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A high volume sampling system, employing Nuclepore filters and designed for sampling particulate in the plumes from industrial sources using a light aircraft, is described. The effluent of kraft paper mills was sampled using this system and then analyzed by electron microscopy.

Size distributions of particles were obtained at several points downwind in the plume from a kraft mill. The size distribution close into the stack was log normal. There was a statistically significant reduction in median particle size a mile to two miles downwind of the stack. Also, the size distribution deviated from log normal. Several possible mechanisms are postulated as causes for this phenomena. Plume dilution with particles of smaller average size appeared to be a significant factor in causing the decrease. The median particle size close to the kraft mill was about 0.35 micrometers. At downwind points it was found to be as low as 0.15 micrometers.

Chemical identification of kraft mill particles was accomplished using electron diffraction techniques. Kraft mill salt cake was identified in particulate samples collected as far downwind from the mill as eight miles. Sodium sulfate (Na_2SO_4) and calcium carbonate $(CaCO_3)$ particles were both identified. Morphological associations were made with chemical identity. Sodium sulfate morphology was related to sampling technique. Due to the presence of water in the plume this compound appeared to have been fluid when sampled, and to have crystallized as a hydrate in a flat, smeared form on the filter. Calcium carbonate was a relatively large flaky particle appearing in both anhydrous and hydrated forms.

Approximately 100 electron micrographs including both transmission and scanning micrographs are presented which support the sizing and morphological results.

Airborne Sampling of Particles Emitted to the Atmosphere from Kraft Paper Mill Processes and Their Characterization by Electron Microscopy

by

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AIRBORNE SAMPLING OF PARTICLES EMITTED TO THE ATMOSPHERE FROM KRAFT PAPER MILL PROCESSES AND THEIR CHARACTERIZATION BY ELECTRON MICROSCOPY

I. INTRODUCTION

Statement of the Problem

The most widely used process for the manufacture of pulp and paper in the United States is the Kraft process. Plants using this process are numerous and widespread throughout the country. Two components of this process, the recovery furnace and the lime kiln, emit particles which contribute to air pollution problems in the areas where plants exist. Although most Kraft plants control over 90 percent by weight of their particulate emissions, the remaining particles, by nature of their small size, can constitute a significant air pollution problem.

The fundamental reason for this problem is because the particles which are emitted are in the sub-micrometer size range. Although the amount is small by weight percentage, the number of particles is large. It is well known that the particles in this size range contribute more to loss of visibility and possible health effects than larger particles which are more evident in fallout and soiling problems. How important the effects of small particles are with respect to visibility and health problems can be appreciated by reading the review of such problems in Stern (1968).

The need for the study of such particulate emissions has recently been emphasized by a report of the National Academy of Engineering (1972). This report recommends federal support for "an expanded and coordinated experimental program designed to gather information on the size distribution, especially in the fine particle range, and on the chemical composition of particles and carrier gas emitted from stationary sources" (p. 5). The immediacy of the problem of small particle emissions from pulp mills in the Willamette Valley of western Oregon is delineated in the report, "Environmental Quality in Western Oregon" (Advisory Committee on Environmental Science and Technology, 1971). This report describes the persistent haze problems of this region which are attributable to the combination of its restricted natural ventilation and concentration of population and industry. One of the major components of this industrial complex are the pulp mills located in this region.

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It was intended that this research, the characterization of particles emitted from kraft paper mill processes, would contribute information to the solution of general problems of particulate pollution given by the NAE report cited previously and at the same time develop data which would lead to a better understanding and control of specific air pollution problems in western Oregon. With reference to the latter, the capability to characterize particles in atmospheric aerosols would be quite useful in tracing the types and sources of particles which are contributing to local pollution problems.

Objectives of the Study

Whereas natural atmospheric aerosols have been the subject of considerable research, atmospheric aerosols from industrial sources have only been lightly treated, and kraft mill aerosols not at all. Therefore, it was the general objective of this research to study the physical and chemical properties of a particular industrial aerosol and at the same time develop methods which could be applied to sampling and analysis of other industrial effluents in the atmosphere. The problem of characterization of an aerosol and its reactions in the atmosphere can be extremely complex and broad in scope. Therefore, it was necessary to limit this investigation to the development of basic information without regard to the explanation of any particular phenomena (such as atmospheric reactions, etc.).

The specific objectives of this research were: 1) the study of certain physical properties of kraft aerosols such as size distribution and morphology subsequent to their emission into the atmosphere; 2) to perform chemical identification of as many of the various chemical species as possible and to relate, if possible, chemical identity to visual identification through morphological characteristics; and 3) the development of sampling and analytical techniques which would permit the accomplishment of tasks 1 and 2 in a reasonably effective manner.

The Kraft Process

A brief explanation of the recovery portion of the Kraft process as it applies to this research is in order to orient the reader.

The essential part of the pulping operation is the cooking process in which wood chips are reduced to cellulose fiber in a large drum called the digester. The cooking liquor used for digestion is an aqueous solution of sodium sulfide (Na₂S) and sodium hydroxide (NaOH) called "white liquor." This process dissolves the lignin, the glue that holds the cellulose fibers together, and other non-cellulose components of wood.

After digesting, the cellulose fibers, now called "pulp," are separated from the spent liquor called "black liquor." The pulp goes through several processes until it becomes paper or is sold as dried pulp. The spent cooking liquor is then treated to recover the process chemicals. It is this last process that is the source of particulate emissions and the concern of this research.

The "black liquor" is first concentrated through an evaporation process and then goes to a mixing tank where makeup sodium sulfate (Na_2SO_4) is added. The liquor is then pumped into the recovery furnace where the organic materials in the liquor are burned and sodium sulfate is reduced to sodium sulfide. The sodium salts are recovered as smelt or molten ash, its form being sodium carbonate (Na_2CO_3) and sodium sulfide.

The combustion zone of the furnace, in addition to the burning of organics, oxidizes the sodium sulfide to sodium sulfate and combines sodium hydroxide with carbon dioxide (CO_2) to form sodium carbonate. These salts then fall to the reducing zone where again sodium sulfide is formed and carbon dioxide is released. Not all the salts are reduced, however. Some sodium sulfate and sodium carbonate are carried over with the flue gases. It is these salts that are recovered by the control equipment both for purposes of process economy and air pollution control. At the two plants sampled in this research, the control on the recovery furnace is an electrostatic precipitator.

The second major source of particulate in a Kraft mill is the lime kiln. The output of the recovery furnace, sodium sulfide and sodium carbonate, are dissolved in water to form "green liquor" which in turn is causticized by slaked lime $[Ca(OH)_2]$ to convert the sodium carbonate to sodium hydroxide. Solid calcium carbonate $(CaCO_3)$ is recovered from this process by settling and is returned to the kiln where it is converted to lime. The exhaust gases of the lime kiln are controlled by wet scrubbers and the effluent consists of calcium carbonate, sodium carbonate and sodium sulfate.

In both plants sampled during this research, the effluent of both recovery furnaces and the lime kiln were combined into a single tall stack for disposal in the atmosphere.

The proportions of the particulate emitted from both processes were roughly 80 percent sodium sulfate and the remainder sodium carbonate and calcium carbonate.

II. SUPPORTING WORK

There have been a number of analyses of Kraft particulate based on samples taken from stacks. Among these are studies by Bosch (1971), Day (1937), Murdock (1939), and Okita (1967). Doubtless there are many more which have not been widely distributed. To this author's knowledge, no studies have ever been made to determine the characteristics of Kraft particulate after it has been discharged into the atmosphere.

In order to accomplish the objectives of the study it was necessary to study and apply the results of much other aerosol research to problems peculiar to this new field of endeavor. The applicable research which supports the methods and techniques of this project is discussed in this and the following section.

Airborne Sampling

The techniques of airborne sampling of air pollutants have been applied to a variety of pollution and meteorological problems in recent years. To a large extent these investigations have placed most of their emphasis on the sampling and analysis of gaseous pollutants. Several have, however, measured particulate concentrations using optical particle counters. Adams and Koppe (1969) developed a very elaborate airborne sampling system for CO_2 , CO, hydrocarbons and

 SO_2 . They used a Charlson-Ahlquist nephelometer for measuring visual range and a "bulk sampler" to collect particles for mass and microscopic analysis. The latter system was not described in detail in this paper. Blumenthal and Ensor (1972) have described another quite sophisticated airborne sampling system developed by MRI, Incorporated to trace the movement of pollutants in the atmosphere. The concentrations of CO, O_3 , and NO_x are measured. The aerosol sensors are an integrating nephelometer for measurement of visual range and mass loading and a condensation nuclei counter used for measurement of particle concentrations under a size of 0.1 micrometer (µm).

Other investigators who have used light scattering instruments mounted in aircraft to measure vertical and horizontal profiles of particle concentration and/or mass loading include Ahlquist and Charlson (1968), Bach and Hagedorn (1971), McCaldin and Sholtes (1971), and McCormick <u>et al.</u> (1972).

Among those who have developed airborne sampling techniques which are suitable for the collection of particles for subsequent detailed analysis are MacCready and Todd (1964), McCaldin and Johnson (1969), and Raynor (1972). MacCready and Todd, in their studies of cloud physics, have developed a means of capturing ice crystals and water droplets continuously in a softened Formvar film. The Formvar film is then allowed to harden, forming a permanent

replica of the crystal or droplet. The collection mechanism was impaction and was suitable only for large particles. In this study isokinetic sampling was not required. One of the most interesting aspects of this study which might be related to the present research was the analysis of water droplet distortion and estimate of the minimum size of particle which would break up on impaction. McCaldin and Johnson have used rather unsophisticated but effective techniques in their studies of power station and forest fire plumes. They have measured particle concentration at various points downwind in plumes using a Bausch and Lomb particle counter. To collect particles for microscopic examination they used a coated microscope slide held in the airstream just outside the aircraft. This was rather effective for relatively large particles but collection of particles below the size of about 2 µm was unlikely.

The particle collection system which most closely resembled that used in the present research was the sampler designed by Raynor. It was intended for determining size distributions and composition of power station stack effluents. It was an isokinetic sampler that matched the intake velocity of the sampler to the aircraft velocity. It was designed to utilize membrane filters with a high pressure drop. A flow rate sufficient to maintain isokinetic velocity was provided by a high volume blower powered by a 24 volt dc battery system. The design feature which made this system particularly suitable for

sampling was its use of membrane or nuclepore filters which are efficient samplers and lend themselves to such analytical techniques as electron microscopy and neutron activation analysis. The isokinetic feature, of course, was required in determining number and mass concentration of highly dispersed particulate. Another excellent design characteristic was the close proximity of the filter holder to the entrance cone of the sampler. This eliminated the possibility of particle deposition within the system prior to its encounter with the filter.

Application of Electron Microscopy to Air Pollution Research

The electron microscope has an important role in air pollution and atmospheric research. Its primary application is in the analysis of sub-micrometer particles since it has resolution capabilities some three orders of magnitude lower than the light microscope. The information which can be obtained using electron microscopy is similar to that obtained in light microscopy; namely, size distribution and morphology (size, shape and surface characteristics). While such information as refractive index and birefringence cannot be obtained, chemical identification can be achieved using selected area electron diffraction (SAED). A description of these techniques follows in the next section.

The capabilities of the electron microscope have been used by several investigators in the field of atmospheric and air pollution research. In the process, techniques of sample collection and sample preparation for aerosols have been well developed. Among the important contributors using electron microscopy is Junge (1953), who used electron diffraction to identify ammonium sulfate as a constituent of natural aerosols. Cadle et al. (1950) and Cartwright, Nagelschmidt and Skidmore (1956) were early investigators of air pollutants using the electron microscope. Several investigators have used electron microscopy to verify the self preserving size distribution theory of Junge for atmospheric aerosols. These investigations are summarized by Clark and Whitby (1967). An even more recent study of the size distribution of atmospheric aerosols was conducted by Simon (1971) in Hungary. Hemenway et al. (1964a, b) and Witt et al. (1964)conducted a rather extensive investigation of noctilucent cloud particles in which the samples were gathered during a sounding rocket probe to altitudes between 75 to 98 km. The major methods for analysis of the samples were electron microscopy and diffraction, neutron activation and electron microprobe analysis. Size distributions and morphological data were successfully obtained. However, results of composition studies using electron diffraction were inconclusive. Electron microprobe studies were more successful in identifying chemical composition of the particles. Certain elements (Fe, Ni, etc.) were

identified which led to the conclusion that the particles were of extra terrestrial origin. This study points up the importance of using, where possible, several analytical tools which complement each other. Later investigators who were more successful in identification of atmospheric aerosols using electron diffraction were Heard and Wiffen (1969). They successfully collected extensive samples of ammonium sulfate and conclusively identified it. Their micrographs also show interesting morphological and compositional features which are quite similar to those encountered in this research; namely, shape features and rapid decomposition of crystals under heating of the electron beam.

In recent years the study and identification of small particles by morphological characteristics has been the interest of Frank and Lodge. Their findings are reported in several papers (1967, 1970a, b; Cadle <u>et al.</u>, 1968) together and with co-authors. These papers contain many very interesting and striking micrographs. They have perfected the art of specimen preparation and examination to a high degree and this is a distinct contribution to the state of the art.

Particulate Sizing and Morphology

In relation to the research at hand, the subject of particle sizing and size distribution can be divided into two major areas. The first concerns the methods, techniques, and statistics of particle sizing.

In this area there is a large body of literature since particle technology has application to a wide range of industries including cement, ceramics, paints, and soil sciences to name a few. Industrial hygienists have been among the major contributors to the advancement of particle sizing techniques. In this thesis, only a few of the more fundamental papers on particle sizing will be reviewed.

The second major area investigated was the measurement and analysis of atmospheric aerosols. There are a number of theoretical and experimental works in this area, mostly concentrating on natural aerosols. These will be reviewed briefly. Few, if any, atmospheric experimenters have concentrated on aerosols generated by specific man made sources.

On the subject of particle sizing, perhaps the most fundamental and comprehensive work in existence is <u>Small Particle Statistics</u> by Herdan (1960). The contents include fundamental concepts of particle statistics, principles of sampling and size measurement, graphical representation, statistical testing, physical and chemical properties of materials that depend on size, experimental design, and experimental errors related to particle size.

The measurement of particle size is important because of the properties and effects of aerosols which are functions of size. For atmospheric aerosols the properties and effects of most interest are residence time, visibility, and lung deposition.

Depending on the properties to be investigated, one or another of the various measures of particle size may be of interest. For instance, visibility and light scattering effects are dependent on surface area and, in turn, on an equivalent diameter which will yield projected area. Lung deposition on the other hand is dependent on aerodynamic diameter which depends on the mass and drag characteristics of a particle. Excellent discussions of the various particle diametric measurements have been given by Davies (1961a, b), Hodkinson (1965), and Kaye (1968). In the first two works, the relation of various diameters to particle properties is discussed. Of particular interest in this research was the relation of projected area of particles to their surface area. Both Davies and Hodkinson point out a theorem due to Cauchy which states that the mean projected area of particles is a quarter of the total surface area, independent of their shape. This is true, however, only of particles which are randomly oriented, i.e., in suspension, whereas most particles measured microscopically are in a settled orientation. The factor which relates random orientation to settled orientation is called a shape factor. This factor has been the subject of experimental research. Both Corn (1964) and Ellison (1954) have made experimental determinations of the ratio of settled projected area to random projected area. Their results show that this ratio varies from about 1.1 to 1.4 for micrometer size particles. Many other types of particle shape factors exist including the ratio of

settled projected area diameter to Stokes diameter, ratio of volume diameter to surface diameter, etc. These shape factors are discussed by Davies (1964), Herdan (1960), and Hodkinson (1965). Shape factors vary from one material to another and, consequently, experimental determination of these factors is usually required. Many experimental measurements have been reported, for example, Cartwright (1962), in addition to those named above.

Stein <u>et al.</u> (1968) studied the shape of particles in ambient Pittsburgh air in the size range 1.5 μ m to 16 μ m. Aerodynamic diameter (d_e) was measured by elutriation techniques and projected area diameter (d_p) by microscopic techniques. It was found that aerodynamic diameter could be successfully used to estimate mass distributions but not projected area diameter. Large variations in the ratio d_e/d_p were found, reflecting variations in shape and which precluded the translation of particle size distribution data collected on the basis of one parameter to distributions associated with the other.

An interesting approach to the measurement of area/perimeter ratios and volume/surface ratios using a counting technique is reported by Kaye (1968) and is due to Chalkley <u>et al.</u> (1949). The technique utilizes a needle of length δ dropped randomly on particle profiles. If h is the number of times that both ends of the needle lie within the particle profiles and if C is the total number of times the needle cuts

the particle profile, then:

$$\frac{\delta h}{C} = \frac{\text{Area of particle profiles}}{\text{Perimeter of particle profiles}} = 4 \left(\frac{\text{particles}}{\text{Surface}}\right) \quad (2-1)$$

Kaye (1968) also presents an excellent discussion of Martin's and Ferret's Diameters, two common indicators of particle size. Another technique for geometric shape characterization has been developed by Byers <u>et al.</u> (1970), using a computer to process scanning electron microscope images. An ellipse of best fit is calculated for each particle. From this an aspect ratio, which is log normally distributed, is derived.

The statistical reliability of particle size distributions has been studied by Corn (1965). Corn reviews some of the literature on the number of particles counted to achieve a reasonably accurate size distribution curve. He finds that the number recommended varies from 100 to several thousand. He states that in actual practice most industrial hygienists assume 200 is an adequate number. Ettinger and Posner (1965) conducted an extensive comparison study of sizing results on a given aerosol when done by eight participating laboratories. They found that geometric means agreed to within 10 percent while geometric standard deviations agreed to within 15 percent. The typical number of particles ranged from 200 to 600 with an average of about 500.

Watson (1948) and later Irani (1959) have discussed abnormalities

Volume of

which cause size distributions to depart from the usual log normal distribution. Irani suggest as possible causes either a truncation (at either the high end or low end) in size of particles during particle formation process or a heterogeneous mixture of size distributions.

