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The Mechanism of Seasonal Variation in the Size Distributions of Atmospheric Chloride and Nitrate Aerosol in Tokyo

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The volatility of ammonium chloride and nitrate was demonstrated to be responsible for the seasonal variation in size distributions that is the atmospheric fine-mode (<2 μm) chloride and nitrate aerosol were predominant in winter, but the coarse mode (>2 μm) was more pronounced in summer. An ion-balance examination and heating of winter aerosol samples demonstrated that fine-mode chloride and nitrate species are ammonium salts which are volatile at summer atmospheric temperatures. Both volatilized and unvolatilized concentrations of these chloride and nitrate species were determined both in winter and in summer to prove that the gas-solid interconversion took place in the atmosphere. The log-normal distributions of the ionic-component concentrations and the seasonal changes in the ionic composition of fine-mode aerosol were also discussed.

Chloride, like sulfate and nitrate[1,2] is one of the major ionic components of atmospheric aerosol. As yet, however, sufficient attention has not been paid to this component compared with sulfate and nitrate. Chloride has been considered to be of natural origin, such as sea spray and volcanic emission, whereas sulfate and nitrate have been studied in connection with photochemical air pollution and acid precipitation problems. Recently, however, the direct emission of hydrochloric acid associated with the burning of fossil fuels and of municipal refuse was noted, along with chlorine loss during the breakdown of seasalt by photoxidation with nitrogen dioxide along with aldehydes and through acidic displacement reactions.[3] Some of the HCl emitted into the atmosphere is expected to be transformed into ammonium chloride, which has been directly identified by means of X-ray diffraction analysis[4,5] or the IR spectrometry[6] of atmospheric aerosol, and has been speculated to exist in atmospheric aerosol on the basis of the observed seasonal trends in the chloride concentration[7,8] and in ammonium and nitrate losses from high-volume glass-fiber filters stored at room temperature.[9]

In the study of atmospheric aerosol, size distribution is a fundamental physicochemical parameter, like component concentrations, for the particle size is closely related to the source and restricts its aerodynamic behavior.[2,10,11] The size distribution of an aerosol mass is generally composed of fine (<2 μm) and coarse (>2 μm) modes, with a distribution minimum at about 1—2 μm. The coarse-mode aerosol is directly emitted into the atmosphere, as seasalt aerosol and soil dust, for instance, whereas the fine is formed through gas-to-particle conversion, as sulfuric acid mist and automobile exhaust particles, for example. The fine- and coarse-mode concentrations are, however, essentially independent of each other.

Size-fractionated sampling and subsequent analysis has recently become a common procedure in aerosol chemistry. While there is a value in short term monitoring exercises, a full picture can only be drawn from data collected over lengthy periods.

On the basis of our June 1979—July 1982 observations in Tokyo, using an 8-stage Andersen sampler, we have discovered a seasonal variation in the size distribution of chloride aerosol and that the variation is air-temperature dependent.[7] The fine mode is predominant in winter, whereas the coarse is predominant in summer, which was comparable with the seasonal variation in the nitrate size distribution.[12,13] Similar seasonal changes have been noted in the U.S.[14] and England.[15]

We interpreted this variation as being due to the temperature dependence of the volatility of the chloride under the assumption that it was present as ammonium chloride.[7,8] A general review of this observation was given in a previous publication.[7]

This paper will report a further analysis of the data and experiments with collected aerosols in order to understand the variation mechanism of the distribution of chloride aerosol and to evaluate its significance in aerosol chemistry.

