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TROPOSPHERIC SAMPLING WITH AIRCRAFT

P. H. Daum and S. R. Springston
Environmental Chemistry Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

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ABSTRACT

Aircraft constitute a unique environment which places stringent requirements on the instruments used to measure the concentrations of atmospheric trace gases and aerosols. Some of these requirements such as minimization of size, weight, and power consumption are general; others are specific to individual techniques. This review presents the basic principles and considerations governing the deployment of trace gas and aerosol instrumentation on an aircraft. An overview of common instruments illustrates these points and provides guidelines for designing and using instruments on aircraft-based measurement programs.

I. INTRODUCTION

In situ measurements have always been an important component of atmospheric chemical studies due to the enormous complexity of the atmosphere and the impossibility of realistically simulating the interactions between all of the relevant species in the laboratory. Surface level measurements are extremely useful in identifying important species and characterizing the chemical processes in which they are involved. However, atmospheric composition and chemical reactivity are spatially variant quantities, and surface measurements are not capable of providing data for study of many important chemical phenomena. Furthermore, these features of the atmosphere are frequently linked to static and dynamic meteorological phenomena that occur over a vast range of scales and cannot be understood by sampling at a fixed location.

In theory, spatially resolved measurements of concentrations of atmospheric trace substances could be made by remote sensing techniques deployed from either surface based, or satellite platforms, but remote sensing capabilities have not yet been developed for many species. Furthermore, both surface and satellite based remote sensing methods have distinct limitations with respect to their ability to resolve horizontal and vertical variations in concentrations on scales that may be important to understanding various atmospheric chemical properties. For these reasons there will remain a need for *in situ* sampling of atmospheric regimes inaccessible to surface or satellite based measurements (by altitude, geographic or technical constraints) for the foreseeable future.

Platforms capable of conducting such measurements include, tethered balloons, free balloons such as those deployed for meteorological soundings or for stratospheric measurements, and aircraft. While each of these platforms has been employed in atmospheric chemical studies, only aircraft have been used by a relatively broad community. This is because payload and electrical power limitations, or cost (the latter an especially important consideration for stratospheric

measurements) limits the use of balloons to study of phenomena not readily accessible by other means. More importantly however, balloons sample the atmosphere in fundamentally different ways than aircraft. Tethered balloons, because they only have access to a narrow cylinder above their mooring, essentially sample in a Eulerian framework. Free balloons, essentially sample in a Lagrangian framework. Although sampling in such frameworks is important for study of specific classes of problems, such measurement strategies do not provide the information necessary to understand many of the important chemical properties of the atmosphere.

As the atmospheric chemical community focuses more intensely on issues of global concern, requiring survey of the chemical composition of the remote atmosphere and study of chemical processes occurring well above the surface, a larger number of programs will use aircraft as either the principal sampling platform, or to augment measurements made by other means. Because aircraft measurements impose different, and frequently more stringent sets of requirements on techniques used to measure trace atmospheric species than surface measurements, there is a need to review these requirements and to show how various measurement methods have been designed or altered to meet the needs of aircraft use. We will focus our attention here on measurement of trace chemical species, that definition including trace gases as well as aerosol particles and cloud droplets. Measurements of winds, atmospheric state parameters, solar radiation, and similar parameters will not be treated. Furthermore, we restrict our attention to use of aircraft and instruments for tropospheric measurements. This chapter is divided into two main sections: the first section emphasizes general issues involved in sampling from aircraft; the second section surveys specific techniques that have been used for aircraft measurement of species that we have identified to be of common interest to a large segment of the chemical community.

II. GENERAL CONSIDERATIONS

Aircraft measurement of trace atmospheric species emphasizes several problems in the composite sampling/analytical process that are not routinely encountered to the same degree during measurements at a stationary surface site. The first problem is distortion of sample composition during the sampling process. For aerosol species this is an especially significant problem because sampling is accomplished at high relative velocity (50-200 m/s) and fractionation of the aerosol by size due to non-isokinetic sampling, turbulence, and inertial losses at bends in the sampling lines can occur. For trace gases special attention must be paid to design and implementation of inlet and distribution systems to avoid adsorptive losses or contamination of the sampling system. Second, there are often important engineering problems associated with use of instruments in an aircraft that are not usually encountered in surface sampling applications. Weight, size, and electrical power consumption are frequently severe constraints on aircraft. Furthermore, instruments may be subjected to extreme variations in temperature and humidity, and to high levels of vibration. Thus, it is frequently not possible to deploy conventional state-of-the-art analytical instruments on aircraft without substantial modifications to minimize the influence of these factors on instrument performance. Finally, aircraft measurements are frequently made over a wide range of altitudes, and instruments will be exposed to a range of pressures more extreme than would ever be encountered during operation at the surface (depending on whether the aircraft is pressurized, and how the sample inlet system is designed). Since instruments frequently exhibit large changes in sensitivity with pressure, using a sensor on an aircraft requires that the pressure response of the composite instrument/sampling system be well understood. No instrument, whether commercial or custom made, can be deployed in an aircraft without considering the effects of this environment. The purpose of this section is to explore these and related issues, and to give some guidelines on how these problems can be resolved.

A. Concentration units. Any discussion of aircraft measurements must begin with a review of various ways in which abundances of trace atmospheric constituents are specified. Such nomenclature is frequently a point of some confusion. In addition, because instruments used on aircraft are operated over a range of pressures, the fundamental way that an instrument senses a species and generates an output signal that is then converted to a measure of abundance, is an important issue. The latter will be discussed in the next section.

Several methods are commonly used to specify the abundance of substances in the atmosphere. For gaseous constituents common practice is to specify abundances as mixing ratios, or equivalently as mole fractions of the species in air. This quantity is simply the ratio of the partial pressure of a substance divided by the total pressure. The advantage of this unit is that it is independent of pressure and temperature, and for an atmospheric component that is well mixed, the mixing ratio will be constant as the pressure and/or temperature changes. Common units for specifying mixing ratios are parts per million (ppmv), parts per billion (ppbv), and parts per trillion (pptv), meaning respectively, ratios of the partial pressure to the total pressure (or molar ratios) of 1 in 10^6 , 1 in 10^9 , and 1 in 10^{12} . For clarity, and to distinguish from common usage in specifying solution phase concentrations, where ppb, etc., indicates the mass mixing ratio, the suffix v is added to indicate mixing ratio by volume.

Other common ways of expressing abundances, particularly of solid or liquid particles is to express them as concentrations in units of $\mu\text{g}/\text{m}^3$ or $\text{nanomoles}/\text{m}^3$. For purposes of consistency, concentrations expressed in these units should be normalized to standard conditions of temperature and pressure. Since there is some confusion as to what constitutes standard conditions in atmospheric chemistry (273°K , and 1.013 bar commonly used in chemistry and physics, or 293°K and 1.013 bar used in engineering) it is important to define the standard conditions that are assumed when reporting data. This is frequently not done. Concentrations

expressed in the above units can be easily converted to mixing ratios by use of the Ideal Gas Law, viz.,

$$MR(ppbv) = C(\mu g/m^3) \times 22.4/M = C(nanomoles/m^3) \times 0.0224,$$

where MR is the mixing ratio, M is the molecular weight, C is the concentration expressed in the specified units, and standard conditions are assumed to be 273°K and 1.013 bar.

B. Altitude response. Pressure response is an issue that needs to be addressed for every instrument deployed on an aircraft. First, it must be decided how chemical abundances are to be reported. If standard practice is followed and they are reported as mixing ratios, then it must be determined whether the instrument is fundamentally a mass or a concentration dependent sensor, because this defines the first order means by which instrument response is converted to mixing ratios as a function of pressure. In this context, a mass sensitive detector is a device whose output signal is a function of the mass flow of analyte molecules; a concentration sensitive detector is one where the response is proportional to the absolute concentration, i. e., molecules/cm³.

For sensors that are truly mass sensitive, and for which the mass flow of sample through the sensing element is held constant as a function of pressure (for example by use of electronic mass flow controllers), instrument response is proportional to the mixing ratio independent of the pressure. For concentration sensitive detectors, such as simple spectrophotometric instruments measuring absorbance or fluorescence, instrument response is a function of the absolute concentration, and the response will decrease for a constant mixing ratio as the pressure decreases. For example, the response of a pulsed fluorescence SO₂ instrument sampling air containing a fixed mixing ratio of SO₂ will be less at 850 mb than at 1000 mb because there will be 15% fewer SO₂ molecules present in the active volume of the detector. The correct mixing ratio can be obtained by multiplying the

instrument response by the ratio P_0/P_i , where P_0 is the pressure at which the calibration was performed, and P_i is the pressure at which the measurement is made. Similar first order corrections are adequate for most instruments based on concentration sensitive detectors, such as the UV photometric O_3 , NDIR CO, and similar instruments. The response of concentration sensitive detectors having sensing chambers that operate at constant absolute pressure, should not need to be adjusted for altitude if concentrations are reported as mixing ratios.

The need for more complicated considerations in conversion of instrument response to mixing ratios usually arises when employing instruments that are based on mass sensitive detectors. Common reasons are that either the mass flow is not held constant, or the conditions of the process whereby the flow of analyte molecules is converted to an electrical signal proportional to that flow, change, as the pressure changes. We illustrate these effects below by discussing the pressure response of two instruments commonly used to measure atmospheric trace gases, both based on detection schemes that are inherently mass sensitive.