Particle size distribution for atmospheric aerosols has been studied by Blifford and Ringer (1969), Clark and Whitby (1967), Friedlander (1961, 1965), Junge (1953, 1955), Pasceri and Friedlander (1965), and Simon (1971). The major thrust of these investigations has been the study of the so-called "self-preserving" size distributions of atmospheric aerosols. These size distributions of aerosols may be described by an equation of the form

$$\frac{\mathrm{dN}}{\mathrm{dr}} = \mathrm{Kr}^{-4} \tag{2-2}$$

where N is the aerosol concentration in particles /unit volume and r the particle radius and K a constant. This phenomenon was first noted experimentally by Junge. A theory was developed by Friedlander explaining the phenomena in terms of the effects of coagulation and sedimentation. Subsequent investigations by those authors named, and others, have tended to confirm the theory.

The test of a "self-preserving" size distribution was not applied to the data of this research because of the time requirements necessary to count and establish particle concentrations on a statistically sound basis. It would be interesting and useful to do so and should ultimately be done. The information actually exists in data already acquired and merely needs processing.

Filter Efficiency and Retention

The present theoretical and experimental basis for the calculation of membrane filter efficiency and retentive capability has largely been the work of two investigators, Spurny and Pich of the Institute of Physical Chemistry, Prague, Czechoslovakia. Together and with other authors they have authored a series of 19 papers under the title, <u>Analytical Methods for Determination of Aerosols by Means of</u> <u>Membrane Ultrafilters</u>. These have been published in the <u>Collection</u> <u>of Czechoslovak Chemical Communications</u> in the period from 1957 to the present. The early part of the series is devoted largely to cellulosic (Millipore) type filters while the latter part is devoted to Nuclepore filters. Some of the most pertinent of these papers are discussed below.

The basic theory of membrane filtration and some experimental results can be found in two papers by Spurny and Pich (1963, 1965). A theoretical development by Pich can be found in the book, <u>Aerosol</u> <u>Science</u>, edited by Davies (1966). In these works modeling schemes for the filter pore structure are proposed and equations developed for the filtration mechanisms of impaction and diffusion. Filtration efficiency is found to be a function of pore size, aerosol diameter and gas velocity at the filter face.

The filtration efficiency of Nuclepore filters is discussed by

Spurny and Lodge in the Czechoslovak journal (1968a, b). The basic theory of membrane filters developed earlier applies, with the addition of an empirical term to account for the filtration mechanism of direct interception. Essentially the same information is contained in two subsequent papers by Spurny, Lodge, Frank and Sheesley in the American journal, <u>Environmental Science and Technology</u> (1969a, b). These papers contain some excellent electron micrographs illustrating the various filtration mechanisms. The last paper in the Czechoslovak series is by Spurny and Madelaine (1971) and contains a comparison of theoretical and experimental data on Nuclepore filters. A significant drop off in actual efficiency at high filter face velocities (> 50 cm/s) was shown. These data had important implications for the present research.

Particle Deposition and Anisokinetic Sampling

Some of the major sources of error in aerosol sampling are those which are associated with particle deposition, anisokinetic sampling and angularity of flow relative to the sampling orifice. The theoretical treatment of these problems is covered by Davies in two works. In <u>Aerosol Science</u> (1966), Davies discusses the fundamental physics of particle deposition in a turbulent boundary layer. In the second (1968), Davies gives a parametric treatment of anisokinetic

sampling deriving bounds in sampling parameters such as probe diameter, sampling velocity, wind velocity, and particle diameter within which sampling can be considered 100 percent efficient. He also derives sampling efficiencies for point sinks in winds and limiting sizes for sampling at 100 percent efficiency at arbitrary orientation in a wind. Vitols (1966) calculated particle trajectories and correlated the results in terms of the Stokes Number, S/D, where S is the particle stopping distance and D is a characteristic dimension, in this case probe diameter. The results allow the corrections of observed concentration to actual concentration. Vitols was able to obtain agreement between his predictions and the experimental data of Badzioch (1960) and Hemeon and Haines (1954). Nelson (1971) has adapted Vitol's data to a form usable in correcting experimental data.

Much of the recent experimental work in particle deposition and isokinetic sampling has been done by Sehmel (1970). Percentage of particle deposition as a function of a deposition velocity parameter, Reynold's number and particle size is given. Concentration ratios are given for anisokinetic sampling conditions as a function of Stokes number, velocity of the sampled stream, and particle diameter. Concentration ratios were found not to correlate perfectly with Stokes number although the same general trend as calculated by Vitols is shown. It can be observed, however, from Sehmel's data that sampling errors become small at particle diameters below one

micrometer. Another interesting result, pertinent to computation of aerosol concentration, is the measurement of concentration ratios of particles in the cross section of a sampling duct. Schmel shows that concentrations are definitely non-uniform across a filter placed in the duct.

Finally, May in <u>Airborne Microbes</u> (1967) discusses anisokinetic sampling and angularity of flow with respect to the sampling probe. His conclusion is that angularity of flow up to about 50 degrees can be tolerated with 10 percent error or less for particle sizes up to 5 µm.

III. EXPERIMENTAL METHODS

Airborne Sampling System Description

The primary means of sampling in this project was with a light aircraft equipped with a high volume sampling system. The principal ground rules in developing this system were that it should be sufficiently simple so as not to entail any modification to the sampling aircraft, and that it should easily be installed and removed from the aircraft for each sampling flight. This approach avoided the necessity of leasing an aircraft on a continuous basis, keeping the cost within bounds, and avoided a time consuming FFA certification procedure. The aircraft used was a Piper Cherokee 140.

A laboratory setup of the high volume sampling system with its major components labeled is shown in Figure 3-1. The equipment as installed in the aircraft is shown in Figures 3-2 and 3-3.

The system served two functions, the primary one was to collect particulate on a membrane filter and the second was to indicate when the aircraft entered and exited the plume. It consisted of the sampling probe which was constructed so that it protruded outside the window of the aircraft and was roughly aligned with the airstream. The probe introduced the sampled air into an integrating nephelometer mounted inside the aircraft. The nephelometer was a light scattering device which served to indicate when the aircraft entered



Figure 3-1. Laboratory setup of high volume sampling system.



Figure 3-2. High volume sampling system installed in the sampling aircraft.



Figure 3-3. Sampling probe installation in the aircraft.

and exited the plume. Not only did this instrument give a more precise indication of this than could be made visually, but it could also serve to locate the plume at distances far downwind and/or under lighting conditions where the naked eye could not. From the nephelometer the sampled stream passed through approximately two feet of tubing to the filter holder. This holder was a standard 4 inch Gelman filter holder modified to hold 90 mm Nuclepore or Millipore filters. The flow next passed through an orifice flowmeter, then into the Gelman Hi-volume blower powered by a 1/4 hp electric motor. The blower delivered a flow rate of 5 to 6 CFM through a 1 μ m Nuclepore filter. The power supply for the system was a 12 volt storage battery and DC-AC inverter. Flow rate, and thus velocity at the filter face was controlled with a Variac device in the circuit.

The sampling probe was equipped with an inlet nozzle designed to give approximately isokinetic flow when sampling with a 3 μ m Nuclepore filter. When it was determined that 1 μ m pore size filters and lower filter face velocities were needed to maintain filter retentivity in a quantifiable regime, the velocity decrease in the system resulted in a sampling velocity/airspeed ratio of about 0.4. Rather than reduce nozzle diameter and cause a further restriction in flow, it was decided to retain this nozzle. It will be shown that the errors due to this anisokinetic sampling ratio are negligible. A picture of
the aircraft sampling the plume, taken from a second aircraft, is shown in Figure 3-4.¹ In the background is the American Can Company plant at Halsey, Oregon. The plume is barely visible in the picture attesting to the excellent pollution control at this plant and to the need for the nephelometer in locating the plume.



Figure 3-4. Sampling aircraft passing through the plume at the American Can Company plant, Halsey, Oregon.

¹Photo credit to Mr. Ed Meyer, Graduate Student, Department of Mechanical Engineering, Oregon State University. Pilot of the Photographing aircraft was Dr. R. W. Boubel.

If a plume is to be sampled at a given point downwind, the aircraft must fly across the plume. The usual duration in the plume on such a pass is a matter of seconds. It has been found through experience that many passes must be made through the plume to collect a sample sufficiently dense for analysis. To get the total volume sampled during these multiple sampling runs, it was necessary to time each pass with a stopwatch and record the flow rate during the pass using the orifice flowmeter. The system is equipped with a filter holder bypass and valving system such that, by operating two valves, the sampled flow could be delivered to the filter and stopped at the proper times indicated by the nephelometer. Thus, with total volume measured and by using particle count on the filter, the plume concentration in terms of particle number /unit volume could be estimated. Exposed filters were removed from the holder and placed in plastic containers to prevent contamination during transfer to the laboratory.

The orifice flowmeter constructed for this experiment was necessarily much shorter than the standard length and therefore it was necessary to calibrate it independently. Calibration was accomplished using the actual sampling system set up in the laboratory and flowing through a precision rotameter. Several filters with a range of pore sizes were run and it was determined that there was no difference in calibration due to filter pore size.

The calibration curve is given in Figure 3-5. Flow rate through the filter is given as a function of a pressure head parameter which characterizes the actual flow conditions. Required pressure measurements are Δp_0 , the pressure drop across the orifice; Δp_a , the pressure differential between ambient and static pressure ahead of the orifice (flowing pressure), and the barometric pressure at altitude. The first two measurements were made with the Magnehelic gauges shown in Figure 3-1. Barometric pressure was read from the aircraft altimeter.

Nuclepore Filters

Both Nuclepore and Millipore filters were considered for use in this program. Nuclepore became the primary sampling filter for several reasons. The flow rate through Nuclepore filters is approximately four times that through a Millipore of comparable pore size. Nuclepore also makes an excellent substrate for electron microscopy and seems considerably easier to prepare for microscopic examination. Nuclepore filters do have poorer particle retention characteristics than Millipore but their efficiency is quantifiable, removing much of the disadvantage. This quantifiable nature is due to the cylindrical geometry of the pores which lend themselves readily to modeling. Plate SM01 of Appendix B shows the smooth surface and regularity of the Nuclepore pore geometry. The filtration efficiencies and



Figure 3-5. Calibration curve for orifice flowmeter flow rate in cfm versus pressure head parameter, $\sqrt{\Delta P_0 \Delta P_a}$.

structural characteristics have been studied in some detail by Spurny <u>et al.</u> (1968) and will be discussed below. The uniformity of pore diameter for Nuclepore filters is indicated in Table 3-1 which details characteristics of some typical Nuclepore filters. The rated pore size is generally the upper limit with the mean pore size somewhat less. For example, for a 1 μ m filter the mean pore size is about 0.88 μ m. The standard deviation of the pores ranges from 15 to 30 percent of nominal. Filters are typically 10 μ m to 12 μ m thick and made of a tough polycarbonate plastic film.

Sampling Errors

There are several possible sources of error associated with the sampling system described above. Briefly, these are:

- 1) Errors due to Anisokinetic Sampling.
- 2) Particle deposition in the sampling train.
- Angularity of flow relative to the sampling probe due to prop wash.
- 4) Filter retention characteristics.
- 5) Filter contamination due to engine exhaust.

A thorough search was made of sampling literature and analysis to determine how serious the errors were and whether or not they could be tolerated.

In the first four problems mentioned, the key parameter is

Nominal pore diameter (µm)	Mean pore diameter (µm)	Standard deviation (µm)	No. pores/ cm ²	Porosity ^a (P= V_P/V_F)	Filter thicknes s (µm)
0.5	0.42	± 0.16	3×10^{7}	5.1 x 10 ⁻²	12
0.8	0.482	± 0.12	1×10^7	2.52 x 10 ⁻²	11
1.0	0.882	± 0.24	1×10^{7}	3. 9 x 10 ⁻²	10
2.0	1. 724	± 0.38	2×10^{6}	6.28 x 10 ⁻²	8
5.0	4.102	± 1.56	1×10^{5}	7.8 x 10 ⁻²	8
		· · · · · · · · · · · · · · · · · · ·			

Table 3-1. Structural properties of nuclepore filters. (Source: Spurny et al., 1969a)

 ${}^{a}V_{P}$ = total volume of the pores in the filter, cm³ V_{F} = total volume of the filter, cm³

particle inertia and its effects can be expressed in terms of the Stokes Number, S/D. This is the ratio of the inertial parameter, particle stopping distance, S, to some characteristic distance, D (sampling probe inlet diameter, for instance). In the first three cases, it has been determined that the errors incurred are negligible due to the small size (95% $\leq 1 \ \mu m$) of the particles being sampled. In the fourth case, filter retentivity problems are aggravated due to small particle size.

Anisokinetic Sampling

The correction factors for anisokinetic sampling developed by Nelson (1971) based on Vitol's data (1966) were applied to the size distribution of Filter 050 to test the effect of sampling at a subisokinetic velocity ratio of 0.4. The correction to particle concentration at a particle size of 1 μ m is about 4 percent and 10 percent at 1.5 μ m. In the case of Filter 050, neglect of these corrections would cause an error of about 0.6 percent in concentration.

With respect to morphological data there would be no loss of information since at subisokinetic velocities large particles on trajectories in line with the probe entrance are captured due to their inertia.

Particle Deposition

Concerning the problem of possible particle deposition in the sampling train it seems quite certain that this should not have seriously affected sampling effectiveness. Schmel (1970) has shown that for fully developed turbulent flow in straight tubing, 10 feet long, diameters ranging from 0.6 inches to 1.15 inches and flow rates up to 12 and 40 cfm respectively, that particle deposition for 1 μ m particles is generally less than 0.1 percent. It is true that the system used in this report was not a straight tube and the flow path was somewhat tortuous, especially through the nephelometer. This was of some concern until it was learned that air pollution personnel have operated nephelometers continuously over long periods (one year or more) without noting any evidence of deposition.² Care was taken to avoid as much as possible the use of plastics in the sampling train in order to minimize any deposition due to electrostatic charge.

Angularity of Flow

Possible sampling errors due to angularity of flow at the nozzle

² Personal communication from Mr. John Kowalcyzk of Columbia-Willamette Air Pollution Authority, Portland, Oregon.

inlet due to the propeller can be neglected for the same reasons as given for the two previous errors. Particles as small as 1 µm simply follow the airstream and can be treated as a gas, relative to large openings. There is no reason to believe that the concentration or distribution of particle sizes should be changed due to the propeller action. Therefore, based on the error estimate of May (1967) quoted in the previous section, it was assumed that there was no significant error from this source.

Filter Retention Characteristics

The problem of filter retention characteristics depends heavily on the same inertia parameter discussed above, the Stokes Number, as well as on particle diffusion and particle interception. In this case, however, the tendency of small particles to act like a gas is disadvantageous, since it is because of this characteristic that the smaller particles tend to flow right on through the filter pores. In this case, the characteristic distance, D, in the Stokes Number is the pore diameter which is usually much smaller than a typical probe diameter and there is, therefore, a reasonable possibility of retaining a sufficient number of particles on a filter surface due to impaction. As discussed in the previous section, the theory and experimental data on filter retention characteristics have been well developed by Pich (1966) and Spurny and Pich (1963, 1965). Papers that are most important to this research are two by Spurny <u>et al.</u> (1969a, b). In the first, theoretical equations for filter efficiency are given. The efficiency equations which follow are taken from this paper. In the second, a comparison is made of theoretical and actual efficiencies as a function of filter face velocities. An empirical correction to the theoretical equations is also made.

The important collection mechanisms for these filters are impaction, diffusion, interception, and electrostatic effects. Separate partial efficiencies can be computed for each mechanism, except electrostatic effects, and summed as follows:

$$E = \epsilon_{i} + \epsilon_{D} - \epsilon_{i} \epsilon_{D} + \epsilon_{R} I^{(1-N_{R})} (1-\epsilon_{i})$$
(3-1)

where E = filter efficiency

 ϵ_{i} = partial efficiency of impaction

 $\epsilon_{\rm D}$ = partial efficiency of diffusion

 $\epsilon_{\mathbf{p}}$ = partial efficiency of interception

I = empirical constant = 0.63

 N_{R} = ratio of particle radius to pore radius, r/R_{o}

The definition of the equations for partial efficiencies is as follows:

The partial efficiency of impaction is from Pich (1966).

$$\epsilon_{i} = \frac{2\epsilon_{i}'}{1+\xi} - \frac{\epsilon_{i}'^{2}}{(1+\xi)^{2}}$$
 (3-2)

where

$$\epsilon_{i}^{\prime} = 2 \operatorname{Stk} \sqrt{\xi} + 2 \operatorname{Stk}^{2} \xi \exp\left[-\frac{1}{\operatorname{Stk} \sqrt{\xi}}\right] - 2 \operatorname{Stk}^{2} \xi \qquad (3-3)$$

$$\xi = \frac{\sqrt{P}}{1 - \sqrt{P}}$$
(3-4)

$$P = V_P / V_F$$
, filter porosity
 $V_P = total volume of the pores in the filter, cm3 $V_F = total volume of the filter, cm3$$

Stk = Stokes Number

$$Stk = \frac{2r^{3}\rho v}{9\eta rR_{0}}$$
(3-5)

r = particle diameter, cm

 ρ = particle density, gr/cm³

v = velocity of gas at filter face, cm/sec

 R_{o} = pore radius of filter, cm η = gas viscosity, cm²/sec

The partial efficiency of diffusion ϵ_D was computed by the formula attributed by Spurny to Gormley and Kennedy (1949).

$$\epsilon_{\rm D} = 2.56 \,{\rm N}_{\rm D}^{2/3} - 1.2 \,{\rm N}_{\rm D} - 0.177 \,{\rm N}_{\rm D}^{4/3}$$
 (3-6)

where N_{D} is the coefficient of diffusive collection given by:

$$N_{D} = \frac{LDP}{R_{O}^{2}v}$$
(3-7)

L = filter thickness or pore depth, cm

Equation (3-6) is valid for $N_D \leq 0.01$ which was the case for all instances pertinent to this research.

