NASA Contractor Report 3465

In Situ Sensors for Measurements in the Global Troposphere

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	angstrom
APEX	Acid Precipitation Experiment
Ar	argon
cm	centimeter
CO	carbon monoxide
CO_2	carbon dioxide
COS	carbonyl sulfide
CS_2	carbon disulfide
DACOM	differential absorption CO monitor
EAA	Electrical Aerosol Analyzer
ECD	electron capture detector
EDTA	ethylenediamine tetraacetate
EERM	Establissement d'Etudes et de Rechercher Meteorologiques
EPA	U. S. Environmental Protection Agency
EPR	electron paramagnetic resonance
FAA	Federal Aviation Administration
FID	flame ionization detector
FPD	flame photometric detection
FTIS	Fourier Transform Infrared Spectroscopy
GASP	Global Air Sampling Program
GC-FPD	gas chromatograph - flame photometric detector
GHz	gigahertz
HCl	hydrogen chloride
H_2S	hydrogen sulfide
HO_2	hydroperoxy radical
Hz	hertz
I^-	iodide
IR	infrared
kg	kilogram
kHz	kilohertz
KI	potassium iodide
km	kilometer
Kr	krypton

LIST OF SYMBOLS AND ABBREVIATIONS
(continued)

kW	kilowatt
L	liter
LDL	lower detectable limit
MHz	megahertz
MST	mesosphere stratosphere troposphere
™J	microjoule
mJ	millijoule
mL	milliliter
™mb	micromillibar
mm	millimeter
MRI	Meteorology Research Incorporated
MSL	mean sea level
ms	millisecond
m/s	meters per second
mV	millivolt
mW	milliwatt
NaOH	sodium hydroxide
NASA	National Aeronautics and Space Administration
NAVAID	Navigational Aid
NCAR	National Center for Atmospheric Research
NBS	National Bureau of Standards
NDIR	nondispersive infrared
Ne	neon
nm	nanometer
NMHC	nonmethane hydrocarbon
NMOC	nonmethane organic carbons
NO	nitric oxide
N_2	nitrogen
NO_x	oxides of nitrogen
NO_2	nitrogen dioxide
NWS	National Weather Service
O_2	oxygen

LIST OF SYMBOLS AND ABBREVIATIONS
(concluded)

O_3	ozone
OH	hydroxyl radical
OPC	Optical Particle Counter
PAN	peroxyacetyl nitrate
PASS	pure acoustic sounding system
pH	negative log of the hydrogen ion concentration
PIXE	proton induced x-ray emission
PMT	photomultiplier tube
ppb	parts per billion
ppbC	parts per billion carbon
ppm	parts per million
ppmC	parts per million carbon
ppq	parts per quadrillion
ppt	parts per trillion
RASS	radio acoustic sounding system
Rh-B	Rhodamine B
rms	root-mean-square
RPA	Remotely Piloted Aircraft
RTD	Resistance Temperature Devices
SiC	silicone carbide
ST	stratosphere troposphere
TBAH	tetrabutylammonium hydroxide
TiO_2	titanium oxide
TROP	Tropospheric Orbital Program
UHF	ultra high frequency
URL	upper range limit
U_s	speed of sound
UV	ultraviolet
VAD	velocity azimuth display
VHF	very high frequency
WBRT	Weather Bureau Radio Theodolite

1.0 INTRODUCTION

1.1 Background

As part of its continuing efforts to direct its applications programs toward relevant national needs, NASA is conducting a Tropospheric Air Quality Research Program with the objective of applying NASA's space technology to assess and predict human impact on the troposphere, particularly on the regional to global scale where both the synoptic view afforded by satellites and the increasing importance of pollution on those scales suggest that space observations can play a unique and critical role. Because the large scale troposphere is so poorly understood at the present time, the initial step toward this objective is to conduct a strong interactive program of theoretical modeling, laboratory study, investigations aimed at developing and improving instrumentation for atmospheric measurements, and field studies aimed at characterizing the large scale troposphere and identifying the most promising, highest payoff areas for future operational space measurements. A further objective is to apply NASA's existing and developing technology for atmospheric measurements to immediate local and regional air pollution problems through measurement programs conducted jointly with and at the request of agencies, particularly the U. S. Environmental Protection Agency (EPA), responsible for developing control strategies for such problems. In order to achieve these objectives, substantial effort must be directed toward in situ and remote sensors for atmospheric measurements.

1.2 Purpose

The purpose of this report is to present the current status of in situ instrumentation for the measurement of selected tropospheric air pollutants. The report does not include every instrumental technique currently in use but it is intended to describe the available in situ techniques that are, or can be, made to be aircraft-compatible.

In Section 2 of the report, real-time in situ measurement techniques are discussed. By "real-time in situ" it is meant that the actual measurement occurs at essentially the same time and location where the sample is obtained. Both commercially-available instruments and research or prototype instruments are discussed and arranged by pollutant. The section begins with a discussion of the instrumentation for EPA criteria pollutants and continues to other important pollutant species of interest to NASA and the scientific community.

Section 3 of the report describes both the commercial and prototype techniques that require some form of laboratory analysis. In these methods, the samples are collected in situ by either a filter, a container or some chemical sorbent. The analysis of these samples, however, is completed at some later time under laboratory conditions. This section is structured by technique for classes of compounds rather than by individual species.

In Section 4, meteorological sensors are discussed. Modeling efforts concerned with air pollution transport and chemistry must have a representative data base of the area modeled as input. The principal meteorological measurements required for tropospheric modeling are vertical profiles of wind speed and direction, temperature and dew point, and surface measurements of pressure and solar insolation. The discussion begins with descriptions of present and planned in situ measurement techniques and the systems used to obtain vertical soundings of the parameters mentioned above. The important measurement systems to obtain vertical distributions of meteorological variables include the use of instrumented towers, tethered balloons, radiosonde balloon releases, dropsondes, and both unmanned and manned aircraft, among others. The use of acoustic sounders, radar and microwave remote measurement techniques are now becoming useful for obtaining additional meteorological information. These techniques will also be discussed.

Finally, in Section 5, a summary of the report highlighting potential problems of the various techniques described in Sections 2, 3 and 4 is presented. Problems concerning aircraft mounting, pressure effects, sampling time, reliable calibration, sensitivity and data processing are discussed as each of these problems may affect an instrument's ability to adequately perform in aircraft correlative missions with a remote sensor.

1.3 Requirements of Instrumental Techniques

An important part of an atmospheric sampling program is the definition of sensitivity, vertical and horizontal resolution, and sampling times required for the measurement of individual chemical species. Preliminary requirements have been established by NASA so that data generated during the program could be optimally used in atmospheric modeling studies. The characteristics of each instrument described are discussed in the report. Some of the instruments described in this report do not meet all of the criteria desired by NASA for the measurement of particular pollutants. The best possible existing measurement techniques have been described and any proposed modifications to specific instruments that may stretch the limits of a particular technique are also discussed.

For the special case of nonreactive species, such as carbon dioxide, that are of interest because of long-term impacts on stratospheric ozone or climate modification, it is assumed that accurate long-term surface monitoring will be sufficient as a comparison measurement for the remote sensors. For these species, it is assumed that they become mixed and homogeneous throughout the mixed layer.

Use of trade names or names of manufacturers in this report does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

2.0 REAL-TIME IN SITU MEASUREMENTS

Real-time measurement instruments are those that employ a detection principle that is capable of producing an output signal directly relatable to the concentration of the species in a sample drawn into the instrument from ambient air. Certain requirements are therefore necessary for real-time instruments. They must be relatively portable, rugged, and have a self-contained means of drawing a sample, selectively detecting and quantifying the pollutant of interest, disposing unused sample and displaying a stable response signal.

In situ instruments which operate in real time are commercially-available for all of the EPA criteria pollutants as well as for some other interesting pollutants. Instruments for other pollutants or for special sensitivity requirements for the criteria pollutants are in either a prototype stage or in developmental stages. This section of the report describes the principles and specifications of all the commercially-available instruments on the market and those prototype or research instruments that show promise in ambient air measurements. The requirements for aircraft sampling programs present additional considerations to the requirements of fixed location surface measurements. The limitations of these instruments for use aboard airborne platforms are also discussed.

A description of the techniques used and a short summary of the operating characteristics of the commercially-available instruments are included for each criteria pollutant. Those research or prototype instruments that have been described in the literature are also described by pollutant. A detailed list of the specifications of the commercial instruments is included as an appendix to this report.

2.1 Ozone

2.1.1 Commercially-Available Instruments. - Ozone is a well-studied trace constituent of the atmosphere. There have been many measurement techniques suggested and through the years many techniques have been used. The commercial instruments presently available all operate either by the method of chemiluminescence, or ultraviolet (UV) photometry. The commercially-available chemiluminescent instruments measure ozone by determining the quantity of light emitted by the chemiluminescent reaction of ethylene (C_2H_4) and O_3. The chemiluminescent product of this reaction is an electronically excited state of formaldehyde and the instruments based on this detection principle are highly linear in the concentration range of interest for tropospheric studies. The amount of light emitted by the reaction of ozone in the sample and constant source of ethylene is proportional to the ozone concentration in the sample.

