Multiple Thin Film Method for Simultaneous Detection of Sulfate and Nitrate Ions in Individual Particles and Its Application to Atmospheric Aerosols

By Gong Wang Qian, Hiroshi Tanaka, Masahiko Yamato1 and Yutaka Ishizaka

Water Research Institute, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

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Abstract

A new thin film chemical method has been developed for the simultaneous detection of individual sulfate-containing and nitrate-containing aerosols. It is based on the reactions of the sulfate ion with barium chloride and of the nitrate ion with nitron. Multiple thin films are prepared by successive depositions of nitron and barium chloride. Both reactions of sulfate with barium chloride and of nitrate with nitron proceed in the octanol saturated atmosphere. Under this reaction condition, existence of sulfate and nitrate in individual particles is indicated by the appearance of the Liesegang rings and of a bundle of needle-like crystals, respectively. These reactions are reproducible and not interfered with carbonate and chloride ions. The method is specific for sulfate and nitrate ions and can be applied to soluble sulfate and nitrate. Examples of the method applied to atmospheric aerosols are shown. Particular interest is concerned with the observation of the mixed salt of sulfate-nitrate in the atmosphere.

1. Introduction

It has been shown that sulfate and nitrate ions constitute a substantial portion of the ambient aerosols (Junge, 1963; Lundgren, 1970; Meszaros and Vissy, 1974; Okita et al., 1976; Kadowaki, 1976, 1977; Appel et al., 1978; Mamane and Mehler, 1987). Both of them are thought to be formed either by homogeneous oxidation of SOx and NOx in the gas phase, or by some heterogeneous processes in the aqueous phase of aerosol particles. Knowledge of the size, number concentration, chemical composition and mixture state of individual aerosol particles is essential to interpret their origin and transformation processes in the atmosphere. The mixture state of aerosols introduced by Winkler (1973) is divided into three categories: internal mixture, external mixture and intermediate mixture. Internal mixture is a state of mixing of various substances within an aerosol particle. External mixture is a state of coexistence of pure particles with different substances.

Winkler (1973) and Charlson et al. (1974) indicated that aerosols with perfect internal mixture show different behavior in the uptake and release of water from aerosols with perfect external mixture. Externally mixed aerosols show increased water uptake when compared with internally mixed aerosols. Aerosols will behave depending on the mixture state in the formation processes of fog and cloud particles. It is, therefore, important to recognize whether sulfate and nitrate components are internally mixed or not.

Properties of sulfate and nitrate aerosols have been studied extensively (Orr et al., 1958; Winkler, 1973; Chen, 1974; Tang, 1976, 1980; Tang et al., 1978, 1981; Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983, 1984). Tang et al. (1978) demonstrated that mixed salt aerosol particles grow stepwise and the phase diagrams are useful in understanding these processes. Stelson and Seinfeld (1982) and Bassett and Seinfeld (1983) have made a phase diagram of the NH4NO3-(NH4)2SO4-H2O system which indicates four stable phases: NH4NO3, (NH4)2SO4, 3NH4NO3, (NH4)2SO4, 2NH4NO3 and (NH4)2SO4. However, existence of the mixed sulfate-nitrate salts in atmospheric individual particles has not been well demonstrated until recently because of lack of simultaneous detection of ionic composition in an individual particles.

Sulfate and nitrate ions are usually simultaneously analyzed for bulk samples in which information on individual particle has been lost. Electron microprobe analysis is available for simultaneous de-
tection of chemical elements included in individual particles. However, chemical elements with atomic number lower than Na, especially N, cannot be detected by the standard electron microprobes. What is more important is that electron microprobe analysis can only detect elemental components but cannot detect ionic components. Bigg et al. (1974) outlined the method of chemical tests for individual particles, which was based on the reactions of vacuum-deposited thin film of reagents with test particles. Chemical tests for identification of sulfate ion (Bigg et al., 1974; Ayers, 1978b; Mamane and de Pena, 1978), nitrate ion (Bigg et al., 1974; Ayers, 1978a; Isawa and Ono, 1979; Mamane and Pueschel, 1980) and ammonium ion (Weisweiler and Schwarz, 1988) have been developed as thin film methods. For the mixed salt particles of sulfate and nitrate, however, a usable chemical test has not been reported.