The partial efficiency of interception, ϵ_R , was computed using the expression credited to Natanson (1957).

$$\epsilon_{\rm R} = N_{\rm R} (2 - N_{\rm R}) \tag{3-8}$$

When $N_R \ge 1$ the filter efficiency is obviously 1 and the formula is invalid.

The electrostatic collection mechanism in Nuclepore filters is not yet understood and therefore no quantitative evaluation is possible. However, Spurny (1968b, 1971) has discussed this effect and attempted to measure changes in efficiencies due to it. He concludes that electrostatic forces may be responsible for increasing efficiencies above theoretical by about 10 percent in some cases. The greatest effect was at smaller face velocities (\simeq 5 to 10 cm/sec) well below the range used in this experiment.

A study of the equations above will indicate that for a given filter pore size the effects of particle radius and filter velocity have opposite effects on the two major collection mechanisms, impaction and diffusion. Impaction efficiency is directly proportional to particle momentum which, in turn, is proportional to particle radius cubed (or mass) and velocity. Higher particle velocities enhance impaction because the turning radius or stopping distance of a particle becomes larger and thus more difficult for it to turn and pass through a nearby pore. On the other hand, diffusive collection is inversely proportional to particle diameter and velocity. The diffusion mechanism acts both next to the surface and within the filter pores and results from the tendency of a particle to gravitate from its position in a streamline to the surface or a pore wall due to interaction with gas molecules. For this interaction to be significant the particle diameter must be small and its velocity low.

As a consequence of these relationships, Nuclepore filters usually exhibit a minimum efficiency at some particle size for a given face velocity. This effect and the effect of filter pore size are illustrated in the curves of Figure 3-6 taken from Spurny's paper (1969a).

The contribution of the direct interception mechanism seems also to be relatively less important than the value given to it by equation (3-8) and it must be reduced by some empirical factor. A value was estimated by Spurny (1968) and later revised in 1971. This revised value is that used in equation (3-1).



Figure 3-6. Computed dependency of efficiency on particle size, r, and pore size, R_{o} . (Source: Spurny <u>et al.</u>, 1969a)

Filter efficiencies as functions of filter pore size, particle size and face velocity were computed based on the equations given above. These data are given in Figures 3-7, 3-8, and 3-9. They were used to correct the actual particle counts on filters to give true size distributions.

The result given by Spurny and Madelaine (1971) in comparing theoretical and measured filter efficiencies had a significant effect on the conduct of the experimental program. These data show that there is a sharp dropoff in filter efficiency for face velocities of about 50 cm/sec. The data for one set of conditions is given in Figure 3-10. In the initial stages of sampling, a 3 μ m pore size Nuclepore filter











Figure 3-9. Theoretical efficiencies of Nuclepore filters as a function of particle size, d, and filter face velocity, v. Nominal pore diameter = $3 \mu m$.





Figure 3-10. Measured dependence of filter efficiency, E, on face velocity, v. (Source: Spurny and Madelaine, 1971)

had been selected in order to keep flow rate as high as possible and minimize the amount of time required to be spent in the plume to collect a reasonable sample. At the maximum flow rate of the sampling system (15 cfm) for this pore size, the filter face velocity was approximately 150 cm/sec. Although rather good samples were obtained with this pore size filter, it was felt that the filter face velocity and pore size should be reduced to 45 cm/sec and 1.0 μ m respectively to insure reasonable sampling efficiency. In spite of the dropoff in efficiency indicated in Figure 3-10, the theoretical efficiency curves were used to correct the data for 3 μ m filters. Comparison of size distributions obtained with 1 μ m and 3 μ m filters seems to indicate that, while theoretical efficiencies for high face velocities are probably somewhat high, they are not as inaccurate as might be expected from the data of Figure 3-10.

Although the data on theoretical and actual efficiencies by Spurny are adequate to give warning to avoid certain combinations of sampling conditions, the range of the data is limited. It would be useful and helpful to have more comparison data for a larger range of particle to pore size ratios and face velocities.

Exhaust Contamination

The presence of the sampling probe in the propeller slipstream raised the question of possible contamination of filters by exhaust from the aircraft engine. This possibility was examined by using Neutron Activation analyses performed by OSU Radiation Center personnel. A sample was taken of aircraft engine exhaust on a Nuclepore filter by placing the sampler below the aircraft engine exhaust stack while the aircraft was on the ground. This sample was compared to samples taken at the normal sampling point in flight. The exhaust sample was found to have relatively heavy concentrations of the elements bromine and vanadium, which are common to aviation fuels. The filter taken at the sampling point had no evidence at all of these elements, proving conclusively that exhaust contamination was not a problem. These results are summarized in Table 3-2.

	Sampling Point		Presence of tracer	
Filter		Sample source	compounds (µg)	
			bromine	vanadium
014	Below aircraft exhaust stack (on the ground)	Aircraft exhaust	13.75	0.05
015	Aircraft window	Background air	0.00	0.00
016	Over top of cabin ^b (in flight)	Background air	0.04	0.00
017	Aircraft window (in flight)	Plume	0.00	0.00
018	Over top of cabin ^b (in flight)	Plume	0.06	0.00

Table 3-2. Results of neutron activation analyses testing for engine exhaust at the sampling point.^a

^aThis analysis was performed by Mr. Ed Shum, Graduate Student, Oregon State University Radiation Center.

^bSample taken through plastic tubing with open end attached to the top of the aircraft cabin.

Stack Sampling

Several stack samples were taken at the American Can Company

plant in order to make a comparison of particle characteristics in the

stack with those of atmospheric samples.

These samples are listed in Appendix A along with the

atmospheric samples and were obtained with equipment normally used at American Can for stack sampling. The Nuclepore filters were placed in a standard 47 mm filter holder fitted to a 3/8 in. stainless steel probe with a 1/4 in. nozzle. Flow through the sampling system was induced by an air eductor in the plant high pressure air system. With this system is was possible to achieve whatever velocity was necessary to insure isokinetic sampling.

Samples were taken at two points just prior to the effluent entry into the stack. At one sampling point, effluent from the recovery boiler is collected and at the other effluent from the lime kiln. The filters from these points are labeled RB and K, respectively. Both sampling points were downstream from the control equipment.

Some difficulty was encountered in obtaining a sample which could be considered representative of the particulate as it exists in the gas stream due to condensation problems. The temperature of the recovery furnace effluent is about 420 ^oF and it is about 35 percent steam, by volume. When the first set of samples were taken in the recovery boiler effluent, it was feared that the Nuclepore filters would not withstand the high temperature and, therefore, the sampling probe was placed in the stream only long enough to achieve is okinetic velocity and take the sample. The total time involved was perhaps two minutes at most. When these filters were analyzed it appeared

that there may have been a good deal of condensation on the filter surface due to the cold probe. Analysis of the filters revealed that they had withstood the high temperature gas quite well. Therefore, a second set of filters was exposed, allowing a longer time for the probe system to come to equilibrium temperature before the actual sample was taken. The results of both of these sets of samples are discussed in the Results and it appears that the second set was probably much more representative since the particles appear to have been much drier. In any future research it would be useful to take several more samples to confirm just what the particulate from the stack should look like.

The effluent from the kiln was from a wet venturi scrubber. It was at a low temperature $(165^{\circ}F)$ and was saturated. It was almost impossible to avoid condensation in this sampling situation. Most of the particles examined from these filters had the appearance of having been combined with some water. This was probably quite representative of the real situation in the atmosphere since the stack effluent probably carries a good deal of condensed water in it.

IV. ANALYTICAL METHODS

Electron Micsocropy

The principal analytical tool in this research was the electron microscope. Light microscopy was not adequate for these studies since the practical limit of resolution with such instruments is about 0.5 micrometers, greater than the median size of the particles being studied. Electron microscopes, on the other hand, have resolution capabilities on the order of angstroms ($10^{-4} \mu m$) and their much greater magnification permits accurate sizing and morphological studies of sub-micrometer particles. An additional feature of the electron microscope is its capability for electron diffraction analysis which can be used for chemical identification of crystalline substances.

Instrument Description

Two types of electron microscope were utilized in this research. The transmission electron microscope (TEM), which forms images by transmission of electrons through the specimen, was used for high magnification, sizing, morphological studies and electron diffraction. The scanning electron microscope (SEM) was used for morphological studies. The latter instrument forms its images by bombarding the specimen with an electron beam causing the emission of secondary electrons which are, in turn, used to form the image. The specimen is scanned with the beam at an angle to it and thus the instrument forms an image which has a three dimensional perspective. This added perspective was very useful in supporting and confirming conclusions reached concerning particle morphology with the TEM.

Three instruments were used in analysis of particles during this research. The first was a Hitachi HU-11B-3, a 125 KV instrument with magnification capability up to 150,000 X. This instrument, belonging to the Department of Mechanical and Metallurgical Engineering at OSU, was used until the instrument was placed out of commission due to a breakdown in its high voltage transformer. Subsequently the Phillips 300 instrument of the Botany Department was used. This was a 100 KV instrument with magnification up to 250,000 X. The scanning instrument was a Cambridge Stereoscan Mk II at the University of Washington.

Figures 4-1 and 4-2 are pictures of the Hitachi and Phillips instruments respectively. Figure 4-2 is a sectional diagram of the microscope column of the Phillips instrument showing its essential components. At the top of the column is the gun chamber containing the electron gun and the filament from which the electron beam is generated. The dual condenser lenses are the illuminating system serving the same purpose as a condenser in light microscopy, to concentrate the illuminating source on the specimen. The objective lens forms the image of the specimen, controls the focus and is the



Figure 4-1. Hitachi electron microscope type HU-11B-3.



Figure 4-2. Phillips 300 electron microscope.

primary magnification lens. The intermediate, diffraction and projector lenses are the magnifying system. The multiple lens arrangement provides a greater magnification range and incremental magnification. It also reduces the total height of the magnification column and permits corrections for distortion. The entire column is maintained at a high vacuum (10^{-4} torr) in order to permit passage of the beam without ionization and arcing. The specimen stage includes an airlock, specimen holder, and specimen tilt and translation mechanisms. The various lens apertures are for the purpose of reducing electron scattering and improving image contrast.

Below the lens system is the image recording system which includes the phosphorescent viewing screen and camera. The viewing screen is used for study and scanning of the image and the camera for recording images. The camera is a simple box camera containing 3-1/4 in. x 4 in. electron image plates. When an image has been selected on the viewing screen and it is desired to record it, the viewing screen is lifted, and an automatic exposure control is activated which exposes the plate for the proper time.

Instrument Operation

The operating techniques which must be acquired in order to effectively use the electron microscope are several. None are difficult, but time and experience are required to put them all together

to achieve satisfactory results. System alignment is the process of aligning the optical and geometrical axes of the electron gun and the lenses; stigmation is the compensation for astigmatism in the condenser and objective lenses, and focusing of the images is accomplished using Fresnel fringes. Focusing for selected area diffraction and image recording required some practice. The technique of getting proper exposure of selected area diffraction was quite different from normal image exposure, and trial and error was required before satisfactory images were achieved.

The technique of specimen preparation presented the most difficulty, and the particular approach used here deserves explanation in detail because of its impact on experimental results. There are as many techniques for specimen preparation as there are varieties of specimens, from biological to metallurgical. A good overview of the general methods of preparation can be found in <u>Techniques of Electron</u> <u>Microscopy</u> edited by Kay (1965).

Specimen Replication

Since transmission microscopy requires a very thin substrate for transmission, a replication process is normally used. In many cases the actual specimen is not examined but a replica of the specimen formed by the vacuum evaporation of a thin film (200-1000 Å) of an appropriate substance on the specimen. Common materials used to

form this film are carbon, palladium and silicon monoxide (SiO). These films have been found to make very faithful replications of the parent material. The replication is removed from the specimen for examination in the microscope by any one of several techniques depending on the nature of the specimen material.

Specimen replication was also required in this analysis due to the fact that the Nuclepore filters were at least 10 μ m thick, which would not permit electron transmission. Therefore the material collected had to be transferred to a thinner substrate for microscopic examination.

The technique adopted for this research was one developed by Evelyn Frank Ackerman (referenced Evelyn Frank) and reported in 1970b. Mrs. Ackerman is at the National Center for Atmospheric Research in Boulder, Colorado and has been associated with Dr. J. P. Lodge in atmospheric chemistry research.

The basic process of replication is sketched in Figure 4-3. The first step is to evaporate on the filter surface a metal shadowing substance to a thickness of about 200 Å at a low angle of incidence. Either chromium or aluminum was used. The next step was to evaporate a silicon monoxide film (SiO) to a thickness of about 1000 Å at vertical incidence. Silicon monoxide was chosen because it forms a tough film much less fragile than carbon. A small piece of filter thus treated was then carefully excised and placed on a specimen grid.







E.M. Specimen grid Mesh - 150 or 200 per inch



Wash three times in separate dishes for 8 min, 5 min, 5 min

Filter Removal

Figure 4-3. Specimen preparation from Nuclepore filters.

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These grids are normally made of copper and come in varying mesh sizes. In this experiment, 150 mesh (divisions per inch) and 200 mesh grids were used. The filter was then removed by a dissolution process. Nuclepore filters are soluble in ethylene dichloride and chloroform. For this process chloroform was found to be the best solvent. The specimen grid and filter square were placed on a small piece of foam saturated in a chloroform bath in a covered petri dish. The filter was allowed to dissolve for several minutes until it was completely removed. As the filter was removed, the silicon monoxide film adheres to the grid mesh and entraps the particles on the filter surface or forms exact replicas of them. Ackerman's process calls for a single wash of seven minute duration. In this process it was found that a single mesh did not, for some reason, satisfactorily remove all the filter material and it was necessary to use a multiple wash process. After much trial and error it was found that a three petri dish setup with a first wash length of eight minutes followed by two washes of five minutes duration each worked quite well. A good source for form material of approximately the right thickness was the foam packing that is found in the top of the boxes of electron image plates.

The substrate formed as described was a very thin replica of only the upper surface of the filter. It was normally quite smooth with the circular shape of the pores replicated and particles either trapped or their shape preserved.

Replication Problems

Although the process described above worked well in many respects and is probably the best available, there were several problems which introduced some confusion and uncertainty into the analysis. This was especially true in the early stage of experimentation. Some effects of the problems were overcome by better understanding of what was being observed on the specimen, but the problems of replication were not completely solved.

The chrome shadowing technique was not perfected and was finally abandoned after the first three dimensional morphological data were obtained using the SEM. Nevertheless, a shadowing effect was observed in the micrographs and it is believed that this resulted from the way the SiO was deposited. The SiO being evaporated was placed in a conical basket made of coiled tungsten wire. It is believed that interference of the basket wires must have caused the deposition from a direction other than vertical. The shadowing effect was manifested on the micrograph by an open area on one side of each particle where SiO did not deposit, which gave the appearance of a shadow. Also the pore replicas showed evidence on one side of the pore that SiO was deposited at an angle on the pore wall below the edge. These pore shadows were always oriented in the same direction as the particle shadows. Actually, the inadvertent shadowing of the SiO appeared to have been more effective than the intentional shadowing.

The problem of so-called filter "artifacts" seems to be unavoidable. These artifacts are the crescent shaped objects that sometimes resemble a fern leaf. Ackerman has said that the artifacts are somehow derived from the material next to the pores as the filter is dissolved away. In any case, this type of contamination can sometimes be very distracting and can mask effects associated with real particles. Fortunately, the artifacts do not always appear since their frequency of appearance varies from lot to lot of Nuclepore filters. Some lots are nearly free of them while in other lots they are quite annoying. Most of the micrographs selected for presentation are relatively free of these objects, but some are present on micrographs where it was necessary to show an effect in spite of them.

A major problem of the replication process was the uncertainty of whether or not some particles were carried away or dissolved during the filter dissolution process. It is obvious that many were not but in many other cases it appears that particles are partially or completely missing. This phenomena is discussed in some detail in the section on particle morphology and possible explanations advanced for it. Suffice to say here that one explanation might be the replication process. Not that replication did not work, but that particle entrapment was a good deal less than 100%. Good replicas always remain wherever particles seemed missing.

There was also some uncertainty about filter residue remaining after the dissolution process. Many filters showed what might be likened to water spotting. In some cases these actually were the results of a liquid droplet impacting the filter and leaving a residue. It seems to be fairly obvious when this was the case (see discussion of particle morphology in Section V). In other cases such as in plates 10-8 and 12-6 in Appendix B this spotting seemed to be definitely residue plastic from the filter. These two plates exhibit plastic looking threads that span the pore giving credence to the idea that this was residue. It appeared in these cases that the filter had nearly completely dissolved, but a very thin plastic sheet was left over which has parted and rolled up on itself, clung to the SiO film underneath and dried there. This phenomena then suggests that the dark area often seen around the periphery of particle replicas might be filter residue rather than particle residue. The author is inclined to think it is particle residue but the question has not been satisfactorily answered.

A problem which may be due, at least in part, to replication is the variability in intensity which will be observed in many of the micrographs in Appendix B. Variable thickness in the replica or evaporation on a surface which is not completely flat are possible causes. It may have been due to microscopic technique, that is, uneven illumination due to poor condenser system adjustment (in spite

of attempts to control this). These were problems of practice and technique which apparently take a good deal of time to perfect.

In spite of these problems, many satisfactory replications were achieved after a period of several weeks trial and error. And certainly the Nuclepore replication seems to be much easier than replication of a Millipore filter. The latter was tried several times with a process similar to that described except that the solvent was acetone. A truly successful replication was never achieved. The Millipore seemed to be much more delicate than the Nuclepore and tended to part during the dissolution process. Also, its surface was very rough compared with a Nuclepore and it was difficult to tell what was Millipore surface and what was a particle. Perhaps insufficient time was devoted to this technique since micrographs of Millipore replicas have appeared in the literature and, therefore, their replication has been demonstrated. Mrs. Ackerman, who has had several years of experience in this field, has confirmed that a Millipore filter is much harder to replicate than a Nuclepore filter.