The principle of UV photometry applied to ozone detection measures the attenuation by ozone of a specific wavelength of UV light from a source after traversing the sample measurement pathlength.[1] The attenuated wavelength is 254 nm which is strongly absorbed by the O_3 molecule. The sample cell is alternately filled with ambient air containing ozone and ambient air which has been drawn through a scrubber to remove ozone. The difference in the transmitted light between reference and sample is proportional to the ozone concentration in the sample. Because the UV photometer uses a differencing scheme to obtain the ozone measurement, it will suffer an interference if exposed to rapidly changing concentrations of ozone or of other UV absorbers.[2] Therefore, in the case of aircraft measurements crossing the boundary of elevated plumes, excessively high or low ozone concentrations may be indicated by the UV instruments.

Table 2-1 summarizes some of the important operating characteristics of the commercially-available ozone monitors. Detailed specification sheets of each of these instruments are included in the appendix. In all cases, the information sources for these tables were the manufacturers' brochures for each instrument and personal contact with representatives of the manufacturer.

2.1.2 Research or Prototype Instruments. - Ozone is also active in a chemiluminescent reaction with nitric oxide (NO). This is the principal chemiluminescent detection technique for oxides of nitrogen. The reaction of O_3 and NO produces an electronically excited state of NO_2 which emits light. Modification of a high sensitivity NO_x detector based on

Table 2-1.

SUMMARY OF OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS

VENDOR	MODEL #	LOWER DETECT. LIMIT (ppm)	RISE TIME (seconds)	POWER REQUIREMENT (watts)	DIMENSIONS (centimeters)	WEIGHT (kg)	COST	COMMENTS
AID	560	0.001	< 3	8	29 x 19 x 38	9	$3560	Portable
Beckman	950-A	0.009	72	250	23 x 45 x 56	32	$3830	
Bendix	8002	0.010	120	350	22 x 42 x 47	20	$4225	
CSI	1100-2	0.011	12	250	27 x 48 x 46	25	$3795	
CSI	2000	0.010	< 30	10	18 x 20 x 46	10	$3468	Portable
Dasibi	1003-AH	0.009	36	110	13 x 36 x 56	14	$4004	
*Dasibi	1003-AAS	*						
*Dasibi	1006-AG							
*Dasibi	1008-AH						$5170	
Meloy Labs	OA-325-2R	0.010	24	250	31 x 48 x 51	18	$3455	
Monitor Labs	8410 E	0.009	2-90	250	24 x 46 x 43	21	$3550	
Thermo-Electron	49				22 x 43 x 58	16	$6175	

*Information not available at this time.

this principle operated in the reverse mode has been reported by R. Pearson and D. H. Stedman to achieve a high sensitivity O_3 detector. This instrument provides a quicker response time and a higher signal to noise ratio for the determination of eddy correlation flux of ozone from an instrumented aircraft than do the commercially-available instruments. The internal O_3 source of the NO monitor was replaced with a NO source for use as an O_3 monitor. For the eddy correlation flux application to be used aboard an aircraft traveling at 100 m/s, it was necessary to develop an instrument that would respond with a bandwidth of 10 Hz and have a signal to noise ratio of 30:1. Modifications to the flow system and the signal processing electronics were required to achieve these specifications.

The flow system modifications were designed to minimize the lag time in introducing the sample to the detector volume. A vacuum pump providing 5 L/s capacity operated at a reactor cell pressure of 10 torr is used to draw the sample. Inlet plumbing was designed to insure the quickest possible delivery of the sample which is drawn through a sintered frit of 316 stainless steel.

A one-inch diameter photomultiplier tube cooled to 10° C views the chemiluminescence in the reaction cell. The cooling elements require 3.5A at 14.2 Vdc and the high voltage for the PMT is supplied from an AC-DC converter, all operated by the 28 Vdc power supply aboard the aircraft. The signal processing electronics circuit consists of a 160 Hz bandwidth electrometer and 12.0 Hz Butterworth lowpass filter and a variable gain DC amplifier. Full-scale ranges of 250, 100, 50 and 25 ppb are available. The total weight of the instrument is 51 kg, 24 kg of which is in the vacuum pump, surge tank (to minimize pressure effects) and the mounting bracket. The total power requirement is 725 W. The instrument showed a flat response at a sampling frequency of 5 Hz. At a sampling frequency of 2 Hz, the response time, both rise and fall times, was 42 ms ± 5 ms. Maximum instrument noise was 1.4 ppb at a constant ozone concentration of 70 ppb. The PMT dark current was 0.05 ppb at 15° C. In use aboard an aircraft flown at 75 m/s, the instrument responded to an ozone inhomogeneity only 8 m wide. This instrument has been successfully operated on both an Aero Commander and Queen Air research aircraft.

The instrument described above was used by D. H. Lenschow et al. in a program to obtain a measurement of the vertical ozone flux. The use of the same data generated in reference 4 to measure the time rate of change of the ozone concentration in the boundary layer has also been described in an unpublished report.

Another chemiluminescent technique based on the solid phase chemiluminescence of the reaction of solid phase Rhodamine-B and O_3 has also been used.[3] This technique was used to measure stratospheric ozone profiles from a dropsonde. A ballast volume evacuated upon ascent to 60 km draws an ambient sample past a disk impregnated with Rh-B upon descent. A small transmitter radios the signal to a ground-based receiver. The detection limit of this instrument is 1 μmb or 20 ppb at an altitude of 18 km. The accuracy of the instrument is reported to be ±20% over the altitude range of 65 km to 20 km.

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2.2 Oxides of Nitrogen

2.2.1 Commercially-Available Instruments. - All commercially-available instruments for the measurement of oxides of nitrogen in ambient air operate on the principle of chemiluminescence. The reaction of NO and O_3 to produce an electronically excited state of NO_2 is the basis of this measurement technique. Sample air containing the oxides of nitrogen is mixed with an excess of O_3 in a reaction chamber at reduced pressure. Some of the excited NO_2 decays to a stable molecule by luminescence, and the amount of this radiation, which is proportional to the concentration of NO in the sample, is measured by a photomultiplier tube. A measurement of total oxides of nitrogen is obtained by passing sample air through a reducing converter where all the NO_2 in the sample is converted to NO while the NO originally in the sample is unchanged. The measurement of NO_2 is made by electronic subtraction of the total oxides of nitrogen signal from the NO signal. Table 2-2 lists some of the important operating specifications of the commercial NO_x analyzers. A more complete list of instrument specifications appears in the appendix. The information was obtained from either the manufacturers' brochures describing each instrument or by personal communication with a representative of the manufacturer.

2.2.2 Research or Prototype Instruments. - The measurement of oxides of nitrogen aboard instrumented aircraft and in remote rural locations has presented some difficulties since the ambient concentrations in such locations are usually below the minimum detectable concentrations of the commercial analyzers. As early as 1974, efforts were described by Ridley and Howlett[1] to improve the sensitivity of the NO-O_3 chemiluminescence technique.

The instrument was originally designed for stratospheric measurements aboard a balloon-borne platform. The same instrument was also used in the Global Air Sampling Program (GASP) sponsored by NASA.[2] The reaction chamber was constructed from a gold-coated tube. The PMT was positioned so

Table 2-2.

SUMMARY OF OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, NITROGEN DIOXIDE MONITORS

VENDOR	MODEL #	LOWER DETECT. LIMIT (ppm)	RISE TIME (seconds)	POWER REQUIREMENT (watts)	DIMENSIONS (centimeters)	WEIGHT (kg)	COST	COMMENTS
Beckman	952-A	0.010	90	600	23 x 45 x 56	35	$5819 (GSA)	
Bendix	8101-C	0.004	60	500	22 x 42 x 43	23	$6430 (GSA)	
CSI	1600	0.002	90	500	27 x 48 x 69	34	$6650 (GSA)	
CSI	2200	0.010	20		20 x 18 x 46	9	$5875 (GSA)	Portable
Meloy Labs	NA-530R	0.004	5-300	300	31 x 48 x 51	27	$7700 (LIST)	
Monitor Labs	8440E	0.002	90		See Comments	35	$6300 (LIST)	Two Cases
Monitor Labs	8840	0.002	180	320	22 x 43 x 61	27	$6200 (LIST)	
Thermo-Electron	14A	0.0002	1-30	1100	43 x 48 x 46	75(?)	$8425 (LIST)	
Thermo-Electron	14 B/E	0.002	120	475	43 x 48 x 46	34	$6128 (GSA)	
Thermo-Electron	14 D/E	0.0025	60	475	43 x 48 x 50	34	$6631 (GSA)	

as to view the chemiluminescence along the entire length of the tube. A 6-10% solution of O_3 in CF_3Cl was stored in a stainless steel cylinder which was cooled with dry ice. The ozone supply system allowed a vaporized flow of 10 standard cm^3/s.

The operation of the instrument proceeds in three cycles. In the zero mode, the O_3 source is added to the sample prior to a mixing volume where all of the NO is reacted. The chemiluminescence occurs within the mixing volume out of sight of the PMT. This mode establishes a background count rate due to PMT dark current and any other miscellaneous chemiluminescence due to the presence of excess O_3. The sample mode introduces the O_3 source at the PMT where the chemiluminescence of the NO-O_3 reaction is viewed. The difference in count rates is proportional to the NO concentration in the sample. A calibrated mode is also included between every purge. A known concentration of NO is added while the sample is diverted.