Experimental

The procedures have been described in detail elsewhere.[7,16] Aerosol was collected onto Teflon filters (Sumitomo Denko, Fluoropore FP 065) using an 8-stage Andersen sampler (Koritsu, KA-200P) on the rooftop (24 m) of the Institute of Public Health, about 3 km west of Tokyo Bay (Fig. 1). The water soluble components were extracted with an ion-chromatography eluent (0.0030 $\mathrm{mol\,dm^{-3}}$ $NaHCO_3$-0.0024 $\mathrm{mol\,dm^{-3}}$ Na_2CO_3) in an ultrasonic bath and were analyzed by two procedures: ion chromatography for chloride, nitrate, and sulfate (Dionex, System 10), and indophenol blue spectrophotometry for ammonium (Jasco, UV-1).[17]

Hydrochloric and nitric acids and ammonia in the atmosphere were sampled over the period from July, 1981, to February, 1982, with cellulose filters impregnated with

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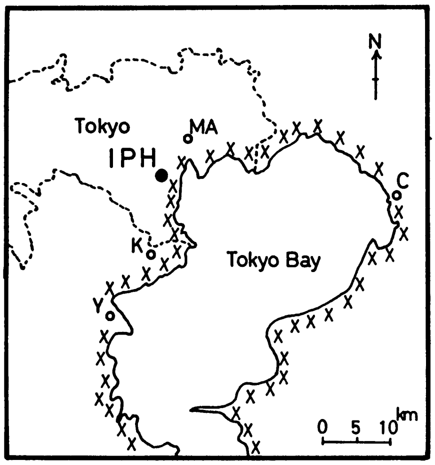

Fig. 1. Location of the sampling site: IPH, the Institute of Public Health; MA, Meteorological Agency; Y, Yokohama City; K, Kawasaki City; C, Chiba City. The coastal areas on Tokyo Bay are industrialized (x).

sodium carbonate, sodium chloride, and oxalic acid respectively.[17] Each of the gases was extracted with doubly-distilled water and determined by means of spectrophotometry: the mercury(II)-thiocyanate, the hydrazine-reduction, and the indophenol-blue methods for hydrogen chloride, nitric acid, and ammonia respectively.[17]

Results and Discussion

Temperature Dependence of the Fine Fraction. The size-distribution data were quantitatively analyzed as a function of the temperature. The distribution pattern was quantified by defining an index, "Fine Fraction" (FF), as $F/(F+C)$, where C and F represent the concentration sums of Stages 0—4 (coarse mode) and Stage 5 to the backup filter (fine mode), because the 50% effective cutoff diameters (ECD) for Stages 4 and 5 are 2.1 and 1.1 μm respectively.

Each value of FF was plotted as a function of the temperature for chloride and nitrate (Fig. 2) and for sulfate and ammonium (Fig. 3). The mean temperature in the sampling period was calculated from the daily mean data determined by the Meteorological Agency in Chiyoda-ku, 6.5 km northeast of the sampling site (Fig. 1). As is shown in Fig. 2, the FF's for chloride and nitrate were evidently temperature-dependent; they increased drastically with a decrease in the temperature. In contrast, sulfate and ammonium exhibited fine-mode-dominant distribution irrespective of the temperature (Fig. 3).

Temperature Dependence of Fine- and Coarse-Mode Concentrations. A high FF value will be a result either of a high fine-mode concentration or of a low coarse-mode one. The fine- and coarse-mode concentrations were plotted against the temperatures for chloride and nitrate. The fine-mode chloride concentration was temperature-dependent, similar to the FF for chloride (Fig. 4 (a)). However, coarse-mode chloride seemed to demonstrate the opposite temperature dependence, but with a narrower variation range than that of the fine mode (Fig. 4 (b)). The concentration slightly increased with the temperature. Similar features appeared in nitrate (Fig. 5(a) and (b)), where the fine-mode concentrations also controlled the size distribution. We interpret these data for both anions as indicating that, schematically, the fine-mode concentration decreased profoundly with the temperature, while the coarse-mode concentration increased when the temperature rose within a limited variation range compared with those of the fine mode.