Ayers (1978a) proposed a detection method for nitrate only, using multiple thin films of SiO, nitron, BaCl₂, CaCl₂ and CaF₂ in order to prevent interference with sodium sulfate and sulfite. The method is postcoating with nitron and uses water vapor to promote reaction. According to Mamane and Pueschel (1980), the postcoating method is not suitable to analyze a volatile nitrate particle such as ammonium nitrate. The precoating method is suitable (Mamane and Mehler, 1987). Moreover, Isawa and Ono (1979) proposed a method using octanol vapor instead of water vapor to promote reaction to prevent interference with sulfate and sulfite. This method is more reliable than Ayers'. Based on the above results, we proposed a method using multiple thin films of barium chloride and nitron for the detection of sulfate and/or nitrate ions. The reactions are promoted in the octanol vapor and not interfered with the carbonate ion. The purpose of this paper is to establish a new method for the simultaneous detection of submicrometer and micrometer size sulfate and nitrate particles extending Bigg's technique (Bigg et al., 1974). This method should satisfy the following requirements: (a) to be specific for sulfate and nitrate ions and distinguishable from each other, (b) to be able to distinguish internal mixture from external mixture of sulfate and nitrate, (c) to provide the size distribution of sulfate and nitrate particles, and the number ratio of sulfate and/or nitrate particles to total particles, (d) to be able to differentiate liquid particles such as sulfuric acid from solid particles such as sodium sulfate, (e) to be sensitive enough to enable sampling times of seconds to a few minutes in the atmosphere.

2. Method

The method developed for simultaneous detection of sulfate and nitrate ions in individual particles is basically a modified spot test. When a sulfate- and nitrate-containing particle contacts multiple thin films composed of nitron and barium chloride, chemical reactions occur under adequate solvent vapor supply. Liesegang rings formed are composed of insoluble barium sulfate, and bundles of needle-like crystals formed are composed of insoluble nitron nitrate. These characteristic spots are observed by the transmission electron microscope (TEM).

As shown in Fig. 1, the method consists of several steps described below:

(a) An electron microscope screen, being covered with a nitrocellulose film and a carbon film and then with a nitron film, is used as a surface for particle collection. Nitron can be deposited on the screen in a vacuum chamber at a low pressure (2 × 10⁻⁶ mmHg). As these screens are usually placed in the jet impactors, the screen is so thin that there is no significant influence on the collection efficiency of the particles.

(b) Sampling time is normally from seconds to minutes depending on the purpose of the study, specification of the sampling device and particle concentration. Prior to impaction of particles on multiple thin films, water vapor contained in the ambient air should be removed using a diffusion drier. The dehydration is necessary because recrystallization of the reagents often appears on the precoated screens through exposure to the ambient humid atmosphere during particle collection.

(c) Non-volatile particles can be coated with a film of barium chloride in a vacuum evaporator. Volatile particles should be collected on a screen precoated with barium chloride. Figure 1a is a photomicrograph of the reaction spots of a sulfuric acid particle before the solvent vapor treatment. The reaction spot is almost circular, and called a Liesegang ring. But for other particles, no reaction spot can be seen before octanol treatment because the particles are usually not liquid at room temperature in dry air, except for sulfuric acid particles.

(d) The samples are then exposed to octanol vapor for 16–20 hours at a room temperature to promote the reaction of sulfate and/or nitrate with the multiple thin film.

(e) Next, the samples are examined by the transmission electron microscope (TEM) and are photographed. The particles containing the nitrate ion can be identified by the appearance of bundles of needle-like crystals. Figure 1b is an example of the reaction of sodium nitrate particles with multiple thin films. The particles containing the sulfate ion can be identified by the appearance of Liesegang rings. Figure 1c is an example of the reaction of ammonium sulfate with multiple thin films. Particles containing both nitrate and sulfate ions can be identified by the simultaneous appearance of bundles of needle-like crystals and Liesegang rings. Figure 1d shows the reaction of an internal mixture of ammonium nitrate and ammonium sulfate with multiple
The Multiple Thin Films Method

<table>
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<tr>
<th>Thin Films</th>
<th>(a) $\text{H}_2\text{SO}_4$</th>
<th>(b) $\text{NO}_3^-$</th>
<th>(c) $\text{SO}_4^{2-}$</th>
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Fig. 1. Conceptual display of the multiple thin film method.
thin films. Information of the mixture state of the sulfate and nitrate in aerosol particles can be obtained by the multiple thin film method.