Particle Sizing

Particle size for purposes of this report is defined in terms of equivalent area diameter. This diameter is defined as the diameter of a circle with a projected surface area equal to that of the particle. Sizing was accomplished using a Porton graticule (see Figure 4-4)



Figure 4-4. Porton graticule used in particle sizing.

adapted from one used in a light microscope. This graticule was photographed and enlarged so that, when placed in the binocular optics used for magnifying the image on the viewing screen of the electron microscope, it encompassed the field of view. The Porton graticule contains nine circles with diameters graduated in the ratio $\sqrt{2}$. It also contains a central grid whose spacings continue the graduations from Porton #9 to Porton #13. The sizing process was accomplished by focusing the image of the Porton graticule on the viewing screen and translating the image of the specimen past it, matching the area of each particle with the appropriate circle and recording the size, in terms of Porton number. The Porton eyepiece was calibrated by matching the graduations of Porton #13 with a metric measure as
viewed in the binoculars for each magnification setting of the microscope. This measurement determined the size of all Porton circles. A fixed magnification was maintained during the sizing of any one specimen.

Based on the practice of industrial hygienists as reported by Corn (1965), an endeavor was made to size at least 200 particles per filter. In a few cases the total fell slightly below this. On the other hand, in other cases, where there was initial doubt about the results, up to 1200 particles were sized. In most cases there was little change in results as the number of counts increased over 200. The actual count for each filter is given in the Results.

Size distributions determined in the manner described above were determined for a number of filters covering several downwind sequences and the results reported in Section V. The statistical analysis of these data is also reported in that section.

The statistical test used in analyzing differences in size distributions was the t test. Discussions of this testing procedure can be found in any elementary text on statistical methods. The test was used to establish that samples taken close in to the stack were from different populations than those taken downwind from the stack. One means of doing this was to compare measures of central tendency, in this case the medians, of the size distributions. The appropriate test for such a comparison is the t test. Since all of the particle size distributions in this research were described in terms of the parameters for a log normal distribution and plotted on log probability paper, the equation for the t test was formulated using these parameters. For a population which is assumed to be distributed log normally the parameters of the distribution are the geometric mean and the geometric deviation. The best estimator of the geometric mean is the median of the distribution; thus the equation for the t test in terms of these parameters is:

$$t = \frac{\ell n m_1 - \ell n m_2}{\sqrt{\frac{\ell n^2 \sigma_{g1}}{N_1} + \frac{\ell n^2 \sigma_{g2}}{N_2}}}$$

where m = median of the distribution

 σ_g = geometric deviation of the distribution N = sample size

The parameters m and σ_g were determined graphically from the log probability plots. In the test above it was assumed that the medians and geometric deviations were also best estimators of the sample means and standard error of the means. This is a good approximation if the sample sizes are large which was the situation in all samples tested. The large samples also allowed the test to be applied to non log normal distributions since, by the Central Limit Theorem, the distribution of their means approaches normality.

Selected Area Electron Diffraction

Selected area electron diffraction (SAED) or selected area diffraction (SAD) was the basic analytical method used in establishment of the chemical identity of particles in this research. The method of analysis is applicable to crystalline structures only. The analytical techniques are those of crystallography and use its structural modeling and terminology. Only the very briefest of explanations will be given here in order to orient the reader to some concepts necessary to follow the analysis which was performed. For more detailed expositions of the method the reader is referred to Kay (1965) and Andrews, Dyson, and Keown (1967). The explanation here is taken from the latter.

Principles of Selected Area Diffraction

Selected Area Electron Diffraction, as its name implies, involves the passage of a focused electron beam through a specimen and if the substance is crystalline the beam will be diffracted and produce a unique pattern on the viewing screen. This pattern may contain many rings of varying diameter or it may be a pattern of individual spots. These types of pattern will be discussed shortly. The term "selected area" is derived from the fact that diffraction apertures are normally used to limit the incidence of the electron beam to a specific, desired area on the specimen. With the Phillips 300 instrument the minimum aperture size for is 20 μ m and the focused electron beam during diffraction is about 1 μ m in diameter. Therefore, the uncertainty in the portion of a particle to be associated with a given pattern could be as much as 0.5 μ m.

When a suitably focused electron beam is passed through a crystal, diffraction will occur if the proper conditions are fulfilled. These conditions are represented by the Bragg Law and are illustrated in Figure 4-5.



Figure 4-5. Basic geometry of diffraction. Source: Andrews, et al. (1967)

In the circular inset a parallel beam of electron waves impinges on a crystal and makes an angle of incidence θ with a set of crystallographic planes of interplanar spacing, d, and Miller indices (h k l). By the construction shown, diffraction occurs when the paths via successive planes in the system differ from each other by a whole number of wavelengths. The diffracted ray then leaves the plane at angle θ . When this occurs the path difference, which is n λ , must equal the extra lengths along successive ray paths which is 2d sin θ and we have the Bragg's Law relationship,

$$n\lambda = 2d \sin \theta \qquad (4-2)$$

An alternative form of equation (4-2) with n equal to unity is:

$$\frac{1}{d} = 2 \left(\frac{1}{\lambda}\right) \sin \theta \qquad (4-3)$$

In the inset of Figure 4-5, a sphere of radius $1/\lambda$ is constructed with its center at O!. This intersects the direct beam of O" and the diffracted beam at P". The distance O"P" is seen to be 2 sin θ/λ which is therefore equal to 1/d. Furthermore, the direction of O"P" is parallel to O'N which is perpendicular to (h k ℓ). The construction of this "sphere of reflection" or "Ewald sphere" is a device for interpreting diffraction patterns.

Equation (4-3) is thus a useful form for interpreting the diffraction pattern from a single crystal in the electron beam. The pattern is recorded on the image plate which is normal to the incident beam direction O'O in Figure 4.5. The diffracted ray proceeds along O'P' and makes a diffraction spot on the film at P.

Now using the geometric relationships of Figure 4-5 and equation (4-2) it can be seen how interplanar, or d spacings, can be obtained by measuring the distance $\frac{D}{2}$ recorded on an electron image plate and knowing the camera constant for the instrument being used. From Figure 4-5 we have:

$$OP = \frac{D}{2} = L \tan 2\theta$$

$$OP' = 2 L sin\theta$$

Now, since θ is normally very small (< 3[°]), we can say:

$$\frac{D}{2} = 2\theta L$$

$$\lambda = 2\theta d \quad \text{from (4-3)}$$

and

giving

$$d = \frac{2L\lambda}{D}$$
(4-4)

which is the desired result. The quantity $L\lambda$ is known as the camera constant for the instrument and is usually determined through a calibration procedure by recording a diffraction pattern of a substance with known d spacings, such as gold.

One of the better diffraction spot patterns obtained during the analysis is shown in Figure 4-6. This is plate 9201 corresponding to the crystal of plate 9199 shown in Appendix 2. It has been identified as calcium carbonate hydrate (CaCO₃ \cdot H₂O).



Figure 4-6. Plate 9201 electron diffraction pattern from $CaCO_3 \cdot H_2O$.

This spot pattern results when the plane of the image plate intercepts the "sphere of reflection" or Ewald sphere. Normally this sphere has a radius so large that the area of interest on the sphere can be considered planar. The interpretation of the spot pattern so formed is done with a device known as the reciprocal lattice. This construction is explained below with the aid of Figure 4-7.

The reciprocal length 1/d is defined as the reciprocal lattice vector d*. The single crystal diffraction pattern is quite similar to a network of points that are at distances from the center, O, of the diffraction pattern proportional to $\frac{1}{d}$ or d*. Furthermore, the line joining O to any point is also parallel to the normal to the





Figure 4.7. Reciprocal lattice relationships for rectangular and oblique plane lattices. Also shows the relationship of the zone axis and planes in a zone. Source: Andrews <u>et al.</u> (1967)

diffracting plane (see Figure 4-5) and so represents the vector d* on a suitable scale. The array of points, therefore, determine vectors from the origin, O. Because it is a regular network it is regarded as a layer of a reciprocal lattice. The reciprocal lattice is a regular three dimensional pattern of points which is related to the three dimensional crystal lattice by the requirement that the vector distances in the former, d*, are perpendicular to their respective planes in the crystal lattice and have lengths inversely proportional to the corresponding interplanar spacing, d.

In the reciprocal lattice a point represents a plane of the crystal lattice and is defined by a set of Miller indices (h k ℓ). The formation of these indices is explained in terms of the two dimensional construction of Figure 4-7 and the parameters of the unit cell. The basic structure of a given substance is the unit cell. It may be made up of the atoms from one or more molecules of the substance. Its dimensions a, b, c, and angles α , β , γ are the fundamental crystal (or lattice) parameters of the substance and determine in which crystal system it belongs. The definition of the various crystal systems is given in Table 4-1.

Figure 4-7 covers the two dimensional rectangular axes (a) and oblique axes (b). Three dimensional lattices (except triclinic) follow by adding Z axes normal to the plane of the diagram. In the figure the Miller Indices are illustrated for the (230) plane. In crystal space

Table 4-1. Crystal systems.

Cubic	a = b = c
	$\alpha = \beta = \gamma = 90^{\circ}$
Tetragonal	$\mathbf{a} = \mathbf{b} = \mathbf{c}$
	$\alpha = \beta = \gamma = 90^{\circ}$
Orthorhombic	a≠b≠c
	$\alpha = \beta = \gamma = 90^{\circ}$
Hexagonal	$a = b \neq c$
	$\alpha = \beta = 90^{\circ}, \gamma = 120^{\circ}$
Rhombohedral	a = b = c
	$\alpha = \beta = \gamma 120^{\circ} \neq 90^{\circ}$
Monoclinic	a≠b≠c
	$\alpha = \gamma = 90^{\circ} \neq \beta$
Triclinic	a≠b≠c
	$\alpha \neq \beta \neq \gamma$

this plane intercepts edge a of the unit cell at a/h, or in this case, a/2. It intercepts the b edge of the unit cell at b/k, in this case b/3 and the plane is parallel to the Z axis so the third intercept is $\frac{1}{\infty}$. Thus the Miller indices of the point, P' in the reciprocal lattice representing this plane are the reciprocals of these intercepts, namely (230). The vector d* to the point (230) is the reciprocal of the d spacing.

The interplanar spacing formulas which will be discussed shortly can be deduced from this diagram. A simple case is the orthohombic case (here with l = 0) for rectangular and orthogonal axes. The relationship between spacing, d, and the unit cell dimensions for a given h k 0 is:

$$\frac{1}{a^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2}$$

This can be derived simply from Figure 4-7, considering that

$$d* = \frac{1}{d}$$
, $a* = \frac{1}{a}$, and $b* = \frac{1}{b}$ so:
 $(OP')^2 = (d*)^2 = h^2 (a*)^2 + k^2 (b*)^2$

The relationship of interplanar angles and the zone axis, [uvw] in the crystal lattice is shown in (c) of Figure 4-7. The zone axis is defined such that the normals to it are the reciprocal vectors of the planes. Thus these normals radiate from [uvw] like spokes from a wheel. It can be seen that the angle between two reciprocal vectors as projected on the photographic plate is, directly, the angle between the two planes. The relation between the zone axis and its associated planes is given by:

$$h\mathbf{u} + \mathbf{k}\mathbf{v} + \mathbf{\ell}\mathbf{w} = 0 \tag{4-5}$$

It also can be seen that the zone axis is nearly the direction of the incident beam since the angle, θ is very small. The zone axis can be computed from the following equations:

$$u = k_{1}\ell_{2} - k_{1}\ell_{1}$$

$$v = \ell_{1}h_{2} - \ell_{2}h_{1}$$

$$z = h_{1}k_{2} - h_{2}k_{1}$$
(4-6)

As alluded to previously, interplanar spacings and interplanar angles for any crystalline compound of a given crystal system and for any set of Miller indices can be computed based on formulas which are the result of the geometry of the crystal system. Examples are the equations which govern the orthorhombic system:

$$\frac{1}{d^2} = \frac{h^2}{a} + \frac{k^2}{b^2} + \frac{\ell^2}{c^2}$$
(4-7)

$$\cos \theta_{12} = \frac{\frac{h_1h_2}{2} + \frac{k_1k_2}{2} + \frac{\ell_1\ell_2}{2}}{\sqrt{\left[\frac{h_1}{2} + \frac{k_1}{2} + \frac{\ell_1}{2} + \frac{\ell_1}{2}\right]}} \sqrt{\left[\frac{h_2}{2} + \frac{k_2}{2} + \frac{\ell_2}{2}\right]}$$
(4-8)

The equations become rather complex as the crystal geometry becomes complex.

Equations of this type (for the appropriate crystal system) along with (4-4) can be used in the identification of unknown substances. Using equation (4-4), d spacings of the unknown, along with a measured interplanar angle θ_{12} , can be compared to theoretical d spacings and angles computed with (4-7) and (4-8). It is a trial and error process where a possible compound is selected, d spacings and θ 's computed and compared one by one to the experimental results.

Computer Analysis of Diffraction Patterns

The equations can be extremely tedious for hand computation and if all the possible combinations and permutations of Miller Indices for several compounds must be treated it is necessary to have a computing program to perform the computations and necessary comparisons automatically. Fortunately it was found that the needed programs were in existence. These programs were the SADSP and RINGS programs and were written by Dr. R. A. Ploc (1972) of the Canadian Atomic Energy Commission. The SADSP program analyzes the spot patterns described above and the RINGS program analyzes ring patterns. Ring patterns occur when a substance is made up of multiple crystals of many orientations having planes in the right position for diffraction. The diffracted rays then lie anywhere on a cone as would result from rotating O'P' about O'O in Figure 4-5.

The basic equations solved by the programs are the lattice

formulae, (4-4), (4-7) and (4-8) (RINGS does not use (4-8). The programs also contain the necessary logic to test and compare solutions with certain error criteria.

Much more success in chemical identification of particles was achieved with SADSP than with RINGS. Results from the latter were considerably more ambiguous than those from the former, as the discussion which follows will indicate. It will be seen in the Results for SAD that often apparently satisfactory solutions are obtained for more than one compound. This seems to be because there are so many ways to divide a unit cell. Thus in these cases, for each of the inorganic salts considered, one could find planes which would satisfy the required d spacings within 5 percent (the criterion of the programs for retaining solutions). Since the SADSP program has an additional constraint to satisfy, namely, the angular relationship, many solutions can be eliminated, usually bringing the total number of solutions down to a tolerable level. These solutions are then further analyzed using the criteria described in Section V. On the other hand, the lack of the additional angular constraint in RINGS increases the number of solutions tremendously. An examination of results of this program showed that, in most cases, for every compound and every ring, some solution could be found which satisfied the required d spacing within a few tenths of a percent. An additional criterion was needed to eliminate solutions. Conversations with Dr. Ploc indicated

that a program to compute expected ring intensities for comparison with those on the plate could provide a rough guide to the elimination of many solutions. This program was not available to the author but Dr. Ploc did compute some intensity data based on crystal structural data provided to him. The results were of limited assistance because such data were not available for all of the many compounds tested. Furthermore, it appeared that these data could not be applied without a great deal of experience and judgement. Finally, most of the patterns achieved had only three rings, which, according to Dr. Ploc, is not really adequate for identification.

A sample of the printout of data for the SADSP program is given in Table 4-2. This run corresponds to the pattern of plate 9201 discussed previously. Input data include the name of the compound being tested, its lattice parameters, and the measured data; θ_{12} , R_1 and R_2 ; and the camera constant, L λ (LL). These are listed at the top of the printout. The computed d spacings are D_1 and D_2 . (h k l) from -6 to 6 in all combinations were tested and the computed d spacings and angles printed for those with less than 5 percent error. Below this are printed some minimum error comparisons. In this case all solutions appear to be acceptable, varying only with the direction one is looking along the zone axis or the way the crystal is turned with respect to the zone axis. The first solution was accepted since it matched that on plate 9200, a different pattern from the same particle.

Table 4-2. Sample printout of the SADSP program.

CAC03H20 H

A=10.620		
B=10.620		
C= 7.430		
ALPHA= 90.00	LL=	2.494
SETA= 90.00		
SA MMA=120.00	THET12=	63.60
01= 4.510	R1=	.553
02= 4.619	R2≠	.540

HKL RANGE - 6TO 6

H1K1L1	H2K2L2	DC1	DC2	THETA	0/0-01	8 70- 05	070 - 145TA	
0 2 0	-2 2 0	4.599	4.599	60.000	-1.928	.433	1.315	$ZA = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}$
0 2 6	2 0 0	4.599	4.599	65.060	-1.928	.433	1.316	ZA = [0 0-1]
2 -2 0	2 0 0	4.599	4.599	60.400	-1.928	• 433	1.316	$\underline{Z}A = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}$
2 0 0	025	4.599	4.599	6L.000	-1.928	•433	1.316	$\frac{2}{2} = \begin{bmatrix} 0 & 0 & 1 \end{bmatrix}$
200	2 - 2 0	4.599	4.599	60.000	-1.928	• +33	1.316	2A = [0 0-1]

BASED ON A MINIMUM	ADDITIVE	ABSOLUTE	PERCENTAGE	ERROR, THE	BEST SOLUT	FION IS AS	FOLLOWS	
H1K1L1	H2K2L2	DC1	DC2	THETA	0/0-01	0/0-02	0/0-THETA	
0 2 0	200	4.599	4.599	60.000	-1.929	.433	1.316	·74 = [Ū 0-1]

ALTERNATIVELY,	IGNORING THE	MAGNITUDE OF	THE ANGUL	AR ERROR,	THE BEST	SOLUTION	FOLLOWS IF THE	CAMERA CONSTANT = 2.513	
H1K1L1	H2K2L2	001	002	THETA	0/0-D1	0/0-02	0/0-THETA	DIFFERENCE IN C-SPACING	ERRORS (0/C)
2 - 2 0	2 ũ U	4.599	4.599	6u.ü0î	1.175	+1,254	1.316	2.379	ZA = [0 0 1]

THE M	INIMUM TOTAL	ERROR IS GIVE	N BY THE	FOLLOWING	IF THE C	AMERA CONSTA	NT = 2.5	1?		
	H1K1L1	H2K2L2	DC1	002	THETA	0/0-01	0/0+02	070-THETA	TOTAL ARS ERROR(D/U)	
	200	0 2 0	4.599	4.599	63.300	1.175	-1.2.4	1.316	3.095	7A = E 0 0 1 J

Recommendations for Improving Experimental and Analytical Methods

If research is continued along the lines begun during the course of this program, it is recommended that certain equipment be acquired and certain steps be taken to improve experimental methods:

- Automatic data logging equipment be acquired to record ambient air temperature, pressure, system flow rate, and time of entry into and exit from the plume.
- 2) More effort should be devoted to the optimization of filter pore size and system flow rate in order to minimize the sampling time in the plume.
- 3) Instrumentation which will measure humidity in the ambient air and in the plume should be acquired or developed.
- 4) A micro-balance capable of weighing masses down to 0.1 μ g should be acquired. This is required in order to measure mass concentration in the plume using airborne sampling.
- 5) Automatic particle counting equipment should be acquired to speed up the sizing process and to permit the counting of enough filter samples to permit estimation of particle concentration.
- 6) Improved methods of handling filters be developed.
- 7) More experimental data on filter efficiency as a function of particle size, filter pore size and filter face velocity needs to

be developed. Existing data is sketchy and there are many gaps to be filled.

