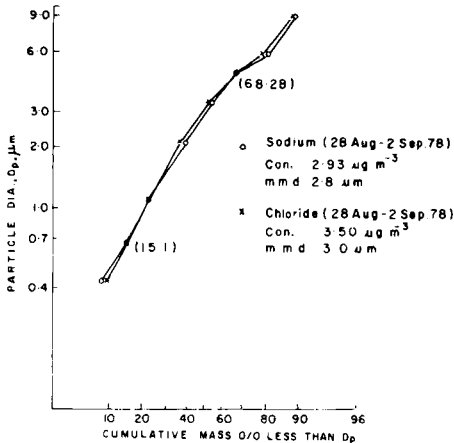


Fig. 5. Cumulative size distributions for sodium and chloride (monsoon).

for Sudan (Penkett et al., 1979). The higher concentrations observed at Poona are due to the maritime influence in the region.

5.3. Ammonium and sulphate

The average concentration of ammonium did not show a marked difference between the monsoon and winter, but sulphate showed a difference which is about 25% less in winter (Table 2). The mmd's of these two components exhibited differences between the two seasons, and the differences are significant according to the Mann-Whitney test. The

mmd's of ammonium and sulphate during the monsoon were the same (1.5 µm).

The distributions representative of the monsoon and winter conditions are shown in Figs. 6 and 7 respectively. The curves exhibited a bimodal distribution during the monsoon and a unimodal distribution during the winter.

The cumulative mass distributions of ammonium and sulphate for the monsoon and the winter are

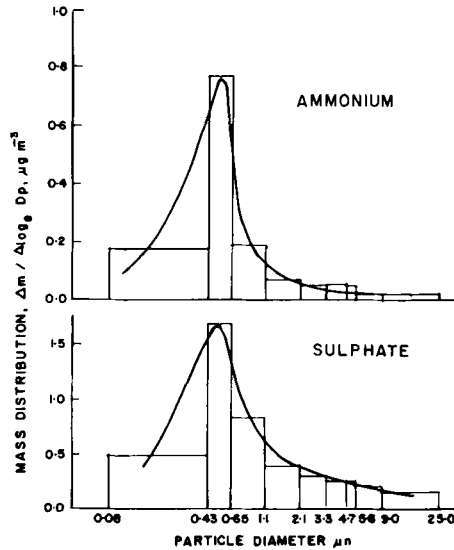


Fig. 7. Histogram and size distribution for winter condition (21-25 November 1978).

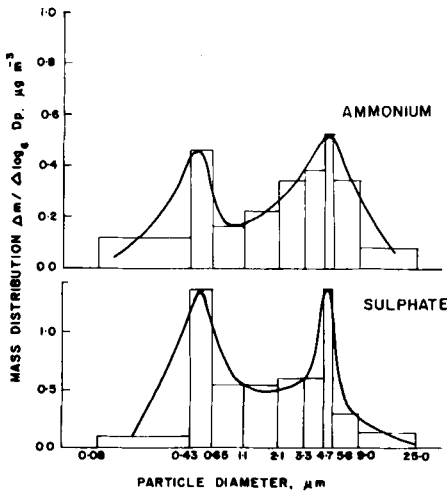


Fig. 6. Histogram and size distribution for monsoon condition (25-26 July 1978).

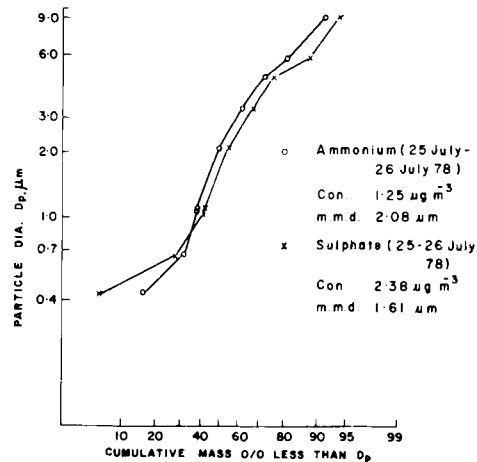


Fig. 8. Cumulative size distributions for ammonium and sulphate (monsoon).