(f) Several hundreds of reaction spots were photographed, analyzed, counted and sized. Comparing the number density of the reaction spots in nitron-barium chloride screens with the total number density of particles in non-treated screens sampled simultaneously, we can obtained the number concentration of sulfate and/or nitrate particles. The relationship between diameter of the reaction spot and original particle is useful in obtaining the size distribution of sulfate and/or nitrate particles. The size distribution of these particles also can be obtained by using a size-fractionated impactor.

3. Results of laboratory experiment

In order to examine the reaction condition, reproducibility, interference, and detection limit of the multiple thin film method, laboratory experiments were carried out focusing on the following factors.

3.1 Solvent

With respect to the thin film method, it has been considered that chemical reactions proceed in very concentrated solution when the thin films are exposed to solvent vapor, and as a result some substances are separated and then precipitate (Bigg et al., 1974). The first step for the new thin film method is to find out the most suitable solvent vapor to promote chemical reactions and to obtain reproducible reactions on the multiple thin films.

Two kinds of solvent vapors have been used: one is water vapor and the other is octanol vapor. Water vapor strongly reacts with the thin film but octanol vapor does not. Testing many of the samples, we found that the reaction product exposed to octanol vapor is more clear-cut than that exposed to water vapor.

As was described before, the present method is based on the appearance of a Liesegang ring in detecting the sulfate ion and on the appearance of bundles of needle-like crystals in detecting the nitrate ion. It is important to ensure that any interaction among nitron, barium chloride and octanol vapor does not occur. Blank tests were performed by the exposure of multiple thin films without particles to octanol vapor. As shown in Fig. 2, no Liesegang rings or bundles of needle-like crystals were observed.

An exposure time of 16–20 hours seems sufficient. If the exposure time is shorter, the reaction is not completed. If the exposure time is too long, recrystallization of the reagents occurs.

3.2 Thickness of the reagent film

The control of film thickness is essential to obtain reproducible reaction products. If the film of reagent is too thin, the reaction is not completed due to the shortage of reagent. If the film is too thick, small particles are masked. In addition, the size of the recrystallized grain of the film, which is closely related to the detection limit, is determined by the film thickness; the thinner the better.

Assuming that the source vapor is emitted from a point source and is spherically distributed around the vapor source, the film thickness is estimated by a simple formula described by Preuss (1959):

\[
t = (M \sin \theta)/(4\pi \gamma^2 \rho),
\]

where \(\gamma\) is the distance between the screen and vapor source, \(\rho\) the density of the reagent, \(M\) the mass of the reagent to be evaporated, \(\theta\) the angle between the screen and vapor source, and \(t\) the film thickness.

In order to obtain uniform layers of the reagents, we placed a narrow slit between the screen and vapor source as shown in Fig. 3. Through the slit a uniform current of reagent can be obtained. Because the vapor source is not exactly a point source and gas molecules are not spherically distributed exactly around the source, it is difficult to produce a perfectly uniform film thickness. The presence of the slit prevents heating by the hot source. The heating may damage the sample during the postcoating process.

The thickness of the reagent has been studied by many researchers. For the determination of sulfate-containing particles in the size range between 0.1
and 4 µm, they agree that an adequate thickness of barium chloride film is from 2 to 5 nm. But, for nitrate-containing particles, an adequate thickness of nitron film is subject to scatter (Ayers, 1978a; Isawa and Ono, 1979; Mamane and Pueschel, 1980) and no definite value has been shown, since the density of nitron was unknown (Isawa and Ono, 1979; Mamane and Pueschel, 1980).