Our first example is the O_3 /ethylene chemiluminescent detector for measurement of O_3 . Such detectors are inherently mass sensitive since the photomultiplier current is a function of the flow of O_3 molecules through the detector, provided other factors controlling response remain constant. Thus, as long as the mass flow of sample is fixed, instrument response will be proportional to the O_3 mixing ratio, independent of pressure. However, all of the commercially available O_3 /ethylene detectors of which the authors are aware, use flow restrictors to control sample flow. If these restrictors operate under choked flow conditions, the mass flow will decrease as the pressure decreases and the response of the instrument to a fixed mixing ratio of O_3 will decrease with pressure. If the decrease in mass flow with pressure is linear, the O_3 detector will exhibit characteristics of a concentration sensitive detector (response to fixed mixing ratio decreasing with pressure) even though it is inherently a mass sensitive detector, and mixing ratios

can be calculated from instrument response in the same way as concentration sensitive detectors. (This is the case because the process generating the chemiluminescent signal is not a strong function of pressure.) Behavior of a commercial O₃ chemiluminescent detector using choked flow restrictors to control sample flow was evaluated (1), (see also (2, 3)). Under operating conditions of the instrument, response to a fixed O₃ mixing ratio decreased with pressure in a manner that could be predicted from Ideal Gas Law considerations, i.e., the change in response was virtually identical to the change in response of a UV O₃ sensor in parallel measurements. If it had been assumed that the response was proportional to the mixing ratio (mass sensitive), then O₃ concentrations would have been reported incorrectly. It was also demonstrated that maintaining constant sample mass flow caused the O₃ sensor response to be proportional to the mixing ratio, independent of pressure, i. e., to respond as a mass sensitive detector.

The second example is the commonly used flame photometric detector for measurement of SO₂ and aerosol sulfur. In this detector, sulfur compounds are determined by measuring the light emitted by excited state S₂ molecules formed when sulfur compounds are introduced into a hydrogen rich flame. Since two sulfur atoms combine to form the emitting species, detector response is approximately proportional to the square of the sulfur concentration. The detector is mass sensitive in the sense that the signal is proportional to the mass flow of sulfur molecules passing through the detector; it is concentration sensitive in the sense that the signal is proportional (approximately) to the square of the sulfur concentration in the active region of the detector. In its commercial form, sample flow is determined by a flow restrictor and thus mass flow decreases with pressure, and it would be predicted that the response to a given sulfur mixing ratio would decrease with altitude. However, because of the way in which the hydrogen flow is controlled, the H₂/O₂ ratio in the flame also changes with pressure. This causes not only changes in sensitivity larger than would be predicted based on mass flow

reduction with pressure, but also large shifts in the background emission of the flame. The dependency of both the baseline response and sulfur sensitivity on pressure can be minimized (4) by controlling the mass flow of sample and hydrogen. The small residual dependency on pressure is presumably a manifestation of the concentration sensitive characteristics of the detector due to the reduction in burner pressure with altitude.

The above discussion points out several issues that need to be addressed when considering deployment of an instrument on an aircraft. First, it cannot be assumed that an instrument based on a mass sensitive detector will give a response proportional to the mixing ratio independent of pressure. Response may vary because the flow control system does not maintain constant mass flow over a relevant range of pressures. Similarly, it cannot be assumed that a flow control system based on restrictors will operate under choked flow conditions over the required range of pressures. Pumping efficiency changes with pressure, and at higher altitudes, pumps may not be able to maintain the pressure drop required for choked flow. Under these conditions, the flow will not be a simple function of the ambient pressure, and instrument response cannot easily be converted to either mixing ratios or absolute concentrations. For these reasons, it is good practice to use electronic mass flow controllers to control sample flow either directly or by difference, on any mass sensitive detector used on an aircraft.

However, even the use of mass flow controllers may not be sufficient to stabilize instrument response as the pressure changes. For many detectors, chamber pressure varies with altitude even if the sample mass flow is maintained at a constant value. This may cause a change in the efficiency of the process(s) converting analyte flow to an electrical or optical signal proportional to concentration. As demonstrated by the examples given above, it is difficult to predict, a priori, the pressure response of a composite sampling system/detector. It is thus necessary to characterize instruments, particularly mass sensitive

instruments based on chemiluminescent processes, before employing them in aircraft measurements to assure that the pressure response is well understood.

C. Instrument Time Response. Instrument response time is always a consideration in aircraft measurements because aircraft velocities can be very high, upwards of 200 m/s. Since instruments have a finite response time, spatial resolution is often an important consideration when sampling from an aircraft. About the slowest speed that can be maintained on a conventional aircraft with any realistic payload capability is 50 m/s. Thus, if an instrument has a 10 s response time, the spatial resolution of the measurement is on the order of 0.5 km; for an aircraft sampling at 200 m/s, the spatial resolution is on the order of 2 km. Slow instrument response distorts the signal in regions of strong spatial gradients, decreasing peak heights and smoothing the signal. Reconstruction of the actual signal is not trivial and will generally require extensive laboratory characterizations of instrument response characteristics in order to derive an adequate differential transform. A more complete discussion of this topic is given in (5) and references contained therein.

Whether response time is a significant issue in an aircraft sampling program depends on the objective of the measurements. For sampling programs designed to characterize spatially compact regions of the atmosphere such as power plant plumes, or single cumulus clouds, fast instrument response time is of paramount importance because these features may only be 0.5 to several km in extent. Features of interest in some cloud studies may have scales of only a few meters. For measurement programs where the objective is characterization of remote regional air masses where concentrations are relatively homogenous, instrument time response may not be important.

For most measurement techniques a trade-off exists between time response and sensitivity. Instruments can be made to respond more rapidly, but in doing so noise levels and detection limits increase. To fulfill certain measurement objectives

where sensitivity is not a problem, it may be useful to enhance the time response of the instrument and accept the decrease in sensitivity. In any event, careful consideration must be made in the design of any sampling program to ascertain what level of concentrations need to be measured and what time/space resolution is required. These issues will determine the characteristics of the airborne platform and instruments that will be used, and how they will be deployed.

D. Sample Inlets The design and construction of any system for aircraft sampling involves implementing an inlet that will not alter the composition of the sample air. For trace gases this means an inlet that will not change the concentration of trace gases as they transit the inlet system; for aerosol sampling this means preserving the size distribution of the aerosol particles during the sampling process. For trace gases, the type of inlet that is required depends strongly on the characteristics of the gases that are being sampled. For substances that are relatively inert, such as CH_4 , CO , NO , etc., common materials such as glass, Teflon, and stainless steel will suffice; for reactive gases, or gases that have a tendency to adsorb on surfaces (e.g. HNO_3), the choice of materials for sample inlet lines is much more critical. Surface adsorption on the tubing material is only part of the problem. Clean surfaces, made of even the most inert material, quickly become coated with a layer of moisture and fine particles. Short residence times and laminar flow conditions minimize the influence of the wall and aid in preserving the integrity of sample components.

Sampling aerosols from an aircraft is inherently a difficult process, and no generally accepted method for sampling over the entire size range of interest (0.01 - 10 μm) has been developed. The problem is difficult because aircraft sample at a high velocity, and the aerosol particles must be brought to that velocity during the sampling process. Because of this, distortion of the size distribution (by size selective sampling at the probe tip, or by evaporative losses of volatile components

due to adiabatic heating), and losses at the inlet or in subsequent tubulation by turbulent deposition or inertial impaction, are of great concern.

The first requirement for sampling aerosols is to preserve their size distribution. To accomplish this, sampling must be conducted isokinetically, that is the sampling rate must such that the velocity of air relative to the probe tip is the same just inside the probe as it is outside. If these velocities are different, sampling is anisokinetic and this will lead to a distortion in the size distribution of the sampled aerosol. If air is sampled sub-isokinetically, large particles will be oversampled relative to smaller particles; the smaller particles will follow the streamlines around the probe tip, while the large particles will still penetrate the inlet. If sampling is super-isokinetic, smaller particles will be over sampled. This is illustrated in Figure 1. A second requirement is to move the aerosol particles from the probe tip to the sample collection point, or to the inlet of an instrument without losses either by turbulent processes or inertial deposition at bends in the inlet tubing. These losses can be minimized by keeping the inlet lines as straight as possible, and where bends are required, using a large radius of curvature.

A typical aircraft sampling probe consists of conically shaped tip with sharp leading edges, Figure 2. The probe is shaped in this way to minimize distortion of the airstream by the nozzle at the point of sample entry into the system. The diameter of the probe increases behind the nozzle (usually at an angle of about 70°) to decrease the linear flow rate to minimize losses at bends in the tubing bringing the sample into the interior of the aircraft. The radius of curvature of required bends can be quite large particularly if coarse mode aerosol particles are to be sampled. For example, Sheridan and Zoller, (6) used an inlet with a radius of curvature of ca 75 cm to minimize losses of large particles by inertial deposition.

Figure 1. Representation of an aircraft aerosol sampling inlet showing flow streamlines for sub-isokinetic, super-isokinetic and isokinetic sampling. Under sub-isokinetic conditions large particles will be oversampled; under super-isokinetic conditions small particles will be oversampled; under isokinetic conditions, the particle size distribution will be preserved.

An alternate probe design using a rounded profile on the leading edge following criteria developed for aircraft engine intakes at low Mach numbers, has been applied to aerosol sampling from aircraft (7). This intake is reported to avoid distortion of the pressure field at the nozzle tip and the resulting problems associated with flow separation and turbulence. This design has been reported to be much more efficient at collecting coarse aerosol particles than isokinetic inlets with sharp leading edges, and presumably because of its shape is more forgiving of slight misalignment with the local airflow.

The ability of currently used aircraft probes to accurately sample aerosols has been recently questioned. Huebert et. al., (8) conducted a comparative study of several different types of aerosol probes, all mounted on the same aircraft. The results suggested that substantial losses of particles occurred in all of the inlet systems. Because of the limited nature of the study, however, the cause(s) of the aerosol losses could not be identified. The results of the Heubert study prompted a recent workshop to re-examine the entire issue of aerosol sampling from aircraft (9). An important conclusion of the workshop was that currently, there is insufficient knowledge to "adequately describe important characteristics of air-flow and particle trajectories at flight speeds" of aerosol sampling probes used on aircraft. A second conclusion is that coarse-mode particles are typically undersampled by currently used aircraft probes, and that while the sampling efficiencies for accumulation mode particles seem higher, there is insufficient experimental data to assure that currently used sampling methods are adequate. It was also suggested that inlet performance is highly sensitive to both orientation with respect to the local airflow, and to location on the airframe and that aerosol sampling problems are more severe at higher aircraft speeds.

Figure 2. Diagram of a typical knife edged probe for isokinetic sampling of aerosol particles from an aircraft. Probe is sized to provide ca 500 l/m at a sampling velocity of 50 m/s. Note the 7° expansion of the probe behind the probe tip to slow the air velocity. Interior surfaces of the probe are polished to a mirror surface.