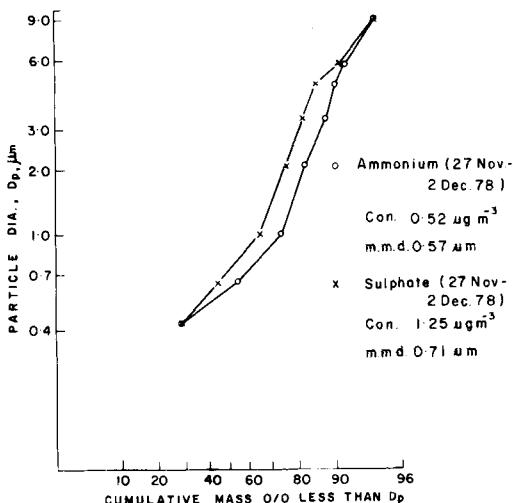


Fig. 9. Cumulative size distributions for ammonium and sulphate (winter).

shown in Figs. 8 and 9 respectively. The agreement between the distributions is better in the monsoon than in winter in the higher size range (0.7–0.6 µm). The percentage contribution of coarse size aerosols (2–10 µm) was greater in the monsoon, whereas that of fine size aerosols (0.1–2 µm) was greater in winter (Table 4).

At Poona, the concentration of ammonium is slightly higher and the sulphate concentration slightly lower than that reported for the Sudan (Penkett et al., 1979). These differences were due to differences in the local anthropogenic processes.

5.4. Nitrate

The average concentration of nitrate showed no marked difference between the monsoon and the winter (Table 2). However, the mmd's differed, being 2.3 µm in the monsoon and 1.5 µm in winter. The difference in the mmd's was significant. Also, a significant correlation between relative humidity and mmd was observed ($r = 0.4$, significant at 5% level). A sample histogram, representative of the monsoon conditions, is shown in Fig. 10. The distribution was bimodal.

The cumulative size distribution curves for sodium and nitrate are shown in Fig. 11. There is good agreement between the two distributions. A significant correlation between ammonium and nitrate was observed during the winter ($r = 0.72$, significant at less than 1% level). No such correlation was observed during the monsoon.

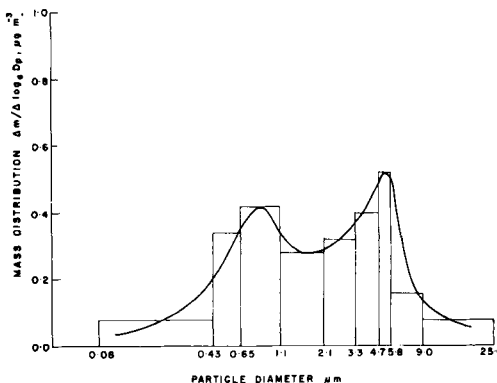


Fig. 10. Histogram and size distribution for nitrate (25–29 September 1978).

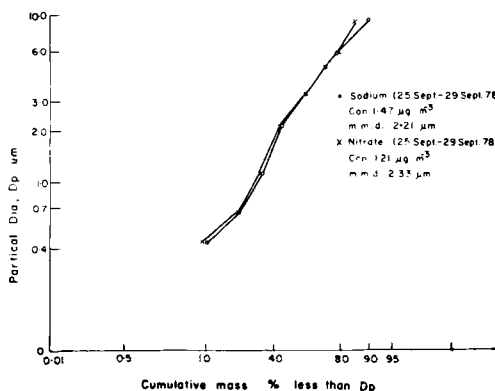


Fig. 11. Cumulative size distributions for sodium and nitrate (monsoon).

The concentration of nitrate at Poona is lower than that reported for Sudan (Penkett et al., 1979) which may be due to differences in the sources of these particles.

6. Discussion

The concentration of the total aerosol in the surface air layers at Poona was found to be higher during the winter than during the monsoon by over 70%. This feature is attributable to the transport of aerosols of continental origin by the air masses travelling over land from the east. The higher value of the mmd and the predominance of aerosols in the size range 5–6 µm (B mode) observed during the monsoon are consistent. During this period, the

region will be under the influence of maritime air masses which transport giant size aerosols from the Arabian sea.

6.1. Chloride and sodium

The average concentrations of chloride and sodium were significantly higher during the monsoon. The cumulative size distributions of chloride and sodium showed good agreement (Fig. 5). The mole ratio of Cl/Na for fine and coarse aerosols during both seasons was around 1. Also, the correlation coefficient between chloride and sodium was significant ($r = 0.89$). This feature suggests that a good fraction of chloride and sodium are present in the atmosphere in the form of sodium chloride. The size distributions of chloride and sodium were approximately log-normal and were in good agreement with mode B of the curve for total aerosol. This observation indicates that chloride and sodium are mostly present in the giant size range, which is in agreement with the reported findings by other investigators (Junge, 1963; Meszaros, 1968).

