Final Report Covering the Period from 1 February 1980 through 31 January 1987:

Condensation Nuclei Measurement in the Stratosphere for the NASA ACE Program

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Project Objectives.
The objectives of the research funded by this grant were to develop, design and construct a condensation nucleus counter (CNC) for use in the stratosphere on NASA U-2 aircraft and to use the instrument in the Aerosol Climatic Effects program. In addition the instrument was to be calibrated in the laboratory and provided with an inlet which permitted near isokinetic sampling.

Project Accomplishments.
A condensation nucleus counter which operated at stratospheric pressures was developed, designed and constructed. It was calibrated in the laboratory. Its response as a function of particle size and concentration was reported. The was the first time that the response of such an instrument was verified in the laboratory.

An inlet was constructed which provided near isokinetic sampling. The resulting instrument, the U-2 CNC, was deployed on NASA U-2 aircraft in the study of the climatic effects of aerosol. These studies occurred in March, April, May, July, November and December of 1992 and in April, May, June and December of 1983.

The U-2 CNC was used in the study of the aerosol cloud resulting from the eruption of El Chichon. It permitted the observation of new particle formation in the stratosphere.

Publications.
Reprints of papers resulting from this research are found in Appendix A.

Wilson, J. C. , Hyun, J. H., Blackshear, E. D., "The function and response of an improved stratospheric condensation nucleus counter," *J. Geophys. Res, 88, 6781-6785, 1983.*

Wilson, J. C., Blackshear, E. D., Hyun, J. H., "Changes in the sub-2.5 micron diameter aerosol observed at 20 km altitude after the eruption of El Chichon", *Geophys. Res. Lett., 10, 1029-1032, 1983.*

Subsequent Work.
Following the completion of the Aerosol Climatic Effects study, the U-2 CNC and its successors, the ER-2 CNC and the ER-2 CNCII, have been used in a number of studies. They include: Stratosphere-Troposphere Exchange Project, Airborne Antarctic Ozone Experiment, Airborne Arctic Stratospheric Expedition, Airborne Arctic Stratospheric Expedition II, Stratospheric Photochemistry, Aerosols and Dynamics Expedition, Airborne Southern Hemisphere Ozone Experiment and Measurements for Assessing the Effects of Stratospheric Aircraft. Appendix B contains a partial list of papers making use of the CNC data from these experiments. The instrument developed on this grant has made a significant contribution to understanding stratospheric aerosol, chemistry and dynamics.

Appendix A.

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The Function and Response of an Improved Stratospheric Condensation Nucleus Counter

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An improved condensation nucleus counter (CNC) for use in the stratosphere is described. The University of Minnesota CNC (UMCNC) has a sequential saturator and condenser and uses *n*-butyl alcohol as the working fluid. The use of a coaxial saturator flow, with aerosol in the center and filtered, alcohol-laden air around it, speeds the response of this instrument and improves its stability as pressure changes. The counting efficiency has been studied as a function of particle size and pressure. The UMCNC provides an accurate measure of submicron aerosol concentration as long as the number distribution is not dominated by sub 0.02 μm diameter aerosol. The response of the UMCNC is compared with that of other stratospheric condensation nucleus counters, and the results of a (near) comparison with a balloon-borne condensation nucleus counter are presented. The UMCNC has operated 14 times on a NASA U-2 aircraft at altitudes from 8 to 21.5 km.

INTRODUCTION

The University of Minnesota condensation nucleus counter (UMCNC) utilizes a sequential saturator and condenser and *n*-butyl alcohol as the working fluid. The use of a coaxial saturator flow has improved the response of the instrument. The instrument has operated 14 times on NASA U-2 aircraft at altitudes ranging from 8 to 21.5 km.

The response of the instrument has been studied and is compared with that of other condensation nuclei counters (CNC's). The UMCNC provides an accurate measure of submicron aerosol number concentration as long as the distribution is not dominated by particles smaller than 0.02 μm in diameter. This response is similar to the response expected of other stratospheric CNC's.

The UMCNC was flown in an airmass which (it was hoped) had been sampled the previous day by a University of Wyoming CNC. The two measurements are quite similar.

CONDENSATION NUCLEUS COUNTERS (CNC's): TYPES AND RESPONSE

CNC's are often used to measure the number concentration of particles in the diameter range from about 0.01 to about 1.0 μm. When used with a size selecting device such as a diffusion battery or electrical mobility analyzer, a CNC can be used to obtain size distribution measurements. They are particularly useful in studying particles that are too small to be conveniently detected by more direct means.

CNC's function by creating a supersaturated vapor which condenses on particles in the aerosol sample being measured. These nuclei then grow to sizes that permit easy detection. Alcohol or water is often used as a working fluid, and the resulting droplets are usually detected by optical means.

A number of different techniques have been used to create the supersaturated vapor. Expansion chamber instruments are reviewed and described by *Nolan* [1972], *Liu et al.* [1975], *Miller and Bodhaine* [1982*a*] and *Schmitt et al.* [1982]. Thermal gradient diffusion chambers that create sufficient supersaturations to detect submicron particles have been described by *Rosen et al.* [1974, 1978] and *Hoppel et al.* [1979]. Continuous flow counters with sequential saturation and condensation chambers are described by *Bricard et al.* [1974, 1976], *Sinclair and Hoopes* [1975], *Agarwal and Sem* [1980], and *Rosen and Hofmann* [1981]. *Cadle and Langer* [1975] and *Kousaka et al.* [1982] describe mixing type CNC's.

Not all particles are counted by CNC's. Several factors determine whether a given particle can be caused to grow to a detectable size in a given counter. They include the supersaturation of the vapor and the period of time the particle is exposed to the supersaturation; the physical properties of the working fluid; the wetability, reactivity, or solubility of the particle; and the working fluid and the sensitivity of the droplet detector. Concentrations indicated by a condensation nucleus counter may differ from the actual aerosol concentration because small particles may be lost in the sampling tubes and instrument components by diffusion, electrostatic removal, thermophoresis, or diffusiophoresis. Some particles may evaporate if they are heated in the instrument. Large particles are often lost in the instrument plumbing by impaction or settling.