The workshop report suggests that use of shrouds around sharp edged inlets to align streamlines along the probe axis may be an effective means of reducing turbulent losses of aerosols at the probe tip. Such inlet systems have been used on conventional aircraft and helicopters (9,10) but have not been adequately tested at typical aircraft sampling speeds. Double diffuser inlets in which the sample air-velocity is decreased in two stages also seem promising.

Several types of inlets can be used to provide air for trace gas sampling. In many instances a forward facing "ram air" inlet is used (so called because the forward motion of the aircraft "rams" air into the tube). Ram air inlets do not sample isokinetically, and are not suitable for aerosols, but this is generally not a problem for trace gases. Ram air inlets are usually vented to the aircraft cabin to

avoid overpressurization of the instruments and consequent errors in instrument response. Venting also maintains high air velocities through the sample lines which minimizes sample losses and improves response speed. Vented inlet lines can only be used in unpressurized aircraft because pressurization may cause the airflow to reverse, or be insufficient to meet the needs of the instrumentation, resulting in sampling cabin air. Reverse flow inlets, in which the opening of the inlet faces away from the airflow are also common. Reverse flow inlets are frequently used to avoid ingestion of cloud droplets and precipitation into the sampling line. These lines cannot be vented because the venturi effect will cause sufficient negative pressure in the line to extract cabin air. We also note that the negative pressure generated by such lines can render certain instruments such as the sulfur flame photometric detector inoperable because the reduced pressure extinguishes the flame.

Other more sophisticated sampling lines have also been employed. Heikes et al., (11) used a constant pressure sampling line to eliminate the pressure dependent response of a flame photometric detector used for SO_2 measurements. In this system the sampling line was connected to a high capacity pump which evacuated the sampling line to a pressure equivalent to the highest altitude at which measurements were made. A feedback system consisting of a pressure sensor and fast acting valve, maintained the pressure at the set value as the altitude changed.

Regardless of which inlet system is chosen for trace gas sampling, minimization of wall losses during the sampling process is an important consideration. As a general rule, losses can be minimized by keeping the inlet volume flow as high as possible. A further consideration is constructing the inlet of materials that do not have a high affinity for the species that is being sampled. A common practice is to use various types of Teflon, either in the form of a tube that is inserted into a metal shell which together form the sampling system, or by coating the Teflon directly on the tube. Whatever material is chosen for the sampling line,

it should be rigorously tested for possible losses in the laboratory, prior to installation on an aircraft.

An additional issue that seems obvious, but which is frequently overlooked in installations, is to insure that the sampling line is not in a position to sample the aircraft engine exhaust, heater fumes, and is not directly behind the propellor envelope. The sampling inlet should also be placed sufficiently far from the fuselage so that it is in the free airstream and not within the boundary layer of the aircraft.

E. Weight, power and size considerations. One of the axioms of aircraft sampling is that if an instrument has sufficient sensitivity and time response for the intended measurement, then it either weighs too much, or draws too much power to be used on the available aircraft. Such considerations are important when designing an instrument for aircraft use or when preparing a commercial instrument for use on aircraft. One of the typical problems that is encountered in aircraft sampling are limitations on the amount of power available. This problem is especially significant on small aircraft (where the power available may be as little as 3 - 4 KVA), but is also a consideration when using large aircraft. Normally aircraft electrical systems provide 28-V DC and 400-Hz AC power. Unfortunately most laboratory instruments operate on 110 or 220-V, 60 Hz, power. Thus, most aircraft set up for atmospheric research use 60 Hz, 120-V AC inverters to meet the electrical requirements of research equipment. Since some power loss is involved in the inversion process, it is important when planning any aircraft installation to minimize the amount of 60 Hz power that is required. Because many measurement techniques (such as filter pack sampling systems, or chemiluminescence detectors for oxides of nitrogen) use high capacity pumps requiring large amounts of power, one way of maximizing efficiency is to drive these pumps with 28-V DC motors, to avoid losses from the inversion process. This is common practice in aircraft installations. Another source of high power consumption are instrument heaters

(such as those typically used on gas chromatographs), and it is important when employing these systems to minimize the capacity of the heater that is required, or to redesign the method/instrument so that they are not needed.

The electrical power available to equipment is subject to interruptions. These outages may be predictable, such as for takeoffs and landings in some aircraft, or random due to circuit overloads or pilot discretion. Instrument systems must often operate without lengthy warm-up periods, both at the beginning of a flight, and after in-flight power interruptions. Data systems must be sufficiently robust to recover data taken before unexpected power outages. Battery backup for the data system is one alternative, but greatly adds to the weight. A better solution is to write all data to disk or tape back-up as it is recorded. The data processing program must be able to recover data streams that terminate unexpectedly.

Weight and size of instruments are also important considerations. The first order (and most obvious) consideration is that the sampling system cannot exceed the payload of the available aircraft. For many aircraft, particularly small twin engined aircraft, the payload can be quite small (<250 kg), and when designing a sampling system it is important to minimize weight wherever possible. Even for large aircraft, weight is a consideration because there is a tradeoff between instrument payload and fuel, and range. While this may not be an important issue for local sampling of short duration, the payload/fuel tradeoff may be the limiting factor when planning long range flights for sampling in remote regions.

Equipment installations must meet the center of gravity (CG) requirements of the aircraft. Every aircraft has a range of CG's that can be tolerated, thus one is not free to install an instrument, particularly a large one, at an arbitrary position within the aircraft. As a first order approximation, installation of the heaviest equipment (e.g., large pumps) should be planned to be near the normal CG of the aircraft. Center of gravity considerations can be quite critical for small aircraft; somewhat less so for larger aircraft.

The influence of vibration on instrument operation must also be considered in aircraft installation. If problems arise, they can usually be solved using standard vibrational analysis techniques to select appropriate devices (such as dashpots) to isolate instruments from the airframe. Vibrational problems with instruments incorporating precisely aligned optical components may require more complex solutions, including redesign or remounting some of the critical components in the instrument. Electrical noise, arising from aircraft radio transmissions, is also a frequent problem. It is important to identify this problem early in an installation so that sensitive instruments can be mounted at a location where the potential for these interferences is minimal (away from radios and antennas). It is also good practice to shield all data transmission leads. Installation of instruments on aircraft may also require modification to strengthen the equipment to the point where it can withstand the "g" load requirements imposed by applicable FAA regulations.

III. A SELECTIVE REVIEW OF TECHNIQUES FOR MEASUREMENT OF TRACE GASES AND AEROSOLS FROM AIRCRAFT

Techniques used in aircraft sampling can be divided into several categories: those providing concentration information on a continuous basis and those providing such information on a sporadic basis. The latter techniques can be further divided into techniques wherein the sample is collected by some means and is returned to the laboratory for subsequent analysis, and techniques where the sample is collected and analyzed on the aircraft.

It is important to measure continuously as many species as possible to achieve the maximum possible time/space resolution. However, the complexity of instrumentation required for measurement of certain classes of compounds may be such that aircraft installation is not feasible. Alternately, the analytical procedure may be so time consuming that it is not worthwhile to install the equipment on the aircraft. In these cases it will be necessary to collect samples for subsequent analysis in the laboratory. There are two fundamental problems with batch sampling

techniques: as mentioned above, time/space resolution is limited, but also, batch sampling imposes the requirement that the composition of sample not change between the time of collection and the time of analysis. Analysis of collected samples in a laboratory setting, however, allows application of a broad array of techniques that would be impossible to operate in an aircraft environment.

In selecting instruments for installation on an aircraft it should be noted that commercially available instrumentation should not be used for aircraft sampling until their operation is understood in that environment. An equally important consideration is that many commercial instruments have been designed for purposes of determining whether or not pollutant concentrations exceed environmental standards. Since these concentrations are frequently quite high, such instruments may not be able to quantify abundances of species at levels significant to understanding of atmospheric processes, particularly those occurring in the remote or upper troposphere. For these reasons, significant effort has been devoted by atmospheric chemists over the last several decades to developing techniques that can measure low concentrations, and to a lesser extent adapting these techniques for aircraft use.

We give here a review of instruments and techniques that have been used and/or specifically developed for aircraft measurement of trace species. To limit the scope, we restrict our focus to species that we have identified to be of interest to a large segment of the atmospheric chemical community. The objective is to give the reader a starting point from which to either choose, or to develop an instrument or technique for aircraft sampling. This section is divided into two parts: the first covers techniques that are used for batch sampling and/or analysis of atmospheric constituents; the second is a review of continuous analysis methods.

A. Systems for batch sampling

1. Filter Packs. One of the most reliable and adaptable methods for measuring concentrations of atmospheric trace gases and aerosols is the filter pack sampling

system. Indeed, collection by filter is one of the few methods available for obtaining comprehensive information on aerosol composition. In filter methods, sample air is passed through a sequence of filter elements each of which is designed to collect a different species. The various collection elements are designed and positioned in the filter pack assembly so that each element selectively collects the desired component(s) at high efficiency, and passes components to be collected on downstream filters with equally high efficiency. The exposed filters are analyzed in the laboratory to determine the mass of the collected substances. Atmospheric concentrations are then computed from the mass of material collected on the filter, and the sample air volume.

A number of sequential multistage filter pack sampling systems have been used in aircraft. Since many of these systems are similar, it is useful to provide a general description pointing out different approaches for measurement of various species as they arise. The first stage in all filter pack systems is a particle filter for collecting aerosol. Several types of materials are used, the most common are made of treated quartz (12) or Teflon (6, 13, 14). Size segregated sampling of the aerosol has been accomplished by use of two filters of different pore size arranged sequentially. John et al., (15), describe a system in which coarse ($>1.0\text{ }\mu\text{m}$) and fine ($<1.0\text{ }\mu\text{m}$) fractions are collected using an $8\text{-}\mu\text{m}$ (pore size) nucleopore filter, followed by a $2\text{-}\mu\text{m}$ (pore size) Zefluor, Teflon filter. This system has been used in several aircraft sampling programs (e.g., 7, 16). Subsequent to exposure, the filters are returned to the laboratory for analysis of the collected materials. Usually, aerosol filters are extracted with water and the extract analyzed for various soluble materials, commonly strong acid, Na^+ , NH_4^+ , Ca^{++} , Mg^{++} , NO_3^- , $\text{SO}_4^{=}$, Cl^- . Representative examples of the various extraction and analytical procedures have been published (13, 17).