No attempts seem to have been made to discuss the concentrations of either chloride and nitrate in each

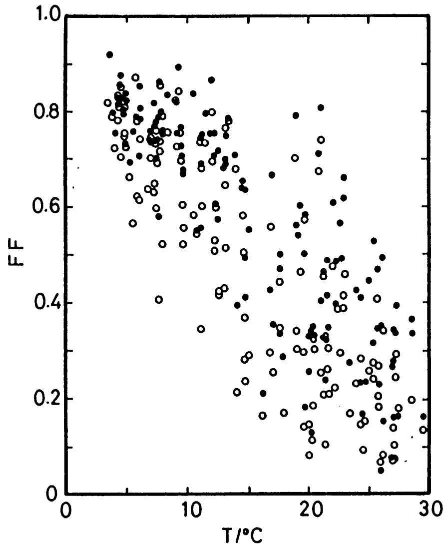

Fig. 2. Temperature dependence of FF's for chloride (O) and nitrate (●).

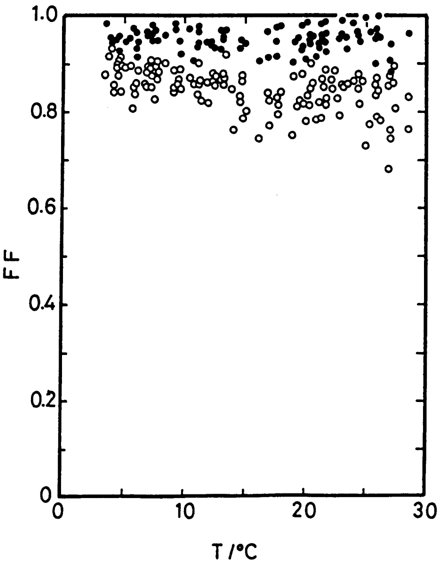

Fig. 3. Temperature dependence of FF's for sulfate (O) and ammonium (●).

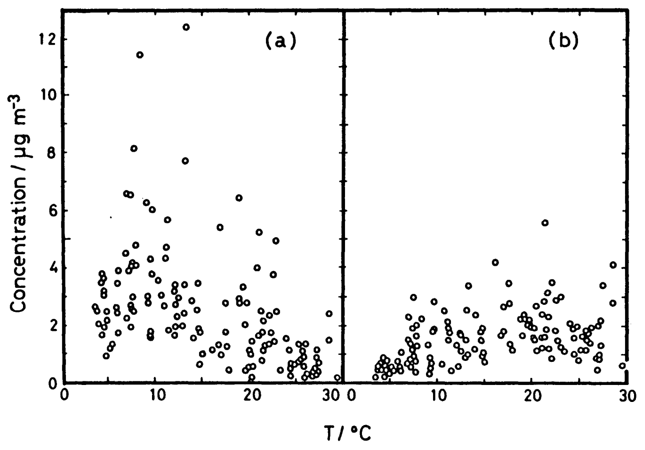

Fig. 4. Temperature dependence of (a) fine- and (b) coarse-mode chloride concentrations.

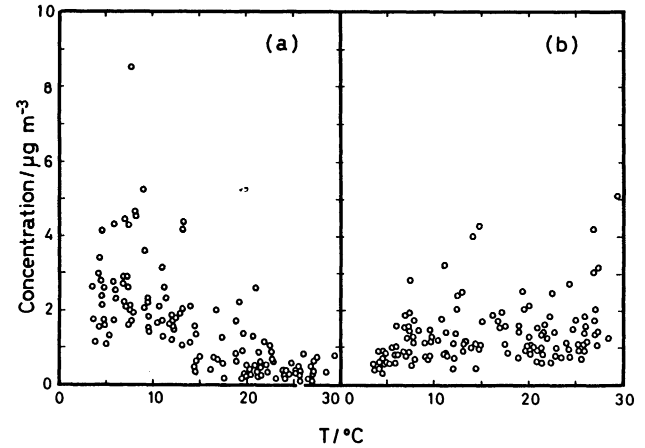

Fig. 5. Temperature dependence of (a) fine- and (b) coarse-mode nitrate concentrations.

mode in terms of the temperature, although it was pointed out nitrate aerosol shows a seasonal variation in its size distribution.