The accuracy of this method is typically better than ±15% and the minimum detectable concentration is less than 1 ppb. The instrument's dimensions measure 400 cm x 400 cm x 250 cm, and it weighs 45 kg without the ozone supply and inlet-outlet systems.

The same basic instrument, with minor modifications so that it could be flown aboard a Convair 990 aircraft, has also been described.[3] Ozone was provided by passing dried cabin air over an ozonizer built into the instrument and the PMT was cooled by a thermoelectric housing. The instrument was flown in a Convair 990 aircraft at altitudes up to 12.5 km. The minimum detectable concentration was determined to be 0.05 ppb. At very low concentrations, however, the uncertainty of the method was ±50 percent with a sample flow of less than 300 cm^3/s, and operation at ambient pressure.

Further modifications to improve the sensitivity of the technique described by Ridley and Howlett in reference 1 have been reported.[4] A very short inlet of 1.5 m length was used for delivery of ambient air directly to the instrument and a high response PMT was used. An expansion orifice, as well as a stainless steel trap cooled to -78° C by dry ice, were placed in the sample line to insure the removal of water vapor. Rapid changes in the sample's water content, as is experienced when entering a cloud, was suspected of creating interference in the NO signal. Background signals of 10 counts/sec were produced and the NO sensitivity was 200 counts/sec per ppb of NO. In this configuration with flowrates of 250-300 cm/s and reaction vessel pressure of 150-200 torr, the minimum detectable limit was improved to 0.02 ppb.

Continued use of this basic design has led to additional improvements, as well as problems. A photodissociation converter to reduce NO_2 to NO was added to the instrument so that it could be used to measure both NO and NO_2.[5] A photodissociation converter was used to avoid interferences from PAN, N_2O_5 and HO_2NO_2 as are observed using thermal converters in the commercial instruments. However, interference from HONO and NO_3 may still be present. It was found that the O_3 luminescence was different in the zero and sample modes which evidently results from differences in the mixing in the two modes. This can produce error due to uncertainty in the background signal, particularly if the instrument is dirty. If ozone is added upstream of the reaction vessel, the artifact NO signal, which was more of a problem at night than in the day, was eliminated. However, this decreases the sensitivity because some of the luminescence occurs outside the view of the PMT. Once again, rapid changes in water content were found to produce erroneous signals.

While the NO_2 photodissociation converter is very efficient, some problems are associated with its use. At NO and NO_2 concentrations less than 50 ppt, the lights can produce an interferent that chemiluminesces with O_3 which can result in a signal as high as 500 ppt NO. With low NO but no NO_2 at all, and with the converter lamp turned on, the NO signal decreased. These two problems are always active together but with varying ratios of NO destruction and production; therefore, the accuracy of the NO_2 measurement with this technique has been no better than ±10 ppt. Ideally, this instrument should provide a minimum detectable limit of one ppt at 60-100 seconds averaging time. However, in practice the minimum detectable NO concentration is 7 ppt when operated with one-second averaging time and a signal-to-noise ratio of unity. The same instrument was used aboard a ship to make NO measurements in the equatorial Pacific region.[6] The nighttime artifact NO signal was once again observed. The detection limit aboard the ship was reported as 1 ppt for a 3-min averaging time. This same basic instrument has also been used in studies around Lake Michigan with a ferrous sulfate NO_2 converter to measure NO and NO_x with a minimum detectable limit of 20 ppt using a 12-second averaging time and a signal-to-noise ratio of unity.[7]

A chemiluminescent NO analyzer for high altitude measurements aboard a rocket platform has been described.[8] This system is designed for launch aboard a Nike-Cajon sounding rocket. It uses the principle of $NO-O_3$ chemiluminescence. The ambient sample is drawn through a sample tube one meter in length which terminates 25 mm from the PMT window surface. A source of O_3 in oxygen is supplied from a pressurized container and is also introduced 25 mm from the PMT window. The reaction chamber is made of polished aluminum surfaces and is 230 mm long and 75 mm in diameter. The flow of ozone is controlled by a specific restriction in the delivery line which is dependent on the pressure of the container. The sample flow is also pressure controlled and is, therefore, dependent on the velocity of the rocket. In the initial description, the instrument obtained a minimum detectable limit of 1 ppb for altitude range between 45 km and 90 km. The complete instrument weighs 31 kg, is 1.55 m long and 180 mm in diameter. An improved design of the same rocket-borne instrument was later described.[9] The basic instrument was unchanged; however, it was modified so as to obtain a direct measure of a background signal generated by ozone chemiluminescence with other species or surfaces in the sample. To measure the ozone background, ozone injection upstream of the reaction chamber was not possible due to the short time in which the rocket experiment was conducted. Instead, pure nitrogen was injected in the entrance of the sample tube thereby effectively preventing ambient air from entering the sample tube. Introducing the nitrogen gas at the entrance was important since the background signal was found to be more dependent on flow conditions than any other property. The instrument responded to the alternating flow usually within 0.2 seconds. The technique operates successfully in the ppb range of sensitivity. The instrument is calibrated in a laboratory prior to launch under conditions closely resembling those estimated to be encountered in flight.

A method for the specific measurement of NO_2 by laser-induced fluorescence was investigated.[10] A one-watt argon ion laser was used to excite the NO_2 sample. The laser was directed through a 4880 Å interference filter with 54% transmittance and 150 Å bandwidth. A 5-cm pathlength absorbing filter of 360 g/L $CuSO_4$ with 50% transmittance at 7600 Å and a bandwidth from 0.70 to 0.83 μm was placed in front of the PMT. The attenuation of the filter at 4880 Å was 10^{17}. A lens was used to focus the fluorescence on a cooled PMT. The cooling and a magnetic focusing assembly provided a dark count rate of one per second. The instrument was calibrated by passing N_2 gas over an NO_2 permeation tube. A concentration of 285 ppb NO_2 produced 2100 counts/min which places the sensitivity of the instrument at 3 ppb. A measure of total oxides of nitrogen was obtained by passing the sample over an oxidizing converter to convert NO in the sample to NO_2. At flowrates of 2-3 L/min of 5 ppm NO in N_2, the conversion efficiency was near 100%. The precision of the instrument was 50 ppb at low ppb concentrations and 100 ppb at ppm concentrations with an accuracy of $\pm$10%. Aerosol was found to produce signals several times greater than the NO_2 fluorescence; therefore, the sample was filtered before entering the fluorescence cell.

Further work with this technique proved that the sensitivity was increased by a factor of 100 when a light source at 442 nm was used to excite the sample.[11] Therefore, a 10 mW He-Cd laser at 442 nm replaced the 1-watt argon ion laser used previously. The basis of the two instruments is the same. Absorbing filters and 442 nm mirrors are arranged so as to minimize the background fluorescence produced by the laser and to maximize the NO_2 fluorescence. There are no interferences from NO, O_3, SO_2 or water vapor. Linearity from 10-1000 ppb for filtered and unfiltered samples was demonstrated. The instrument, when operated with a flowrate of 0.075 L/s and an integration time of 80 seconds, achieved a minimum detectable concentration of 0.6 ppb.

Although exact size and weight figures were not presented for the laser-induced fluorescent instrument, it has been mentioned that the size and weight made field applications difficult. Therefore, a portable model using a xenon arc flash lamp to pump the NO_2 excitation was developed.[12] All of the major features included in the laser instrument to maximize the sensitivity are incorporated in the flash lamp instrument. The flash lamp output was checked over several weeks and was reproducible to better than 0.2%. The instrument was found to be linear from 5-1000 ppb and the detectability for 80 seconds (1024 flash lamp pulses). Integration time was 10 ppb. The instrument measures 48.3 cm in width, 44.5 cm in height, 45.7 cm in depth and weighs 31 kg. The power requirements are 3.4 amps at 116 Vac (390 watts). The size and power requirements make this instrument suitable for aircraft operation.

The operations of the laser fluorescence and flash lamp fluorescence instruments were compared in side-by-side tests.[13] The comparison was made with respect to sensitivity, size, specificity, reliability and economy. In general, the performances of the two instruments were nearly the same. Use of the laser system for excitation achieved can produce 0.1 ppb sensitivity compared to 1 ppb for the flash lamp system.