Frequently, the second element in a sequential system is used to collect gaseous HNO_3 . Both NaCl impregnated filters (18), and nylon filters (e. g. 13, 19) have been

used for this purpose. Both of these filters have been shown to exhibit high collection efficiency (>90%) for nitric acid. Nylon filters have an advantage in that they generally require no pretreatment or impregnation prior to use, in contrast to the NaCl cellulose filters which require both. However, Nylon filters can exhibit high and variable blanks which may compromise their use in sampling regimes where low HNO_3 concentrations are expected. The third element in a sequential filter system may be a base treated cellulose filter for collection of SO_2 , or an impregnated filter for collection of gaseous NH_3 . SO_2 filters are usually pre-washed cellulose filters impregnated with an aqueous solution of K_2CO_3 with glycerol added as a humectant. Daum and Leahy (17), and Anlauf et al. (13), give preparation procedures that call for an impregnating solution containing 250 g K_2CO_3 , and 100 mL of glycerol per liter. It has been reported that use of a less concentrated solution leads to lower detection limits for SO_2 when ion chromatography is used as the method for analyzing the filter extract (20). Filters for collecting of gaseous ammonia have been fabricated from either cellulose filters impregnated with an aqueous solution of citric acid and glycerol (21) or with oxalic acid in ethanol (22).

The detection limit for measuring a species by filter collection and subsequent analysis is determined by either the uncertainty in the filter blank, i.e., the variability in the amount of a species in an unexposed filter, or by the limit of detection imposed by the analytical method. Most frequently, the limit of detection is determined by blank variability, and thus care in preparation and handling of filters is important when using such systems for aircraft sampling, particularly if sampling is conducted in remote areas where concentrations are low. In this regard, it is crucial to establish the blank level, or residual material (and its variability) of unexposed filters. This may be accomplished by carrying extra filters on each sampling mission and exposing them to all of the deployment procedures with the exception of actual air sampling. It has been our practice to carry at least one such filter on every flight.

The time/space resolution that may be achieved with filter sampling techniques is dependent on the collection rate, limit of detection, and ambient concentrations. In aircraft applications, filters are typically operated at high flows (100-500 slpm) to maximize the mass accumulation rate. At these flow rates, sampling times on the order of 20 to 30 min are generally sufficient for measurement of substances in the urban troposphere. For sampling in the upper troposphere, or in areas remote from pollutant sources, collection times of several hours may be necessary to obtain measurable quantities of material.

One of the important concerns in the application of filter methodology to aircraft sampling is generation of artifacts, particularly as they pertain to measurement of aerosol nitrate, nitric acid, and ammonia. These species are in dynamic equilibrium and under conditions where HNO_3 and NH_3 concentrations are sufficiently high to form the solid NH_4NO_3 , the possibility of evaporation of this material followed by collection of artifact HNO_3 and NH_3 should be considered (for a recent discussion of these artifacts, see articles in *Atmospheric Environment*, **24A**, 1990). Similarly, artifact gaseous HCl may be formed by interaction of HNO_3 , or H_2SO_4 with NaCl particles previously collected on an aerosol filter. Such artifacts can be minimized in the first instance by restricting collection of samples to a single air mass so that the collected sample is not exposed to air that has significantly different concentrations of HNO_3 or NH_3 . In the second instance, artifact formation can be minimized by keeping filter loading as small as possible, consistent with limit of detection requirements.

2. Cloudwater and precipitation collectors. Several methods have been developed for collecting cloudwater samples (23-25). Probably the device most commonly used in warm clouds, is the slotted rod collector developed by The Atmospheric Science Research Center at SUNY Albany. Commonly known as the ASRC collector (24), this collector consists of an array of rods constructed from Delrin. Each rod is hollow with a slot located at its forward stagnation line. The rod

radius determines the collection efficiency as a function of particle size; the rods are sized to collect cloud droplets, but not sub-micron aerosol particles, the 50% cutoff is calculated to be at about 3 μm .

The original design of the collector has been refined several times to enhance collection efficiency, and to more firmly establish the operational characteristics of the collector. Major modifications have included: lengthening the collector rods to give a larger collection area; sheathing the rods in steel to prevent bending and the consequent drop of collection efficiency at higher airspeeds, and; constructing the rods of Teflon rather than Delrin to reduce the possibility of losses of sample constituents (particularly nitrate) during the collection process (26). Further modifications include mounting the rods in a single row, in contrast to the staggered multi-row configuration of the original collector, to prevent interaction of the aerodynamic flow around the rods (27). With this modified collector, collection efficiencies upwards of 80% have been measured, based on the collection area of the rods, cloud liquid water content, and mass of collected water.

Mounting of the cloud water collectors on the aircraft is a critical issue since flowfield effects can easily distort the size distribution of drops. If at all possible, the collector should be mounted on a pylon so that the collector is in the free airstream. It has been further noted that substantially greater efficiencies can be achieved if the collector is mounted with a forward inclination of about 12 to 15° relative to a perpendicular from the aircraft longitudinal centerline. This accounts for the nose up attitude at which most aircraft fly under cruise conditions, and also provides a component of the airstream to drive impacted cloud droplets down the rod into the collection vessel, minimizing losses due to blow-off (27).

Supercooled cloud droplets can be collected as ice through the riming process. Isaac and Daum (28), report use of several different types of collectors. Collection of warm precipitation from aircraft has generally been accomplished with a SUNY collector consisting of a single large diameter (circa 8 cm), slotted rod (circa 2 cm slot

width) (V. Mohnen private communication). To our knowledge this collector has never been subjected to realistic laboratory or field testing so that neither actual size distributions collected, nor collection efficiency have been determined. Collection of snow from aircraft has been attempted, but with limited success. The most promising approach is use of a cyclone wherein the air is required to follow a circular path and the snow particles are centrifuged out of the air in which they are suspended. The snow particles settle to the bottom of the cyclone whence they can be drawn off into a collection bottle for analysis. Several different types of cyclones have been used to collect snow from aircraft (28).

3. Gas samples for subsequent laboratory analysis. Collection of air samples for later analysis in the laboratory is a common technique used for aircraft sampling. Whole air sampling for stable compounds (CO , CO_2 , halocarbons, and low molecular weight hydrocarbons) is usually accomplished by filling a container to a pressure of about 2 atm using a metal bellows pump. Alternately, containers may be evacuated in the laboratory to a low pressure, and filled during flight by simply opening a valve at the appropriate time. Containers are typically constructed of stainless steel that has been electropolished and/or treated in some way to reduce surface activity (29-31). Samples have also been collected in glass flasks (34) and in bags fabricated from inert materials (35-36). An alternative whole air sampling method involves cryogenic collection by submerging flasks in liquid nitrogen while pressurizing the container with sample air (37).

An important concern in applying any of these techniques is losses from wall reactions or other processes during pumping, or in the container during the time between sampling and analysis. Apparently, stability is not altogether predictable. Oliver et al., (32), report sample composition to be unaffected by storage in steel containers for up to 30 days in the presence of water, CO_2 , NO_x , and O_3 . Similarly, Ehhalt et al., (31), reported no measurable loss of light hydrocarbons over periods of months. However, other studies have indicated the possibility of

substantial losses (29). Materials that have been collected by cryosampling techniques may experience losses during the analysis when the collected sample is heated. The basic problems of collecting gaseous samples for laboratory analysis have been outlined elsewhere (38).

4. Other batch sampling techniques. Solid adsorbents, such as Tenax or Poropak-Q, have been used to sample higher molecular weight hydrocarbons ($> C_8$) (39-41). Tenax does not trap water or permanent gases which simplifies the subsequent gas chromatographic analysis. Thermal desorption of these traps can produce artifacts arising from degradation of the sample or the trap. The presence of O_3 can further reduce sample integrity (42).

Samples of OCS and CS_2 have been collected by passing air through coils of Teflon tubing submerged in liquid argon (43). Collecting the sample in this way concentrated the species of interest. However, blockage of the coil by ice formed by condensation of ambient water vapor limited the sampled air volume to ~600 mL. The coils were kept refrigerated by the cryogen prior to analysis. Gold wool has been used to trap DMS after first removing SO_2 (44). The sample is later thermally desorbed and analyzed by GC with flame photometric detection.

5. Chromatographic techniques. Chromatographic techniques have long been applied to the problems of separation and analysis of trace atmospheric species. For stable species, batch samples are usually collected as described above and transported to the laboratory for subsequent analysis. However, some compounds are not sufficiently stable to survive transport intact. In this case it has been necessary to implement *in situ* chromatographic analyses of samples. Usually, chromatography is used on aircraft in a batch mode wherein samples are collected, preconcentrated, separated on a column, and the individual species detected as they elute; the process is then repeated for the next sample. Thus, as with other batch techniques, time resolution is limited.

Packed column technology has been used in airborne gas chromatographs for the separation and quantitation of sulfur species (45, 46) and PAN (47). The combination of sample preconcentration and sensitive detectors has yielded detection limits that are superior to corresponding continuous sensors. For SO₂, a detection limit of 25 pptv was claimed, and for PAN, the detection limit was roughly 60 pptv for a ~50-cm³ air sample. Analysis times for samples were on the order of 10 min.

Several engineering factors have discouraged more frequent utilization of gas chromatographs aboard aircraft. Laboratory research instruments are large, heavy, and have power requirements that exceed the capabilities of most aircraft. However, smaller, high-quality gas chromatographs are now commercially available and can be easily modified to reduce power consumption.

Some altitude effects on operation on chromatographic instruments are anticipated. To achieve reproducible retention times for identifying compounds, mobile phase flows need to be controlled so that they are independent of ambient pressure. Detectors may also respond to changes in pressure. For example, the electron capture detector is a concentration sensitive sensor and exhibits diminished signal as the pressure decreases. Other detectors, such as the flame ionization detector, respond to the mass of the sample and are insensitive to altitude as long as the mass flow is controlled.