The response of various CNC's to aerosols of known size, composition, and concentration has been experimentally studied. *Sinclair* [1982], *Liu et al.* [1982], and *Miller and Bodhaine* [1982*b*] provide reviews and reports of these studies that support several generalizations. Many CNC's count nearly 100% of those submicron particles that are larger than 0.05 μm in diameter regardless of the chemical composition of the aerosol or working fluid. Counting efficiencies generally begin to decrease with particle size at some diameter between 0.01 and 0.05 μm. In this size region, the counting efficiency may depend upon the chemical composition of the aerosol as well as on the design of the counter.

STRATOSPHERIC CONDENSATION NUCLEUS COUNTERS

The heat and mass transfer processes that govern CNC response depend upon pressure and temperature. Instruments that operate in the stratosphere must sample from air at low and varying pressures, and different techniques have been used to produce the necessary supersaturations in stratospheric instruments. A number of investigators have built CNC's that use rapid expansion of a water-vapor saturated sample to achieve the necessary supersaturation. To operate in the

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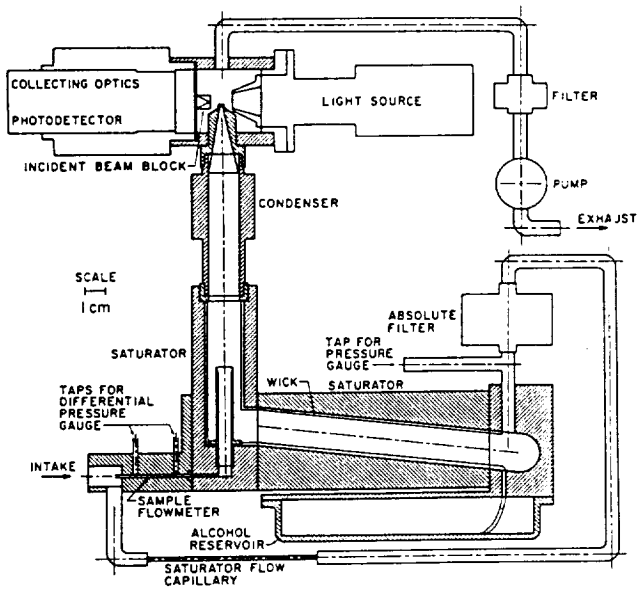

Fig. 1. Diagram of the University of Minnesota condensation nucleus counter showing the coaxial flow saturator, condenser, and particle detection optics. The elements whose dimensions are important in determining the supersaturation are drawn to scale.

stratosphere, these instruments require sample pressurization prior to the expansion [*Junge et al.*, 1961; *Kaselau*, 1974; *Haberl*, 1975]. The *Cadle and Langer* [1975] instrument that creates the supersaturation by mixing cold air with the humidified sample was also pressurized for operation in the stratosphere.

A number of instruments that operate at ambient stratospheric pressures have been developed. *Rosen et al.* [1974, 1978] deployed thermal gradient diffusion cloud chambers that use ethylene glycol as the working fluid. In the instrument developed by *Bricard et al.* [1974, 1976], *n*-butyl alcohol vapor diffuses into the sample as it flows through a heated saturator; then, the supersaturation develops as the sample flows through the cooled condenser. *Rosen and Hofmann* [1981] use ethylene glycol in an instrument which also has a sequential saturator and condensor and which functions to altitudes of 30 km.

Various comparisons and tests have been made by using these instruments. *Cadle et al.* [1975] compared the Langer, Rosen et al., and SANDS (Haberl) instruments with a Pollak counter which had been calibrated by *Liu et al.* [1975]. This work was done at pressures near one atmosphere. The Rosen et al., SANDS, and Pollak counters generally agreed to within 30% or better when counting aerosols generated from sulfuric acid solution and having diameters as small as 0.04 μm. *Rosen et al.* [1978] operated the Kaselau and Rosen et al. instruments on the same balloon flight and found they generally agreed to within a factor of 2 while counting concentrations that varied over 2 orders of magnitude. Most investigators report laboratory measurements made on generally uncharacterized aerosols as pressure is reduced. These measurements often were used to determine the altitude range over which the instruments function. Rosen and Hofmann tested their instruments in the stratosphere by increasing the supersaturations in flight. When the particle count did not increase, they concluded that the supersaturations they normally used were sufficient to detect stratospheric aerosols. In a theoretical study, Junge et al. estimated the effects of particle losses by diffusion and settling in the instrument and predicted that losses of both small and large particles would increase with altitude.

Although detailed experimental studies of these instruments' responses as a function of pressure, particle size, and composition have not been carried out, the studies cited above and experience with atmospheric pressure counters suggest the following generalizations. The various stratospheric instruments that use different mechanisms for creating supersaturations, different working fluids, and operating within their specified altitude ranges probably detect, with a relatively high or predictable efficiencies, sulfuric acid particles having diameters somewhat larger than a few hundreths micron. The instruments would, therefore, be expected to agree when sampling stratospheric aerosols having number distributions dominated by submicron particles with diameters larger than this size. The losses of particles by diffusion will vary from instrument to instrument and will increase for smaller particles at higher altitudes, and like the conventional CNC's, the stratospheric counters are likely to be increasingly inefficient for particles smaller than 0.01 μm. Thus, the various instruments would be expected to disagree when measuring aerosols where the number distribution is dominated by ultrafine aerosol. Such distributions may have occured during events of new particle formation reported following the eruptions of Alaid [*Hofmann and Rosen*, 1981], St. Helens [*Hofmann and Rosen*, 1982], and El Chichon [*Wilson et al.*, 1982; *Rosen and Hofmann*, 1982].

THE UNIVERSITY OF MINNESOTA CNC

The University of Minnesota condensation nucleus counter (UMCNC) (Figure 1) is a continuous-flow instrument with sequential saturator and condenser which functions on a NASA U-2 aircraft at altitudes from 8 to 21.5 km at near-ambient pressure. The instrument uses *n*-butyl alcohol as the working fluid and differs from prior designs using the sequential saturator and condenser. The principal innovation is the use of a coaxial flow: The aerosol sample is introduced on the axis of the vertical saturator and is surrounded by a flow of filtered, alcohol-laden air. After the coaxial flow is formed, it passes out of the saturator section and into the condenser where it is cooled. This coaxial flow system shortens the instrument response time, reduces the losses of particles in the saturator by diffusion, and causes all particles to experience nearly the same supersaturations and flow velocities. The use of this system greatly reduced the variations in instrument response which were observed as pressure was changed in a prototype lacking it [*Wilson et al.*, 1982].