- 8) Experimentation with specimen preparation should continue to overcome the preparation problems discussed in this section.
 An experimental program should be devised to study the characteristics of filter residue and devise methods to eliminate it. Shadowing techniques should be improved, and replica thickness should be controlled.
- 9) Analytical techniques should be expanded to include electron microprobe analysis. A number of the elements can be identified using this means and it would be a valuable adjunct to the method used in this research.
- 10) SAD analysis techniques should be improved especially through a study of how to use the RINGS program more effectively.

V. RESULTS

Introductory Remarks

The results presented in the following section are given in the form of graphs, tables and electron micrographs. The graphs and tables are presented in the text as they are discussed and the micrographs in Appendix B. References will be made to particular filters and micrograph plates by number providing a shorthand notation to identify certain pieces of data without having to use a descriptive name such as "the third filter in the second downwind sequence." The filters are logged in Appendix A and descriptive information about them given including the date, place, and position the sample was taken, filter type and pore size, and micrographs associated with the filter. In discussions of micrographs related to chemical identification the plate numbers listed in the tables correspond to the actual diffraction patterns. Plate numbers of the pictures of the corresponding crystals which appear in Appendix B are in brackets adjacent to that indicating pattern. It would be well for the reader to review the sampling log before reading this Results section and become somewhat familiar with it.

The micrographs were placed in Appendix B to avoid breaking up the text with a large number of pages of pictures. A word of caution is given that will perhaps avoid some distraction. Some of the

micrographs exhibit a rather large number of artifacts which should not be confused with particles (see Section IV for a discussion of these artifacts).

Particle Size Distribution

The numerical size distributions of particles in two kraft mill plumes were determined. Numerical size distribution (cumulative) is defined as the fraction of particles less than a stated size and is given as a function of size. The size measured for these distributions was the equivalent area diameter defined in Section IV and will be referred to hereafter as particle diameter or size. These diameters were measured by comparing particles with reference circles of given diameter. Each particle counted was assigned the diameter of the circle closest in area to it.

Downwind Sequences

Size distributions for several different downwind sequences are given in Figures 5-1 through 5-7. With exception of the sequence in Figure 5-2, all were taken from the plume of the same mill, the American Can Company at Halsey, Oregon. The data in Figure 5-2 were obtained from the plume of the Western Kraft mill at Albany, Oregon. The distributions were obtained at several points in each plume, from as near to the stack as possible (usually about 0.25 mile) to points several miles downwind.



Figure 5-1. Particle size distribution at selected downwind points in a kraft mill plume. Filters 019, $\overset{\infty}{N}$ 020, 021, and 022.



Figure 5-2. Particle size distribution at selected downwind points in a kraft mill plume. Filters 023 and 024.



Figure 5-3. Particle size distribution at selected downwind points in a kraft mill plume. Filters 026 and 027.



Figure 5-4. Particle size distribution at selected downwind points in a kraft mill plume. Filters 034 and 035.



Figure 5-5. Particle size distribution at selected downwind points in a kraft mill plume. Filters 046, 047, and 048.



Figure 5-6. Particle size distribution at selected downwind points in a kraft mill plume. Filter 050, 051, 052, 053, and 054.



Figure 5-7. Particle size distribution at selected downwind points in a kraft mill plume. Filters 058, 059, and 060.

Several distinct characteristics of the particulate in these plumes can be deduced from these curves. The most obvious is the marked decrease in the count median size particles in the plume with distance downwind. The statistical significance of this decrease is established in Table 5-1 where the difference in median size is tested. For a log normal distribution, the count median particle size is a measure of central tendency of the distribution and therefore a good parameter to use in testing for differences in distributions. The statistical data were taken from the size distribution curves and are presented in Table 5-2.

A null hypothesis formulated for each case was "the count median particle size in the plume was invarient with distance downwind from the source." This hypothesis was resoundingly rejected as indicated by the significance levels of Table 5-1, which are all less than 0.1 percent. In two cases there was some evidence that median particle size achieved a minimum at about two miles downwind and increased somewhat further downwind. It was a phenomena worth noting and appeared to be statistically significant at the 1 percent level for filter pairs 021, 022 and at the 5 percent level for 047 and 048. No explanation has been found for this phenomena except perhaps that less dilution was taking place in the plume when the downwind filters were taken due to changing meteorological conditions. There was probably a half-hour time delay between the taking of successive

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	< 0.1
019 0.55 0.57 0.057 10.4	
023 0.25 0.28 0.040 7.0	< 0.1
024 3.0	
026 0.2 0.95 0.047 20.0	< 0.1
027 1.6	
034 0.35 0.19 0.033 5.8	< 0.1
035 1.5	
046 0.3 0.54 0.041 13.2	< 0.1
047 1.3	
050 0.4 0.71 0.057 12.5	< 0.1
053 6.0	

Table 5-1. Significance levels for changes in count median particle size with distance downwind based on the t statistic.

Filter no.	Count median particle size (µm)	Geometric deviation (σ_g)	Particle counts (N)
019	0.36	1.83	197
020 ^a	0.20	1.90	304
021 ^a	0.16	1.87	1275
022 ^a	0.18	1.90	645
023	0.46	1.51	247
024 ^a	0.35	1.55	216
026	0.35	1.70	401
027 ^a	0.14	1.73	196
034	0.33	1.45	263
035 ^a	0.27	1.45	239
036	0,23	1.45	216
046	0.38	1.69	234
047 ^a	0.22	1. 62	458
048^{a}	0.24	1.65	373
049	0.18	1.67	178
050	0.45	1.49	317
051	0.43	1.49	241
052	0.45	1.49	290
053	0.22	2.09	200
061 ^a	0.23	1.67	282
062 ^a	0.30	1.60	233
063 ^a	0.30	1.60	227

Table 5-2. Statistical data used in statistical tests for differences in size distributions.

^aData given for log normal range of curves.

downwind filters. It is possible but does not seem probable that dilution could change so markedly relative to some upstream point in the plume. Actually no very significant changes in wind or turbulence were observed during the period of sampling.

In all sequences but one it appeared that the initial size distribution of the material could be represented reasonably well by a straight line on log probability paper indicating a log normal size distribution for particles sampled close in to the stack. All these data were taken within about 500 to 600 yards of the stack where the plume was still concentrated. Downwind of the stack the size distribution curves were distinctly non-linear indicating a heterogeneous size distribution, probably made up of two different distributions. In these cases it appeared that there was a shift in the peak of the frequency distribution toward smaller sizes. This indication was confirmed by examination of the frequency distributions such as that depicted in Figure 5-8.

There were several possible physical mechanisms which could have caused the observed changes in size distribution with distance downwind. Among these mechanisms were an initial breakup of agglomerated particles shortly after exit from the stack, loss of water from particle droplets due to evaporation, dilution of the plume with particles of a smaller average size, and downwind agglomeration of particles resulting in a larger percentage of particles in the



Figure 5-8. Frequency distribution in selected samples of kraft mill effluent. Filters 019 and 020.

high end of the size range. The latter would contribute to the nonlinearities observed.

Most probably all of these mechanisms were in operation to a greater or lesser degree. In fact, there were evidences which could be attributed to each in the experimental data.

The possibility of an initial breakup of particles after they exit the stack can be seen by a comparison of the median particle size of the stack sample shown in Figure 5-9, to the medians of the samples taken close to the stack shown in Figures 5-1 through 5-5. There was a decrease of about 25 percent in median size. This could also be due to dilution, although the plume was normally quite dense at the close in sampling point.

Evidence of particle evaporation might be inferred from comparison of particle morphology from close in samples compared to downwind samples. The former showed much more evidence of larger (1 to 3 μ m) smeared particles resulting from droplet breakup on impact while the latter showed more evidence of smaller (0.5 μ m), spherical particles. This could be the result of evaporation, with the smaller particles retaining their shape due to greater surface tension. A great deal more research is required to definitely establish the effects of relative humidity on particle size in this plume.

A possible mechanism which might have accounted for the nonlinearity exhibited by the downwind size distributions was the growth



Figure 5-9. Particle size distribution of recovery boiler effluent samples taken in the stack of a kraft mill. Filters 8RB plus 10RB.

or agglomeration of particles in the larger end of the size spectrum at the same time as the infusion of smaller particles in the smaller end was taking place. Although no reasons were evident as to why this might have happened it would explain the fact that the curves representing the size distributions of the downwind samples, which had steeper slopes, crossed the curves of close in samples at approximately $1 \mu m$. This intersection indicated that the downwind distributions actually had more particles in the larger size range than the close in samples. More research will be required to study and explain this phenomena.

Plume Dilution

There was also evidence that plume dilution with background particles of a smaller average size was a significant factor in the reduction in median particle size in the plume. The non-linearity exhibited in the downwind size distributions could result from the mixture of two size distributions.

The theory that plume dilution was a significant cause of the observed phenomena is based on the comparison of the actual and derived downwind size distributions shown in Figures 5-10 and 5-11. The derived distributions are simply the result of combining the distributions from background samples and close in samples taken on the same days. Comparisons for two ratios of background particle



Figure 5-10. Comparison of derived and actual size distributions. Filter 035, Filter 034 plus 036, Filter 034 plus 2x036, and Filter 036.


Figure 5-11. Comparison of derived and actual particle size distributions. Filter 047, Filters 046 plus 049, Filters 046 plus 2x049, and Filter 049.

concentration to plume particle concentration are shown, a one to one ratio and a two to one ratio. It was estimated that these ratios are representative of dilutions that could have occurred. This estimate was based on measurements of particle counts made in the background and in the plume, and plume dilution calculations using a Gaussian plume model.

On the day the sequence 034, 035, and 036 was sampled, a count of particles larger than 0. 1 μ m was made in the plume at the close in sampling point. A count was also made in the background air upwind of the plant. A Gardner particle counter was used. The counts were 59,000 particles/cm³ and 7800 particles/cm³ respectively.

The Gaussian plume model used for dilution calculations was described by Turner (1969). The coordinate system for this model and the relationships of stack height and plume centerline height, H, is given in Figure 5-12. The x axis extends horizontally in the direction of the mean wind. The y axis is in the horizontal plane perpendicular to the x axis and the z axis extends vertically. The plume travels parallel to the x axis. The concentration, χ , of aerosols at x, y, z from a continuous source with an effective emission height, H is given by:

$$\chi(\mathbf{x}, \mathbf{y}, \mathbf{z}, \mathbf{H}) = \frac{Q}{2\pi \sigma_{\mathbf{y}} \sigma_{\mathbf{z}} \mathbf{u}} \left\{ \exp\left[-\frac{1}{2} \left(\frac{\mathbf{y}}{\sigma_{\mathbf{y}}}\right)^{2}\right] \right\} \left\{ \exp\left[-\frac{1}{2} \left(\frac{\mathbf{z}-\mathbf{H}}{\sigma_{\mathbf{z}}}\right)^{2}\right] + \exp\left[-\frac{1}{2} \left(\frac{\mathbf{z}+\mathbf{H}}{\sigma_{\mathbf{z}}}\right)^{2}\right] \right\}$$
(5-1)



Figure 5-12. Coordinate system showing Gaussian distributions in the horizontal and vertical. Source: Turner (1969).

Use of this equation assumes the following: the plume spread has a Gaussian distribution in both horizontal and vertical planes, with standard deviations of plume concentration distribution in the horizontal and vertical of σ_{v} and σ_{z} , respectively; the mean wind speed affecting the plume is u; the uniform emission rate of pollutants is Q; and total reflection of the plume takes place at the earth's surface, i.e., there is no deposition or reaction at the surface. The values for $\sigma_{\mathbf{y}}$ and $\boldsymbol{\sigma}_v$, which are functions of x, are given by Turner in the form of vcurves. These data are attributed to Pasquill (1961) as converted by Gifford (1961). The method of estimating these standard deviations for an assumed Gaussian plume spread in the absence of detailed wind data was suggested by Pasquill. He estimated values of vertical and angular spread of plumes from existing experimental data for various classes of atmospheric stability. These estimates were later converted to horizontal and vertical deviations, σ_x and σ_y , by Gifford.

To obtain an estimate of plume dilution between any two downwind points in the plume, ratios were formed of concentrations at the two points using equation 5-1. This equation was simplified considerably using the following assumptions and approximations. Only the effect of downwind dispersion was of interest, therefore the first expotential in equation 5-1 became unity. It was assumed that the close in sampling point was on the plume centerline (z=H). At the plume altitudes of interest, the reflection term, $\exp\left[-\frac{1}{2}(\frac{z+H}{\sigma})^2\right]$ was

negligible in all but one case. This was for Class B stability at the downwind sampling point where this term contributes 20 percent to dilution. In all other cases it contributes 0.1 percent or less. Using these assumptions and approximations, then, the concentration ratio used for calculations in this specific situation was:

$$\frac{x_1}{x_2} = \frac{\sigma_{y_2} \sigma_{z_2}}{\sigma_{y_1 \sigma_1} \exp\left[-\frac{1}{2}\left(\frac{z_2 - H_2}{\sigma_{z_2}}\right)\right]}$$
(5-2)

If it was further assumed that the plume centerline rose with distance downwind so the sample at the downwind point was also taken on the plume centerline $(z_2 = H_2)$, the ratio reduced to:

$$\frac{\chi_1}{\chi_2} = \frac{\sigma_y \sigma_z}{\sigma_y \sigma_z} \frac{\sigma_z}{\sigma_z}$$
(5-3)

The plume dilution calculations were made based on the sampling conditions of Filters 034, 035, and 036, and the plume and background particle counts quoted previously. Filter 034 and the plume particle count were taken at a point 1100 ft above sea level and 0.35 miles downwind (Point 1). The height of the ground surface was 250 ft above sea level and the stack height was 300 ft. Thus, the centerline was 850 ft above the surface and the plume rise was approximately 550 ft. Filter 035 was sampled at a point 1.5 miles downwind and 1250 ft above sea level (Point 2). Since the practice during sampling was to fly across the plume centerline (as closely as could be determined by eye), it was assumed that the plume centerline had risen another 150 ft between Point 1 and Point 2 ($z_2 = H_2$). Calculations of dilution were also made without this assumption to check the effect of sample dilution due to vertical dispersion ($z_2 - H_2 = 150$ ft). The results of these calculations are given in Table 5-3.

Table 5-3. Plume dilution calculations.

 $x_1 = 0.35 \text{ mi}, H_1 = 850 \text{ ft},$ $x_2 = 1.5 \text{ mi}, H_2 = 1000 \text{ ft}$

Stability class			σ _{y2}	σ _z 2		Background/Plume			
	°У ₁	σz,			v 1v	conc.	/ conc.		
	1	1			×1′×2	z ₂ = H ₂	^z 2 ^{-H} 2 ⁼		
	(11)	(11)	(11)	(11)			<u>150 ft</u>		
В	305	194	1150	950	18.5	2.9	2.9		
С	204	118	790	460	15.1	2.0	2.1		
D	131	68	510	187	10.6	1.3	1.9		
E	98	47	378	125	10.2	1.3	2.8		

Results are shown for several stability classes and include all but the most unstable (A) and stable classes (F). The conditions which prevailed at the time of sampling most probably corresponded to a Class D (neutral) stability since the sample was taken in the late afternoon of a clear summer day. Plume dilution ratios were translated into the ratio of background particle concentration to plume particle concentration at Point 2. The results in the table indicate that reasonable upper and lower values for the concentrations of background to plume particles were about 1.0 and 2.0 respectively.

It should be emphasized that the plume dilution model is only an approximation and considering the assumptions with regard to atmospheric conditions and sampling positions in the plume, the dilution calculations must be regarded as very approximate. Nevertheless, they served as an indicator of how the plume could be expected to dilute and did not negate the possibility of dilution as a contributor to observed phenomena. In support of the modeling it should be pointed out that the plume was emitted into a reasonably steady wind field blowing over smooth terrain, well clear of the ground. These are conditions for which the dispersion data are applicable according to Turner.

The comparison of actual and derived size distributions of Figures 5-10 and 5-11 shows that a background/plume ratio between 1.0 and 2.0 might explain the reduction in median size quite well. The limiting cases in dilution were the pure background distributions. These are also given in Figures 5-10 and 5-11.

Effect of Reduced Precipitator Collection Efficiency

Some special discussion of the downwind sequence depicted in Figure 5-6 is appropriate. Through the cooperation of the American Can Company and the Oregon Department of Environmental Quality, arrangements were made to sample the American Can plume during a period when one of the two electrostatic precipitators normally used in series for salt cake recovery and pollution control on the recovery boilers was shut down. Recovery efficiency dropped from 99.5 percent to about 94 percent by weight. In this situation the effluent plume appeared to be at least an order of magnitude more dense than the normal situation. From Figure 5-6 it can be seen that the median particle size was about 25 percent larger than normal and that the decrease in particle size did not begin to be significant until about 4 miles downwind from the stack. This phenomena was consistent with the dilution theory. Since the plume was considerably more dense it took a longer travel distance before the dilution effect became apparent.