While the modification of existing gas chromatographs for flight is not trivial, no fundamental problems prevent use of this separation technique on aircraft. The presence of a chromatographic system aboard the Viking mission to Mars confirms that a chromatographic instruments can operate within stringent weight, power, and size limitations in an inhospitable environment (48). We anticipate that as the atmospheric community expands its interest to include a larger number of species, chromatographic techniques will be more widely used on aircraft. Analysis times can, in principal, be decreased to one or two minutes (49), a time response that is

comparable to some of the slower continuous sensors. Furthermore, implementation of capillary columns, such as those used in laboratory analyses of air samples (30), will greatly enhance the scope of measurements that can be made during an aircraft sampling program.

B. Continuous measurement methods for trace gases and aerosols

1. Ozone. Three basic types of ozone instruments have been used in aircraft: the ultraviolet photometric method, and two chemiluminescent techniques measuring respectively, light emitted from the reaction of O_3 with ethylene, and from reaction of O_3 with NO. Ultraviolet absorption photometry is one of the preferred methods for measuring O_3 from aircraft because of the stability and reliability of commercially available instruments. The method is specific for O_3 provided there are no immediate sources of aromatic hydrocarbons (50). However, because of the small absorption coefficient of O_3 at the 254-nm measurement wavelength, commercially available detectors have time responses between 30 and 60 sec, and it is not possible to resolve fine features of the O_3 distribution.

The O_3 /ethylene chemiluminescent instrument measures the luminescent signal at 435 nm resulting from the reaction of a large excess of ethylene with O_3 . The chemiluminescent reaction is second order, and to achieve a response that is rapid and linear with changes in the O_3 mixing ratio, the ethylene concentration is controlled at a high value, typically by adjusting the pressure across a flow restrictor. Sample flow is controlled by use of a flow restrictor downstream of the reaction chamber. Because the detector is inherently a mass sensitive detector, commercially available detectors can be modified to respond to the O_3 mixing ratio independent of altitude by use of mass flow controllers (see also discussion under altitude response). Such modifications are described in Gregory et al., (3). Ethylene chemiluminescent detectors exhibit response times that are considerably less (typically, $1/e$ response times of <3 s) than UV photometric instruments, and are thus more broadly applicable to aircraft measurements.

The final O₃ measurement technique that will be discussed here is based on the O₃/NO chemiluminescent reaction. Essentially this instrument is an NO/O₃ chemiluminescent detector for determination of NO operated in reverse. That is, a high concentration of NO is used to measure O₃ as opposed to a high concentration of O₃ to measure NO. Because of the kinetics of the ozone/NO reaction, this detector responds faster than the ethylene based detector and 1/e response times of less than 0.1 s have been reported. Design and operating characteristics of an instrument capable of providing eddy correlation measurements of O₃ flux from an aircraft are given by Pearson and Stedman, (51). A revised version of this instrument that uses considerably less power, and which thus places fewer constraints on its use in aircraft, has been recently reported (52). The instrument uses a smaller reaction chamber than the Pearson/Stedman instrument, requires less power, and generates less heat. The detection limit of this instrument is reported to be 1-2 ppbv, with a 1/e response time of 0.45 s, and a precision of about 2% or 2 ppbv. This instrument has been used for airborne O₃ flux measurements in the Amazon (53).

2. Sulfur dioxide. Both flame photometric and pulsed fluorescence methods have been applied to the continuous measurement of SO₂ from aircraft. In the flame photometric detector (FPD), sulfur compounds are reduced in a hydrogen-rich flame to the S₂ dimer. The emission resulting from the transition of the thermally excited dimer to its ground state at 394 nm is measured using a narrow bandpass filter and a photomultiplier tube. The response of the instrument is roughly proportional to the square of the sulfur concentration. Two major problems are associated with use of commercially available flame photometric detectors on aircraft. First, major changes in background current and more modest changes in detector sensitivity occur as the inlet pressure changes. Second, commercial detectors exhibit detection limits (> 1ppbv, depending on make and model) that are too high to measure ambient concentrations away from SO₂ source regions.

These problems have been largely eliminated by modifying commercial detectors with the addition of mass flow controllers to maintain constant flows of sample air and hydrogen as the altitude changes, and by the use of SF₆ doped hydrogen to enhance sensitivity (4, 54, 55). Controlling the mass flow holds the burner H₂/O₂ ratio at a value independent of altitude, and fixes the sulfur mass flow for a given atmospheric sulfur mixing ratio, greatly stabilizing instrument response. The use of H₂ doped with 60 ppbv SF₆, decreases the limit of detection. Since the atmospheric signal is measured on top of a 60 ppbv background, the response is linear up to ~15 ppbv concentrations of atmospheric SO₂ even though the FPD is inherently non-linear. The limit of detection for aircraft measurements using this modified detector have been reported to be as low as ca 0.1 ppbv, increasing to ca 0.3 ppbv under turbulent atmospheric conditions (56).

Because the FPD responds to both aerosol and gaseous sulfur species it has also been possible to modify these instruments to continuously measure aerosol sulfur by selectively removing gaseous sulfur compounds with a lead(II) oxide-glycerol coated denuder (54). Use of such an instrument for airborne measurements of aerosol sulfur in and around broken clouds has been reported (56). In principle, speciation between aerosol sulfate, bisulfate, and sulfuric acid by selective thermal decomposition (57, 58) can also be achieved. Flame photometric detectors have also been used as selective detectors for gas chromatography. Thornton et al., (59), report the use of a chromatographic system with a flame photometric detector for airborne measurement of SO₂ and OCS with a detection limit of 25 pptv.

The pulsed fluorescence method operates by optically stimulating SO₂ molecules using a UV source (190 - 230 nm), and measuring the resultant fluorescence. The excitation source is pulsed to achieve high excitation intensity, and to encode the concentration information in the form of a chopped signal. By chopping the signal, dark current drift of the photomultiplier tube is eliminated. A scrubber is used to remove hydrocarbon interferences that fluoresce at similar

wavelengths. A commercially available version of this detector (Thermo Environmental 43S, Hopkington MA) has a detection limit better than 0.3 ppbv and a time constant of roughly 2 min. This system has several advantages over the FPD for aircraft use: there are no consumable gases as with the FPD; the detector is simple to operate; exhibits nominal zero shift with altitude, and; the output is easily converted to mixing ratios. For these reasons, the pulsed fluorescence detector has largely supplanted the flame photometric detector for aircraft measurement of SO_2 in the relatively polluted lower troposphere. The relatively slow response of commercial instruments is not optimal for aircraft sampling, but can be improved at the expense of sensitivity. The instrument does not, however, have sufficient sensitivity for measurements in remote regions, or in the upper troposphere

A third measurement technique for SO_2 that may have future application in aircraft measurements has been recently described (60). In this method gaseous SO_2 is removed from the airstream with a diffusion scrubber containing 1-mM H_2O_2 . The scrubber eluant is analyzed in flight for $\text{SO}_4^{=}$ by ion chromatography. Since H_2O_2 quantitatively converts SO_2 to sulfate in the scrubber, the $\text{SO}_4^{=}$ concentration is proportional to the gaseous SO_2 concentration for a given set of sampling conditions. SO_2 was measured at concentration levels of 20 pptv, with 6-min time resolution. The diffusion scrubber method was recently compared with the pulsed fluorescence and filter techniques in airborne tests (20). All three techniques operated with no difficulty in both pressurized and unpressurized aircraft, and were shown to give equivalent response to ambient SO_2 mixing ratios, although there was significant scatter below 200 pptv.

3. Oxides of nitrogen. Two highly sensitive techniques for determining odd nitrogen compounds have been developed based on chemiluminescence reactions with either NO or NO_2 . The first group of detectors measures the chemiluminescence resulting from the reaction of NO with O_3 . Three classes of instruments based on this reaction can be considered for aircraft use. The first are

commercial instruments which typically have detection limits on the order of 1-10 ppbv. These instruments are not particularly suitable for aircraft-based monitoring of ambient air outside of urban areas because of their limited sensitivity. Relatively minor modifications have been described that can improve the sensitivity of these instruments by ten to one-hundred fold, thus making them suitable for monitoring continental air (61-63). This intermediate class of instruments is capable of detection limits on the order of 0.1 ppbv. Finally, a class of instruments has been developed for measuring concentrations in the low pptv range. These typically employ high intensity ozone sources, large vacuum pumps for high sample throughput, cryogenically cooled photomultiplier tubes to reduce background noise, and photon counting electronics to improve measurement statistics. These detectors are custom made on an individual basis, (for example, see 64), and have been extensively compared in flight to sensors based on other techniques (47, 65, 66).

Various approaches have been described to convert other nitrogen species to NO prior to detection by the ozone chemiluminescence reaction. The most common converter is hot molybdenum which converts all of the higher oxides of nitrogen including NO₂, HNO₃, peroxyacetic nitric anhydride (PAN), N₂O₅, NO₃, and many organic species to NO (collectively these species are referred to as NO_y). Heated gold catalysts (67) have also been used for determinations of NO_y. The conversion efficiency of these hot converters is usually close to 1, but must be periodically checked. Selective photolytic conversion of NO₂ to NO by irradiation with UV light has been used to measure NO_x (the sum of NO₂ and NO). NO₂ is then determined by difference (68). The conversion efficiency of NO₂ to NO is less than one and must be measured by performing a gas-phase titration of standard NO mixtures with O₃. NO chemiluminescence detectors generally do not use expendables, but require large pumps to achieve high sample throughput. This imposes considerable weight and power requirements on an aircraft.

NO_2 has also been selectively determined based on its chemiluminescent reaction with luminol (LMA-3, Scintrex/Unisearch, Concord, Ontario). Incoming air impinges on a wick containing a proprietary luminol solution. Emitted light is then detected by a photomultiplier tube. The instrument is mechanically simple, light weight, compact, and consumes little power making it practical for use in aircraft. The luminol reaction is specific for NO_2 ; however, NO can be determined by oxidation to NO_2 . Drawbacks associated with the luminol chemiluminescent detector include nonlinear response below a few ppbv, a minor interference from ozone, and partial response from PAN. These problems can be significant when measuring low concentrations (<3 ppbv). However, correction factors can be applied to account for their effect. Evaluation of the use of this instrument for aircraft sampling, including modifications to eliminate pressure dependence, has been reported (69). A commercial instrument (LPA-4, Scintrex/Unisearch, Concord, Ontario) is also available to determine PAN by catalytic conversion to NO_2 and detection by means of luminol chemiluminescence. In general though, the low concentrations and wide assortment of individual organic odd nitrogen species require sample preconcentration and subsequent analysis by gas chromatography. Some of these approaches are discussed in the previous section on chromatography.