In order to obtain the density of nitron, a simple experiment was carried out. Nitron is not soluble in water and usually precipitates. We found that the nitron density remains in an equilibrium with aqueous solutions of 22.2 % of K$_2$CO$_3$, 39.1 % of (NH$_4$)$_2$SO$_4$, 22.0 % of Na$_2$SO$_4$, or 24.1 % of CaCl$_2$. Thus we determined the nitron density to be 1.21 g/cm$^3$. For the identification of sulfate- and nitrate-containing particles in the size range between 0.1 and 4 µm, we found that a barium chloride film of 2–5 nm and a nitron film of 9–13 nm were most appropriate.

3.3 Applicability, reproducibility and interference

In order to examine the applicability, reproducibility and interference of the present multiple thin film method, we carried out the following experiments:

(a) Standard particles were produced by spraying a dilute solution of each material.

(b) After removing water vapor through a drier tube, we collected particles on an electron microscope relocation screen.

(c) The screen was observed and photographed by a TEM with the lowest beam intensity and shortest time as possible to prevent the sample from damage.

(d) After the octanol vapor treatment, the same framework of the screen was photographed again by TEM.

(e) Figures 4a and 4b show the pictures of ammonium nitrate particles before and after the octanol vapor treatment, respectively. When Fig. 4b is superposed on Fig. 4a so as to coincide with the grid marks in the two photomicrographs, we find that the reaction spots are exactly on the particles. The chemical reactions are completed between the particles and multiple thin films. In addition, a relationship between the reaction spot and the original particle can be also determined.

For examining reproducibility of the reactions, the same procedures were applied to other nitrate-containing particles: sodium nitrate (NaNO$_3$), magnesium nitrate [Mg (NO$_3$)$_2$] and calcium nitrate [Ca (NO$_3$)$_2$]. As shown in Fig. 5, similar reaction products appeared when these nitrate particles were exposed to octanol vapor. These experimental results imply that bundles of needle-like crystals are caused by the reaction of nitron with nitrate ions contained in the particles.

The same procedures were also applied to sulfate-containing particles: sulfuric acid (H$_2$SO$_4$), ammonium sulfate [(NH$_4$)$_2$SO$_4$] and sodium sulfate (Na$_2$SO$_4$). As shown in Figs. 6, 7 and 8, only Liesegang rings are observed in these cases instead of bundles of needle-like crystals. Figures 6a and 6b
correspond to ammonium sulfate particles before and after the octanol vapor treatment, respectively, and Fig. 7 shows the case of sulfuric acid droplets. Liesegang rings are formed the octanol vapor treatment and remain unchanged by the treatment for sulfuric acid droplets, but are formed only after the octanol vapor treatment for ammonium sulfate particles. Therefore, we can distinguish sulfate-containing particles from sulfuric acid particles.

Mixed particles containing the sulfate and nitrate were produced in the laboratory and treated in the same manner as described above. These mixed particles reacted with thin films selectively as shown in Fig. 9. Figures 9a and 9b show the particles of mixed ammonium nitrate and ammonium sulfate \([3\text{NH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4]\) before and after the octanol vapor treatment, respectively. Note that bundles of needle-like crystals are not always produced every particle. However, when these particles were treated without first TEM observation (procedure (c)), bundles of needle-like crystals are observed in most of the particles as shown in Fig. 10. These experimental results imply that particles containing both sulfate and nitrate ions can be identified by the simultaneous appearance of Liesegang ring and bundles of needle-like crystals.

Interference tests were carried out for chloride and carbonate ions. The morphology of the reaction spot is different from the cases of sulfate and nitrate particles. The photomicrographs of the reaction spots of sodium chloride (NaCl) and ammonium chloride (NH₄Cl) on the multiple thin films are shown in Figs. 11a and 11b, respectively. The reaction spot of sodium carbonate (Na₂CO₃) is shown in Fig. 12. None of these reaction spots is either a bundle of needle-like crystals nor a Liesegang ring. This fact implies that none of these materials interacts with sulfate and nitrate on the multiple thin films.

Thus, we have come to the conclusion that
Fig. 7. Application of the multiple thin film to (NH₄)₂SO₄ particles. The particles are indicated in the same framework before (a) and after (b) octanol vapor treatment.

Fig. 8. Products of the reaction of multiple thin film with Na₂SO₄ (a) and MgSO₄ (b) particles produced in the laboratory.