Table 1 lists the operating conditions and component dimensions which have been used in the UMCNC. The instrument performance is not very sensitive to small variations in these conditions.

TABLE 1. Operating Conditions of the UMCNC

	Variable
Instrument pressure range	40–400 mbar
Saturator temperature	29°C
Condenser temperature	5°C
Sample flow rate	~4.5 cm^3 s^{-1}
Total flow rate	~30 cm^3 s^{-1}
Working fluid	*n*-butyl alcohol
Condenser length	6 cm
Condenser diameter	1.5 cm

The UMCNC operates at nearly constant volumetric flow rate. The sample flow rate is monitored continuously by a capillary tube flow meter, where the output is used to control the pump. The ratio of sample flow to saturator flow remains nearly constant over the range of operating pressures due to the use of capillary flow elements in both branches.

Droplets formed in the condensor are individually counted in an optical particle counter. The present electronics permit concentrations up to 2500 cm^{-3} to be counted. The coincidence correction is about 20% at this concentration.

The number of particles per unit mass of air is calculated from the count rate, the sample flow rate, the absolute pressure in the instrument, and the temperature of the sample flowmeter. These variables are continuously recorded by a data logger. The calculation of ambient concentration requires ambient pressure and temperature data which are supplied by other investigators on the U-2. The ambient pressure differs slightly from the instrument pressure due to the airplane velocity (approximately Mach 0.7). Ambient temperatures are considerably lower than instrument temperatures. The stratospheric, ambient number concentrations generally exceed those in the instrument by about 25% due to these differences.

Laboratory Determination of UMCNC Performance

The quantity measured by condensation nuclei counters is usually referred to as the concentration of condensation nuclei or Aitken nuclei. To define more precisely the meaning of the UMCNC output, laboratory measurements were made of instrument response to monodisperse, singly charged particles at a range of pressures. The experimental setup is shown in Figure 2. Di-octyl phthalate (DOP) particles of 0.054 μm in diameter were generated by a system consisting of an atomizer, a radioactive neutralizer, a condensation generator, a differential mobility analyzer (DMA), a second neutralizer and a second DMA. The second neutralizer and DMA served to reduce the number of doubly charged particles in the test aerosol to near zero. *Liu and Lee* [1975] and *Liu and Pui* [1974] describe the components used in the generation of the DOP aerosol. Particles between 0.006 μm and 0.01 μm in diameter were generated by using a flat flame aerosol generator [*Vikayakumar*, 1982] fed with sodium chloride. The chemical composition of the resulting particles is unknown. Since very few particles in that size range carry two charges after neutralization, only one neutralizer and DMA were used to select the test aerosols.

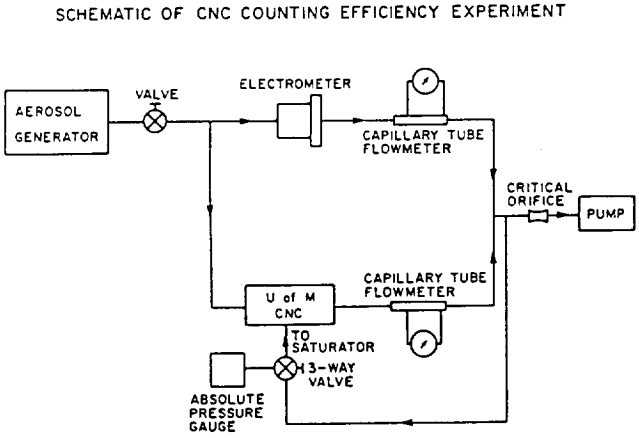

Fig. 2. Diagram of experimental setup used to determine the response of the UMCNC to singly charged, monodisperse aerosol.

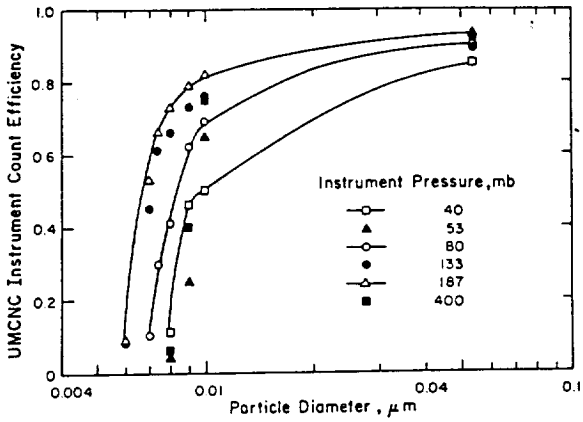

Fig. 3. Response of the UMCNC to monodisperse, singly charged aerosol. The vertical axis gives the fraction of the particles entering the instrument which are counted. The 0.56 μm aerosol was DOP. The smaller particles were produced in a flat-flame generator fed with sodium chloride and are of unknown chemical composition.

The test aerosols were passed through a pressure-reducing valve and then divided with approximately 30 $cm^3\ s^{-1}$ passing through a tube 35 cm in length to the UMCNC and the rest passing through a tube 16 cm in length to a Faraday cage mounted on a Cary 401 electrometer. The total flow was approximately 156 $cm^3\ s^{-1}$ or 212 $cm^3\ s^{-1}$ depending upon the critical orifice used in the test. Volumetric flows and absolute pressure were measured in each branch. The electrometer current and the flow data were used to calculate the concentration of the singly charged particles reaching the electrometer. Corrections were made for pressure differences and for diffusion losses in the tubes by using the formula of *Gormely and Kennedy* [1949] in order to calculate the concentration of the aerosol actually entering the UMCNC. The ratio of the concentration determined by the UMCNC to the actual value is plotted as a function of particle size and pressure in Figure 3. A range of ± 0.06 represents a reasonable measure of the repeatability of the efficiency measurements.

Figure 4 shows the chamber detection efficiency as a function of particle size. The chamber detection efficiency equals the fraction of the particles actually reaching the saturator which are counted. This figure is determined from the data in Figure 3 by accounting for the diffusion losses in the sample flowmeter and injection tube which have a combined length of 10.4 cm. The curves are nearly horizontal from 0.054 to 0.01 μm which suggests that the changes in efficiency shown in Figure 3 in this size range are caused by diffusion losses in the instrument itself. Thus, the curves in Figure 3 between 0.01 and 0.056 μm were drawn with this assumption.