Tunable diode laser absorption spectroscopy (TDLAS) has been used to measure oxides of nitrogen during flight (70). By tuning the laser to specific infrared absorption bands, the technique can selectively measure each compound. Detection limits are higher (25- 100 pptv for a 3 min response time) than the best chemiluminescent methods, and the instrumentation is less amenable to aircraft operations than the chemiluminescence techniques because of weight and size.

A sensor based on two-photon laser-induced fluorescence has been described for detection of $\text{NO}/\text{NO}_x/\text{NO}_2$ (71). NO is detected directly based on its fluorescent properties. NO_2 is first converted to NO by photofragmentation at 353 nm with a XeF excimer laser. Detection limits approach the low pptv level for 2-min

integration times. This technique is still in the developmental stage, but holds promise for future aircraft measurements.

4. Carbon monoxide. Methods for determining carbon monoxide include detection by conversion to mercury vapor, gas filter correlation (GFC) spectrometry, tunable diode laser absorption spectroscopy (TDLAS), and grab sampling followed by gas chromatographic analysis. The quantitative liberation of mercury vapor from mercury oxide by CO has been used to measure CO (72). The mercury vapor concentration is then measured by flameless atomic absorption spectrometry. A detection limit of 0.1 ppbv was reported for a 30-s response time. Accuracy was reported to be $\pm 3\%$ at tropospheric mixing ratios. A commercial instrument providing similar performance is available.

GFC spectrometry is based on measurement of the absorption of broadband infrared radiation by carbon monoxide. Specificity for CO is achieved by alternating the infrared beam between wavelengths that are absorbed and transmitted by CO. In practice, this is done by chopping the light with a gas filter containing CO. When the filter is in place, all of the absorption bands are saturated and the beam cannot be further attenuated by CO in the sample cell. This provides a reference signal. Absorption of the unfiltered light by CO in the cell is measured relative to the reference beam to determine the CO concentration. A multipass White cell increases sensitivity. Detectors based on this technology are commercially available, but lack sufficient sensitivity for aircraft measurements. Modifications of a commercial GFC detector to improve its sensitivity have been described (73). This instrument has been used in several aircraft sampling programs (e. g., 74, 75).

TDLAS measures the absorption of monochromatic light by CO in a multipass flow cell (76). The time response is controlled by the flow of air through the cell. In theory, the instrument is fast enough for application to aircraft measurement of CO flux by eddy correlation. A reported precision of ~ 1 ppbv or $\sim 1\%$ is superior to other techniques. The instrument is not commercially available.

Grab samples obtained during flight can be subsequently analyzed by GC. Because CO is stable in passivated containers, this approach is straightforward. Discrete sampling limits the resolution of rapid changes in concentration. The TDLAS and two different GC trapping methods have been evaluated during an airborne intercomparison (77).

5. Gaseous hydrogen peroxide. Methods for determination of gas phase hydrogen peroxide have been recently reviewed (78-80). Hydrogen peroxide is determined by either scrubbing air with an aqueous solution and measuring the resultant liquid phase peroxide, or by measuring the peroxide directly with a spectroscopic technique. The method that has been most commonly used for aircraft sampling is the POHPAA (p-hydroxyphenylacetic acid) technique developed by Lazrus and co-workers (81, 82). In the PHOPAA technique, peroxides are removed from the air using a scrubber coil and subsequently undergo the horseradish peroxidase catalyzed reaction with PHOPAA to form a fluorescent dimer species. The fluorescent intensity of the dimer is measured and is directly proportional the peroxide concentration in the air. Since the method is sensitive to all peroxides, a second channel is employed in which H_2O_2 is selectively destroyed by catalase; H_2O_2 is computed by difference. The accuracy and precision with which H_2O_2 can be determined using this technique is critically dependent on the catalase activity. Thus, the catalase activity must be periodically monitored and adjusted to assure that it is at an appropriate level to minimize errors in the determination of H_2O_2 . The method is reported by various aircraft users (84 and references therein) to have a detection limit of <0.1 ppbv and a time delay of ca 3 min, although the time response is considerably faster, ~ 1 min. A non-enzymatic method has been developed which avoids the catalase activity problem in distinguishing H_2O_2 from total peroxide (83).

6. Particle measurements. A variety of instruments are available for measuring the number density and size distribution of particles sampled from

airborne platforms. We restrict our considerations here to instruments that measure particles smaller than 50 μm (cloud droplets and aerosol particles) because these are of most interest to atmospheric chemists.

Particle Measurement Systems (Boulder, CO) has developed a series of probes for aircraft measurement of atmospheric particles. Several of these probes will be discussed here. The airborne Active Scattering Aerosol Spectrometer Probe (ASASP-100X) measures the number concentration and size distribution of particles in the size range (approximate) 0.12 to 3.12 μm by measuring the light scattered when the particles pass through the active cavity of a laser. In this probe, particles are forced into a conical deceleration chamber by the motion of the aircraft. A pump pulls about 1 cm^3/sec of this air into the detection region through a narrow nozzle that aerodynamically focusses the particle stream to a diameter (150 μm) that is small with respect to the diameter of the laser beam. During transit of the laser beam, particles scatter radiant energy which is sensed by a photodetector. The output of the photodetector is a series of pulses (one for each particle) whose size is proportional to the scattering intensity. A pulse height analyzer groups the pulses into counts by size; the ASASP uses a pulse height analyzer with 15 channels. Since scattering intensity is proportional to particle size, the count in each channel represents the number of particles within a specified size range. A newer version of this probe, the Passive Cavity Aerosol Spectrometer Probe (PCASP-100X) has recently been introduced. It utilizes the same sampling techniques as the ASASP but the sensing area has been moved external to the laser, and the laser has been changed to improve sensitivity and stability.

Scattering intensity measured by the pulse height analyzer is related to particle size by calibration with mono-disperse latex spheres, or nearly monodisperse NaCl particles. Calibration uncertainties have been studied and discussed (85-90). These studies show that the smallest size particles that can be sensed by the ASASP probe is somewhat higher than the 0.12 μm stated by the manufacturer. Similarly, it is

reported that detection of particles larger than about 2 μm is unreliable due to attenuation of the laser power.

Distortion of the particle size during the sampling process is a concern in use of this probe on an aircraft. Compressional heating due to deceleration of the particles may distort the size distribution, since evaporation of water from aerosol particles reduces their diameters. Likewise, particle sizes can be reduced by use of a heater incorporated into some models of this probe to prevent icing when flying through supercooled clouds. One study (87) indicates that the probe heater removes most of the water from aerosol particles sampled at relative humidities of 95%. It is concluded that size distributions of aerosol particles measured with the probe heater on, corresponds to that of the dehydrated aerosol. These results were confirmed by a later study (89) where size distributions of aerosols measured with a non-intrusive probe were compared to size distributions measured with a de-iced PCASP probe. Measurement of the aerosol size distribution with the probe heater on may be an advantage in certain studies.

The PMS Forward Scattering cloud droplet Spectrometer Probe (FSSP-100) determines particle size by measurement of the scattering intensity over a prescribed range of angles during particle interaction with a focused laser beam. Similar to the ASASP probe, scattered light pulses are measured by a photosensor and sized with a pulse height analyzer; the height of the pulses is proportional to the particle size. The FSSP can measure particles with diameters between 0.5 and 47 μm in four selectable size ranges. Each range divides particles into 15 equally spaced size classes. The response of the FSSP has been shown to be a function of particle shape, refractive index, and absorption as well as size. Furthermore, the response function is multivalued because scattered intensity is not a smooth function of the particle diameter. This can lead to errors in determination of the size distribution of both aerosol particles and cloud droplets (85, 90). Extensive information regarding calibration and operation of this probe has been published (90-96).

A newer version of the FSSP-100, the FSSP-300, is currently available. The probe is similar to the FSSP-100 except that the electronics are faster, and it uses a different laser, and slit arrangement. The major difference is that it is configured to measure particles in the size range ~ 0.3 to $20\text{ }\mu\text{m}$ etc. in 31 separate size channels in comparison to the FSSP's 15 size channels. The additional channels in the lower portion of the size spectrum overlap the sizes measured by the ASASP and the PCASP probes and have allowed intercomparisons between aerosol size distributions measured by these two probes (89). Dye, et al, have recently evaluated the capabilities of this probe for measuring the number density and size distribution of atmospheric aerosols (97).

The integrating nephelometer (98, 99) measures the extinction coefficient, b_{sp} , due to light scattering from gases and aerosols. A sample cell is illuminated with a diffuse source and the scattered light is measured in both the forward and back-scattered directions with a photodetector. The geometry of the system physically integrates the intensity of scattered light providing a close approximation to the scattering component of extinction. Correction for Rayleigh scattering by gases is done by filtering particles from the incoming airstream. Calibrations are performed by measuring the extinction of pure gases such as carbon dioxide and dichlorodifluoromethane (Freon).

The integrating nephelometer has been employed on aircraft for several purposes. The most common uses are to measure visual range in atmospheric haze studies, or to locate atmospheric boundaries such as temperature inversions by noting discontinuities in b_{sp} . However, it has also been shown that submicron aerosol mass can be estimated from b_{sp} measurements. This stems from the observation that the ratio of light scattering coefficient to aerosol particle volume is approximately independent of the size distribution of the aerosol, for particle radii comparable to the wavelength of light employed (100-102). It has also been noted that b_{scat} can serve as a surrogate measurement of sulfate in areas where sulfate, and

associated species comprise a fairly uniform fraction by volume of the sub- μm aerosol (55 and references cited therein). In these applications, the relationship between b_{scat} and mass of an aerosol constituent holds only to the extent that the amount of water associated with the aerosol particle is constant. Thus, it is common practice to employ a pre-heater in the b_{sp} instrument to bring particles to a reference relative humidity. The application of b_{sp} for airborne study of the distribution of sulfate in broken clouds has been described (55).