The temperature dependence of the coarse-mode chloride and nitrate will be explained in terms of both meteorology and chemistry on the assumption that those components originate from seasalt aerosol. The prevailing wind direction in Tokyo is northeast in winter and southwest in summer. Because of the location of Tokyo Bay relative to the sampling site (Fig. 1), the coarse-mode chloride is favored in the summer. Coarse-mode nitrate is attributed to the sodium nitrate[13,18] resulting from the chlorine-loss reaction:

$$\mathrm{NaCl + HNO_3 \longrightarrow NaNO_3 + HCl} \qquad (1)$$

Much more of the reactant, HNO_3, is photochemically formed in summer than in winter.

The temperature dependence of the fine mode will be discussed below.

Ion Balance. The next question is what is the chemical form of this fine-mode chloride responsible for the temperature dependence? In a previous paper,[7] we have speculated that this chloride is ammonium chloride, considering the reported identifications of this compound by means of IR spectrometry[6] and X-ray diffraction analysis.[5] Harrison and Pio[19] and Stevens et al.[20] also showed the ion-balance method, that ammonium chloride was one of the major compounds present in atmospheric aerosol. A similar analysis was applied to the present data.

Figure 6 is a plot of ammonium against the sum of the chloride, nitrate, and sulfate concentrations in the fine mode; the corresponding coarse-mode plot was not attempted because the sodium and calcium components, two major coarse-mode cations, were not determined in this study. The ion concentrations were expressed in units of µmol dm^{-3} to enable testing of the ion charge balance. Most of the points located on or slightly below the diagonal dotted 1 : 1 line were interpreted as corresponding to the condition in which all the anions cited were associated with ammonium ions.

The points falling below the line were attributable to the sulfuric acid and/or the ammoniumhydrogen sulfate, and possibly also to the sodium and calcium ions, which were not determined in this study. In some samples, a larger amount is obtained for ammonium than the three-anion sum. This may result from imprecision in analytical measurements, but in part it may also be due to the existence of organic salts of ammonium.

However, the data in Fig. 6 strongly suggest that the fine chloride and nitrate are in the form of the respective ammonium salts.

Simulation of Summer Temperatures. Another examination determined the chemical forms of fine-chloride and nitrate. Winter aerosol samples were subjected to heating in order to simulate summer

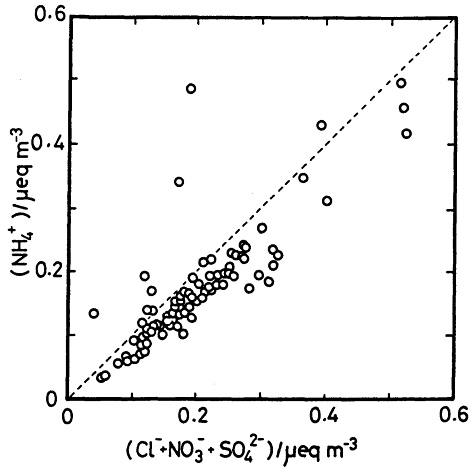

Fig. 6. Comparison of ammonium, and chloride, nitrate and sulfate concentrations in the fine mode on an equivalent basis.

temperature conditions. If the seasonal variation is derived from the temperature dependence of the gas-solid equilibria (Eqs. 2 and 3), the winter aerosol sample may be expected to exhibit a similar variation upon being heated to a summer temerature. Coarse- and fine-mode aerosol samples in winter were heated as follows. The filter at Stage 3 (50% ECD: 3.3 μm) and the backup filter were chosen to represent particles in the coarse- and fine-mode respectively. Filters with samples on were cut along a diagonal line into two equivalent parts. One part was directly subjected to the ion analysis as the reference. The other was heated, prior to the ion determination, in a temperature-controlled oven for 24 or 48 h at a typical summer temperature (between 25 and 30 °C).

Table 1 shows the ratio, C_a/C_b, of the concentrations after- (C_a) to before-heating (C_b), the subscripts a and b denote "after" and "before" respectively. For the coarse mode, the ratios were almost unity, which indicated that no vaporization took place at these temperatures. The coarse-mode ammonium was not determined because the concentration in this sample part was immeasurably small. In contrast, the fine-mode chloride, nitrate, and ammonium decreased in the C_a/C_b ratio, showing the vaporization losses of these ionic species. Nevertheless, the ratio of fine sulfate showed no appreciable change: $C_a/C_b=1.00\pm0.06$.