Liesegang rings obtained above are caused only by the reaction of sulfate with barium chloride and that bundles of needle-like crystals are caused only by the reaction of nitrate with nitron. It is also concluded that octanol vapor is the most suitable solvent vapor to promote the reactions of both sulfate and nitrate with multiple thin films. The present method can be applied to the simultaneous detection of atmospheric sulfate and nitrate.

3.4 Detection limit
For the estimation of the detection limit in the nitron-barium chloride thin film method, it is necessary to obtain the smallest mass of the particles that form a recognizable reaction spot. Usually, the mass of the original particle is calculated by the product of particle volume and particle density. In the laboratory, the volume of each particle is to be estimated by the assumption of a semi-spherical cap (Ayers, 1978b) in terms of apparent particle diameter and shadow length. However, we cannot obtain the shadow of a particle directly. In order to get the empirical relationship between shadow length and apparent particle diameter, separately collected particles under the same experimental condition were shadowed in a vacuum at a known angle with gold-palladium alloy, and the apparent particle diameter and the shadow length were measured. Using the derived empirical relationship, the volume of the particles can be estimated.

The smallest sizes of particles that form recognizable reaction spots were obtained for standard particles of NaNO₃, (NH₄)₂SO₄ and [3NH₄NO₃·(NH₄)₂SO₄]. The same particles were observed and photographed by the TEM before and after the octanol vapor treatment. Comparing many pairs of particles in the photographs, the smallest sizes of the particles that form recognizable reaction spots were obtained. The smallest sizes are about 0.05 µm in radius for pure sulfate particles, about 0.1 µm for pure nitrate particles, and about 0.2 µm for internally mixed sulfate-nitrate particles. Then, the detection limits of pure particles can be calculated by particle size and density. The detection limits are about 10⁻¹⁷ g for pure sulfate particles, and about 10⁻¹⁴ g for pure nitrate particles. For internally mixed sulfate-nitrate particles, on the other hand, there is no simple answer as to how the detection limit may be determined. More information on individual mixed particles is needed before any conclusion can be drawn. The reason will be given later.
4. Application

Applicability of the multiple thin film method to the detection of atmospheric aerosols was tested at Nagoya University campus during the period from February to December in 1988. Both the sulfate and nitrate ions were detected in the ambient aerosol in Nagoya urban air (cf., Kadowaki, 1976, 1977; Okada, 1985; Wu et al., 1987). Atmospheric aerosols were fractionated by a two-stage cascade impactor into two size ranges: coarse particles \( r > 1.0 \mu m \) and submicron particles \( 1.0 \geq r > 0.1 \mu m \), analysis being focused on morphology and composition of the particles. This method gave the positive results in identifying the atmospheric particles, especially internally mixed particles (see Fig. 13). There are several aerosol particles in the photograph of Fig. 13 that form Liesegang rings only which are identified as sulfate containing particles. Several aerosol particles form both Liesegang rings and bundles of needle-like crystals, and are identified as mixed particles of sulfate and nitrate.

The samples were analyzed to obtain the percentage of sulfate- and nitrate-containing particles. It was found that, in the submicron size range, sulfate particles, nitrate particles and internally mixed particles are 25%, 15% and 11% in number concentration to the total submicron particles, respectively. In the coarse size range, on the other hand, the number concentration of nitrate particles was about 10% to the total coarse particles, but no sulfate particle was observed.
To validate the results of number concentrations obtained by the multiple thin film method, the number concentrations of sulfate- and nitrate-containing particles were measured by using the barium chloride thin film (Bigg et al., 1974; Okada, 1985) and the nitron thin film (Isawa and Ono, 1979; Mamane and Mehler, 1987), respectively. The result indicated that the total number concentrations of sulfate-containing particles and nitrate-containing particles measured by these method are similar to those measured by the multiple thin film method. However, no information on mixed particles could be obtained.

The multiple thin film method was also applied to samples collected in a coastal area of Sakushima Island, eighty miles south from Nagoya city. Particles were collected on precoated nitron screens and then treated with barium chloride. Many samples were analyzed to obtain the ratio of sulfate and nitrate particles. Sulfate-containing particles were 47% and nitrate-containing particles were 18% to the total particle number. Internally mixed sulfate-nitrate particles were only 2–3%. Figure 14 shows a typical TEM photograph of internally mixed sulfate-nitrate particle collected on the multiple thin film on 21 September 1988 under very humid condition.