Since the number distribution of stratospheric aerosol is dominated by submicron particles, the upper size cutoff of the UMCNC is not critical. However, it is expected that particles larger than a few microns will be lost in the plumbing by impaction.

Stratospheric Performance of the UMCNC

The temperatures and flow rates essential for correct operation of the UMCNC are monitored continuously in flight. In the 14 research flights undertaken to date, the thermodynamic conditions for efficient particle counting have been maintained in actual use on the U-2 aircraft. In another flight, a filter was placed on the inlet, and the indicated particle concentrations

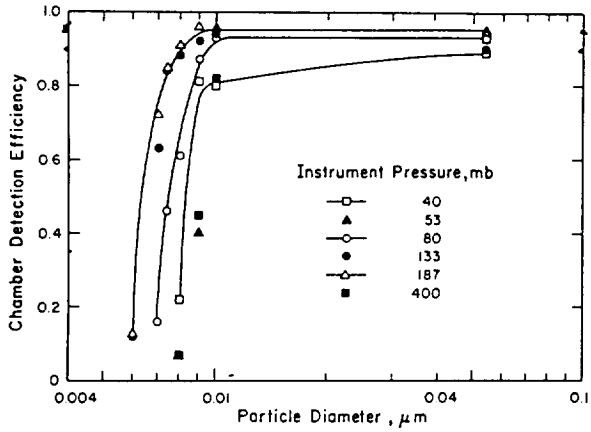

Fig. 4. Detection efficiency of the saturator-condenser and optical system for the test aerosol. The vertical axis shows the fraction of the particles reaching saturator which are counted.

were usually zero. Occasional nonzero counts were observed and may have been artifacts but were infrequent enough so that their contribution to UMCNC output can be neglected.

The UMCNC inlet is designed to draw samples from outside of the aircraft's boundary layer and to avoid sampling bias due to the mismatch between sampling and aircraft velocity. Thus, on the aircraft the sampled aerosol passes through 28 cm of tubing at a flow of 30 $cm^3\ s^{-1}$ before reaching the instrument. Additional losses of particles by diffusion can occur in that tube. These losses have been estimated and incorporated into Figure 5, which shows the estimated counting efficiency of the UMCNC in the stratosphere as a function of altitude and particle size for the usual inlet configuration. In this case, the instrument pressure equals 1.1 times the ambient pressure due to partial dissipation of the ram pressure.

The chemical composition of the aerosol may also effect the counting efficiency. The gradual decrease in counting efficiency shown in Figure 5 is due to losses of particles by diffusion. The sharp decrease occurs when the system is no longer able to cause the particles to grow efficiently. The dashed line in Figure 5 indicates the efficiency which would be observed if the chamber detection efficiency remained high (92% in this case). Comparisons of various calibrations done on the TSI CNC, a commercial instrument using *n*-butyl alcohol as the working fluid, suggest that it detects sub-0.01 μm sulfuric acid particles more efficiently than flame generated aerosols [*Agarwal and Sem*, 1980; *Madeline and Metayer*, 1980; *Brockmann*, 1981; *Vijayakumar*, 1982]. Stratospheric submicron aerosols are mainly sulfuric acid and water, and the TSI CNC and UMCNC are chemically similar. If they respond similarly, the lower size limits for efficient counting of stratospheric aerosols may be smaller than indicated for the test aerosols, and the efficiency curves would follow the dashed lines in Figure 5 to smaller sizes and then decrease sharply.

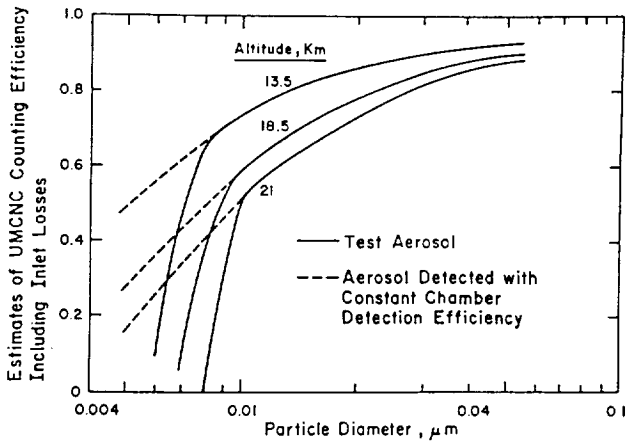

Fig. 5. Estimates of UMCNC counting efficiency at various altitudes. Losses in the inlet are included.

COMPARISON OF THE UMCNC WITH THE COUNTER OF *ROSEN AND HOFMANN* [1981]

On December 8, 1982, the University of Wyoming group flew a balloon with a Rosen and Hofmann counter into the stratosphere above Laramie, Wyoming. On the next day, a NASA U-2 flew to Grand Junction, Colorado, in hopes of meeting the same air mass that had been over Laramie the previous day and whose trajectory had been estimated at NASA Ames Research Center. (The planned, more intimate rendezvous had been prevented by technical difficulties.) A portion of the December 9 Wyoming data (D. Hofmann, personal communication, 1982) is plotted on Figure 6 with the UMCNC data from December 10. The UMCNC data at altitudes below 20 km were gathered during a nearly steady descent lasting 25 min. The data above 20 km were taken about 90 min later in the flight.

Assuming that the measurements occurred in the same airmass, the instruments seem to respond similarly. The two profiles show many of the same features, and a small shift in altitudes would bring the two profiles into close agreement. The Wyoming instrument samples stratospheric aerosol at nearly 13 $cm^3\ s^{-1}$ through a tube 15.2 cm long after which the aerosol enters a saturator (D. Hofmann, personal communication, 1982). The diffusion losses in transport to the saturator are about 1/3 those suffered in the UMCNC at the same altitude. Additional losses may occur in the saturator itself. The efficiencies of the two instruments approach one another for larger particles and as long as the sampled aerosol is not dominated by sub-0.02 μm particles, they should agree.