Samples Taken Underneath the Plume

More special cases in size distributions are shown in Figure 5-13. These samples were taken close in to the stack but well under the centerline plume in order to assess the effects of particulate



Figure 5-13. Particle size distribution of samples taken underneath a kraft mill plume. Filters 061, 062, and 063.

fallout. Filter 061 was taken underflying the plume from about 500 yards downwind to 2 miles downwind at an altitude of 150 to 200 feet above the ground. At this time the plume centerline was at an elevation of 300 to 400 feet. The apparent dilution effect in the size distribution can be seen. Filters 062 and 063 were sampled on the ground directly underneath the plume. Filter 062 was taken on top of the pulp mill about 150 yards downwind. The top of this building was about 100 feet above the surface of the ground but was at least 200 feet below the plume centerline. Filter 063 was taken on the surface directly underneath the plume at a point about 500 yards downwind. Both of these size distributions showed the apparent dilution effect with 063 showing more than 062, as would be expected. Even though both filters were taken close to the stack they were well below the centerline and it appears that what was sampled was the result of downward turbulent mixing from the plume. No particular evidence of fallout can be seen from examining the micrographs taken from these filters. Both large and small particles are present with small particles predominating.

Size Distribution of Stack Samples

Figures 5-9 and 5-14 are size distributions of effluent samples taken in the ducting prior to entry into the stack at American Can Company. Filters labeled RB are recovery boiler effluent and those



Figure 5-14. Particle size distribution of recovery boiler and kiln effluent samples taken in the stack of a kraft mill.

labeled K are from the lime kiln. In both cases the effluent passed through control equipment (electrostatic precipitators for the recovery boiler and a wet scrubber for the kiln) and was about to be mixed in the stack. There was an apparent discrepancy between the size distributions of Figures 5-9 and 5-14. This was most probably due to effects related to the heating of the probe, as explained in section III. A study of the micrographs (Plates 8964 and 9032 in Appendix B) for these samples indicated that water condensation and subsequent crystallization of what most probably were agglomerated particles has increased average particle size in the distribution of Figure 5-14. A second set of samples was taken from the recovery boiler duct where the probe and filter were thoroughly heated before sample collection. This size distribution is given in Figure 5-9. It is felt that this size distribution was much more representative of the particles as they exist in the stack. Micrographs indicate that the primary particles are about 0.2 μ m to 0.3 μ m in diameter with agglomerations of these particles up to several micrometers in diameter (Plates 9151 and 9152). In sizing these particles it was decided to size only primary particles and those small agglomerates that could definitely be considered a single particle. Plate 9156 is representative of such particles. The results of this sizing compare very favorably with the distributions sampled just downwind of the stack, having a median of 0.45 μm and a standard deviation, $\sigma_{_{\rm CP}}$, of

1.7. The particles sized in Figure 5-14 may not entirely be unrepresentative, however, since many of them resemble morphologically particles sampled in the wet plume and which crystallized on the filter. A comparison of Plates 8964 and 10-5 illustrates this point.

It was not possible to achieve a dry sample of kiln effluent since this stream was saturated with water vapor at all times.

Chemical Identification of Particles

Chemical identification of a number of particles was achieved using selected area diffraction. Considerable success was achieved in the analysis of single crystal (spot) patterns using Ploc's SADSP program described in Section IV. Twenty-six particles were analyzed and in 20 cases the results were worthy of presentation. These results are summarized in Tables 5-4, 5-5 and 5-6. Micrographs of the crystals corresponding to these patterns appear in Appendix B. Results of the analysis of multiple crystal or ring patterns were poor in quality and were not adequate for presentation. The reasons for this are given in Section IV.

The primary identification criterion for a given crystal was the matching of its calculated interplanar spacings (d spacing) and angles with those calculated from the crystal parameters of a given compound using the SADSP program. It was necessary, however, to rely heavily on other factors to complete or confirm the identification due to ambiguities which remained after the computer analysis.

	Filton		Created	Miller	indices	· · · · · ·	7.000			
Plate no.	no.	Compound	system	$\mathbf{h}_{1}\mathbf{k}_{1}\mathbf{h}_{1}$	$\frac{h_{2}k_{2}l_{2}}{2}$	θ ₁₂	axis	d ₁	d ₂	θ ₁₂
8961 (8962)	6RB	$Na_2SO_4 \cdot 10H_2O_2$	Monoclinic	42-1	003	88.8	1-20	-0. 60	0.60	1.38
8965 (8964)	5RB	$Na_2SO_4 \cdot 10H_2O$	Monoclinic	10-4	40-1	78.6	0-10	1.63	-1.09	. 916
9094 (9095)	021	$Na_2SO_4 \cdot 10H_2O_4$	Monoclinic	102	40-2	84.4	010	1.53	0. 31	-1.31
^a 9307A (9308)	061	$^{Na}_{2}SO_{4} \cdot 10H_{2}O_{4}$	Monoclinic	32-4	-360	72.7	212	1. 34	-0. 62	-1. 32
^a 9307B (9308)	061	$Na_2SO_4 \cdot 10H_2O_2$	Monoclinic	32-4	-14-1	58.5	212	0.75	-0.95	2.63
9245 (9246)	057	$Na_2SO_4 \cdot 10H_2O_2$	Monoclinic	132	-13-2	74. 9	-201	-0.62	-0. 62	0. 85
^a 9290A (9291)	065	$CaCO_3 \cdot H_2O$	Hexagonal	02-2	-330	71.7	111	0.82	-1.51	-1.83
^a 9290B (9291)	065	CaCO ₃ · H ₂ O	Hexagonal	11-2	- 220	90. 0	111	- 1. 41	-1.03	0
9309 (9310)	061	CaCO ₃	Hexagonal	010	100	60.0	00-1	1.27	0.91	0.50
^b 9200 (9199)	062	CaCO ₃ · H ₂ O	Hexagonal	2-20	310	73.9	001	-0. 12	0.18	1.34
^b 9201 (9199)	062	$CaCO_3 \cdot H_2O$	Hexagonal	020	-220	60.0	001	-1.93	0. 43	1.31
8-6(8-7)	012	$C_{aCO} \cdot H_{2O}$	Hexagonal	020	-220	60. 0	001	0. 98	0, 98	0

Table 5-4. Selected Area Diffraction Summary - Probable identification.

^aTwo distinct patterns recorded on a single plate for one particle.

^bSame particle with patterns recorded from different areas of particle.

Filton		Cruzetal	Millers	indices		7	Error (%)		
no.	Compound	system	$\begin{array}{c}\mathbf{h} \mathbf{k} 1 \\ 1 1 1 1 \end{array}$	^h 2 ^k 2 ¹ 2	θ ₁₂	axis	d 1	^d 2	0 ₁₂
2K	CaCO ₃	Orthorhombic	030	002	90.0	100	0. 43	-0.93	0
5RB	$Na_2SO_4 \cdot 10H_2O_2$	Monoclinic	103	40-2	90.4	010	-2. 78	1.71	-0.40
060	CaCO3	Hexagonal	-112	-101	57.1	1-11	1. 10	-0.26	-2.87
062	$Na_2SO_4 \cdot 10H_2O$	Monoclinic	-511	-133	71.4	01-1	-2,29	0.55	1,95
012	$N_{2}SO \cdot 10H_{2}O$	Monoclinic	222	-110	89.0	-1-12	3. 40	0.85	1.07
023	$Na_2SO_4 \cdot 10H_2O$	Monoclinic	600	030	90.0	001	-1.46	-2.5	0
	Filter no. 2K 5RB 060 062 012 023	Filter no.Compound2K $CaCO_3$ SRB $Na_2SO_4 \cdot 10H_2O$ 060 $CaCO_3$ 062 $Na_2SO_4 \cdot 10H_2O$ 012 $Na_2SO_4 \cdot 10H_2O$ 023 $Na_2SO_4 \cdot 10H_2O$	Filter no.CompoundCrystal system2K $CaCO_3$ Orthorhombic5RB $Na_2SO_4 \cdot 10H_2O$ Monoclinic060 $CaCO_3$ Hexagonal062 $Na_2SO_4 \cdot 10H_2O$ Monoclinic012 $Na_2SO_4 \cdot 10H_2O$ Monoclinic023 $Na_2SO_4 \cdot 10H_2O$ Monoclinic	Filter no.CompoundCrystal systemMillers h h l 11112KCaCO3Orthorhombic0305RBNa2SO4 \cdot 10H2OMonoclinic103060CaCO3Hexagonal-112062Na2SO4 \cdot 10H2OMonoclinic-511012Na2SO4 \cdot 10H2OMonoclinic222023Na2SO4 \cdot 10H2OMonoclinic600	Filter no.CompoundCrystal systemMillers indices $h_1k_1l_1$ Millers indices $h_2k_2l_2$ 2KCaCO3Orthorhombic030002SRBNa2SO4 · 10H2OMonoclinic10340-2060CaCO3Hexagonal-112-101062Na2SO4 · 10H2OMonoclinic-511-133012Na2SO4 · 10H2OMonoclinic222-110023Na2SO4 · 10H2OMonoclinic600030	Filter no.CompoundCrystal systemMillers indices $h_1k_1l_1$ $h_2k_2l_2$ θ_{12} 2KCaCO3Orthorhombic03000290.0SRBNa2SO4 · 10H2OMonoclinic10340-290.4060CaCO3Hexagonal-112-10157.1062Na2SO4 · 10H2OMonoclinic-511-13371.4012Na2SO4 · 10H2OMonoclinic222-11089.0023Na2SO4 · 10H2OMonoclinic60003090.0	Filter no.CompoundCrystal systemMillers indices $h_1^k h_1^1 1$ Zone $h_2^k h_2^1 2$ Zone θ_{12} Zone axis2KCaCO3Orthorhombic03000290.01005RBNa2SO4 · 10H2OMonoclinic10340-290.4010060CaCO3Hexagonal-112-10157.11-11062Na2SO4 · 10H2OMonoclinic-511-13371.401-1012Na2SO4 · 10H2OMonoclinic222-11089.0-1-12023Na2SO4 · 10H2OMonoclinic60003090.0001	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Filter no.CompoundCrystal systemMillers indices h k 1 1 1 1Zone h 2 22Zone d 1Error (%) d 22KCaCO3Orthorhombic03000290.01000.43-0.935RBNa2SO4 · 10H2OMonoclinic10340-290.4010-2.781.71060CaCO3Hexagonal-112-10157.11-111.10-0.26062Na2SO4 · 10H2OMonoclinic-511-13371.401-1-2.290.55012Na2SO4 · 10H2OMonoclinic222-11089.0-1-123.400.85023Na2SO4 · 10H2OMonoclinic60003090.0001-1.46-2.5

Table 5-5. Selected Area Diffraction Summary - Possible Identification.

^aSame particle as 9201, 9202.

	E:14		()	Miller indices				Error (%)		
Plate no.	no.	Compound		h_k_1	^h 2 ^k 2 ^l 2	θ 12	Zone axis	d 1	^d 2	θ 12
8945 (8946)	5K	$Na_2SO_4 \cdot 10H_2O_4$	Monoclinic	301	0-40	90.0	10-3	-0.63	1.03	0
8945 (8946)	5K	CaCO3 · HO	Hexagonal	012	-420	90. 0	-1-21	0.56	-1.54	0
^a 9186 (9188)	059	$Na_{3}SO_{4} \cdot H_{2}O$	Monoclinic	005	2-42	61.7	-2-10	-1.72	0.06	-1.12
^a 9186 (9188)	059	$Na_{3}SO_{4}$	Orthorhombic	034	0-34	61.8	100	2.06	0.33	-1.33
^a 9186 (9188)	059	CaCO	Hexagonal	2-20	202	61.0	-1-11	-0.48	0. 92	-0.01
^a 9187 (9188)	059	Na SO · HO	Monoclinic	005	2-42	60.8	-2-10	-1.47	0.96	-0.56
^a 9187 (9 188)	059	Na _s SO ₄	Orthorhombic	034	0-34	61.8	100	0.42	2. 32	-2. 17
^a 9187 (9188)	059	CaCO	Hexagonal	022	-220	61.0	-1-11	1.01	-0. 22	-0.84
9659 (9660)	060	$Na_2SO_4 \cdot 10H_2O$	Monoclinic	12-2	-122	84.7	201	1.91	1.75	2. 28
9659 (9660)	060	Na SO 4	Orthorhombic	12-1	022	85.2	3-11	0.02	1.38	1.82
9659 (9660)	060	CaCO3 · H2O	Hexagonal	201	02-1	85.2	-112	-0.34	-0.50	1.79
9336 (9337)	064	Na ₂ SO ₄	Orthorhombic	102	120	62.3	-211	-2.26	2. 10	1.11
9336 (9337)	064	CaCO	Hexagonal	1-12	0-10	63.5	20-1	-4.54	0.30	-0.81
8-18 (9-2)	012	$Na_2SO_4 \cdot 10H_2O$	Monoclinic	22-1	-12-1	60.0	012	3.71	-1.11	. 946
8-18 (9-2)	012	CaCO3	Hexagonal	010	-11-1	61.0	-101	-4.68	-1.06	-0.67
10-7 (10-8)	013	$Na_{2}SO_{4} \cdot 10H_{2}O$	Monoclinic	22-1	-12-1	60.0	012	2.85	-1.91	-0, 38
10-7 (10-8)	013	CaCO3	Nexagonal	01-1	10-1	58.0	-1-1-1	-2.49	-1.86	3.03

Table 5-6. Selected Area Diffraction Summary - Ambiguous Cases.

^aTwo exposures of the same particle.

At the suggestion of Dr. Ploc, the error criterion in matching d spacings and interplanar angles was taken to be 2 percent. Heard and Wiffen (1969) also used this error margin in their identification of atmospheric ammonium sulfate. Those solutions which satisfied this and other criteria are presented in Table 5-4 as probable identifications. Those in which one or more of the errors exceeded the 2 percent criterion by a small amount are presented in Table 5-5 as possible identifications. So-called "ambiguous" solutions, those for which the errors for more than one compound satisfied the 2 percent criterion, are presented in Table 5-6. These multiple solutions are given to point out the difficulties in identification using diffraction data alone.

The SADSP program printed out all combinations of crystal planes and angles which match theoretical interplanar spacing and interplanar angles to within 5 percent. The solution with the minimum absolute value of error was also selected and printed out. Some compounds had solutions numbering in the hundreds but most ranged from about 5 to 10 or 20. In addition to the minimum error criterion, it was necessary to examine the zone axis for validity. The zone axis [uvw] is approximately the direction of the incident electron beam with respect to the crystal lattice.

Normally, crystals that yield diffraction patterns at all are oriented such that a low order zone axis [uvw] results, say[101]. If

the minimum error solution for a compound had a high order zone axis, say [825], it was rejected. The other solutions printed out for a given compound were then examined for their zone axis and error size. If a result was found which was satisfactory in both cases then this compound was tentatively accepted. If one or another of the criteria was not met, then the compound was rejected.

Other important aids to identification which were used were the source of particles, process characteristics, chemical properties, and morphology. For instance, in the case of the patterns associated with the filters 5 RB and 6 RB, where the sample source was the recovery boiler only, solutions indicating sodium sulfate in some form or sodium carbonate were possible but any indicating calcium carbonate were rejected.

An important result which was deduced with regard to chemical identity and morphology became an aid to further identification of particles. In the initial analysis only an anhydrous form of sodium sulfate was used in comparisons, but after a search of crystallographic data yielded the parameters of sodium sulfate decahydrate $(Na_2SO_4 \cdot 10H_2O)$, this too was tested and yielded numerous solutions. These results provided an explanation for a morphological phenomena which had been observed many times previously but not understood. The explanation is that the highly deliquescent sodium sulfate particles have absorbed water from plume condensate and after

collection, dried and crystallized on the filter surface in the hydrated form. This resulted in a "smeared" appearance on the filter surface. This is illustrated in plate 8964 corresponding to the pattern of plate 8965. In this case the micrograph of the particle was taken prior to the diffraction pattern, which was fortunate, for these types of particles usually experienced considerable particle deterioration due to beam heating.

Particle deterioration or lack of it provided another identification clue. Hydrated sodium sulfate melts at 33°C and looses its water of hydration at 100 °C. This was undoubtedly the cause of much particle decomposition which was observed under beam heat. The micrographs of plates 8962, 9121, and 9246 are examples which show damage due to beam heat and have been identified as $Na_2SO_4 \cdot 10H_2O$. The appearance of the particles in these pictures correlates well with many of the medium to larger size particles, more or less circular in shape, which were frequently observed. It is postulated that these are agglomerated particles of Na_2SO_4 which have absorbed enough water to become fluid droplets and would form the flat circular particles on impact with the filter. The particle of plate 8-13 corresponding to the pattern of 8-12 is in the same class as those discussed above, a flat smear. This can probably be identified as $Na_2SO_4 \cdot 10H_2O$ even though the identification error percentages are large.

In contrast to sodium sulfate, calcium carbonate is not very soluble in water, although it does exist in hydrated form. Several of the particles identified as anhydrous CaCO₃(Calcite) look quite different than the $Na_2SO_4 \cdot 10H_2O$. They tend to be large particles, from one to several micrometers in diameter, appear flaky, and exhibit some evidence of agglomeration. Such particles never showed any evidence of damage due to beam heat. The particles depicted in the micrographs of plates 9188, 9310³, and the large particles of plates 10-8 and 9-2 show these characteristics. It is suspected that those large particles in plates 10-8 and 9-2 are indeed anhydrous CaCO3 in spite of the large error shown by the program in these cases. The only exception is the particle of plate 9191 which was identified as calcite but looks more like the $Na_2SO_4 \cdot 10H_2O$ of 9308. Hydrated CaCO₂ is shown in plates 9291, 9199, and 8-7. These, too, are large, solid, blocky particles which showed no evidence of deterioration but seem to be more homogeneous than the agglomerated Calcite.