For the fine mode, the ratio of the decreased amount of these anions to that of ammonium, $(\Delta\mathrm{Cl}^- + \Delta\mathrm{NO_3}^-)/\Delta\mathrm{NH_4}^+$, was found to be 0.97 ± 0.12, essentially unity (Table 1). The fine-mode anionic species were concluded to form the respective ammonium salts: NH_4Cl, NH_4NO_3, $(NH_4)_2SO_4$, and their mixed salts, such as $(NH_4)_2SO_4\ n\mathrm{NH_4NO_3}$ (n=1, 2).[5)]

These findings show that fine-mode chloride, nitrate, and ammonium are highly volatile compared with the sulfate. Further, we interpret these results as indicating that the amount of species lost is in the form of NH_4Cl and NH_4NO_3 vapor. For the fine-mode ionic concentration of these winter samples, the averaged atmospheric concentration of ammonium (0.281 μequiv m^{-3}) agreed well with the averaged anion-sum (0.293 μequiv m^{-3}, where chloride: 0.090; nitrate: 0.077; sulfate: 0.126 μequiv m^{-3}).

Concentration Products of NH_3 and HCl, and NH_3 and HNO_3. Because both ammonium chloride and nitrate are volatile, hydrochloric and nitric acids volatalized from the fine-mode aerosol may be expected to exhibit complementary seasonal variations. However, the gaseous concentrations are restricted to the chemical equilibria, Eqs. 2 and 3:

$$\mathrm{NH_4Cl\,(s)} \rightleftarrows \mathrm{NH_3\,(g) + HCl\,(g)}\ K_2 \tag{2}$$

$$\mathrm{NH_4NO_3\,(s)} \rightleftarrows \mathrm{NH_3\,(g) + HNO_3\,(g)}\ K_3 \tag{3}$$

If these equilibria are attained in the atmosphere, the gas-concentration products, $P(\mathrm{NH_3})\cdot P(\mathrm{HCl})$ and $P(\mathrm{NH_3})\cdot P(\mathrm{HNO_3})$, should be equal to the equilibrium constants. The equilibrium constants for Eqs. 2 and 3 have been thermochemically calculated.[21–25)]

In Fig. 7, the logarithm of the observed concentration products for NH_4Cl and NH_4NO_3 are plotted together with calculated and measured equilibrium constants, as a function of the reciprocal temperatures. The error bar corresponds to the assumed uncertainty of the gas concentration, 20% in either direction. The present plots agree very well with the predicted temperature dependences, K_2 and K_3, within the limits of experimental error. This agreement is encouraging.

The concentration product for NH_4Cl was found to be generally larger than that for NH_4NO_3; this was consistent with the fact that K_2 is larger than K_3, judging from both the calculated and measured vapor pressures.[21,24)]

A number of groups have reported comparison of the observed NH_3-HCl[26–28)] and NH_3-HNO_3[24,29–32)] concentration products with calculations. For the NH_3-HNO_3 system, Hildermann et al.[31)] have shown that measurements and theory are in good agreement for inland sites employing filter-based techniques without diffusion denuders. So far as we have sur-