5. Discussion

Deeper discussion is necessary to validate and improve the method of multiple thin films. As shown in Fig. 9b, reactions between the mixed salt particles of sulfate and nitrate and multiple films, especially for the submicron particles, are hardly completed, so that the observed number of mixed particles is likely to be less than the real number. Some reasons for this will be discussed.

5.1 Evaporation

Since ammonium nitrate is low in boiling point and high in volatility, it is likely to be evaporated from the particles, especially when these particles are injected into a high-vacuum chamber of the evaporater during the reagent coating process and when electron beams are radiated during the microscope observation. In the latter case, the electron beams may also heat up the particles and decompose them rapidly. The effects of high vacuum and electron beam on ammonium nitrate particles were also reported by Mamane and Pueschel (1980). When the particles are exposed to high vacuum, 60% of the ammonium nitrate particles does not react with nitron, while almost 95% of the particles does react for the precoated samples. The effect of electron beams is catastrophic and causes particles to evaporate in a few seconds in the TEM.

For the purpose of testing the effects of high vacuum and the electron beam on mixed particles of sulfate and nitrate, particles of NH$_4$NO$_3$ and
\[3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4\] were collected on electron microscope screens. Then, the samples were exposed to high intensity electron beams. All of the \(\text{NH}_4\text{NO}_3\) particles were completely evaporated in a few seconds leaving nothing on the screen. Particles of \([3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\) were also evaporated leaving some residues. But, octanol vapor treatment with the residues showed that the reaction spots only have Liesegang rings. This result indicates that the ammonium nitrate is decomposed more rapidly than ammonium sulfate when they are included in the same particles. Based on the experiment described in this section, atmospheric particles should be collected on precleaned screens when they are abundant in volatile nitrate particles.

5.2 Detection limit of mixed sulfate-nitrate particle

It is important to estimate the detection limit of the multiple thin film method for internally mixed salt particles. The nitrate-to-sulfate ratio in a particle has to be obtained for the purpose. These particles were generated by spraying a bulk solution whose concentration is known. After drying them to solid particles, they were collected on an electron microscope screen. It must be questioned whether the nitrate-to-sulfate ratio has been changed or not after the processes of the particulation and dehydration. For the case of non-volatile materials, it may be considered that, in the size range where the Kelvin effect is negligible, the chemical composition of the particles is likely to be the same as that of the bulk solution. But the situation seems different when volatile salts are included and when Kelvin effect is not negligible (Tang, 1976). The problem has been studied by many investigators. Tang (1980) has studied a chemical equilibrium for the \(\text{NH}_4\cdot\text{HNO}_3\cdot\text{H}_2\text{SO}_4\cdot\text{H}_2\text{O}\) system and indicated that the nitrate-to-sulfate ratio in droplets depends strongly on the relative humidity of the atmosphere as well as the droplet pH. The observations by Forrest et al. (1980) showed that the greatest \(\text{NH}_4\text{NO}_3\) loss occurs at a relative humidity below 60\%, whereas \(\text{NH}_4\text{NO}_3\) is not lost at 100\% relative humidity. Stelson and Seinfeld (1982) gave a reasonable explanation of the result of Forrest et al. based on the relative humidity dependence of the \(\text{NH}_4\text{NO}_3\) dissociation constant at 25°C. Moreover, Friedlander (1977) showed that the chemical composition in a mixed salt particle under varying humidity is too complex to be determined compared with the case of single-component salt particles. Even if the particles have an equilibrium point with relative humidity at the same size, they may have a different chemical composition. The equilibrium vapor pressures of ammonia and sulfuric acid are very low at the surface of solid ammonium sulfate, compared with the vapor pressures of ammonia and nitric acid at the surface of ammonium nitrate (Stelson et al., 1979). It is not surprising that \(\text{NH}_4\text{NO}_3\) is lost more rapidly than \((\text{NH}_4)_2\text{SO}_4\) during the processes of particulation and dehydration.