DISCUSSION

The UMCNC has been tested in the laboratory and is capable of efficiently detecting particles as small as 0.008 μm in

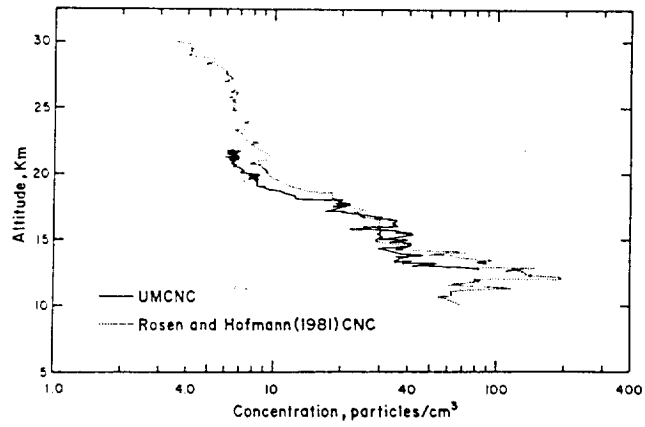

Fig. 6. Aerosol concentration profiles measured on December 9 over Laramie, Wyoming, by the Wyoming group and on December 10 over Grand Junction, Colorado, with the UMCNC. Efforts were made to make the measurements in the same airmass.

diameter. However, diffusion losses in the sample line and sample flowmeter reduce the counting efficiency significantly for stratospheric measurements of particles having diameters below 0.02 μm. The UMCNC provides an accurate measure of the aerosol number concentration as long as the size distribution is not dominated by sub-0.02 μm particles. It is expected that this is also true of other stratospheric CNC's.

Continuous flow counters are well suited for use with diffusion batteries or mobility analyzers to determine aerosol size distributions. In such applications it is essential to know the counting efficiency of the CNC as a function of particle size. The next step in the development of the UMCNC should involve development of a size selective inlet to permit determination of size distributions for particles smaller than 0.1 μm. At that time, the diffusion losses of small particles can be taken into account and reduced by relatively modest design changes.

During its first year of operation, the UMCNC has operated 14 times in the stratosphere, both before and after the eruption of the El Chichon volcano. These measurements have contributed to our knowledge of the stratospheric aerosol size distribution and its evolution following the volcanic injection. Reports concerning these measurements are being prepared.

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REFERENCES

Agarwal, J. K., and G. J. Sem, Continuous flow, single-particle-counting condensation nucleus counter, *J. Aerosol Sci.*, *11*, 343–357, 1980.

Bricard, J., P. DeLattre, and G. Madelaine, Counting of Condensation nuclei at low pressures: Its application to photolysis of gaseous impurities in the stratosphere, in Proceedings of the Third Conference on the Climatic Impact Assessment Program, *Rep. DOT-TSC-OST-74-15*, U.S. Dept. Transp. Washington, D. C., 1974.

Bricard, J., P. Delattre, G. Madelaine, and M. Pourprix, Detection of ultrafine particles by means of a continuous flux condensation nuclei counter, in *Fine Particles*, edited by B. Y. H. Liu, Academic, New York, 1976.

Brockmann, J. E., Coagulation and deposition of ultrafine aerosols in turbulent pipe flow, Ph.D. Thesis, Univ. of Minn., Minneapolis, 1981.

Cadle, R. D., and G. Langer, Stratospheric Aitken particles near the tropopause, *Geophys. Res. Lett.*, *2*, 329, 1975.

Cadle, R. D., G. Langer, J. B. Haberl, A. Hogan, J. M. Rosen, W. A. Sedlacek, and J. Wegrzyn, A comparison of the Langer, Rosen, Nolan-Pollak and SANDS condensation nucleus counters, *J. Appl. Meteorol.*, *14*, 1566, 1975.

Gormley, P. G., and J. M. Kennedy, Diffusion from a stream flowing through a cylindrical tube, *Proc. R. Irish Acad.*, *52-A*, 163–169, 1949.

Haberl, J. B., Stratospheric Aitken nuclei counter, *Rev. Sci. Instrum.*, *46*, 442, 1975.

Hofmann, D. J., and J. M. Rosen, Balloon-borne observations of stratospheric aerosol and condensation nuclei during the year following the Mt. St. Helens eruption, *J. Geophys. Res.*, *87*(C13), 11,039–11,061, 1982.

Hofmann, D. J., and J. M. Rosen, Stratospheric aerosols and condensation nuclei enhancements following the eruption of Alaid in April 1981, *Geophys. Res. Lett.*, *8*, 1231, 1981.

Hoppel, W. A., S. Twomey, and T. A. Wojciechowski, A segmented thermal diffusion chamber for continuous measurements of CN, *J. Aerosol Sci. 10*, 369, 1979.

Junge, C. E., C. W. Chagnon, and J. E. Manson, Stratospheric aerosols, *J. Meterol.*, *18*, 81–108, 1961.

Kaselau, K. H., Measurements of aerosol concentration up to a height of 27 km, *Pure Appl. Geophys.*, *112*, 877, 1974.

Kousaka, Y., T. Nida, K. Okuyama, and H. Tanaka, Development of a mixing type condensation nucleus counter, *J. Aerosol Sci.*, *13*, 231, 1982.

Liu, B. Y. H., and K. W. Lee, An aerosol generator of high stability, *Am. Ind. Hyg. Assoc. J.*, *36*, 861, 1975.

Liu, B. Y. H., and D. Y. H. Pui, A submicron aerosol standard and the primary, absolute calibration of the condensation nuclei counter, *J. Colloid Interface Sci.*, *47*, 155–171, 1974.

Liu, B. Y. H., D. Y. H. Pui, A. W. Hogan, and T. A. Rich, Calibration of the Pollack counter with monodisperse aerosols, *J. Appl. Meteorol.*, *14*, 46, 1975.

Liu, B. Y. H., D. Y. H. Pui, R. L. McKenzie, J. K. Agarwal, R. Jaenicke, F. G. Pohl, O. Preining, G. Reischl, W. Szymanski, and P. E. Wagner, Intercomparison of different 'absolute' instruments for the measurement of aerosol number concentrations, *J. Aerosol Sci.*, *13*, 429, 1982.

Madelaine, G., and Y. Metayer, Note, *J. Aerosol Sci.*, *11*, 358, 1980.

Miller, S. W., and B. A. Bodhaine, Supersaturation and expansion ratios in condensation nuclei counters: An historical perspective, *J. Aerosol Sci.*, *13*, 481, 1982*a*.

Miller, S. W., and B. A. Bodhaine, Calibration of Pollak condensation nuclei counters using charged, monodisperse aerosols, *J. Aerosol Sci.*, *13*, 419, 1982*b*.

