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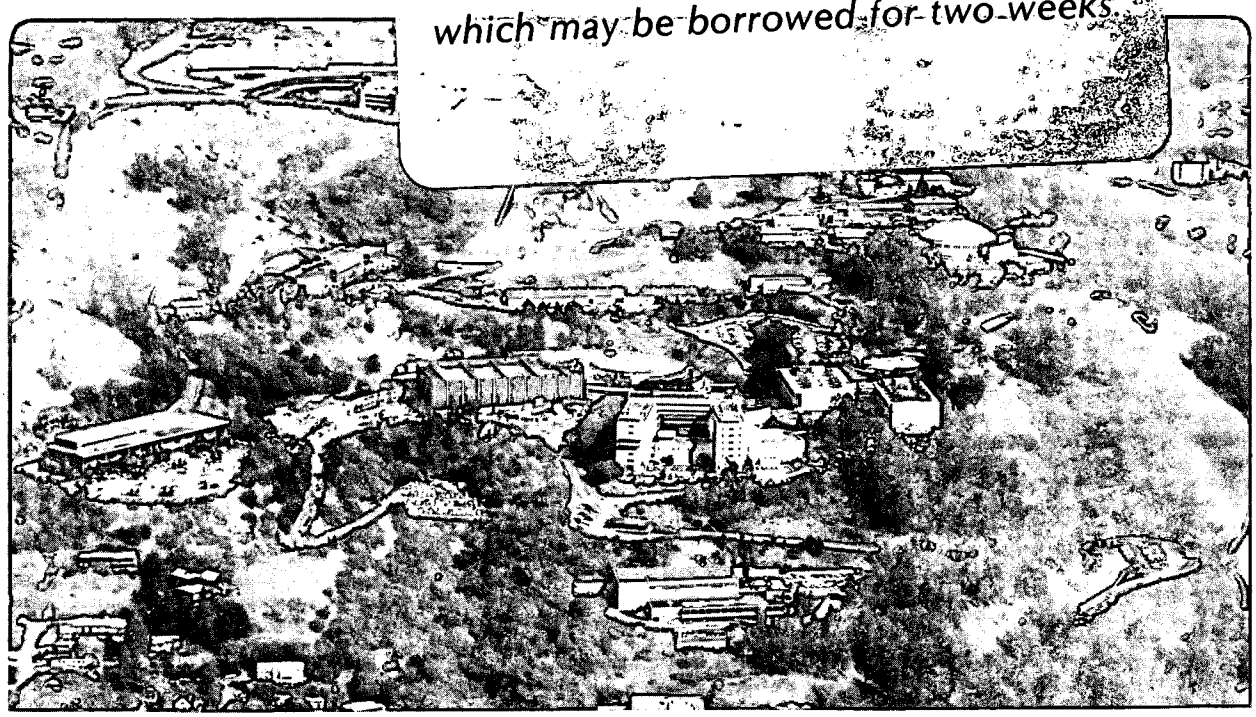

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THE USE OF X-RAY POWDER DIFFRACTOMETRY IN COMBINATION WITH SEM AND MICROENCAPSULATION FOR STUDYING THE PHYSICO-CHEMICAL TRANSFORMATIONS OF CRYSTALLINE PARTICLES ON TEFLON FILTERS

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X-ray powder diffractometry (XPDFT) and scanning electron microscopy (SEM) are being used to study the formation and transformation of microcrystalline particles on teflon filters. The work represented here is directly related to sampling artifacts associated with the recrystallization of particles on the filter and the interaction between a variety of particulate compounds and the dominant particulate sulfate. In addition, polymeric replication of water on and around the particles is being investigated as a means to obtain complementary information on the chemical and physical transformation mechanisms.

BACKGROUND

Several authors have demonstrated the capability of x-ray powder diffractometry (XPDFT) for the chemical characterization of major crystalline species present in ambient atmospheric aerosols [Davis, 1984; Harrison and Sturges, 1984; and Tani et al., 1983]. When combined with other nondestructive analytical methods such as x-ray fluorescence (XRF), XPDFT is a potentially powerful tool for source apportionment studies.

A recent study at LBL involved the XPDFT analysis of approximately 140 course-fine filter pairs acquired in a field study operated in Philadelphia during July and August, 1982 by the EPA. These samples were collected on 1 μm pore size teflon filters using dichotomous samplers [Loo et al., 1979] operating at 16.7 l/m for 12 hr intervals. Table I is a summary of the major crystalline compounds observed in the study and their range of compositions.

Although the results are not inconsistent with the known properties of ambient aerosols, a closer examination of the data set did indicate certain anomalies. The overwhelming predominance of sulfates in the fine fraction, to the exclusion of any other cation particularly nitrate, is suspicious. The presence of zinc and lead ammonium sulfate and the absence of Pb halides indicates the possibility of sampling artifacts involving the particles which produce these sulfates as a final product. Finally, analysis of a subset of the filters yielded x-ray powder diffraction patterns for mascagnite in which the ratios of lines associated with specific refraction indices exhibited anomalous intensities with respect to the remainder of lines. This is an indication of a preferential alignment of the individual particles with respect to a specific orientation, and supports the supposition that the particles were recrystallized after collection on the filter.