In addition, it is not easy in the laboratory to produce the mixed sulfate-nitrate salt with a pure phase. Harrison and Sturges (1984) suggested that \(3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4\), \(2\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4\) and \(\text{Na}_2\text{SO}_4\cdot\text{NaNO}_3\cdot\text{H}_2\text{O}\) are possible in the atmosphere as mixed salt particles of sulfate and nitrate. Production of \([\text{Na}_2\text{SO}_4\cdot\text{NaNO}_3\cdot\text{H}_2\text{O}]\) particles has not been reported so far. Particles of \([3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\) and \([2\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\) were produced by Smith et al. (1962). Later, Coates and Woodard (1963) published X-ray crystallographic data for the two kinds of ammonium nitrate-sulfates, \([3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\) and \([2\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\), and described in detail the production method required to produce these materials with pure phases. These mixed salts can be produced by mixing aqueous solutions of \(\text{NH}_4\text{NO}_3\) and \((\text{NH}_4)_2\text{SO}_4\). But Tani et al. (1983) reported that after evaporation of water from stoichiometric solutions, the residues contain \([3\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\), \([2\text{NH}_4\text{NO}_3\cdot(\text{NH}_4)_2\text{SO}_4]\), \((\text{NH}_4)_2\text{SO}_4\) and \(\text{NH}_4\text{NO}_3\) in varying amounts. In order to obtain a relationship between salt content and particle size, we made mixed solutions of nitrate and sulfate at varying stochiometries. Then we nebulized the solutions, collected the particles, and analyzed them using an X-ray method and a thin film method. No significant relationship could be obtained between salt content and particle size. However, some qualitative data were similar to the results of Tani et al. (1983).

The detection limit of mixed particles obtained by this method depends on the volume of the original particle, the densities of sulfate and nitrate particles, and the nitrate-to-sulfate containing ratio in a particle. In order to obtain the volume of an original particle, first TEM observation (procedure (c)) is needed. However, the nitrate in some of the particles was damaged by the microscope electron beam when observed by TEM. In addition, the product prepared in our laboratory is small droplets of aqueous solution. It is not certain whether these droplets have the same ratio as that of the bulk solution or not. The detection limits for pure nitrate and sulfate were found to be reproducible. For mixed particles, however, no quantitative results have been obtained since the produced droplets in the laboratory are uncertain in composition. More information such as the nitrate-to-sulfate ratio in internally mixed particles is needed to obtain definite conclusion.

6. Summary

A method for the simultaneous detection of sulfate and nitrate ions contained in individual particles has been described. The method is based on
the reaction of the sulfate ion with barium chloride and the reaction of the nitrate ion with nitron. Octanol vapor treatment gives the reproducible reaction product of Liesegang rings for sulfates and bundles of needle-like crystals for nitrates. Results of the reactions show characteristic spots easily recognized by the electron microscope. The particles of the sulfate or/and nitrate are identified by the appearance of the Liesegang ring or/bundles of needle-like crystals, respectively. The detection limits for pure sulfate and pure nitrate are $10^{-17}$ g and $10^{-14}$ g, respectively. For internal mixed particles, however, no quantitative result can be obtained in the laboratory. Some qualitative data show that the smallest size of mixed particle with recognisable reaction spots is about 0.2 µm in radius.

The method has been applied to atmospheric aerosol samples. The analysis simultaneously provided the ratio of nitrate and/or sulfate to total particles, number concentration and the size distribution of nitrate and/or sulfate. It also enables the distinction to be made between sulfate and sulfuric acid. Especially, it is possible to observe the existence of mixed particles of sulfate and nitrate compounds.

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References


Smith, J.P., J.R. Lehr and A.W. Frazier, 1962: Crystallographic properties of the ammonium nitrate-sulfates $3\text{NH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4$, $2\text{NH}_4\text{NO}_3(\text{NH}_4)_2\text{SO}_4$. J. Agric. Fd. Chem., 10, 77–78.

Stelson, A.W., S.K. Friedlander and Seinfeld J.H., 1982: Thermodynamic prediction of the water activity, \( \text{NH}_4\text{NO}_3 \) dissociation constant, density and refractive index for the \( \text{NH}_4\text{NO}_3-(\text{NH}_4)_2\text{SO}_4-\text{H}_2\text{O} \) system at 25°C. *Atmos. Environ.*, 16, 983–992.