Nolan, P. J., The photoelectric nucleus counter, *Sci. Proc. R. Dublin Soc.*, *A4*, 161, 1972.

Rosen, J. M., and D. J. Hofmann, Stratospheric condensation nuclei, *Rep. Ap-61*, Univ. of Wyoming, Laramie, 1981.

Rosen, J. M., and D. J. Hofmann, Aerosol profiles over Laredo, Texas, during May 1982, *Rep. VWY/DPA/AP-72*, Univ. of Wyoming, Laramie, 1982.

Rosen, J. M., R. G. Pinnick, and R. Hall, Recent measurements of condensation nuclei in the stratosphere, in Proceedings 3rd Conference Climatic Impact Assessment Program, *DOT-TCS-OST-74-15*, Dept. of Transp., Washington, D. C., 1974.

Rosen, J. M., D. J. Hofmann, and K. H. Kaselau, Vertical profiles of condensation nuclei, *J. Appl. Meteorol.*, *17*, 1737, 1978.

Schmitt, J. L., J. L. Kassner, Jr., and J. Podzimek, The University of Missouri-Rolla, absolute Aitken nucleus counter, *J. Aerosol Sci.*, *13*, 373, 1982.

Sinclair, D., Particle size sensitivity of condensation nucleus counters, *Atmos. Environ.*, *16*, 955, 1982.

Sinclair, D., and G. S. Hoopes, A continuous flow condensation nucleus counter, *J. Aerosol Sci.*, *6*, 1, 1975.

Vijayakumar, R., Ultrafine aerosol generation using a premixed flat flame, Ph.D. Thesis, Univ. of Minnesota, Minneapolis, 1982.

Wilson, J. C., E. D. Blackshear, and J. H. Hyun, An improved, continuous-flow condensation nucleus counter for use in the stratosphere, *J. Aerosol Sci.*, in press, 1982.

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CHANGES IN THE SUB-2.5 MICRON DIAMETER AEROSOL OBSERVED AT 20 KM ALTITUDE AFTER THE ERUPTION OF EL CHICHON

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Abstract. Measurements of sub-2.5 μm aerosol concentration were made from a NASA U-2 aircraft by several experimenters before and after the eruptions of El Chichon in March and April of 1982. Concentrations of sub-2.5 μm diameter particles encountered between 19.6 and 21.6 km altitude were nearly uniform over large distances in regions thought to be unaffected by El Chichon. Comparisons of measurements made with three instruments suggest that particles smaller than .1 μm in diameter contributed significantly to the number distribution of these non-El Chichon aerosols. Measurements of large concentrations of sub 0.1 μm particles in April and May 1982 imply that new particle formation occured following the eruption. Measurements made in November and December of 1982 showed decreased numbers of sub-0.1μm particles compared to the non-El Chichon measurements. Simultaneous measurements of SO_2 and aerosol volume concentrations made on the lower edge of the volcanic cloud two weeks after the eruption permitted a range of SO_2 conversion rates to be estimated.

Introduction

The University of Minnesota Condensation Nucleus Counter (UMCNC) (Wilson et al.,1983), the Ames Wire Impactor (AWI)(Oberbeck et al., 1983) and the PMS ASAS-X optical particle counter (Knollenberg and Huffman, 1983) provide independent measures of aerosol concentration and were operated simultaneously on NASA U-2 aircraft before and after the eruption of El Chichon. The UMCNC measures the number concentration of particles larger than 0.01 μm in diameter with an efficiency which depends upon particle diameter and altitude. At 20 km altitude, the UMCNC counting efficiencies for 0.01 μm, 0.02 μm and 0.05 μm particles are about 55%, 70% and 90% respectively. The ASAS-X continuously measures size distributions of particles in the 0.1 μm to 3 μm diameter range. The ASAS-X data shown here were provided by Knollenberg and Huffman (personal communication). The ASAS-X sampling efficiency decreases for particles larger than 0.5 μm in diameter due to inertial losses in the sampling inlet. The data shown here have been corrected for these losses using a scheme similiar to that presented by Knollenberg and Huffman (1983). The correction scheme is not yet in final form and may change. The aerosol volumes calculated from the ASAS-X number distributions are quite sensitive to the assumed counting efficiencies. The AWI is used to collect samples of one or two minutes duration which are analyzed to provide size distributions in the range from 0.06 μm to a few microns. AWI data included in this paper were supplied by Oberbeck, Snetsinger and Hays (personal communication). Whenever possible, data from both the ASAS-X and AWI are used when considering particles in their common size range.

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Measurements

Table 1 lists each 1982 flight segment between 19.6 km and 21.6 km altitude for which UMCNC and AWI or ASAS-X data are available. The starting time and distance covered are listed with the UMCNC average concentration and standard deviation for the segment. The number concentration measured with the AWI and/or the ASAS-X number and volume concentrations are also given. The approximate locations (S. Scott, personal communication) of the longer flight segments are indicated on figure 1. The start and end points of the three segments following path d are indicated by different symbols. For most flight segments, the small standard deviations of the UMCNC and ASAS-X measurements indicate that the aerosol was quite uniform over the segment and the AWI data is taken to be representative of the segment in these cases. On 19 April and 5 May, the aerosol shows considerable spatial inhomogeneity and the AWI data can not be considered representative of the segments. Data from these two flights are plotted on figures 2 and 3.

Measurements Free from the Effects of El Chichon

Flight segements a and b were made prior to the eruption and flights c and e were made when the main volcanic cloud was thought to be south of the flight paths. These flights showed spatial homogeneity in the 20 km aerosol. For each of these segments, the standard deviations of the hundreds of UMCNC measurements were less than 7% of the mean concentrations. The standard deviation of the concentrations measured by the ASAS-X over these intervals were almost entirely explained by the random fluctuations in the ten second ASAS-X samples. The variability due to changes in aircraft position was small.

The UMCNC concentration measured on these four segments exceeds the concentrations measured by the AWI and the ASAS-X by a factor of 3 or more. The second AWI sample shown for April 19 and that of May 5 were collected at times when the UMCNC and ASAS-X concentrations were near the non-El Chichon levels (see figures 2 and 3) and show concentrations well below that indicated by the UMCNC. These observations suggest that the number distribution of the non-El Chichon aerosol was dominated by particles smaller than 0.1 μm or 0.06 μm. Note that the agreement among the three

approach that indicated by the UMCNC on many of these segments. Segment m is an exception where the ASAS-X number concentration is not significantly increased over non-El Chichon levels.