As a result of these observations, we attempted to duplicate these effects using laboratory generated aerosols. In addition to explaining the anomalies exhibited in the XPDFT data, such a study has far reaching implications with respect to the chemical analysis of ambient particles collected on inert teflon filters. It also relates to earlier studies on sampling artifacts associated with sulfate and nitrate species.

Insofar as the humidity of the air stream and the resultant hydration of the collected sample were suspected as being strong factors in the chemical reactions, a related study of the distribution of water on the samples was undertaken using a microencapsulation technique. This method uses methyl-2-cyanoacrylate (MCA) polymer to replicate water on particles. The method is known to work well in preserving the size distribution of cigarette smoke, a predominantly liquid-phase aerosol [Holmberg, 1979]. Further work at LBL has shown that the polymer forms a porous matrix replicating condensed water on the particles. The MCA monomer shows no affinity for the teflon filters and will diffuse through blank filters leaving no interfering polymer.

TABLE I. Predominant Crystalline Species Identified on Ambient Philadelphia Aerosol Samples Using XPDFT

Formula	Mineral Form	Maximum Concentration*	Particle Size
$(NH_4)_2SO_4$	Mascagnite	100 $\mu g/cm^2$	Fine
$(NH_4)_3H(SO_4)_2$	Letovicite	60 $\mu g/cm^2$	"
$Pb(NH_4)_2(SO_4)_2$	Lead Ammonium Sulfate	4 $\mu g/cm^2$	"
$Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	Zinc Ammonium Sulfate	4 $\mu g/cm^2$	"
SiO_2	Quartz	20 $\mu g/cm^2$	Coarse
NaCl	Halite	10 $\mu g/cm^2$	"
$CaCO_3$	Calcite	10 $\mu g/cm^2$	"
Aluminum Silicates	Muscovite	20 $\mu g/cm^2$	Coarse
	Dolomite	4 $\mu g/cm^2$	"
	Microcline	4 $\mu g/cm^2$	"

*The miniumum concentration for mascagnite was 10 $\mu g/cm^2$. For all the other compounds it was below the detection limit which varies with the specific compound but is on the order of 2 - 5 $\mu g/cm^2$.

EXPERIMENTAL PROCEDURE

Aerosols are generated using a constant output collision nebulizer (TSI Model 3075*) [May, 1973]. Solutions were prepared from reagent grade salts of the desired crystals. The nebulized solution is mixed with dry air and heated to 70°C. The water vapor is removed using a silica diffusion dryer. The particles are then mixed with dry air creating a nominal 5% R.H. condition and passed through a KR-85 diffusion discharger. Finally 100% R.H. air with no liquid water content can be mixed with the dry aerosol stream to create the desired relative humidity. The aerosol was collected on 1 μm teflon filters (Ghia Corp.*) using the automatic dichotomous sampler. Only fine fractions

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(< 2.5 μm) were used in this study. In experiments where mixtures of compounds were used, the salts were collected sequentially on the filters. Exposure to humid air was accomplished by placing the filters in the dichotomous sampler and filtering particle free humid air for 5 - 20 min through the loaded filter.

XPDFT data were obtained using a Bragg-Brentano diffractometer modified for use with a position-sensitive detector [Thomson, et al., 1982]. Due to the nondestructive nature of the XPDFT analysis, it was possible to perform a series of measurements on the same filters in order to observe the effects of sequential deposition of different salts and the results of exposure to humid air over variable time periods.

Encapsulation and replication of water on the particles was accomplished by 5 min exposures of selected filters to vapors of methyl-2-cyanoacrylate (MCA) heated to 70°C. These samples were then coated with a sputtered gold film and observed in a scanning electron microscope.

RESULTS AND DISCUSSION

Preferred Orientation of Mascagnite

The XPDFT method will produce a diffraction pattern resulting from only those crystals having planes lying parallel to the face of the filter and d spacings satisfying the Bragg condition for a given value of 2θ. Preferred orientation implies a nonrandom orientation of the particles on the filter, and furthermore, some preference of certain crystal orientations to the plane of the filter. The recrystallization of mascagnite was inferred from the Philadelphia fine-fraction diffraction patterns in which a subset of the data had an enhanced intensity of the line corresponding to the Miller indices of <200>. This enhanced intensity was seen by comparison with the strongest line in the pattern (Miller indices, <111>). This enhancement is direct evidence that under some conditions there is a preference for orthorombic mascagnite crystals to be orientated with one face parallel to the surface of the filter. Because of the fibrous nature of the filter, its effective pore size of 1 μm, and the expected submicron size distribution of the mascagnite particles in ambient air samples, this effect can be readily explained. However, one suspects that at least a fraction of these particles exhibiting this orientation were formed after achieving contact with the filters.