2.2.3 Nitrous Oxide Measurements. - Nitrous oxide (N_2O) is not commonly included as a compound in the oxides of nitrogen category (normally $NO = NO_2$), since it is relatively inert and nontoxic at the low concentrations characteristic of the atmosphere. Recently, however, the distribution of N_2O in the atmosphere has been of concern due to the possibility that is might be involved in stratospheric ozone destruction. Since its discovery as an atmospheric constituent in 1938 many measurements of the tropospheric N_2O concentration have been reported.[14] While it is expected that large combustion sources produce some N_2O, and its use as an anesthetic may result in some releases to the atmosphere, the major source of N_2O in the atmosphere is suspected to result from the action of bacteria on nitrogen-containing fertilizers. The methods that have been used to measure N_2O in the atmosphere are infrared spectroscopy, (absorption and emission) mass spectrometry, manometry and gas chromatography coupled with detectors of virtually all types. The principal detectors used are thermal conductivity, flame ionization and electron capture. The wide variety of detection methods used has resulted in variations in the absolute concentrations reported; however, many of the measurements since 1965 have been remarkably consistent averaging between 270 and 320 ppb.[14]

Throughout 1976 and early 1977 a large number of nitrous oxide measurements have been made in situ using gas chromatography and electron capture detection.[14] This method allows an in situ sample analysis within five minutes. The measurements were made with consistent operational and calibration procedures and covered latitude range from 80°N to 90°S, and altitude ranges from the surface to 3600 m (12,000 ft) above the tropopause. The average of literally thousands of measurements was 300 ppb and was not found to vary significantly with latitude or altitude within the troposphere. A small decrease on the order of 10-15 ppb N_2O concentration was associated with the latitudes influence by the northeast tradewinds. Above the tropopause the N_2O concentrations appear to decrease slowly with altitude.

An investigation of all the various reported measurements seems to suggest that techniques that require preconcentration of the sample give measurements below 300 ppb while techniques which are basically in situ in nature give measurements above 300 ppb. It has been recommended that an intercalibration effort be undertaken to establish the relationship between the various analytical methods. At present it has been shown that gas chromatography with electron capture detection can be used to obtain consistent tropospheric N_2O measurements on mobile platforms, both aircraft and ship, and fixed surface platforms.

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2.3 Sulfur Dioxide

2.3.1 Commercially-Available Instruments. - The commercial analyzers for ambient SO_2 detection operate on either the flame photometric detection method or the pulsed fluorescence method.

In the chemical analysis of environmental samples, the flame photometric detection (FPD) principle has seen great usage in the identification and quantification of sulfur-containing molecules.

In the FPD principle, an ambient air sample is either routed directly to a hydrogen-rich flame, or is first preconcentrated by a chemical or cryogenic trap and then flushed into a hydrogen-rich flame. In this flame, the sulfur-containing molecule decomposes and excited-state dimeric sulfur molecules (S_2) are produced through a series of reactions. Light of a characteristic wavelength (350 to 427 nm) is emitted as the excited-state species returns to ground state. A selective optical filter allows only a narrow wavelength of light (around 394 nm) to pass to a photomultiplier tube and thus makes the FPD a specific detector for sulfur containing compounds. Since the flame photometric method responds to all sulfur atoms in a given sample, this technique suffers from a lack of specificity for SO_2 unless scrubbers are used to remove other sulfur compounds.

Ambient air concentrations of sulfur dioxide are often measured with commercially-available flame photometric sulfur dioxide analyzers. These instruments are normally operated in the 0-0.5 or 0-1.0 ppm range. Recent versions of these instruments have been subjected to EPA Equivalent Methods Testing[1,2] in which a full range of possible interferents are tested and sensitivity and response time are determined. The lag time (time from pollutant injection to noticeable response from zero or fixed concentration) is approximately 6 seconds. The 95% rise time (time to reach 95% of the final concentration readout at 0.4 ppm) is 18 seconds or greater.

The major interferents in the method are H_2S and CO_2. H_2S is selectively scrubbed with a filter that allows SO_2 to pass unaffected. The quenching effect of CO_2 on the signal is effectively nulled out by calibrating the analyzer with CO_2 present in the calibration gas.

Continuous FPD SO_2 analyzers have been employed in numerous aircraft studies. There is a notable variation of response with altitude; however, this variation has been characterized[3] and the logarithmic output of the analyzer can be adjusted to compensate. The size (25 cm x 60 cm x 60 cm), weight (50 kg), and current requirement (4 amps) make these units suitable for airborne use. It should be noted that a source of hydrogen is necessary for operation.

In the pulsed fluorescence analyzer, the sample is energized by a pulsed 15W Zn or Cd UV source. As the SO_2 molecules in the sample absorb the light energy, they reach an electronically-excited state. After a lifetime of approximately 10^{-9} seconds they return to their ground state by emission of light energy of a longer wavelength than the exciting radiation. A specific filter which does not overlap the exciting light source passes the fluorescence to a PMT. Signal processing electronics reduces the output of the PMT to a signal proportional to the SO_2 concentration in the sample.

A list of the important operating characteristics of the commercially-available monitors appears in Table 2-3. A complete list of the manufacturers' specifications of all the commercial instruments is given in the appendix.

2.3.2 Research or Prototype Instruments. - The major thrust of research in developing improved techniques for ambient SO_2 detection is concentrated in the field of remote measurement. The limitations of the present measurement techniques for the commercial SO_2 analyzers are not likely to be improved significantly in the near future. The research efforts associated with the basic FPD technique are concentrating on the measurement of atmospheric sulfur containing molecules other than SO_2. These efforts will be described later.

One research method, a fluorescence monitor for SO_2 measurement that uses a Cd or Zn lamp for the excitation energy, has been described.[4] The lamp radiation is filtered through a Cl_2 filter which prevents transmission of wavelengths between 2700 and 3900 Å. The SO_2 fluorescence is passed to the photomultiplier tube by a specific filter that only passes

Table 2-3.

SUMMARY OF OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS

VENDOR	MODEL #	LOWER DETECT. LIMIT (ppm)	RISE TIME (seconds)	POWER REQUIREMENT (watts)	DIMENSIONS (centimeters)	WEIGHT (kg)	COST	COMMENTS
Beckman	953	0.010	< 180	900	31 x 48 x 56	41	$6763	
Bendix	8303	0.009	18	300	21 x 42 x 46	27	$6295	
Lear Siegler	SM1000	0.013	504	150	28 x 28 x 41 20 x 86 x 38		$11620	Two Cases
Meloy Labs	SA 185-2A	0.007	66	250	31 x 43 x 51	18	$4735	
Meloy Labs	SA 285E	0.009	3-10	250	31 x 43 x 51	18	$5450	Fast Response Option
Meloy Labs	SA 700	0.002	90	300	31 x 43 x 51	18	$6300	
Monitor Labs	8450	0.013	45	500	24 x 46 x 59 24 x 46 x 59	46	$5208	Two Cases
Monitor Labs	8850	0.001	204	700	23 x 48 x 57	27	$6487	External Pump
Thermo-Electron	43	0.003	234	150	22 x 43 x 58	25	$7101	

wavelengths from 2900 to 4100 Å. This combination of filters insures that wavelengths from the lamp are not seen by the photomultiplier.

The detection was found to be linear from 0.1 ppm to 500 ppm for the Zn lamp and from 0.1 ppm to 1600 ppm for the Cd lamp. At SO_2 concentrations below 0.1 ppm, the PMT was operated as a photon counter and the signal had to be integrated for one minute. The limit of detection was 20 ppb using one-minute signal integration. This detector, therefore, is primarily useful as a source monitor and is not highly suitable for ambient measurements. The effects of interferents on this method were investigated.[5] The test results showed that napthalene was a significant interferent. This interference could be removed, however, by passing the sample through an oxidizing catalytic converter. The catalytic converter, however, also oxidized other ambient sulfur species, like H_2S, to SO_2. To counteract this, a $HgCl_2$ scrubber was placed in the sample line to remove those reduced sulfur species in the sample prior to the oxidizing converter.

A technique using anodic oxidation of SO_2 and galvanic detection has been described.[6] The system employs two anodes and one cathode submersed in electrolyte. Sample air is passed by each anode; however, the SO_2 is selectively scrubbed out of one of those flows. The differential currently established between the anodes is then proportional to the SO_2 concentration in the sample. In this way, improved sensitivity is attained since background current and current due to interferents are effectively zeroed out. The response time was three seconds and the minimum detection limit was 3 $\mu g/m^3$ (~2 ppb). The flowrate was 180 cm^3/min to each anode. The system was field-tested and found to be stable in terms of anode activity over a ten-month period.

The other important SO_2 measurement technique useful for ambient analysis is filter collection with subsequent laboratory analysis. This technique will be discussed in Section 3.

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2.4 Carbon Monoxide

2.4.1 Commercially-Available Instruments. - The main technique used to measure ambient carbon monoxide in commercially-available instruments is nondispersive infrared (NDIR) detection. Radiation from an infrared source passes through the gaseous sample and the absorption due to the presence of CO is measured. This technique has been described and used for many years.[1] One commercially-available instrument uses the technique of gas filter correlation. A research instrument operating by this technique is described later.

Table 2-4 is a summary of some of the important operating parameters of the commercially-available carbon monoxide instruments. Complete specifications for these instruments are listed in the appendix. The information sources for this information are the manufacturers' brochures for the instrument and personal contacts with representatives of the manufacturers.

2.4.2 Research Instruments for Carbon Monoxide. - Reports of other instruments and instrumental methods for carbon monoxide measurement are listed below. Some of these methods have been specifically designed to be used as airborne monitors. Quick response time, ruggedness and reliability are the major considerations for airborne operations of CO monitors.

A method for airborne measurement of carbon monoxide based on differential absorption of a laser beam has been described.[2] The differential absorption CO monitor (DACOM) measures the absorption of a laser signal through a 10-m absorption path that is mounted to the outside fuselage of a C-54 aircraft. A tunable PbSSe diode laser is used as the light source. This laser has the characteristic that it can be tuned over a wavelength interval by varying the current to the laser source. The current is varied such that the laser wavelength sweeps across an absorption feature of CO. The technique operates with a response time of one second and a sensitivity of 20 ppb.