Aerosol volumes calculated from the ASAS-X data generally show increasing values with time but the cloud may have been settling and apparent temporal variations may have been due to successive sampling of richer and richer cloud layers.

Evidence for New Particle Formation in the Cloud

The elevated concentrations observed on 19 April and 5 May can not be explained by assuming that large numbers of particles were injected into the stratosphere at the time of the eruption. Estimates of free-molecule regime coagulation were made assuming self-preserving (Friedlander, 1977) size distributions. Conservative estimates of the volume of the coagulating aerosol were made by including only the sub-.1 μm aerosol and assuming that its diameter was 0.01 μm. The UMCNC counting efficiency was accounted for in these calculations. They show that arbitrarily large concentrations of injected aerosol would have decayed to concentrations less than 20% and 40% of the peak values observed on 19 April and 5 May. Thus new particle formation occured between the injection of the volcanic material and the measurements. This implies that gas-phase reactions contributed to the formation of secondary aerosol. New particle formation was also observed following the eruptions of Alaid and Mt. St. Helens (Hofmann and Rosen, 1981 and Hofmann and Rosen, 1982).

SO_2 Conversion Rates Consistent with the Measurements of April 19,1982

The conversion of gas-phase SO_2 to particle-phase SO_4 accounts for much of the sub-micron aerosol mass added to the stratosphere by the volcano. Using equation 1, the fraction, F, of injected SO_2 converted to SO_4 was calculated for maximum concentrations observed on 19 April.

$$F=[SO_4s]/([SO_2]+[SO_4s]) \quad (1)$$

$[SO_4s]$ equals the concentration of secondary sulfate molecules added to the aerosol phase as a result of the oxidation of SO_2. $[SO_2]$ is the concentration of sulfur dioxide. F applies to the time interval between the eruption and the measurements of SO_4 and SO_2. The calculation assumes that the gases and particles experience the same dilution and dispersion.

SO_2 concentrations (Vedder, et al. 1983) were reported for periods A (35 pptv) and B (40pptv) shown on figure 2. Aerosol measured during period B shows evidence of new particle formation while period A measurements resemble the non-El Chichon aerosol. Peak concentrations of sub-0.1 μm aerosol occured during 36% of period B and the corresponding peak values of $[SO_2]$ were estimated by assuming that non-peak values in B equaled those measured in interval A.

$[SO_4s]$ was calculated from aerosol volume measured with the ASAS-X or estimated from UMCNC measurements. Woods and Chuan (1983) report that the submicron aerosol measured on the April 19 flight consisted largely of sulfuric acid and that aerosol larger than 3 μm contained minerals. To avoid including these minerals as well as sulfates settling from higher in the cloud, particles smaller than 2.5 μm were used in the calculations. It was assumed that the sulfate consisted of a 65% solution by weight of H_2SO_4 and H_2O (Harder et al., 1983). The use of aerosol volume concentration as a measure of sulfate was tested by comparing filter measurements of sulfate (B. Gandrud, personal communication, 1983) with simultaneous ASAS-X size distributions made on 5 May. The sub-2.5 μm ASAS-X volume concentrations accounted for less than 45% of the filter sulfate on the average. Regression analysis done on the

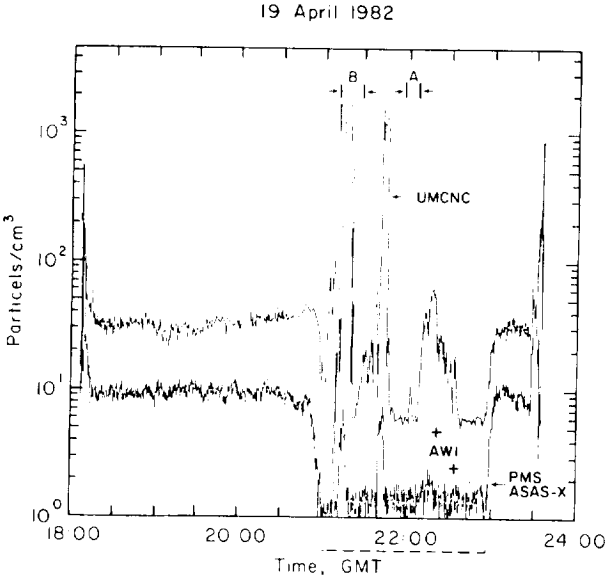

Fig. 2. Aerosol concentrations recorded on flight of 19 April 1982. The dashed line indicates segment >d<. The AWI data are indicated by a +. SO_2 concentrations were measured during intervals A and B.

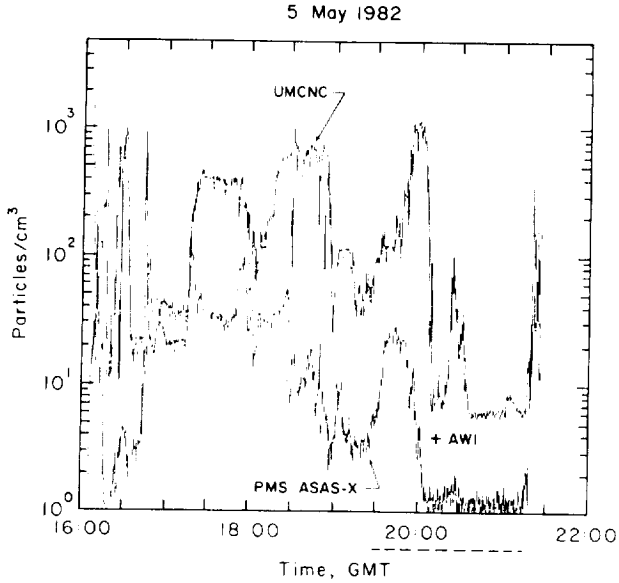

Fig. 3. Aerosol concentrations recorded on flight of 5 May 1982. Flight segment | d | is indicated by the dashed line. The AWI data are indicated by a +.

Appendix B.