Condensation nuclei counters (CNC) measure the concentration of particles in the size range 0.001 to 0.1- μm diameter. They operate by exposing a sample of ambient air to a high supersaturation by humidifying the incoming air then abruptly reducing the pressure to cause adiabatic cooling. Supersaturations on the order of 400% are achieved and this is sufficient to cause even the smallest particles to activate and grow. These larger particles are then usually detected optically by light scattering (103). Since all droplets are, in theory, approximately the same size at a given time following the expansion, the scattered light intensity is directly proportional to the concentration of condensation nuclei.

Adaptation of a CNC for aircraft use is straightforward. Unlike larger particles, condensation nuclei are small enough so that they are not easily deposited to walls by inertial processes so the physical shape of the inlet is not a significant issue. However, metal tubing rather than plastic should be used for sampling lines to avoid electrostatic precipitation of particles (104). Particle concentrations ranging from ca. 1 to 300,000 cm^{-3} can be measured with a CNC, however, to assure reliable measurements, calibrations should be performed over the range of particle concentrations expected (105). It has also been reported that CNC counting efficiency decreases rapidly for particles $< 0.01 \mu\text{m}$ (106).

7. Cloud liquid water content. Three different methods have been used to measure cloud liquid water content from aircraft. The most commonly used instrument is the Johnson/Williams detector (Cloud Technology Inc., Palo Alto,

CA). This device employs an electrically heated resistance wire mounted perpendicular to the airstream to sense the water content. As cloud droplets strike the wire they evaporate, cooling the wire, and causing an imbalance in a bridge circuit of which the wire is one arm. The magnitude of the imbalance is a function of the cloud liquid water content. Another wire, mounted parallel to the airstream so that it is not subject to water drop impingement, serves to compensate for variations in airspeed, altitude, and air temperature. While the operating principle of the Johnson/Williams detector is simple, the device is not absolute, requiring calibration to yield accurate results (107). The device begins to underestimate the mass of droplets with diameters $> 30 \mu\text{m}$. A carefully calibrated probe has a response time of $< 0.1 \text{ sec}$, a detection limit of about 0.03 g/m^3 , and an accuracy of about 20%.

The operating principle of the CSIRO (Australian Commonwealth Scientific and Industrial Research Organization) King Probe (Particle Measuring Systems Inc., Boulder, CO) is similar in concept to the Johnson Williams probe. The King probe measures the amount of power necessary to maintain a heated wire at a constant temperature whereas, the J/W probe measures the change in resistance due to cooling of the wire by water evaporation. The probe consists of a heated coil of wire that is maintained at a constant temperature. The amount of excess power required to maintain the wire at this temperature when impacted by water droplets is measured, and is proportional to the cloud liquid water content. The nominal response time of the instrument is 0.05 sec with an accuracy of 20%. This instrument uses less power than a J/W probe, an important consideration in aircraft applications.

A third commonly used method for determining cloud liquid water content measurements is integration of the droplet size spectrum as measured by a PMS FSSP probe. Estimates of cloud liquid water content using this technique are subject to large errors due to uncertainties in determining the number concentrations of droplets in the largest size ranges.

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LITERATURE CITED

1. Gregory, G. L.; Hudgins, C. H.; Edahl, R. A., Jr. *Environ. Sci. Technol.* 1983, 17, 100-103.
2. O'Brien, R. J.; Hard, T. M.; Mehrabzadeh, A. A. *Environ. Sci. Technol.*, 1983, 17, 560-2.
3. Gregory, G. L.; Hudgins, C. H.; Edahl, R. A., Jr. *Environ. Sci. Technol.* 1983, 17, 562-64.
4. D'Ottavio, T.; Garber, R.; Tanner, R. L.; Newman, L. *Atmos. Environ.* 1981, 15, 197-203.
5. Gregory, G. L. In *In-Situ Air Quality Monitoring From Moving Platforms* American Pollution Control Conference Proceedings, 1982; pp 6-25
6. Sheridan, P. J.; Zoller, W. H. *J. Atmos. Chem.* 1989, 9, 363-81.
7. Andrae, M. O.; Berresheim, H.; Andreae, T. W.; Krita, M. A.; Bates, T. S.; Merrill, J. T. *J. Atmos. Chem.* 1988, 6, 149-73.
8. Huebert, B. J.; Lee, G.; Warren, W. L. *J. Geophys. Res.* 1990, 95, 16369-81.
9. Baumgartner, D.; Huebert, B.; Wilson, C. *Meeting Review: Airborne Aerosol Inlet Workshop*, National Center For Atmospheric Research Technical Note: NCAR/TN-362+1A, 1991; pp 1-285.
10. Torgeson, W. L.; Stern, S. C. *J. Appl. Met* 1966, 5, 205-212.
11. Heikes, B. G.; Kok, G. L.; Walega, J. G.; Lazrus, A. L. *J. Geophys. Res.* 1987, 92, 915-31.
12. Leahy, D. F.; Phillips M. F.; Garber R. W.; Tanner R. L. *Anal. Chem.* 1980, 52, 1779-80.
13. Anlauf, K. G.; Wiebe, H. A.; Fellin, P. J. *Air. Pollu. Contr. Assoc.* 1986, 36, 715-23.
14. Huebert, B. J.; Robert, C. H. *J. Geophys. Res.* 1985, 90, 2985-90.

15. John, W. S.; Hering, S.; Reischl, G.; Sasaki, G.; Goren, S. *Atmos. Environ.* 1983, 17, 373-82.
16. Talbot, R. W.; Andreae, M. O.; Berresheim, H.; Artaxo, P.; Garstung, M.; Harriss, R. C.; Beecher, K. M.; Li, S. M.; *J. Geophys. Res.* 1990, 95, 16,955-69.
17. Daum, P. H.; Leahy, D. F. *The Brookhaven National Laboratory Filter Pack System for Collection and Determination of Air Pollutants*, Brookhaven National Laboratory Report: BNL 31381R, 1985; pp. 1-43.
18. Forrest J.; Tanner, R. L.; Spandau, D.; D'Ottavio, T.; Newman, L. *Atmos. Environ.* 1980, 14, 137-44.
19. Norton, R. B.; Huebert, B. J. *Atmos. Environ.* 1983, 17, 1355-64.
20. Kok, G. L.; Schanot, A. J.; Lindgren, P. F.; Dasgupta, P. K.; Hegg, D. A.; Hobbs, P. V.; Boatman, J. F. *Atmos. Environ.* 1990, 24A, 1903-8.
21. Anlauf, K. G.; MacTavish, D. C.; Wiebe, H. A.; Schiff, H. I.; Mackay, G. I. *Atmos. Environ.* 1988, 22, 1579-86.
22. Solomon, P. A.; Larson, S. M.; Fall, T.; Cass, G. R. *Atmos. Environ.* 1988, 22, 1587-94.
23. Scott, W. D. *Atmos. Environ.* 1978, 12, 917-24.
24. Winters, W.; Hogan, A.; Mohnen, V.; Barnard, S. *ASRC Airborne Cloudwater Collection System*, ASRC-SUNYA Publication No. 728, Albany, NY, 1979.
25. Walters, P. T.; Moore, M. J.; Webb, A. H. *Atmos. Environ.* 1983, 17, 1083-91.
26. Huebert, B. J.; Baumgardner, D. *Atmos. Environ.* 1985, 19, 843-6.
27. Huebert, B. J.; VanBramer, S.; Tschudy, K. L. *J. Atmos. Chem.* 1988, 6, 251-63.
28. Isaac, G. A.; Daum, P. H. *Atmos. Environ.* 1987, 21, 1587-600.
29. Greenberg, J. L.; Zimmerman, P. R. *J. Geophys. Res.* 1984, 88, 4767-78.
30. Westberg, H.; Lonneman, W.; Holdren, M. *Identification and Analysis of Organic Pollutants in Air*, Keith, L. H., Ed.; Butterworth: Boston, 1984; 323-37.
31. Ehhalt, D. H.; Rudolph, J.; Meixner, F.; Schmidt, U. *J. Atmos. Chem.* 1985, 3, 21-9.
32. Oliver, K. D.; Pleil, J. D.; McClenny *Atmos. Environ.* 1986, 20, 1403-12.
33. Singh, H. B.; Viezee, W.; Salas, L. J. *J. Geophys. Res.* 1988, 93, 15861-78.