A series of experiments were performed in which teflon filters were loaded with approximately 50 $\mu g/cm^2$ of mascagnite and XPDFT spectrum were then obtained. The relative intensities of the lines reflected a perfectly random crystalline deposit corresponding to the reference spectrum values. The particle diameters, determined by electron microscopy, range from 0.1 to 0.5 μm. Although mascagnite is an orthorombic crystal, the particles appear round in the micrographs. In a first attempt to induce a preferred orientation, filters were placed in static 100% R.H. at 20°C for two days. The filters were then equilibrated with the room air (approximately 40% R.H.) and XPDFT was repeated. No evidence of change could be detected either in the XPDFT spectrum or SEM micrographs. In a second attempt, 80% R.H. air with no liquid water content was passed through the filter for 15 to 20 min using the dichotomous sampler. This resulted in a preferred orientation that can be correlated, through the Miller indices, with having the faces of the crystal lying parallel to the filter face. The micrographs showed significantly more angular crystals in the

range of 0.3 to 0.6 μm in diameter. The 0.1 μm and smaller particles previously buried deeper in the filter matrix had disappeared. In a third experiment, particles of ammonium bisulfate were deposited on teflon filters and exposed to ammonia gas. The addition of $NH_3(g)$ resulted in mascagnite crystals as expected. This method produced an extremely strong preferred orientation, again with a preference for the faces and edges of the crystal lying in the plane of the filter. Optical microscopy showed that the ammonium bisulfate at a loading of approximately 20 $\mu m/cm^2$ (sulfur) appeared as small droplets on the filter apparently in a coalesced liquid state. This is expected since ammonium bisulfate deliquesce at R.H. values above 30%. Following neutralization with $NH_3(g)$, the particles will recrystallize as they dry. In both mechanisms the randomly deposited particles have the opportunity to slowly recrystallize while on the surface of the filter which provides an opportunity for preferential orientation of the crystals.

Particle-Particle Interactions

Both positive and negative particulate nitrate sampling artifacts on teflon filters have been studied [Mulawa and Cadle, 1985; Anlauf et al., 1985; Appel et al., 1984; Forest et al., 1982; Appel and Tokiwa, 1981; Appel et al., 1980; Doyle et al., 1979]. A summary of reactions that have been observed in the laboratory by one or more of these authors are listed below.

1) $NH_4NO_3(s) \rightarrow NH_3(g) + HNO_3(g)$

2) $H_2SO_4(l) + 2NH_4NO_3(s) \rightarrow HNO_3(g) + (NH_4)_2SO_4(s)$

3) $HCl(g) + NH_4NO_3(s) \rightarrow HNO_3(g) + NH_4Cl(s)$

4) $HNO_3(g) + NaCl(s) \rightarrow HCl(g) + NaNO_3(s)$

The mechanisms associated with these various reactions, and in particular the role that water of hydration, deliquescence, and condensation plays in the transformations are not well understood. Relative humidity has been recognized as a significant variable but has not been fully explored. XPDFT provides an excellent analytical tool for studying the nitrate and other artifact reactions on teflon filters. We have observed the following reactions:

5) $NH_4HSO_4(s) + NH_4NO_3(s) \rightarrow (NH_4)_2SO_4(s) + HNO_3(g)$

6) $2NH_4HSO_4(s) + NH_4NO_3(s) \rightarrow (NH_4)_3H(SO_4)_2(s) + HNO_3(g)$

Ammonium nitrate was deposited on teflon filters and XPDFT spectra were obtained. The complete disappearance of nitrate was observed by adding nearly stoichiometric amounts of ammonium bisulfate to the ammonium nitrate deposits. At this stoichiometric ratio, and under laboratory R.H. of about 40%, mascagnite is formed and the nitrate peak disappears within twelve hours. The addition of twice the stoichiometric amount of sulfate produces letovicite and the disappearance of ammonium nitrate. Repeated XPDFT was performed on ammonium nitrate samples to assure that the result was not induced by intense x-radiation. The filters were subsequently exposed to $NH_3(g)$ to convert any remaining nitric acid to ammonium nitrate and XPDFT was repeated. There was no evidence of ammonium nitrate. In these experiments, approximately 50 $\mu g/cm^2$ of ammonium nitrate was reduced to less than 2 $\mu g/cm^2$, the detection limit.

Water as a Key Factor in Artifact Formation

The differences in particle wetting between the static and flow conditions in the preferred orientation experiments were studied using methyl-2-cyano-acrylate (MCA) polymeric replication of the water on the particles. Immediately following exposure to humid air in the first two methods, the filters were placed over vapors of the MCA monomer. The subsequent micrographs of the filters showed that under static conditions, the larger (0.3 to 0.5 μm) particles on the surface of the filter have grown to 2 to 5 μm, while the smaller particles showed no evidence of nucleating water. In the second flow exposure to humid air, a uniform deposit of water was seen connecting all of the particles. The dimension of the connected particle was still 2 to 5 μm. These are exactly the conditions that would allow the 0.1 μm and smaller particles to coalesce with the larger particles resulting in their disappearance.

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