The problems associated with aircraft operation of this instrument are that the absorption path is necessarily short and the aircraft vibration produces noise modulation of the laser beam. The necessarily short

Table 2-4.

SUMMARY OF OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, CARBON MONOXIDE MONITORS

VENDOR	MODEL #	LOWER DETECT. LIMIT (ppm)	RISE TIME (seconds)	POWER REQUIREMENT (watts)	DIMENSIONS (centimeters)	WEIGHT (kg)	COST	COMMENTS
Beckman	866	0.2	13	500	48 x 34 x 72	41	$5602 (GSA)	
Bendix	8501-5CA	0.5		300	76 x 48 x 27	27	$7315 (GSA)	
Horiba	AQM-10	0.3	60	300	15 x 10 x 86 49 x 48 x 10	34	$5337 (GSA)	
Horiba	APMA-300E/SE	0.1	15	340	22 x 48 x 27 22 x 48 x 27	48	$7690 (LIST)	
Monitor Labs	8310	< 0.1	< 45	400	114 x 48 x 36	30	$7268 (GSA)	
MSA/LIRA	202S	1.00	36	500	110 x 47 x 50		$5748 (GSA)	
Thermo-Electron	48	0.2	120		22 x 43 x 58	41	$6650 (LIST)	
DASIBI	3003	0.2	30		13 x 44 x 57	27	$6750 (LIST)	

absorption path can result in an error of ~5 ppb due to random detector noise. The diode laser nonideality produces wavelength modulation which, accompanied by amplitude modulation, results in an offset of 50-200 ppb in the signal. To minimize these effects, 50% of the laser beam is diverted to a second detector which bypasses the absorption path and the CO absorption signal is obtained by subtraction. This procedure results in an error offset of only ~5 ppb. Additional laser power is diverted to a third detector which is connected to a lock-on amplifier that keeps the laser sweep centered on the fundamental absorption feature, limiting the influence of wavelength modulation.

A study of the influence of aircraft vibration showed that the vibration was dependent on propeller frequency. Both the laser and detector were mounted on 3 Hz vibration isolators to minimize vibration-induced error. Aircraft turbulence introduced a small error at 2 kHz of less than ±2 ppb. A parabolic collector and a large beam of 3 cm diameter minimized the influence of turbulence.

An infrared absorption method using dual isotope fluorescence for carbon monoxide has been used in the Global Air Sampling Program (GASP).[3] This technique uses an IR source to irradiate a sealed cell containing both $C^{12}O^{16}$ and the isotope $C^{13}O^{16}$. A chopper wheel pulses the irradiation source of the sealed cell. The mixture in the cell then fluoresces at the wavelengths characteristic of both isotopes. Another chopper wheel has two gas-filled cells, one of which contains $C^{12}O^{16}$, and the other is $C^{13}O^{16}$ that alternately filters wavelengths of the two isotopes. The radiation of both cells passes through the sample volume where the $C^{12}O^{16}$ in the sample, 98.9% of the ambient CO, can absorb only the wavelengths passed by the $C^{12}O^{16}$ filter. In this way, a cycle of reference followed by signal is produced and the CO in the sample concentration volume can be determined.

The instrument has been operated in the GASP with error of ±3 to ±13% over the altitude range 6 km to 13 km. It has a full-scale range of 1 ppm and a minimum detection limit of 0.02 ppm. The sample flow is 5 L/min. The instrument weighs 30 kg and comes in two packages: an electronics case measuring 23 cm x 50 cm x 18 cm, and an optics case measuring 35 cm x 62 cm x 18 cm.

A gas filter correlation method with an infrared source for the determination of carbon monoxide concentrations is being developed.[4] A glowing SiC rod serves as the IR source. A chopper wheel containing 19 cells rotates and the IR radiation is passed through each cell. Ten of the cells contain pure CO and the other 9 are clear cells with respect to passage of the IR radiation. A sample cell is located after the chopper wheel. The ten cells with pure CO attenuate the IR radiation so strongly that no effect of the sample cell is measurable. The clear cells pass the IR radiation and a small amount is attenuated by the sample cell. The difference in the transmitted radiation is proportional to the CO in the sample cell. The instrument is zeroed electronically and spanned by a calibration volume of known concentration that replaces the sample volume. The minimum detectable concentration is 5 ppm using a one-meter pathlength and a one-second time constant. This instrument, therefore, is not useful as an ambient measurement technique.

A high sensitivity technique based on a coulometric method is available for carbon monoxide.[5] CO in sample air is drawn into a reaction cell where the CO is reacted with I_2O_5 to form free iodine. The free iodine is then passed to a two electrode-measuring cell where the free iodine is reduced to I^-. The electric current established through the solution between the two electrodes is proportional to the CO concentration reacted to produce the free I^-. Ozone, oxides of nitrogen and sulfur compounds are interferents which are scrubbed and the sample air is dried. The only interference is a small one due to reactive hydrocarbons. The minimum detection limit is less than 0.03 ppm and there is a maximum noise of 0.015 ppm. The zero drift is 0.2 ppm in 24 hours and the span drift is ±2% of full scale in 24 hours. The instrument has auto-zero and auto-span capabilities; therefore, it could be operated unattended for long periods of time. The response is linear within ±1% of the indicated value from 0-30° C over a concentration range of 0-180 ppm. At 10 ppm step input, the instrument response is 90% in 300 seconds. The sample flowrate is 300 cm^3/min.

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2.5 Nonmethane Hydrocarbons

2.5.1 Commercially-Available Instruments. - The commercially-available nonmethane hydrocarbon (NMHC) instruments all operate by the principle of flame ionization detection. When hydrocarbons are burned in a hydrogen rich flame, the individual carbon atoms are ionized. This ion stream, when passed through a potential field, produces a current which is proportional to the number of carbon atoms ionized; therefore, these types of instruments are carbon counters. For the measurement of total nonmethane hydrocarbons, a retention column is employed which passes the methane in a sample while retaining all of the other hydrocarbon species. By allowing the sample to bypass the retention column, a measure of the total hydrocarbon in the sample can be obtained. The nonmethane fraction is found by subtraction. There are calibration problems with such instruments as the response to carbon contained in different classes and in different compounds varies to some extent. In addition, the sum of nonmethane hydrocarbons represents data that are difficult to interpret since a similar response is obtained for each carbon atom regardless of the reactivity of the parent molecule with respect to ambient photochemistry. Most of these instruments require a hydrogen source, an oxygen source and an inert gas source such as nitrogen for backflushing the retention column; therefore, the size and weight requirements are prohibitive for some applications.

A list of the basic specifications of the commercially-available nonmethane hydrocarbon analyzers appears in Table 2-5. A more detailed list of the specifications of each instrument appears in the appendix.

2.5.2 Research or Prototype Instruments. - Most commercially-available nonmethane hydrocarbon instruments use a gas chromatographic separation of methane from a sample. This allows a sample of methane only to be diverted to the detector, followed by a sample that is not diverted through the retention column. The actual measurement of nonmethane hydrocarbon is attained by the subtraction of those two signals. These instruments can be large and heavy and require, in most cases, several support gases that must be supplied from compressed gas cylinders, adding to the space and weight

Table 2-5.

SUMMARY OF OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, NONMETHANE HYDROCARBON MONITORS

VENDOR	MODEL #	LOWER DETECT. LIMIT (ppm)	RISE TIME (seconds)	POWER REQUIREMENT (watts)	DIMENSIONS (centimeters)	WEIGHT (kg)	COST	COMMENTS
Baseline	1030A	---	---	100	18 x 31 x 39	9	$4449 (LIST)	General-Purpose GC
Bendix	8202	0.005	180	700	23 x 42 x 45	27	$5875 (GSA)	
Byron	301	0.005	180	200	26 x 51 x 47	25	$6690 (LIST)	
Byron	404	---	720	200	26 x 51 x 47	27	$9575 (LIST)	
HNU	PI-201-250	0.050	< 20	200	25 x 50 x 64	25	$5445 (LIST)	Interferences
Meloy Labs	HC500-2C	0.010	< 30	250	31 x 43 x 51	18	$4170 (LIST)	
MSA	11-2	0.040	< 15	1000	84 x 33 x 51	28	$6460 (GSA)	Flown by EPA

requirements for their operation. The requirements of these instruments make them less than ideal for use aboard aircraft platforms.

One system using this type of separation and measurement principle has been flown aboard an aircraft.[1] The instrument itself was rather large and was mounted in a C-54 aircraft in order to accommodate its size, power requirements (110 Vac), and pressurized support gases: hydrogen and air to produce a hydrogen flame for the FID, and nitrogen to serve as a backflush gas to clear the plumbing between measurements. In addition to these requirements, a large pump was also necessary to provide 10 L/min of sample flow. This large sample flow was required to obtain a measurable sample in a small amount of time to minimize effects of sample averaging due to the airspeed of the C-54. Pressure changes with altitude influenced the response of the FID and the various flowrates in the instrument in the unpressurized cabin but these effects were found to be nearly linear and appropriate corrections could be made to the data. The instrument was successfully flown, and provided altitude profile measurements and constant altitude crosswind measurements of an urban plume.