Table 1. Concentration Ratios of after- to before Heating

No.	Sampling period	Coarse-mode			Fine-mode				ΔCl$^-$+ΔNO$_3^-$
		Cl$^-$	NO$_3^-$	SO$_4^{2-}$	NH$_4^+$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	ΔNH$_4^+$
1	Feb. 5— 6, 1981	0.93	1.03	0.72	0.63	0.49	0.48	0.91	0.91
2	6— 7	0.94	0.98	0.95	0.76	0.62	0.68	1.03	1.11
3	13—14	0.78	0.86	1.13	0.56	0.39	0.65	0.91	0.95
4	16—17	1.00	0.96	1.00	0.69	0.53	0.56	1.01	0.80
5	18—19	1.07	0.97	0.93	0.84	0.71	0.78	0.99	1.08
6	20—21	0.91	0.97	1.25	0.82	0.83	0.69	1.02	0.89
7	26—28	0.82	0.83	1.04	0.71	0.54	0.61	1.05	1.01
8	Mar. 5— 7	0.98	1.04	1.01	0.80	0.36	0.76	1.09	0.90
9	5— 7	0.93	0.83	0.97	0.83	0.57	0.78	1.04	1.19
10	9—11	0.97	0.94	1.13	0.64	0.42	0.65	1.02	0.87
11	9—11	1.01	0.89	1.03	0.73	0.67	0.68	0.96	0.91
	Mean	0.94	0.94	1.01	0.73	0.56	0.67	1.00	0.97±0.12

Two Andersen samplers were simultaneously employed in March, 1981.

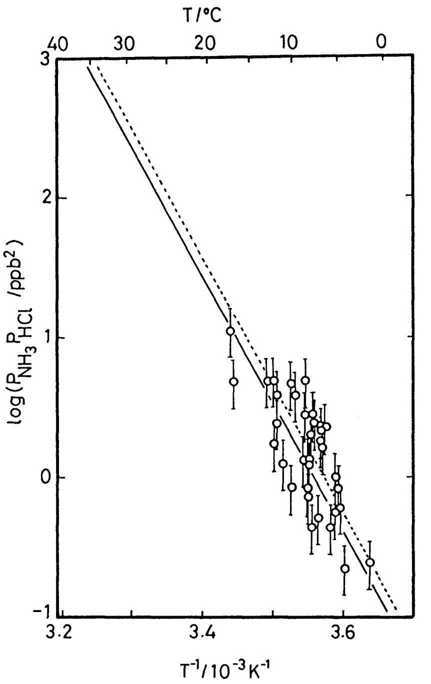

Fig. 7. Relationship between the measured NH_3–HCl products and ambient temperaute. The lines are calculated (——) and experimental (----) equilibrium constant, K_2.

veyed the literature, the other observational results exhibit considerable deviations in either direction from the predicted values even if the denuder method was applied to the nitric acid determinations. The magnitude of potential interference for the nitric acid measurement must be unequivocally determined in order to establish whether the equilibirum relationship, Eq. 3, holds in the atmosphere.

Theoretical models have been developed in consideration of several factors, such as the relative humidity[22,23,25] and such coexisting salts as $(NH_4)_2SO_4$.[25] Recently, however, Jaffe has pointed out potentially unwarranted confidence in the theoretical equilibrium constant.[35] If the free energy and enthalpy values are derived from the experimental equilibrium constants at temperatures well above the ambient conditions, as is the case for NH_4NO_3 (76—165 °C), the extrapolation of the calculated results on the basis of the thermodynamical vaules to ambient temperatures could lead to serious errors in the predicted concentration product.

The atmospheric concentration product in Eqs. 2 and 3 are still open to further discussion. Highly time-resolved observations and more sophisticated theoretical considerations based on reliable thermodynamical data are required to obtain quantitative explanations of these systems.[38—40]

***f*-Values.** In terms of the gas-particle distribution factor, defined as in Eq. 4, the involvement of the equilibria, Eqs. 2 and 3, in the seasonal-variation mechanism of the size-distribution was qualitatively examined. This factor was originally introduced by Grosjean and Friedlander[36] in examining carbonaceous compounds, for the component, X, between the gas and aerosol phases as follows:

$$f(\mathrm{X})=P(\mathrm{X})/(G(\mathrm{X})+P(\mathrm{X})) \qquad (4)$$

where P(X) and G(X) are the aerosol and gaseous concentrations, in $\mu g\,m^{-3}$ as X (Cl^- or NO_3^- in the fine mode or the corresponding gaseous form).