34. Conway, T. J.; Steele, L. P. *J Atmos. Chem.* 1989, 9, 81-100.
35. Evans, L. F.; Weeks, I. A.; Eccleston, A. J. *Clean Air Melbourne*, 1985 19, 21-9.
36. Zimmerman, P. R.; Greenberg, J. P.; Westberg, C. E. *J. Geophys. Res.* 1988, 93, 1407-16.
37. Rasmussen, R. A.; Khalil, M. A. K. *J. Geophys. Res.* 1988, 93, 1417-21.
38. Huebert, B. J. *Atmos. Tech.*, 1980 12, 30-4.
39. Bertoni, G.; Bruner, F.; Liberti, A.; Perrino, C. *J. Chromatog.* 1983, 203, 263-70.
40. Billings, W. N.; Bidleman, T. F. *Atmos. Environ.* 1983, 17, 383-91.
41. Brown, R. H.; Purnell, C. J. *J. Chromatogr.* 1979, 178, 79-90.
42. Walling, J. F.; Bumgarner, J. E.; Driscoll, D. J.; Morris, C. M.; Riley, A. E.; Wright L. H. *Atmos. Environ.* 1986, 20, 51-7.
43. Carroll, M. A. *J. Geophys. Res.* 1985, 90, 10483-6.
44. Berresheim, H.; Andreae, M. O.; Ayers, G. P.; Gillett, R. W.; Merrill, J. T.; Davis, V. J.; Chameides, W. L. *J. Atmos. Chem.* 1990, 10, 341-70.
45. Thornton, D. C.; Drieger, A. R., III; Bandy, A. R. *Anal. Chem.*, 1986, 58, 2688-91.
46. Thornton, D. C.; Bandy, A. R.; Drieger, A. R., III. *J. Atmos. Chem.* 1989, 9, 331-46.
47. Gregory, G. L.; Hoell, J. M., Jr.; Ridley, B. A.; Singh, H. B.; Gandrud, B.; Salas, L. J.; Shetter, J. J. *J. Geophys. Res.* 1990, 95, 10077-87.
48. Novotny, M.; Hayes, J. M.; Bruner, F.; Simmonds, P. G. *Science* 1975, 189, 215-7.
49. Desty, D. H.; Goldup, A. *Coated Capillary Columns - An Investigation of Operating Conditions, Gas Chromatography* 1960, Scott, R. P. W., Ed.; Butterworths: London, 1960; pp 162-83.
50. Grosjean, D.; Harrison, J. *Environ. Sci. Technol.* 1985, 19, 862-75.
51. Pearson, R., Jr.; Stedman, D. *Atmos. Tech.* 1980, 12, 51-5.
52. Gregory, G. L.; Hudgins, C. H.; Ritter, J. A.; Lawrence, M. *Proc. 6th Symp. on Meteor. Observ. and Instr.*, Amer. Meteor. Soc., Boston, MA, 1987, pp 136-9.
53. Ritter, J. A.; Lenschow, D. H.; Barrick, J. D. W.; Gregory, G. L.; Sachse, G. W. Hill, G. F.; Woerner, M. A. *J. Geophys. Res.* 1990, 95, 16875-86.

54. Garber, R. W.; Daum, P. H.; Doering, R. F.; D'Ottavio, T.; Tanner, R. L. *Atmos. Environ.* 1983, 17, 1381-5.
55. Tanner, R. L.; Daum, P. H.; Kelly, T. J. *Int. J. Envir. Analyt. Chem.* 1983, 13, 323-35.
56. ten Brink, H. M.; Schwartz, S. E.; Daum, P. H. *Atmos. Environ.* 1987, 21, 2035-52.
57. Huntzicker, J. J.; Hoffman, R. S.; Ling, C-S. *Atmos. Environ.* 1978, 12, 83-8.
58. Cobourn, W. G.; Husar, R. B.; Husar, J. D. *Atmos. Environ.* 1978, 12, 89-98.
59. Thornton, D. C.; Bandy, A. R. *Globl. Biogeochem. Cyc.* 1987, 4, 317-28.
60. Lindgren, P. F.; Dasgupta, P. K. *Anal. Chem.* 1989, 61, 19-24.
61. Delany, A. C.; Dickerson, R. R.; Melchior, F. L., Jr.; Wartburg, A. F. *Rev. Sci. Instrum.* 1982, 53, 1899-902.
62. Dickerson, R. R.; Delany, A. C.; Wartburg, A. F. *Rev. Sci. Instrum.* 1984, 55, 1995-8.
63. Kelly, T. J. *Modifications of Commercial Oxides of Nitrogen Detectors for Improved Response*, Brookhaven National Laboratory, BNL Informal Report 38000, 1986; pp. 1-A6-5.
64. Drummond, J. W.; Volz, A.; Ehhalt, D. H. *J. Atmos. Chem.* 1985, 2, 287-306.
65. Gregory, G.L.; Hoell, J.; Carroll, M. A.; Ridley, B. A.; Davis, D. D.; Bradshaw, J.; Rodgers, M. O.; Sandholm, S. T.; Schiff, H. I.; Hastie, D. R.; Karecki, D. R.; Mackay, G. I.; Harris, G. W.; Torres, A. L.; Fried, A. J. *Geophys. Res.* 1990, 95, 10103-27.
66. Gregory, G.L.; Hoell, J.; Torres, A. L.; Carroll, M. A.; Ridley, B. A.; Rodgers, M. O.; Bradshaw, J.; Sandholm, S. T.; Davis, D. D. *J. Geophys. Res.* 1990, 95, 10129-38.
67. Bollinger, M. J.; Sievers, R. E.; Fahey, D. W.; Fehsenfeld, F.C. *Anal. Chem.* 1983, 55, 1980-6.
68. Kley, D.; McFarland, M. *Atmos. Technol.* 1980, 12, 63-9.
69. Kelly, T. J.; Spicer, C. W.; Ward, G. F. *Atmos. Environ.* 1990, 24A, 2397-403.
70. Schiff, H. I.; Karecki, D. R.; Harris, G. W.; Hastie, D. R.; Mackay, G. I. *J. Geophys. Res.* 1990, 95, 10147-53.
71. Sandholm, S. T.; Bradshaw, J. D.; Dorris, K. S.; Rodgers, M. O.; Davis, D. D. *J. Geophys. Res.* 1990, 95, 10155-61.

72. Seiler, W.; Giehl, H.; Roggendorf, P. *Atmos. Technol.* 1980, 12, 40-5.
73. Dickerson, R. R.; Delany, A. C. *J. Atmos. Oceanic Technol.* 1988, 5, 424-31.
74. Dickerson, R. R.; et al. *Science* 1987, 235, 460-6.
75. Kleinman, L. I.; Daum, P. H. *J. Geophys. Res.* 1991, 96, 991-1005.
76. Sachse, G. W.; Hill, G. F.; Wade, L. O.; Perry, M. G. *J. Geophys. Res.* 1987, 92, 2071-81.
77. Hoell, J. M., Jr.; Gregory, G. L.; McDougal, D. S.; Sachse, G. W.; Hill, G. F.; Condon, E. P.; Rasmussen, R. A. *J. Geophys. Res.* 1987, 92, 2009-19.
78. Kleindienst, T. E.; Shepson, P. B.; Hodges, D. N.; Nero, C. M.; Arnts, R. A.; Dasgupta, P. K.; Hwang, H.; Kok, G. L.; Lind, J. A.; Lazrus, A. L.; Mackay, G. I.; Mayne, L. K.; Schiff, H. I. *Environ. Sci. Technol.* 1988, 22, 53-61.
79. Sakugawa, H.; Kaplan, I. R.; Tsai, W.; Cohen, Y. *Environ. Sci. Technol.* 1990, 24, 1452-62.
80. Kok, G. L.; Heikes, B. G.; Lind, J. A.; Lazrus, A. L. *Atmos. Environ.* 1989, 23, 283.
81. Lazrus, A. L.; Kok, G. L.; Gitlin, S. N.; Lind, J. A.; McLaren, S. E. *Anal. Chem.* 1985, 57, 917-22.
82. Lazrus, A. L.; Kok, G. L.; Lind, J. A.; Gitlin, S. N.; Heikes, B. G.; Shetter, R. E. *Anal. Chem.* 1986, 58, 594-7.
83. Lee, J. H.; Tang, I. N.; Weinstein-Lloyd, J. B. *Anal. Chem.* 1990, 62, 2381-84.
84. Daum, P. H.; Kleinman, L. I.; Hills, A. J.; Lazrus, A. L.; Leslie, A. C. D.; Busness, K.; Boatman, J. *J. Geophys. Res.* 1990, 95, 9857-71.
85. Pinnick, R. G.; Auvermann, H. J. *J. Aerosol Sci.* 1979, 10, 55-74.
86. Garvey, D. M.; Pinnick, R. J. *Aerosol Sci. and Technol.* 1983, 2, 477-88.
87. Isaac, G. A.; Leaitch, W. R.; Strapp, W. *Atmos. Environ.* 1990, 24A, 3033-46.
88. Kim, Y. J.; Boatman, J. F. *Aerosol Sci. and Tech.*, 1990, 12, 665-72.
89. Strapp, J. W.; Leaitch, W. R.; Liu, P. S. K. In *Meeting Review: Airborne Aerosol Inlet Workshop*, National Center For Atmospheric Research Technical Note: NCAR/TN-362+1A, 1991; pp. 109.

90. Tsonis, A. A.; Lealtch, W. R.; Couture, M. D. *J. Atmos. Oceanic. Technol.* 1987, 4, 518-26.
91. Pinnick, R. G.; Rosen, J. M. *J. Aerosol Sci.* 1979, 10, 533-8.
92. Pinnick, R. G.; Garvey, D. M.; Duncan, L. D. *J. Appl. Met.* 1981, 20, 1049-57.
93. Dye, J. E.; Baumgardner, D. *J. Atmos. Oceanic Technol.* 1984, 1, 329-44.
94. Baumgartner, D.; Strapp, W.; Dye, J. E. *J. Atmos. and Oceanic Tech.* 1985, 2, 626-32.
95. Baumgartner, D.; Spowart, 1990 *J. Atmos. and Oceanic Tech.* 1990, 7, 666-72.
96. Kim, Y. J.; Boatman, J. F. *J. Atmos. and Oceanic Tech.* 1990, 7, 673-80.
97. Dye, J. E.; Gandrud, B. W.; Baumgardner, D.; Sanford, L. A. *Geophys. Res. Ltrs.* 1991, 17, 409-12.
98. Butcher, S. S.; Charlson, R. J. *An Introduction to Air Chemistry*; Academic Press: New York, 1972; pp. 241.
99. Charlson, R. J. *Atmos. Tech.* 1980, 12, 10-14.
100. Pinnick, R. G.; Jennings, S. G.; Chylek, P. *J. Geophys. Res.* 1980, 85, 4059-66.
101. Waggoner, A. P.; Weiss, R. E.; Alquist, N. C., Covert, D. S.; Charson, T. J. *Atmos. Environ.* 1981, 14, 623-26
102. Lewis, C. W. *Atmos. Environ.* 1981, 15, 2639-46.
103. Skala, G. F. *Anal. Chem.* 1963, 35, 702-6.
104. Cooper, G.; Langer, G. *J. Aerosol Sci.* 1978, 9, 65-75.
105. Bodhaine, B. A.; Murphy, M. E. *J. Aerosol Sci.* 1980, 11, 305-12
106. Liu, B. Y. H.; Kim, C. S. *Atmos. Environ.* 1977, 11, 1097-100.
107. Strapp J. W.; Schemenauer, R. S. *J. Appl. Met.* 1982, 21, 98-108.

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