Recently, several other methods have been described to measure all or some fraction of ambient nonmethane hydrocarbon concentrations. Several of these methods have been used on airborne platforms. The nonmethane hydrocarbon instruments lump into a single measurement all of the numerous species present in ambient air, some of which are highly reactive photochemically and others which have been shown to be of only minor importance in photochemical systems. This problem is of utmost concern to photochemical modelers who must arbitrarily assign percentages of the reported nonmethane hydrocarbon concentrations to the various classes treated in photochemical airshed models. As a result of the shortcomings of the commercially-available nonmethane hydrocarbon analyzers, developments have been made to construct small, efficient and species- or class-specific in situ hydrocarbon analyzers that can be operated aboard airborne platforms.

A chemiluminescent monitor for alkene (olefinic) hydrocarbons has been described.[2] The instrument used was a modified chemiluminscent ozone monitor with an O_3 generator from an NO_x instrument replacing the ethylene source. The instrument was found to give a specific response to alkenes. No response was measured to alkenes, aromatics, or saturated hydrocarbons with ester, acid, alcohol, ether, ketone, aldehyde, or aromatic functional groups. Interferences from sulfides and amines, pinene, methyl amine, H_2S, and methyl mercaptane were discovered. The chemiluminescent spectral emissions from the O_3 alkene reaction were sufficiently distant from the spectra for amines and sulfides so that a cut-off filter prior to the photomultiplier tube could eliminate the sulfide and amine interferences. The authors claimed the sensitivity for detecting alkenes could be improved by ten times over that of a FID detector. The other advantage is that the instrument could be light, use power requirements similar to ozone chemiluminescent instruments and would provide continuous measurements. Therefore, this system seems ideal for aircraft application.

In an independent article, a system identical to the one described above was also discussed.[3] It was mentioned that the instrument had been flown on an aircraft although no data were presented and no specific reference was given.

The same detection principle was also employed in conjunction with a gas chromatographic column which separated the sample into individual components.[4] The operating temperatures varied from 50-250° C, and at the higher temperature, a response to paraffins was also measured. At 100° C, however, the instrument responded only to the alkenes in the sample. The technique was found to be very sensitive, provide low minimum detectability and was selective for alkenes at easily achieved operating temperatures.

Improvements in the sensitivity of this technique have been achieved by adding small amounts of sulfur-containing gases to the sample prior to detection.[5] The introduction of small amounts of H_2S or CS_2 was shown to improve the sensitivity of the technique in measuring concentrations as low as 20 ppb in a 5 cm^3 sample. Although the chemistry responsible for the improved sensitivity is not completely understood, the addition of sulfur-containing gases is thought to contribute additional chemiluminescence due to the formation of activated SO_2 and its subsequent chemiluminescence. The formation of activated SO_2 is thought to result from a chemical reaction of CS_2 or H_2S with an intermediate produced by the ozone attack on the olefins. Data are presented showing a marked increase in sensitivity with 8.7 ppm CS_2 added to the sample. The response with added CS_2 was not linear. Data showed that the addition of 1.1 ppm of CS_2 improved the detection limit of the technique for propene by a factor of 200.

Chemiluminescent reactions with oxygen atoms have also been investigated as a measurement technique for unsaturated reactive hydrocarbons.[6] One instrument based on the chemiluminescent reaction of oxygen atoms and reactive hydrocarbons used two photomultiplier tubes with filters for the differentiation of OH emission at 308.9 and 312.2 nm, respectively.[7] The emission results from the formation of the activated state of OH, which is much stronger at 308.9 nm than at 312.2 nm. The difference in the emission intensity at the two wavelengths is proportional, both to the mass and photochemical reactivity of the hydrocarbons in the sample. The oxygen atoms are produced by passing an oxygen in argon source through a microwave cavity. Parameters of nozzle distances from the detector and water concentration in the sample were investigated and the optimum nozzle distance was found to be dependent on both the type of hydrocarbon in the sample and in the water concentration. In the paper, the sample air was dried and the nozzle distance set to optimize the measurement of auto exhaust. The instrument was zeroed by equating the output signal from each PMT with acetylene in the sample air since acetylene is a nonreactive species. The span is produced by introducing a known amount of ethylene and measuring the difference in the output signal from each PMT. Therefore, the instrument provides a quantitative measure of the reactive hydrocarbon in the sample in ethylene equivalent amounts. This measurement is directly related to the photochemical reactivity of the sample.

Another technique using the principle of chemiluminescence of the reaction of oxygen atoms with reactive hydrocarbons has been investigated.[8] The technique described is very similar to that of the previous instrument. A source of oxygen atoms produced in a microwave cavity is mixed with the ambient air sample in a reaction cell and the emission from the OH transition ($A^2\Sigma - X^2\pi$) is measured by a single photomultiplier tube at 306.4 nm. The optical filter used is centered at 305.9 nm and has a bandwidth at half peak transmittance of 25.0 nm ±5 nm. By measuring the emission intensity through that entire waveband, all of the emission for the transition is measured regardless of the rotational state of the OH produced. The work described was intended to be demonstrative and the concentration of all hydrocarbons tested was 1000 ppm. No details of projected specifications were offered.

An analytical technique for measuring hydrocarbons based on the chemiluminescence of the reaction of hydrocarbons with active nitrogen was described.[9] The nitrogen source was activated by use of a 70 to 90 W microwave generator and the resulting analysis yielded results similar to hydrocarbon detection using a FID. This eliminated the potentially dangerous flame associated with FID's for some particular applications. It can be operated in a continuous mode for analysis of total hydrocarbons or in a pulsed mode for use with a gas chromatograph. Argon gas is used as the carrier since helium quenches the active nitrogen. The sensitivity of the instrument was increased significantly by adding HCl to make a solution of 1% HCl in the nitrogen. The detection limit for hydrocarbons was ~4 ng with the 1% HCl solution, while without HCl, the detection limit was ~200 ng. The technique can also be used to detect metal alkyls. The authors projected that sensitivities could be achieved for all hydrocarbon species that would be at least competitive with FID detection.

Another method for the detection of nonmethane hydrocarbons is using the principle of photoionization.[10] The ionizing radiation is generated by a sealed ultraviolet source. The instrument's response was independent of sample flow rate and it had a 90 percent response time of three (3) seconds. The sensitivity was 2 ppm full scale, the repeatability was better than ±1 percent, and both the span and zero drift were less than one percent over a two-week period. The technique is a carbon counter and gives a response similar to an FID except it is nonresponsive to methane. The signal is continuous; therefore, it gives a continuous measurement of nonmethane hydrocarbons that is much simpler than chromatographic techniques using an FID.

The concept of using a photoionization mass spectrometer for analysis of stratospheric air from a balloon platform has been offered by R. W. Stewart (NASA Goddard Space Flight Center). While electron impact ionization results in an apparent concentration of 1 ppb for low masses in air, photoionization does not. The normal constituents of air (N_2, O_2, Ar, CO_2, Ne, Kr) cause responses of approximately 1 ppb for masses between 12 to 48 except 24-27, 31 and 37; therefore, those masses are regarded as undetectable by electron impact ionization. This effect is not seen using the photoionization technique. Ambient air was supplied by a mechanical pump, and a pressure-activated servo valve opened the sample line at the appropriate altitude. Four (4) UV flux lamps supplied the ionizing radiation. Both the analyzer and ionizer were pumped by a liquid helium cryopump using 6 liters of liquid helium and 11 liters of liquid nitrogen. The existing instrument can analyze NO, H_2S, CS_2 and several hydrocarbons with a minimum detectable limit of 0.1 ppb with 10% accuracy in 0.5 to 5 minutes.

Proposed design improvements include the use of a krypton Xenon lamp system which would increase the ionizing flux by a factor of ten and increase the detection limit to 0.01 ppm for species that are presently sensitivity limited (NO_2, NH_3, HCl and sulfur species). Use of an argon lamp could increase the capability for species detection to include HNO_3, H_2O_2, H_2CO, OCS, CH_3Cl, C_2H_6, C_3H_8 and others. A molecular beam inlet system may permit the detection of highly reactive radical species and increase the sensitivity for species that are background-limited.

The advantages of such a system are that it has a high level of discrimination against major components of air and there is no high temperature filament that could have chemical and outgassing effects on the sample. Also, it could be directly calibrated by gas mixtures traceable to NBS, it can analyze a variety of components, and with molecular beam inlet, it could be used to analyze radicals. If the instrument can be operated aboard a stratosphere balloon, it could probably be installed on an aircraft and used for tropospheric analysis.

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2.6 Sulfur Species

2.6.1 Flame Photometric Principle. - Since the FPD detection principle is a method that responds selectively to sulfur atoms in the sample volume, it is not limited to SO_2 alone (Section 2.3). The same principle is applicable to any sulfur-containing molecule that can be separated in the sample volume and burned in a hydrogen-rich flame. Due to this feature of FPD detection, a semicontinuous method for measurement of ambient levels of hydrogen sulfide, methyl mercaptan, dimethyl sulfide and dimethyldisulfide is possible using chromatographic separation and FPD analysis. That is, each compound is identified in a single sampling/analysis run. Two leading references were located. In the method of Stevens et al.,[1] the sample is routed directly through the column without preconcentration. Individual species may be detected down to ~2 ppb concentration. The sensitivity is not defined. The response time would vary depending on the choice of column and carrier flowrates; therefore, discrete samples could be taken probably every 10 to 20 minutes.