The temperature dependence of the values of this factor (the *f*-values) for chloride and nitrate species were examined over a wider range of temperature than that of the concentration products (Fig. 8). Over the range of 5—30 °C, the distribution factors decreased for both chloride and nitrate aerosol from near unity to zero with the temperature. This demonstrates that gaseous forms are favored in the summer period, while aerosol forms are favored in winter. These findings are in harmony with the above equilibria, Eqs. 2 and 3.

Tanaka et al.[28] undertook a similar investigation of gaseous and particulate chloride, nitrate, and ammonium species at a wooded park about 500 m from our institute in June, 1985, and February, 1986. The gas-particle distributions for chloride and nitrate were shown to be affected by the temperature in the same manner. Sasaki et al.[37] measured nitrate aerosol and nitric acid in four sites on the Kanto Plain from 28 to 30 July, 1983; they found that nitrate dominated over nitric acid as the temperature increased.

The restriction of the equilibria (Eqs. 2 and 3),

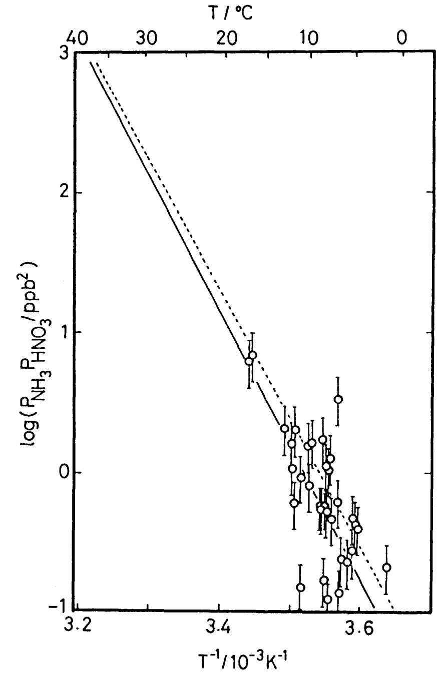

Fig. 8. Relationship between the measured NH_3–HNO_3 products and ambient temperaute. The lines are calculated (——) and experimental (----) equilibrium constant, K_3.

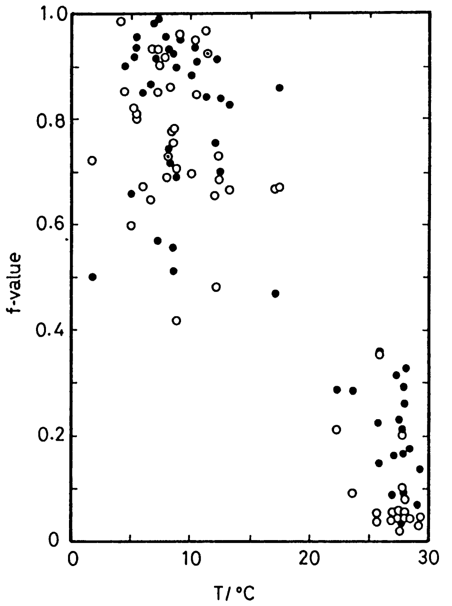

Fig. 9. Temperature dependence of *f*-values for chloride (○) and nitrate (●).

caused the seasonal variation over a wider range in the fine chloride and nitrate concentrations. In Tokyo, the range happens to be significantly both over and under the coase-mode concentrations; this results in our observed variation in the size distributions with the season.

Frequency Distributions. The cumulative distributions for the fine-, coarse-mode, and total concentrations of chloride, nitrate, sulfate, and ammonium aerosols are displayed in Fig. 9. The parameters approximated very closely to the log-normal distributions. Further, fine-mode chloride and nitrate showed bimodal distributions. This bimodal feature probably results from the temperature dependence of the equilibria, Eqs. 2 and 3.