An apparent anomaly occurs with what appears to be a portion of the particle of 9199 and which was identified as $Na_2SO_4 \cdot 10H_2O$ in the pattern of plate 9202. This pattern came from the finger sticking out from the denser portion of the particle. Actually this part of the

³With plate 9310 care should be taken to distinguish the particles from the broken pieces of SiO film which are present in this micrograph.

particle looks more like the smeared crystallized particles earlier identified as $Na_2SO_4 \cdot 10H_2O$. It may actually be part of a different particle which impacted at this spot at an earlier time during the sampling or actually was adhering to the large particle and splashed out on impact.

The particles of plates 8946 and 9660 were placed in the ambiguous class because, strictly speaking, they yielded solutions for more than one compound based on crystallographic data alone. However, based on the morphological theory it is believed that in these two cases the solution is actually $Na_2SO_4 \cdot 10H_2O$. Both particles showed strong evidence of decomposition due to beam heating.

The particles of plates 9095, 9308 and 16-11 were all very similar in morphology and had solutions which indicate $Na_2SO_4 \cdot 10HO$. They all showed small, partially decomposed particles suspended in a pore by a film believed to be plastic filter residue.

The particle of plate 9337 was the only one which yielded a reasonably good solution for anydrous Na_2SO_4 . It is a large, dense particle corresponding to the theory of appearance of particles containing little or no water. Some doubt could be cast on this solution since the material immediately adjacent to it has a strong resemblance to the particle depicted in plate 9310 identified as $CaCO_3$. This pattern also had a solution for $CaCO_3$ but with a rather large error in d spacing (over 4 percent). Since the selected area of

diffraction is finite it is difficult to tell, as close as these particles were, which is really yielding the solution. Therefore, it was felt that the $CaCO_3$ solution should be included as a possibility.

The particles of plates 8946 and 9036 were both from samples taken from the lime kiln effluent. One can expect both sodium sulfate and calcium carbonate in this effluent. As indicated above, the solution for 8946 was $Na_2SO_4 \cdot 10H_2O$. The solution for 9036 was an anhydrous form of $CaCO_3$. Unfortunately this solution is questionable because a micrograph of the particle was not made and there is no means of judging its morphology.

The reason sodium sulfate can be expected in kiln effluent (and, in fact, it may be as much as 90 percent of the effluent) is explained by the following theory which has been postulated by those who work in the industry. ⁴ Sodium compounds are carried over in the lime mud into the kiln. These compounds react with the SO_2 from the burning of non-condensible sulfur compounds in the kiln. The sodium sulfate thus formed is dissolved in the water condensate of the saturated gases leaving the wet scrubbers used to control particulate matter from the kiln. Most of the insoluble calcium carbonate is captured and retained by the scrubber but some sodium sulfate is emitted due

⁴Personal communication from Mr. Rod Schmall of the National Council for Air and Stream Improvement, West Coast Regional Office, Corvallis, Oregon.

to its soluble nature. An examination of the micrographs of kiln effluent seems to bear out the theory since the large majority of particles have the smeared crystallized appearance. There are a few agglomerated, unwetted particles, however, indicating calcium carbonate has passed through the scrubber.

One other means of verification of particle identity was available in two cases. In these cases, 9290 and 9307, two distinct diffraction patterns were obtained on the same plate. This indicates the beam was passing through a particle with two crystals adjacent to each other both yielding diffraction patterns. It was thus possible to cross check the quality of solutions in these cases. For instance, if one pattern yielded a reasonably good solution for Na₂SO₄ and the other did not, then this compound was rejected as a solution for this particle.

The case cited above illustrates the need, in this type of work, for a tilt stage on the instrument to be used for electron diffraction. The tilt stage allows the operator to tilt slightly the specimen altering the beam direction with respect to the crystal lattice and thus giving rise to a second diffraction pattern. This helps immensely in positive identification. The initial part of this work was done on a Hitachi HU-11B equipped with a tilt stage. Unfortunately, before the diffraction analysis was begun in earnest, it became necessary to shift operations to the Phillips 300. The latter was an excellent instrument but was equipped with a three position stage instead of a continuous tilt which was required.

No solutions that were considered valid were obtained for the third possible compound, sodium carbonate, Na₂CO₃. Although some solutions were given by the program, SADSP, in each case they were eliminated by one of the criteria mentioned above. In most cases the errors in these solutions were on the large side. No particular reason can be given for this situation except that this compound is probably 5 percent or less of the total effluent. Calcium carbonate is also a small percentage of the effluent but in this case the particles are apparently rather large and are more evident among their neighbors.

The crystallographic parameters for the compounds tested in the analysis were obtained from Donnay and Donnay (1963) and are given in Table 5-7.

Particle Morphology

The morphology of some types of particles has been discussed in the previous section. In this section those particles will be classified and other types will be introduced and discussed.

Most of the particles that were collected during this research can be placed in one of five classifications. These types and typical examples of them are:

Compound	Crystal	Unit	Unit cell dimensions			it cell ang (deg.)	les	Comments	
	system	A	B	с	α	β	γ		
Na ₂ SO ₄	Orthorhombic	9 . 82 1	12.304	5.821	90	90	90	: · ·	
$Na_{2}SO_{4}$	Orthorhombic	6.953	8.926	5.592	90	90	90	No solutions	
Na ₂ SO ₄	Hexagonal	5.40	5.40	7.27	90	90	120	No solutions	
$Na_2SO_4 \cdot 10H_2O_2$	Monoclinic	12 . 8 2	10. 35	11.48	90	107.67	90		
Na2 ^{SO} 3	Hexagonal	5.441	5.441	6.133	90	90	1 2 0	No solutions	
$Na_2CO_3 \cdot H_2O$	Orthorhombic	6.440	10 . 72 1	5.243	90	90	90	No acceptable solutions	
$2Na_2SO_4 \cdot Na_2CO_3$	Orthorhombic	21, 15	27.63	5.16	90	90	90	No solutions	
$Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$	Orthorhombic	20.11	3.49	10. 31	90	103.13	90	No solutions	
CaCO3	Orthorhombic	5.72	8.94	4.94	90	90	90		
CaCO ₃	Hexagonal	7.135	7.135	8.524	90	90	120		
CaCO3	Rhombohedral	6. 361	6.361	6.361	46. 1	46.1	46.1	No acceptable solutions	
$CaCO_3 \cdot H_2O$	Hexagonal	10 . 62 0	10.620	7.430	90	90	120		
CaCO ₃ · H ₂ O	Hexagonal	6. 150	6.150	4.955	90	90	120	No solutions	
NaCl	Cubic	5.640	5.640	5.640	90	90	90	No acceptable solutions	

Table 5-7. Crystallographic Parameters of Compounds which were Tested against Experimental Data. Source: Donnay and Donnay (1963).

- Type I This was a large, flaky particle which ranged from about l μ m to about 5 μ m in diameter. These particles are most probably CaCO₃. Examples of these are seen in plates 9-2, 10-8, 9188, 9199, 9030, and 9337.
- Type II This was a large, "smeared" looking particle which ranged in size from 1 to 3 μ m in diameter. These were identified as $Na_2SO_4 \cdot 10H_2O$ which has crystallized on the filter surface. They sometimes project several arms which appear much like the petals of a flower. Plate 8964 is an excellent example along with plates 10-5, 10-8. 8943, 8954, 9032, and 9161. Note that there is a definite correlation between samples taken at the recovery boiler and kiln with those taken flying through the plume.
- Type III These were medium sized agglomerates and circular particles which ranged from 0.5 μm to 2 μm in diameter. These particles appear to be formed from smaller primary particles 0.2 μm to 0.3 μm in diameter. In some cases the particles retain some appearances of agglomeration while others have completely coalesced, probably due to absorption of water. Examples of this type appear in plates 10-8, 10-11, 8863, 8906, 9136, and 9657. Some of these particles appear to have partially or nearly completely disappeared with only a replica of the particle shape remaining outlined by what appears to be a residue of

the particle. Others have considerable density. It is extremely difficult to explain the loss of this material but some possibilities will be discussed.

- Type IV This was a chain-like agglomerate made up of primary particles which ranged from 0.05 µm to 0.3 µm. Examples of these are seen in plates 9151, 9152, 9311, 9619, 9621, and 9662. There is a correlation between particles sampled in the recovery boiler and those sampled in the atmosphere especially between 9151 and 9662. The latter was collected at a point 8 miles downwind and did have definite crystalline character since it produced a diffraction pattern. The pattern, however, was too distorted to analyze. The primary particles of plates 9311, 9619 and 9621 are definitely smaller than those sampled in the stack. They may not actually be the same type of particle but, on the other hand, the "primary" particles sampled in stack may be themselves, agglomerates since they do carry strong electrostatic charges.
- Type V This was a small, circular, "fried egg" type of particle that ranged from 0.1 μm to 0.5 μm in diameter. This was the most numerous and the most enigmatic of all the particles collected. It is characterized by a light center area surrounded by a darker halo. Since lightness and darkness imply density gradations in transmission micrographs, it is presumed that

these particles were fluid in character and experienced drying on the filter surface leaving the ring-like residue. This was nearly the only type of particle found in the background samples. It may account for the reduction in average particle size in the plume with distance downwind as was discussed in the section on size distributions. It also seems certain that some of the smaller particles of the stack effluent take on this appearance. This judgement is based on the concentration of particles on the background filters relative to that on filters exposed in the plume and on the fact that this type of particle was observed on the close in samples where relatively little dilution had taken place and also on some of the filters sampled in the stack. Examples of this type of particle are seen in plates 10-8, 10-11, 8910, 9096, 9110, 9111, and 9112. The particle of 8910 is an enlargement (105, 500X) of a typical Type V particle to show details of its morphology. It is approximately 0.22 μm in diameter. Plates 9110, 9111 and 9112 were all from filter 021, a sample collected over 2 miles downwind. They exhibit many small Type V particles approximately 0.15 µm in diameter of the type similar to those found in the ambient air but the concentration of these was much higher. Also, there are particles over 0.5 μ m in diameter which have the Type V morphology. This seems to indicate that some Type V particles

are from the kraft mill. It was never possible to obtain an electron diffraction pattern from this type of particle indicating that it is amorphous in character. This does not eliminate the possibility of their being kraft salt cake since these substances become amorphous if they are super saturated with water.

The most plausible explanation for the apparent loss of material in the Types II, III and V particles is that they were actually fluid when collected, and contained substantial percentages of water. After collection on the filter surface the water simply evaporated leaving the residue that was observed. This probably was actually the case in the larger particles of Type II and III since they appeared to be mostly solid material and to have crystallized. On the other hand, the morphology of the smaller particles indicated that they contained a much higher percentage of water, but in spite of possible evaporation the shape of these particles was well preserved in the replication process with SiO. This seems to imply that they existed on the filter surface at least until the replication took place. This process usually did not take place until a matter of hours after the sample was collected and in some cases days or weeks.

The remaining possibilities seem to be either that the particle was lost in the filter dissolution process or deteriorated due to beam heating in the microscope. Although the latter was observed many times on the larger particles it was never observed on the smaller ones. A possible explanation might be that the heating happened

extremely fast due to the small size and heat capacity of the particles. However, this does not seem likely. Loss of the particles during the filter dissolution process also seems unlikely since the salts in question were only very slightly soluble in chloroform, if at all. It should also be noted that what looked like water spotting on the filter surface might have been the residue of salts carried away in the dissolution process. Plate 10-11 is an example.

The remainder of the micrographs of Appendix B are presented to illustrate typical particles of the size distributions presented and for every sample which has been discussed.

Scanning Electron Micrographs

To complement the morphological studies possible with transmission microscopy, several hours of scanning microscope time were obtained at the University of Washington using their Cambridge Stereoscan Mk II-A instrument. Mr. Al Soldener of the OSU Botany Department operated the instrument and took the micrographs under the direction of the author.

The scanning microscope provided a unique insight because of the three dimensional aspect of its images. In this particular instance it offered two advantages over transmission operations. One was anticipated, the other not. The first of these was simpler specimen preparation which did not require dissolution of the actual filter and thus avoided some of the uncertainties of the replication process alluded to earlier. Specimen preparation simply involved coating the specimen with a thin (150 Å) coating of conducting material to avoid the buildup of electrostatic charge on the specimen. (This was not always avoided completely and resulted in the "white-out" areas observed at discontinuities in surfaces, such as at edges of pores.)

The second advantage was the use of low magnifications (i. e., < 500X) for observation of large particles which were often overlooked or confused with other phenomena at high magnification in transmission microscopy.

The scanning micrographs shown here tend to support and confirm most of the morphological characteristics deduced from transmission micrographs. In addition the observation of very large particles, i. e., 20 μ m or more, lends more credence to the concept of particle agglomeration in the stack and de-agglomeration outside of it.

The scanning micrographs are serialized from SM01 to SM21 in Appendix B. SM01 is a blank Nuclepore filter with 3 μ m pores showing the clean filter surface. SM02 is directly comparable to plate 10-8, being from the same filter, 013. It illustrates most of the particle types including a large flaky particle, some of the thin partially evaporated particles, and the small 0.3 μ m particles. It

does not seem as though these small particles were evaporated in the center as they appear in the transmission micrographs. It is interesting to note that the large particle has smaller particles agglomerated or impacted upon and around it. This could lead to ambiguity in particle identification by electron diffraction. SM03 depicts some large, $3-5 \mu m$ particles which appeared to be agglomerates.

The series of micrographs SM04 to SM08 depict typical samples taken in the plume close in to the stack, downwind in the plume and in the background. Plates SM04 and SM05 can be compared to plates 10-11 and 8863, being taken from the same filters, 028 and 023 respectively. Plates SM06 and SM07 are downwind samples and comparable to plates 9110 through 9112. Plate SM08 is a background sample and is comparable to plates 9612 and 9615. Plate SM04 clearly illustrates how medium size (0.5 μ m to 1 μ m) particles have been formed from agglomerations of smaller primary particles and are nearly completely fused together. Plate SM09 depicts the thin smeared particles that are most probably crystallized Na₂SO₄ · 10H₂O. This plate is comparable to plates 8964, 8943, and 9032. Plate SM10 depicts the chain like agglomerates comparable to that shown in plate 9662.

The remainder of the scanning micrographs relate to particle agglomeration and de-agglomeration. Plates SM11 through SM13 are micrographs of filter 8RB, a sample taken in the duct between the

electrostatic precipitator and the stack. It is seen that there was a strong tendency for these particles to form large clusters. This was, no doubt, due to the existence of an appreciable electrostatic charge on the particles after they left the precipitator. Based on the appearance of the foregoing micrographs this charge does not seem to persist in the atmosphere since the vast majority of the observed particles were below 1 µm in size. This is again illustrated in SM14 which was sampled in the very dense plume which resulted when only a single bank of precipitators was in operation. On the other hand, there are exceptions and some very large agglomerates were observed on the scanning specimens. SM15 is a micrograph of what apparently was a large, 200 µm semi-solid droplet which impacted on the filter. SM16 is a micrograph at much larger magnification of the edge of this droplet. There is abundant evidence of flattened, fused particles. Apparently this was formed from a large globule (such as those in SM 12) remaining intact in the atmosphere and absorbing water. This sample was taken on a very high humidity day at a point 3 miles downwind of the stack. Other such large globules are seen in SM17 and SM18. SM17 was sampled in the kiln effluent before the stack and SM 18 in or near the plume within 2 miles downwind of the stack. The latter flight was intended to be an underflight of the plume centerline to sample for just such large particles as fallout. On this day, however, winds were high and the plume was horizontal out of the

stack and looped down to the surface within a half mile downwind. Therefore, the particle can hardly be considered as fallout but it is of interest to find that such a large particle existed in or near the plume. Looking at the fused and folded appearance of these globules in SM17 and SM18 leads one to believe that the next two particles shown in SM19 and SM20 are most probably kraft effluent which has proceeded even further in the fusing process. These were early micrographs and until SM17 and SM18 were obtained, it was difficult to believe these were kraft particles. SM21 gives an idea of the frequency of occurrence of these large particles. Counts were made of the total number of particles in the 20 to 50 μ m class using the scanning instrument. Based on this, it was estimated that they formed 1 x 10⁻³ to 1 x 10⁻² percent of the total. Thus they were not a factor in the overall size distribution of particulate.

Summary

- 1) The size distributions for particulate in the plumes from two kraft paper mills were determined at several points downwind of their stacks. Just downwind of the stacks the size distributions were found to be log normal and are characterized by two parameters, the count median size and the geometric standard deviation.
- 2) The median size of the particle size distributions in the plume

was found to decrease significantly up to a point some 1.5 to 2 miles downwind. A likely cause for the decrease in median particle size was shown to be plume dilution. Several other mechanisms were postulated which could also contribute to this phenomena. More research would be required to establish their validity.

- 3) Based on size distributions of samples taken on the surface below the plume and underflight of the plume there did not appear to be any significant fallout effect in the immediate vicinity of the plant. These samples showed definite evidence of kraft particulate and had size distributions which showed the dilution effect. These samples were most probably the result of turbulent mixing below the plume rather than fallout.
- 4) The median size of particulates entering the stack was very difficult to determine due to condensation problems and particle agglomeration. However, at least one sample taken at this point showed the particle median size was somewhat larger than that in the atmosphere near the stack.
- 6) Particle size distributions obtained at the American Can Company when one stage of the two stage precipitator was shut down indicated that particle sizes were about 25 percent larger than during normal operation. Micrographs indicated the particles were more dense and more regular in shape. From

visual observation the plume appeared to have concentrations an order of magnitude greater than normal and did not show evidence of dilution with ambient particles until much further downstream than usual.