The second method is similar but involves a preconcentration on sodium bicarbonate.[2] The sensitivity is increased to approximately 0.1 ppb but the analysis time would be lengthier than the direct injection.

Neither of the above methods have been tested aboard an aircraft. Problems similar to those encountered with FPD SO_2 analyzers would be expected.

Measurement of carbonyl sulfide (COS) can be accomplished through a variation of the GC-FPD method. In a paper by Baumgardner et al.,[3] a system is described in which a silver scrubber was employed to quantitatively remove H_2S and allow 98 percent of SO_2 and COS to pass to the chromatograph/FPD system. The minimum detectable concentration of COS is given as "low ppb." The arrangement of apparatus and problem areas expected, if this system were to be employed aboard an aircraft, would be similar to those described in Section 2.3.1.

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2.7 Ammonia

2.7.1 Tropospheric Concentrations. - An important consideration in the assessment of ammonia methods is the instrumental sensitivity which will be required to measure tropospheric levels of this species. The determination of an acceptable sensitivity is complicated by the lack of agreement for a tropospheric background concentration. Several investigators who used various methods have arrived at widely differing values for tropospheric ammonia concentrations. Part of this disagreement could be explained by the large variability in space and time which appears to exist for this species; however, there are also residual differences which cannot be so explained.

Measurements of nonurban, surface ammonia concentrations have generally ranged between 1 and 10 ppb in the temperate zone and between 5 and 30 ppb in the tropic zone. Oceanic air concentrations are, in general, lower than continental air concentrations (e.g., 0.2 to 7.0 ppb). Review of these measurements can be found in the 1977 National Academy of Science Report on Ammonia[1] and in reference 2.

Information concerning the vertical distribution of ammonia in the atmosphere is sparse. Measurements were made from airborne platforms which indicated that the ammonia concentration at an altitude of 3 km above the surface of Western Germany was approximately 1.9 ppb in winter and 7.6 ppb in summer.[4] The surface concentrations were roughly a factor of 2.4 larger than those at 3 km. These values are supported by recent measurements by NASA-Langley where ammonia concentrations in the 1-2 ppb range at altitudes of 1.6 to 3.0 km in June.[5]

The above measurements appear to be in conflict with other studies which suggest that atmospheric ammonia levels are much lower. High resolution absorption spectroscopic measurements were made in which ammonia, if present, was at concentrations below the detection limit of the instrument.[6] If the vertical distribution of ammonia is assumed to be uniform, this research indicated that its concentration was less than 0.08 ppb. Arguments have been made from theoretical grounds that ammonia concentrations would have to be on the order of 0.001 to 0.010 ppb along the east coast in order to explain acidic sulfate and precipitation chemistry measurements.[7]

In view of these discrepancies, it would be desirable to have instrumental sensitivities on the order of one-half of Kaplan's upper limit for atmospheric ammonia concentrations (i.e., 0.04 ppb). This would insure that the in situ instrument would be able to detect the ammonia. However, since all other measurements place the atmospheric ammonia concentrations larger than 0.2 ppb, a sensitivity of 0.1 ppb would probably be acceptable.

2.7.2 Commercially-Available Instruments. - The general principle of this approach is the modification of the conventional NO/NO_x chemiluminescence instrument by the installation of a thermal converter which is capable of transforming ammonia into NO.[8,9] The thermal converter which is normally used with these instruments (e.g., molybdenum at 450° C) will not convert ammonia. However, a higher temperature converter (e.g., platinum at 800° C) is capable of doing so with approximately 100 percent efficiency.

The Thermal-Electron Model 14T utilizes this principle. This instrument has both types of converters, three reaction cells, one photomultiplier tube and a light chopper, and yields measured values for ammonia, NO, NO_2, NO_x and total nitrogen. The specifications for this instrument are listed in the appendix. The manufacturers' specified sensitivity is 4 ppb which is inadequate for tropospheric ammonia measurements.

Better sensitivity has been obtained using a slightly different approach. AeroChem Research Laboratories (Princeton, New Jersey) built a prototype NH_3 instrument for EPA which has a sensitivity (twice the noise level) of 0.5 ppb.[10] This instrument utilizes both types of converters, two reaction cells and two photomultiplier tubes and yields measured values for NO_x and total nitrogen.

An alternate approach for measuring ammonia has been suggested which utilizes an ammonia scrubber, two high-temperature converters and two photomultiplier tubes.[10] This configuration produced results which were similar to that of the AeroChem unit.

It appears that the primary area of difficulty with this technique is the sensitivity of the basic chemiluminescence NO/NO_x instrument rather than the efficiency of the ammonia-to-NO conversion process. Other investigators have reported about the iluminescence instruments which measure NO, NO_2 or HNO_3 to have far greater sensitivity than the chemiluminescence ammonia instruments which have been fabricated to date. For example, a mobile chemiluminescence NO/NO_x instrument has been constructed which has a sensitivity of 0.02 ppb and a cycle time of one minute.[11] Similar sensitivity has been reported by other investigators.[12] An instrument has been described which has an approximately 0.007 ppb NO sensitivity and a 0.010 ppb NO_2 sensitivity.[13]

As a result, it appears that it is feasible to construct a chemiluminescent ammonia instrument with a sensitivity of well under 0.04 ppb.

Mass spectroscopy has been extensively used in the study of gaseous and particulate organic compounds in the atmosphere; however, little work has been done to measure inorganic compounds in the atmosphere by means of this technique. Sciex, Inc. (Thornhill, Ontario, Canada) operates a mass spectroscopic instrument (TAGA™ 2000) which has a sensitivity of 0.001 ppb for ammonia. This sensitivity is made possible by the use of atmospheric pressure chemical ionization to separate trace gas molecules in air samples prior to their introduction into the mass spectrometer itself.[14,15] This can be contrasted with the gas chromatographic techniques which are normally utilized to achieve separation for mass spectrometers. In the single ion monitoring mode, the instrument has a real-time response time on the order of ten seconds. Data were presented in which atmospheric ammonia concentrations in the 1 to 2.5 ppb region were measured in the vicinity of a local emissions source.[14] In addition to these advantages, Sciex's TAGA™ 2000 System has the additional advantage that it has been operated for several years in a mobile laboratory. This fact demonstrates the technique's portability and suggests that it could be used in an airborne configuration. However, it should be noted that the total weight of the instrument (including a computer) is 450 kg.

2.7.3 Research or Prototype Instruments. - The Laser/Opto Acoustic measurement technique is based on the absorption of radiation from a tunable laser by gas in a sample cell. This produces vibrational excitation in the molecules of interest and a consequent increase in the pressure of the gas inside the cell. This can be measured by a sensitive acoustic microphone. Max and Rosengren[16] constructed an opto-acoustic gas detector with a linear range of 0.1 to 10 ppm of ammonia. The minimum detectable concentration was estimated to be 2.8 ppb based on the background signal from filtered air. By subtraction of this background signal from actual samples, it was estimated that the sensitivity could be further improved by an order of magnitude (i.e., 0.3 ppb). McClenny and Russwurm[17] presented similar results for a system specifically designed for ammonia measurements. They obtained a linear response of between 17 and 70 ppb for ammonia in dry air and estimated a minimum detectable (noise equivalent) concentration of 1.4 ppb. Again, it was estimated that an order of magnitude improvement in sensitivity could be obtained by modifying the design of the instrument. These results suggest that this technique potentially has the sensitivity which would be required for tropospheric ammonia measurements.

Rosengren[18] has recently developed an opto-acoustic detector with a much lower background signal. By passing a second beam of light through the sample cell, absorption losses due to the windows of the cell can be eliminated. As a result, it is expected that the detector should measure pollutant gases at the 0.01 ppb level.

McClenny and Russwurm point out that the technique has a problem with respect to interferences from tropospheric gases. A carbon dioxide concentration of 330 ppm has an interference equivalent of 10.3 ppb while a water vapor concentration of 13,000 ppm has an interference equivalent of 22.0 ppb. Consequently, one would expect a total interference equivalent of about 30 ppb at sea level. This is considerably larger than the background signal levels which were obtained for laboratory air. It was suggested that this problem could be circumvented either by measuring the increase in pressure at several wavelengths or by alternately passing the sample air through an ammonia scrubber. Nevertheless, this level of interference could pose serious problems for the measurement of ammonia at the sub-ppb level.

Vibration effects may represent an additional problem in adapting this technique for airborne measurements. Because a microphone is being used as the basic detection element, the noise level of the instrument could be increased if the instrument mounting is not vibration-isolated from the airborne platform.

Microwave rotational spectroscopy is based on the absorption of microwave energy by transitions between purely rotational states of gaseous molecules. The only instrument which has been built to measure ammonia by this method uses a Gunn-diode coupled to a high-Q resonate cavity to generate the microwaves and to provide an absorption cell for the measurements.[19,20] In order to obtain sharp, intense absorption lines, the cavity is maintained at a vacuum of 0.07 torr. Ammonia molecules enter the cavity by permeation through a two-stage dimethyl-silicone membrane molecular separator.