Coarse nitrate and ammonium, as well as fine-mode chloride and nitrate, showed the bimodal distributions. A considerable change in the concentration level of fine chloride and nitrate (Figs. 4(a) and 5(a)) was observed at about 15 °C. At higher temperatures, the concentration level was rather lower than the level at lower temperatures. This change may be ascribed to the temperature dependence of the equilibria, Eqs. 2 and 3, which results in the bimodal distribution of the fine-chloride and nitrate concentrations. Although bimodal characteristics have also been observed for coarse nitrate and ammonium, no feasible explanation can as yet be offered for the distributional features of these species.

Anionic Composition of Coarse and Fine Aerosol. The relative molar-contributions of the three anions were obtained for fine and coarse modes respectively, classified with respect to the temperature (Fig. 10). In both modes, chloride was demonstrated to be a significant component.

For the fine mode, the relative composition depended dramatically upon the temperature. Chloride contributed 45% of the anions at temperatures below 5 °C. Nitrate exhibited a similar, but not so obvious, dependence. Sulfate contributed more as the temperature increased.

For the coarse mode, on the other hand, the composition was rather invariant with the temperature: chloride always constituted nearly half of the anions. Coarse chloride and nitrate are usually considered to be of seasalt origin and to result from the chlorine-loss reaction, Eq. 1, respectively. If the molar ratio of sulfate to chloride of the seawater (0.0517) is conserved throughout its transport as a seasalt particle, the seasalt sulfate was evaluated as contributing one-third of

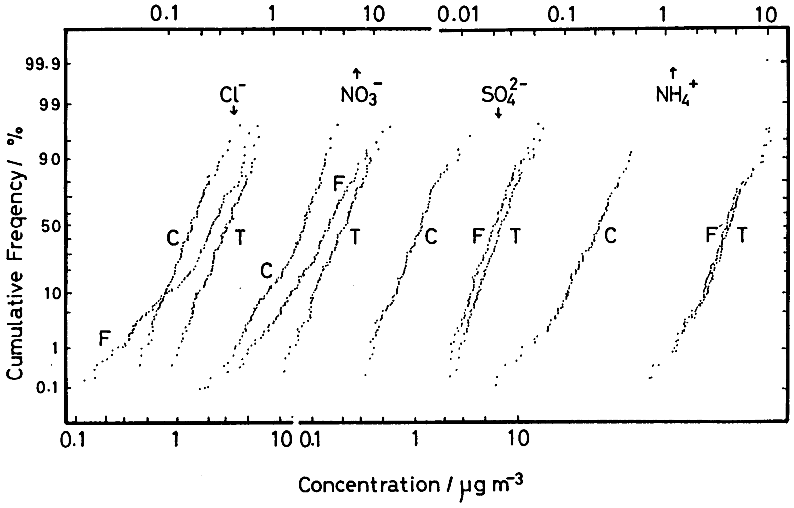

Fig. 10. Cumulative frequency distriubutions of concentrations for indicated species. F, fine-mode; C, coarse-mode; T, the sum of fine- and coarse-modes, F+C. The arrow near the name of a species indicates its concentration scale.

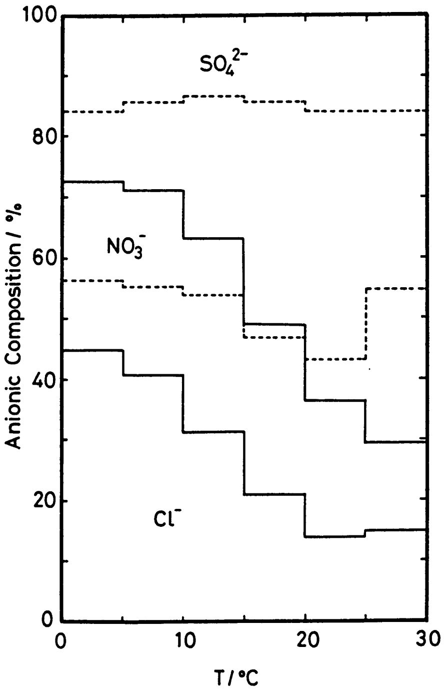

Fig. 11. Relative molar compositons of chloride, nitrate, and sulfate in the fine- (——) and coarse-mode (----) classified by temperature.

the coarse sulfate.

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