- 7) Chemical identification of at least nine separate particles and possibly 11 more was achieved. Both sodium sulfate decahydrate, $Na_2SO_4 \cdot 10H_2O$, and calcium carbonate, $CaCO_3$, were found. No sodium carbonate, Na_2SO_3 , was positively identified in the particles analyzed.
- 8) Some tentative associations of particle morphology were made. It was fairly certain that the soluble Na_2SO_4 appeared in the hydrated form and crystallized on the filter surface as a dark smear (Type II). Calcium carbonate, on the other hand, appeared to be a large, flaky particle about 2 to 3 μ m in size. It was not usually possible to identify particles under 1 μ m in size.
- 9) Particles identifiable as kraft mill salt cake were sampled in the atmosphere as far as 8 miles downwind from the plant.
- 10) At least five morphologically different types of particles were classified. The Type II dark, smeared particle was probably not a natural configuration but a result of the sampling technique. All five of these types were correlated with kraft mill effluent since they appeared on samples taken both in the stack
and the atmosphere. The Type V particles were not identified but could be associated with both background particles and kraft effluent.

Some very large agglomerated particles over 20 µm in size were
found on the filter when scanning them at low magnification.
It was determined that these were not a significant proportion
of the size distribution.

VI. CONCLUDING REMARKS

It should be pointed out that the particle size distributions presented herein are not the actual size distributions that exist in the plume. The mean sizes given in this report are no doubt larger than those which actually exist in the plume due to particle flattening upon impact on the filter. The flattening was quite apparent from a study of the scanning micrographs and resulted from the particles being in a fluid or semi-fluid state. A correction factor with which one could compute actual size distributions was not determined.

No particles other than the normal constituents of kraft mill salt cake were identified chemically. No evidence of condensible hydrocarbons was found or of particles which would not be considered part of the process chemicals. This does not mean, of course, that none of these were present in the effluent. Since most of the particles identified chemically were $l\mu m$ or larger in diameter these identifications can, strictly speaking, be associated with about 5 percent or less of the particles. It is felt that these associations could be extended to particles of smaller diameter by morphology. Nevertheless, a large number of particles remained unidentified, some of which could be material other than salt cake.

The reduction in particle size with distance is most probably due to physical mechanisms such as plume dilution and evaporation of water from fluid particles. There appears to be little likelihood of atmospheric chemical reaction at least among the larger size particles, i. e., greater than 0.5 μ m. It could be possible that a portion of the small Type V particles were formed by a reaction in the atmosphere. Until their identity is known, the question of atmospheric reaction in the plume cannot be fully answered.

The following general conclusions can be drawn based on the results presented in this thesis:

- (1) Size distributions of particulate matter in plumes emitted from stationary sources can be determined with a rather high degree of confidence in their reliability. These size distributions are closely related to the size of particles as they exist in the atmosphere.
- (2) It is possible to chemically identify kraft particles in the atmosphere in the vicinity of the source using airborne sampling and the techniques of electron microscopy. It also appears quite likely that good morphological correlations can be made with particle chemical character.
- (3) The sampling equipment and techniques developed during the course of this research work well and are simple and reliable. They are ready for application to studies of effluent from other industrial sources.

Based on these conclusions it is evident that the objectives of this research, as stated in Section I, have been met.

VIL RECOMMENDATIONS FOR FURTHER RESEARCH

The following recommendations are made for continuation of this line of research. These recommendations pertain both to further research on kraft mill effluent in the atmosphere and to other industrial sources of particulate.

- Further study into the identity and sources of the Type V particles should be undertaken.
- (2) The effect of humidity in the plume and in the ambient air on kraft particle characteristics should be studied and the hygroscopic characteristics of the particles should be determined. The possibility of downwind particle growth should be investigated.
- (3) The effect of process equipment and process variables on particle characteristics should be studied. Both kraft mills sampled during this research employed electrostatic precipitators as their primary control equipment. Other mills employ wet scrubbers and it is expected that such equipment might have a significant effect on particle character. Also, some mills still use direct contact evaporators for concentrating black liquor. This procedure could effect the amount of hydrocarbons entrained in the plume.
- (4) Determination of number and mass concentration of particulate

using the sampling techniques developed during this project should be attempted. Additional equipment including a microbalance and equipment to speed particle counting and sizing will be required. Although there are probably more direct methods of determining concentrations in such plumes, the determination of mass and particle concentration by direct sampling would provide valuable information to be used in correlation of these concentrations measured by other devices. In particular, it would be quite interesting to correlate with concentrations measured by laser radar.

- (5) More extensive study and correlation of particle morphological data with chemical identity should be undertaken. This is a very difficult task and much more work is needed before one can gain confidence that it is possible to establish identity based on morphology alone.
- (6) The use of other types of instruments to study particle identity be employed. The use of electron microprobes is encouraged especially when used in connection with a scanning electron microscope. Neutron activation may also be a help in some instances.
- (7) Finally, the methods of sampling and analysis demonstrated during this research should be exnteded to other sources of fine particulate matter. In particular, the method of selected

area diffraction should be quite useful in identifying metal oxides emitted from metals plants since these are usually crystalline in nature. It would also be of much interest to study the morphology of the particulate associated with wood slash burning and agricultural field burning as it rises to high altitudes. Particulate emitted from fossil fuel power plants would be of interest, and even more so, comparisons of air pollution hazards generated by various types of fuels which might be used in power generation should be studied.

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APPENDICES

APPENDIX A

SAMPLING LOG

Airborne Sampling

Filter	Pore size	Date	Location of sample	Sample description and duration	Micrographs in this report
009	3 μm	3/15/72	American Can	Background sample	SM08
012	3 µm	4/27/72	American Can	Sampled along Centerline of Plume (£) 5 min.	8-7, 8-13, 9-2, 10-5
013	3 µm	4/27-72	American Can	Along C 5 min.	10-8, SM02
014	3 μm	4/20/72		Aircraft engine exhaust	
015	3 µm	4/20/72		Background sample for Neut. Act. Analysis	
016	3 µm	4/20/72		Background sample for Neut. Act. Analysis	
017	3 μm	6/15/72	Western Kraft	Along C, 3 min.	
018	3 µm	6/16/72	American Can	0.5 mi. Downwind (D.W.) 1.5 min.	
019	3 μm	6/30/72	American Can	0.35 mi. D.W., 1 min.	
020	3 µm	6/30/72	American Can	1.7 mi. D.W., 2 min.	12-6, 8920, SM06
021	3 µ m	6/30/72	American Can	2.7 mi. D.W., 2 min.	9095, 9096, 9110, 9111, 9112, SM07
022	$3 \ \mu m$	6/30/72	American Can	4.7 mi. D.W., 2 min.	9099, 8916
023	3 µm	7/06/72	Western Kraft	0.25 mi. D.W., 1 min.	1 0- 15, 16-11, 16-13, 8863, SM05
024	3 µm	7/06/73	Western Kraft	3 mi. D.W., 2 min.	8862
025	0.4 µm	7/08/73	American Can	0.25 mi. D.W., 36 sec.	
026	0.4 µm	7/10/72	American Can	0.2 mi. D.W., 1 min.	10-13, 9619, 9621, 9657, 9658, SM03
027	0.4 μm	7/10/72	American Can	1.6 mi. D.W., 5 min.	10-14, SM19
028	3 μm	7/10/72	American Can	0.2 mi. D.W., 1 min.	10-11, 10-12, 16-16, SM04, SM20, SM21
029	3 µm	7/13/72	American Can	0.25 mi. D.W., 3 min.	9630
030	3 µm	7/13/72	American Can	1.6 mi. D.W., 12 sec.	
031	3 µm	7/13/72		Field burning	
032	3 µm	7/13/72	American Can	0.75 mi. D.W., 3 min.	
033	0.6 µm	9/30/72 (a.m.)	American Can	Above stack, 1.5 min.	

(Continued on next page)

Airborne Sampling (Continued)

Filter no.	Pore size	Date	Location of sample	Sample description and duration	Micrographs in this report
034	0.6 µm	9/30/72 (p. m.)	American Can	0.35 mi. D.W., 2 min.	8905
035	0.6 µm	9/30/72 (p. m.)	American Can	1.5 mi. D.W., 3.5 min.	15-15, 8843
036	0.6 µm	9/30/72 (p.m.)	American Can	Background sample, 7 min.	9615
037	$1 \ \mu m$	11/14/72	American Can	Vertical plume, 3 min.	18-10
038	$1 \ \mu mMP^2$	2 11/14/72	American Can	Vertical plume, 3 min.	
039	$1 \mu m$	11/20/72	Western Kraft	Vertical plume	
040	1 µm	11/30/72	Western Kraft	Along plume Ç, 3 min.	
041	0.6 µm	11/30/72	Western Kraft	Vertical plume, 3 min.	
042	$1 \ \mu m$	11/30/72	Western Kraft	Vertical plume, 3 min.	
043	$1 \ \mu m$	12/28/72	Western Kraft	Along plume Ç, 4 min.	
044	$1 \ \mu m$	12/28/72	American Can	Along plume C, 5 min.	
045	$1 \ \mu m$	12/29/72	American Can	Along plume C, 4 min.	8906
046	$1 \ \mu m$	12/29/72	American Can	0.3 mi. D.W., 2 min.	8910, 8911
047	$1 \ \mu m$	12/29/72	American Can	1.3 mi. D.W., 3 min.	8900
048	$1 \ \mu m$	12/29/72	American Can	2.8 mi. D.W., 3 min.	9128
049	$1 \ \mu m$	12/29/72	American Can	Background sample, 3 min.	9612
050	$1 \ \mu m$	1/29/73	American Can	0.4 mi. D.W., 2.4 min.	9135, 9136
051	$1 \ \mu m$	1/29/73	American Can	1.1 mi. D.W., 4 min.	9161
052	$1 \ \mu m$	1/29/73	American Can	3 mi. D.W., 4.3 min.	9138, SM14, SM15, SM16
053	$1 \ \mu m$	1/29/73	American Can	6 mi. D.W., 8 min.	9139
054	$1 \ \mu m$	1/29/73	American Can	4 mi. D.W., 6 min.	9157
055	$1 \ \mu m$	2/06/73	American Can	Underflight along £ of plume, 2.3 min.	SM18
056	$1 \ \mu m$	2/06/73	American Can	0.35 mi. D.W., 1 min. Recovery furnace shutdown	
057	1 µm	2/06/73	American Can	Along C of plume, kiln only operating, 9 min.	9246, 9251, 9252, SM10
058	$1 \ \mu m$	2/07/73	Am e rican Can	0.35 mi. D.W., 3 min.	9227, 9338
059	1 µm	2/07/73	American Can	2.7 mi. D.W., 10 min. Orbiting in plume	9188, 9295

(Continued on next page)

Airborne Sampling (Continued)

Filter _no	Pore size	Date	Location of sample	Sample description and duration	Micrographs in this report
060	$1 \ \mu m$	2/07/73	American Can	8 mi. D.W., 10 min. Orbiting in plume	9191, 9303, 9660, 9662
061	1 µm	2/07/73	American Can	Underflight of plume along \mathcal{E} , 4 mi.	9305, 9308, 9310
062	1 µm	2/09/73	American Can	Sample taken on top of pulp mill about 50 yd D.W., 10 min.	9193, 9199, 9201, 9229, 9311
063	1 µm	2/09/73	American Can	Sample taken on surface about 500 yd D.W., 10 min.	9332, 9334
064	1 µm	2/21/73	American Can	Sampled parallel to plume about 0.25 mi. from c , 6 min.	9337
065	1 µm	2/21/73	American Can	3 mi. D.W., 6 min.	9291

¹All filters prior to 012 with the exception of 009 were exploratory in nature and are not listed here.

 2 MP = Millipore filter, all others are Nuclepore.

Stack Sampling

Filter 1 no.	Pore size	Date	Location of sample	Sample description and duration	Micrographs in this report
1RB	0.2 μm	1/11/73	American Can Recovery furnace	6 sec.	
2RB	0.2 µm	1/11/73	American Can Recovery furnace	11 sec.	
3RB	0.6 µm	1/11/73	American Can Recovery furnace	3.5 sec.	
4RB	0.6 µm	1/11/73	American Can Recovery furnace	6 sec.	
5RB	1 µm	1/11/73	American Can Recovery furnace	4 sec.	8964, 9121
6RB	1 µm	1/11/73	American Can Recovery furnace	5.5 sec.	8943, 8962
7RB	3 µm	1/11/73	American Can Recovery furnace	5.5 sec.	
8RB	3 µm	1/23/73	American Can Recovery furnace	5 sec.	9151, 9152, SM11 SM12, SM13
9RB	0.6 µm	1/23/73	American Can Recovery furnace	5 sec.	
10RB	0.6 µm	1/23/73	American Can Recovery furnace	10 sec.	9156
1K	0.6 µm	1/11/73	American Can Kiln	11 sec.	
2K	0.6 µm	1/11/73	American Can Kiln	7.5 sec.	
3К	0.6 µm	1/11/73	American Can Kiln	11 sec.	
4K	1 µm	1/11/73	American C a n Kiln	5 sec.	9030
5K	1 µm	1/11/73	American Can Kiln	11 sec.	8946, 8954
6K	3 µm	1/11/73	American Can Kiln	5.5 sec.	9032, SM09, SM17
7K	3 µm	1/11/73	American Can Kiln	11.5 sec.	

APPENDIX B

ELECTRON MICROGRAPHS

Electron Micrographs

The micrographs contained in this appendix are arranged according to filter number and indexed by page number below. The plate number, filter number and magnification are given for each micrograph. There are three series of plate numbers. The dashed series, i. e., 8-7, were taken with the Hitachi HU-11B instrument. The first number corresponds to the camera load sequence and the second to the plate number in that camera load. The four digit sequence plates, i. e., 9110, were taken with the Phillips 300 instrument. The sequence beginning SM01 are scanning micrographs and were taken with the Cambridge Stereoscan Mk II instrument.

Plate Number	Page
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8-13	157
9-2	158
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10-15	165
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15-15	177
16-11	166
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16-16	173
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8843	177
8862	168
8863	167

Plate Number	Page
8900	180
8905	176
8906	178
8910	179
8911	179
8916	165
8920	160
8943	198
8946	203
8954	203
8962	199
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9032	204
9095	161
9096	162
9099	164
9110	162
9111	163
9112	163
9121	198
9128	180
9136	181
9138	182
9139	184
9151	199
9152	200
9156	202
9157	185
9161	182
9188	189
9191	190
9193	193
9199	194
9227	188
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9246	186
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Plate Number	Page
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9311	195
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9334	196
9337	196
9338	188
9612	181
9615	177
9619	169
9621	169
9630	175
9657	170
9658	170
9660	191
9662	191
SM01	156
SM02	159
SM03	171
SM04	174
SM05	167
SM06	161
SM07	164
SM08	156
SM09	204
SM10	187
SM11	200
SM12	201
SM13	201
SM14	183
SM15	183
SM16	184
SM17	205
SM18	185
SM19	172
SM20	174
SM21	175



Plate SM01

Blank Nucleopore Filter



Plate SM08 Filter 009

4060X

3990X



Plate 8-7

Filter 012

19150X



Plate 8-13 Filter 012 10850X



Plate 9-2 Filter 012



Plate 10-5 Filter 012 4100X







Plate SM02 Filter 013 3540X



Plate 12-6 Filter 020 5000X



Plate 8920 Filter 020 12350X



Plate SM06

Filter 020



Plate 9095 Filter 021 12350X



Plate 9096 Filter 021 6400X



Plate 9110 Filter 021 4250X



 Plate 9111
 Filter 021
 6400X



 Plate 9112
 Filter 021
 6400X



Plate SM07

Filter 021



Plate 9099

Filter 022 6400X



Plate 8916

Filter 022



Plate 10-15 Filter 023 5200X



Plate 16-11 Filter 023 6400X



Plate 16-13 Filter 023 4000X







Plate SM05 Filter 023 4150X







Plate 10-13

Filter 026

6800X


Plate 9619 Filter 026 12350X



Plate 9621 Filter 026 12350X







Plate 9658 Filter 026 12350X



Plate SM03

2300X



Plate 10-14 Filter 027 9150X



Plate SM19

Filter 027



Plate 10-11

Filter 028

6200X







Plate 16-16 Filter 028 5000X





Filter 028

4150X



Plate SM20 Filter 028 2300X







Plate 9630 Filter 029 12350X







Plate 15-15 Filter 035 5

5200X

176



Plate 8843 Filter 035 6400X



Plate 9615 Filter 036 10000X

177



Plate 18-10 Filter 037 8600X



6400X

Plate 8906 Filter 045



Plate 8910

Filter 046





Plate 8911 Filter 046 6400X

179



 Plate 8900
 Filter 047
 6400X



Plate 9128 Filter 048

4250X

180



Plate 9612 Filter 049 10000X



Plate 9136 Filter 050 6400X



 Plate 9161
 Filter 051
 6400X



Plate 9138 Filter 052 6400X



Plate SM14

Filter 052



Plate SM15 Filter 052 360X



Plate SM16



6400X Plate 9139 Filter 053







Plate SM18 Filter 055 580X



Plate 9246

Filter 057



Plate 9251 Filter 057 6400X







Plate SM10 Filter 057 5210X







Plate 9338 Filter 058

6400X



Plate 9188 Filter 059 15200X



 Plate 9295
 Filter 059
 6400X

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Plate 9303 Fi

Filter 060

6400X







Plate 9662 Filter 060 25900X







Plate 9308 Filter 061 17000X







Plate 9193 Filter 062 6400X







Plate 9229 Filter 062 6400X







Plate 9332 Filter 063 6400X



Plate 9334

Filter 063



Plate 9337 Filter 064 25900X





Filter 065

19200X



 Plate 8964
 Filter 5RB
 12350X



Plate 9121

Filter 5RB



Plate 8943 Filter 6RB 12350X



Plate 8962

Filter 6RB

25900X



Plate 9151 Filter 8RB 2900X







Plate SM11 Filter 8RB



Plate SM12 Filter 8RB 1100X





Plate 9156

Filter 10RB

4250 X



Plate 9030 Filter 4K 12350X



Plate 8946



12350X Plate 8954 Filter 5K







Plate SM09

Filter 6K