6.2. Ammonium and sulphate

The cumulative size distribution curves of ammonium and sulphate showed better agreement during the monsoon (Fig. 8) than during the winter (Fig. 9). The mole ratio of ammonium to sulphate during the monsoon and the winter in the case of coarse aerosol was around 2, whereas in the case of the fine aerosols during the winter it was 2.6. Quantitative chemical analysis (Table 2) suggests that the mass ratios of ammonium to sulphate during the monsoon and winter seasons are 0.37 and 0.46 respectively. The ratio value 0.37 nearly corresponds to the molecular formula $(\text{NH}_4)_2\text{SO}_4$. Therefore it follows that during the monsoon season the molecular composition of the particles is in the form of ammonium sulphate and during winter the particles may exist in different molecular forms.

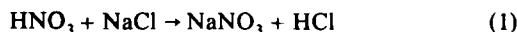
The histogram and size distribution curves of ammonium and sulphate exhibit bimodality during the monsoon (Fig. 6). The average value of the mmd of ammonium was higher by 150% during the monsoon (Table 2). The average values of the relative humidity during the monsoon and winter seasons are $>80\%$ and $<50\%$ respectively. Laboratory experiments on different sulphate particles suggest that the size of the ammonium

sulphate particles increases with relative humidity (Ahlberg and Winchester, 1978). The higher values of the mmd observed during the monsoon thus appear to be consistent with this.

6.3. Nitrate

The size distribution curve of nitrate aerosols (Fig. 10) was similar to that of the total aerosol (Fig. 2). The mean size distributions of nitrate aerosols were bimodal during both the seasons. The percentage contribution of nitrate aerosols in the sub-micron size range was greater during winter than monsoon by 57%, whereas, in the coarse range, it was greater by 24% during the monsoon. It is considered that the sub-micron aerosols may have originated from the gas-to-particle conversion process and the coarse aerosols from the wind erosion process (Whitby, 1978). The above observation suggests that the origin of nitrate aerosols in the two modes could be different. The possible mechanisms are indicated below.

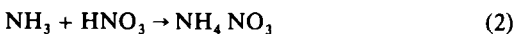
According to Green (1972) nitrate particles can form due to the following reaction:



Formation of HNO_3 in the atmosphere may take place through a number of mechanisms. One of the probable mechanisms could be due to oxidation of NO_2 either by ozone or OH^- radicals (Penkett et al., 1979). Other mechanisms include the formation of HNO_3 due to chemical reactions between NO or NO_2 and the water vapour present in the atmosphere (Vohra et al., 1970).

The average mmd of the nitrate aerosols during the monsoon was significantly higher than during the winter. Since the size of sodium nitrate aerosols, formed by reaction (1) will be in the range $1-10 \mu\text{m}$ (Kadowaki, 1977), the aerosols in the B mode may largely consist of sodium nitrate. The close agreement between the size distribution curves of sodium and nitrate (Fig. 11) further supports this inference.

The nitrate particles in the sub-micron size range may be made up of a different composition. Since ammonium nitrate exists in the sub-micron size range (Kadowaki, 1977) it is considered that formation of nitrate may take place through the following reaction:



The present observations showed a significant correlation ($r = 0.72$ significant at less than 1%

level) between ammonium and nitrate which indicates the possibility of reaction (2).

7. Conclusion

A study of the chemical composition and the mass size distribution of total aerosol at Poona, located in the Deccan Plateau, suggested the following:

(1) The average mass of the total aerosol was lower during the monsoon than during the winter. The distribution was bimodal in both the seasons. Aerosols are predominant in the coarse size range during the monsoon and in the sub-micron size range during the winter.

(2) Chloride and sodium were found in the giant size range.

(3) Ammonium and sulphate exhibited bimodal distribution during the monsoon and unimodal distribution during the winter.

(4) Nitrate exhibited a bimodal distribution both during the monsoon and the winter. In the sub-micron range it could be present in the form of ammonium nitrate formed through the reaction between ammonia and nitric acid. In the coarse size range, it could be present in the form of sodium nitrate formed through the reaction between sodium chloride and nitric acid.

8. Acknowledgement

The authors wish to thank Dr A. S. R. Murty for useful suggestions.

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