Partial list of papers utilizing data from the U-2 CNC, ER-2 CNC or ER-2 CNC II acquired in the following projects: Stratosphere-Troposphere Exchange Project, Airborne Antarctic Ozone Experiment, Airborne Arctic Stratospheric Expedition, Airborne Arctic Stratospheric Expedition II, Stratospheric Photochemistry, Aerosols and Dynamics Expedition, Airborne Southern Hemisphere Ozone Experiment and Measurements for Assessing the Effects of Stratospheric Aircraft.

Refereed Journal Articles:

Fahey, D.W., Kelly, K. K., Ferry, G. V., Poole, L. R., Wilson, J. C., Murphy,D. M., Loewenstein, M., Chan,K. R."In Situ measurements of total reactive nitrogen, total water and aerosol in a polar stratospheric cloud in the Antarctic", *Journal of Geophysical Research,94:11299-11316*, 1989.

Wilson, J.C., Loewenstein, M.,. Fahey, D. W, Gary, B., Smith, S. D., Kelly, K. K.,. Ferry, G. V, Chan, K. R."Observations of condensation nuclei in the airborne antarctic ozone experiment: implications for new particle formation and stratospheric cloud formation",*Journal of Geophysical Research,94:16437-16448*, 1989.

Wilson, J.C.,. Stolzenburg, M. R, Clark, W. E., Loewenstein, M., Ferry, G. V., Chan, K. R. "Measurements of Condensation Nuclei in the Airborne Arctic Stratospheric Expedition: Observations of Particle Production in the Polar Vortex", *Geophysical Res. Lett.,17:361-364*, 1990.

Dye, J. E., Gandrud, D. B., Baumgardner, D., Chan, K. R., Ferry, G. V., Loewenstein, M., Kelly, K. K., Wilson, J. C. "Observed particle evolution in the polar stratospheric cloud of January 24, 1989",*Geophysical Res. Lett., 17: 413-416,* 1990.

Wilson, J. C., Lai,W. T., Smith, S. D. "Measurements of condensation nuclei above the jet stream: evidence for cross jet transport by waves and new particle formation at high altitudes", *Journal of Geophysical Research, 96:17,415-17,423,* 1991.

Wilson, J. C., Stolzenberg,M. R., Clark,W. E., Loewenstein, M., Ferry,G. V., Chan, K. R., Kawa, S. R., Kelly, K. K., "Stratospheric sulfate aerosol in and near the northern hemisphere polar vortex: The morphology of the sulfate layer, multimodal size distributions and the effect of denitrification", *Journal of Geophysical Research, 97:8,7997-8013,* 1992.

Wilson, J. C., Jonsson, H. H., Brock, C. A., Toohey, D. W., Avalone, L. M., Baumgardner, D., Dye, J., E., Poole, L. R., Woods, D. C., DeCoursey, R. J., Osborne, M., Pitts, M. C., Kelly, K. K., Chan, K. R., Ferry, G. V., Loewenstein, M., Podolske, J. R., Weaver, S., "In situ observations of aerosol and chlorine monoxide after the 1991 eruption of Mount Pinatubo: effect of reactions on sulfate aerosol", *Science, 271, 1140-1143,* 1993.

Knollenberg, R. G., Kelly, K. K., Wilson, J. C.,"Measurements of high number densities of ice crystals in the tops of tropical cumulonimbus", *Journal of Geophysical Research, 98, 8639-8664,* 1993.

Kelly,K. K., M. H. Proffitt, K. R. Chan, M. Loewenstein, J. R. Podolske, S. E. Strahan, J. C. Wilson, D. Kley, "Water vapor and cloud water measurements over Darwin during the STEP 1987 tropical mission", *Journal of Geophysical Research, 98, 8713-8724,* 1993.

Brock, C. A. Jonsson, H. H., Wilson, J. C., Dye, J. E., Baumgardner, D., Borrmann, S., Pitts, M. C., Osborn, M. T., DeCoursey, R. J., Woods, D. C., "Relationships between optical extinction, backscatter and aersol surface and volume in the stratosphere following the eruption of Mt. Pinatubo", *Geophysical Research Letters, 20, 2555-2558,* 1993.

Borrmann, S., Dye, J. E., Baumgardner, D., Wilson, J. C., Jonsson, H. H., Brock, C. A., Loewenstein, M., Podolske, J. R., Ferry, G. V., Barr, K. S., "In situ measurements of changes in stratospheric aerosol and the N_2O-aerosol relationship inside and outside of the polar vortex", *Geophysical Research Letters, 22, 2559-2562,* 1993.

Jonsson, H. H., J. C. Wilson, C. A. Brock, R. G. Knollenberg, R. Newton, J. E. Dye, D. Baumgardner, S. Borrmann, G. V. Ferry, R. Pueschel, D. C. Woods, M. C. Pitts, "Performance of a focused cavity aerosol spectrometer for measurements in the stratosphere of particle size in the 0.062 -2.0 μm diameter range", *Journal of Atmospheric and Oceanic Technology*, in press.

Sheridan, P. J., C. A. Brock and J. C. Wilson, " Aerosol particles in the upper troposphere and lower stratosphereL elemental composition and morphology of individual particles in northern midlatitudes", *Geophys. Res. Lett.*, in press.

Fahey, D. W., E. R. Keim, E. L. Woodbridge, R. S. Gao, K. A. Boering, B. C. Daube, S. C. Wofsy, R. P. Lohmann, E. J. Hintsa, A. E. Dessler, C. R. Webster, R. D. May, C. A. Brock, J. C. Wilson, P. O. Wennberg, R. C. Cohen, R. C. Miake-Lye, R. C. Brown, J. M. Rodriguez, M. Loewenstein, M. H. Proffitt, R. M. Stimpfle, S. Bowen, and K. R. Chan. In situ observations in aircraft exhaust plumes in the lower stratosphere at mid-latitudes, 1994: *J. Geophys. Res.*, in press.

Book Chapters and Proceedings

Brock, C. A., Wilson, J. C., Seebaugh, R. W., "Measurement of aerosols and clouds from aircraft", in Aerosol Measurement:Principles, Techniques and Applications, ed. K. Willeke and P. A. Baron, Van Nostrand Reinhold, 1992.

Wilson, J. C., and Fahey, D. W., "Measurements of aerosols and gases from the NASA ER-2", in Proceedings of the International School of Physics "Enrico Fermi" Course CXXIV Diagnostic Tools in Atmospheric Physics, eds. G. Visconti, G. Fiocco, in Press.