The instrument has a minimum detectable limit of 10 ppb and a linear range to 20 ppm.[21] The response time is 30 min to 90% of the final value. The zero drift is less than 0.5 percent of full scale per 24 hours while the peak response stability showed less than 2 percent deviation from the peak maximum in 160 days. Because of the sharpness of the ammonia absorption transition at 23,870.1 MHz and because of the frequency stability of the Gunn-diode/resonant cavity assembly, the technique has no known interferences. The instrument (excluding the vacuum pump) has a weight of 45 kg. It requires 10 amps of power at 115 Vac.

In its current configuration, the instrument does not have the sensitivity to measure tropospheric levels of ammonia. Although it should be possible to improve the sensitivity by redesign of the Gunn-diode/resonant cavity or by the use of more sophisticated electronics, no work is in progress in this area.

Ammonia can also be measured in the atmosphere by Fourier transform infrared spectroscopy. This technique is based on the absorption of infrared radiation at specific spectral frequencies corresponding to vibrational-rotational energy transitions in gaseous molecules. The infrared radiation is produced by a broad-band source and is modulated by a Fourier transform spectrometer before entering the absorption cell. The radiation is measured by an infrared detector after it has traversed the absorption cell. An infrared absorption spectrum is generated from the signal coming from the detector by a computer using inverse Fourier transform algorithms.

The concentration of gaseous molecules in the absorption cell is calculated from the absorption spectrum.

For tropospheric measurements, this technique is preferable over remote-sensing applications of Fourier transform spectroscopy. Airborne stratospheric absorption spectroscopy uses the Sun as its radiation source and thereby can generally provide only an estimate of the total atmospheric burden of a species of interest.[22] Better vertical resolution has been obtained in balloon-borne measurement programs by measuring at various solar zenith angles.[23] However, this approach does not appear to be feasible for tropospheric measurements. As the in situ approach uses both a local radiation source and a known absorption path, point measurements of a species' tropospheric concentration can be made.

Fourier transform spectroscopy has been used for ground-level measurements of ammonia in ambient air.[24,25] The absorption cell was an eight-mirror White cell with a base path of 23 m. It yielded an overall pathlength of approximately 1 km. Over the course of a two-year monitoring program, a number of spectra were identified as having detectable concentrations of ammonia. Because the lowest concentration observed in the spectra was 4 ppb, it was inferred that this represented a minimum detectable ammonia concentration for this instrument. However, theoretical calculations suggest that the technique should be able to achieve a minimum detectable concentration of 0.2 ppb for a pathlength of 500 m.[26] As a result, this technique potentially has the sensitivity for tropospheric measurements. Additionally, the 5-min sampling period which was used for the measurements indicates that reasonable spatial resolution can be attained with this technique.

The only potential problem in applying this technique to airborne monitoring is the sensitivity of the absorption cell to vibration. Several investigators have noted that building vibrations have been a concern.[25,27] Presumably, this is because of the effect that such vibrations would have on the alignment of the absorption cell's optics. As a result, the optics of any Fourier transform infrared spectrometer would have to be vibrationally isolated from its airborne platform if the technique is to be used to obtain tropospheric measurements.

A technique for the measurement of ammonia is based on the conversion of gaseous ammonia into aerosol particles and the subsequent measurement of those particles with a commercially-available condensation nuclei counter. Because there is a reproducible, linear relationship between the ammonia concentration and the number of particles which are produced, the former may be inferred by measurement of the latter. To obtain this conversion, the sample airstream is first passed through a wetted-wall reactor from which gaseous hydrogen chloride diffuses into the sample airstream. The reacting mixture is then passed into a residence flask which allows sufficient time for the formation of an ammonium chloride aerosol which is subsequently measured in the condensation nuclei counter.[28,29]

In one instrument which utilized this technique, a sensitivity of 20 ppb and a maximum range of 8 ppm was obtained.[30] The temperature of the wetted-wall reactor and the aqueous concentration of hydrogen chloride in the reactor were found to be controllable variables which influenced the relationship between ammonia concentration and aerosol production. An order of magnitude increase in sensitivity is expected if the reactor temperature were lowered from 20 to 13 degrees Celsius.

As the result of research into possible military applications of ammonia-particle counters as personnel sensors, an instrument of greatly increased sensitivity was developed at the General Electric Research and Development Center. The gaseous ammonia was reacted with gaseous hydronium ion clusters to form an ammonium ion cluster. The hydronium ions were formed from electric arcs or radioactive sources. The ammonium ion cluster was then reacted with gaseous hydrogen chloride to form an ammonium chloride aerosol. As the reaction between the ammonium ion clusters and hydrogen chloride is much faster than the reaction between ammonia and hydrogen chloride, more aerosol particles were formed using this modified technique. A sensitivity of 0.5 ppb was reported, and as a result, this technique approaches the sensitivity which is required for tropospheric measurements of ammonia.

Two potential problems were found for this technique. The first is a lack of selectivity. For example, low concentrations of carbon monoxide apparently inhibit aerosol formation. It is unclear how serious this problem would be for tropospheric measurements. The second problem is a sensitivity to variations in the relative humidity of the sample air. However, this could be overcome by the use of a cloud chamber which functions both as a wetted-wall reactor and a condensation nuclei counter.

The Environment/One Corporation (Schenectady, New York) has fabricated ammonia-particle counters on a custom-order basis in the past and would consider fabricating additional instruments on the same basis.

Another method known as mercury-sensitized luminescence is based on the measurement of near-ultraviolet light emission from the decay of an excited mercury-ammonia complex.[31] The complex is formed by reacting gaseous ammonia with excited mercury atoms which can be generated by the ultraviolet irradiation of mercury vapor in nitrogen. It was found that the oxygen in the sample would quench the light emission. To circumvent this problem, the sample was injected onto a gas chromatographic column in which the ammonia was separated from the oxygen. The column effluent was mixed with mercury vapor in nitrogen prior to entering the irradiation cell. The ultimate sensitivity of this technique is determined by the degree to which the chromatographic column can separate the ammonia in the sample from oxygen. For the instrument which was discussed, a sensitivity of 4 ppb was achieved. This sensitivity is not adequate for measurement of tropospheric levels of ammonia.

The sensitivity of the chemiluminescence technique for the determination of ammonia in ambient air has been significantly improved by the addition of a gas chromatographic column on the sample inlet of the instrument.[32] The column is used to separate ammonia from NO, NO_2 and other compounds which are present in an injected sample for air. At different retention times, the various compounds emerging from the column are combined with an oxygen stream and enter a high-temperature converter in which they are converted into NO. Subsequently, they enter the instrument where they are detected by chemiluminescence with ozone. The output of the instrument is treated as a chromatogram. The analysis cycle has a period of five minutes.

The chromatographic column acts as a concentrator of the ammonia in the injected sample. An "amplification factor" of 30 was attained as a result of this process. Because the commercially-available instrument which was used had a background noise level of 10 ppb, the estimated minimum detectable concentration was 0.5 ppb of ammonia. It was noted that the amplification factor could be increased by decreasing the oxygen flowrate into the converter. The intrinsic sensitivity of the chemiluminescence NO_x instrument could be improved by decreasing the sample flowrate and the size of the reaction chamber and by the use of a less noisy photomultiplier tube. It is impossible to use the ultra-sensitive chemiluminescence NO_x instruments which are discussed elsewhere because their high sample flowrate requirements would conflict with the low sample flowrates associated with the chromatographic column. In general, this technique is capable of attaining the sensitivity which would be required for tropospheric measurements of ammonia. It would have the advantage of being a real-time instrument.

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2.8 Real-Time In Situ Hydroxyl Radical Methods

2.8.1 Tropospheric Concentrations. - Over the past few decades, recognition of the importance of the hydroxyl radical in atmospheric chemical cycles has grown. The presence of the hydroxyl radical in the atmosphere was first demonstrated by the observation of infrared vibration-rotation emission lines (Meinel bands) in the night sky. This light is associated with the chemiluminescent reaction in the upper mesosphere and lower thermosphere of atomic hydrogen with ozone to form an excited hydroxyl radical. This discovery led to the development of theories describing the important role of this radical in the hydrogen-oxygen cycle, in the conversion of methane and carbon monoxide into carbon dioxide, and in other photochemical processes. In the troposphere, the hydroxyl radical is also a significant contributor to the formation of photochemical smog by being the main chain carrier in the oxidation of hydrocarbons.

Despite such recognition, very few measurements have been made of the concentration of the hydroxyl radical either in the troposphere or in other portions of the atmosphere. This is due, in large part, to the extremely low levels at which this radical is present in the atmosphere. Theoretical calculations have predicted that the tropospheric hydroxyl radical concentration is on the order of tens to hundreds of parts per quadrillion (ppq). In order to measure such low concentrations, very sensitive and sophisticated methods have had to be developed. Measurements of the tropospheric hydroxyl radical concentration have been reported only in the last seven years. In general, these measurements are consistent with the theoretical predictions; however, there is substantial spatial and temporal variations in the reported values. This may be the result of real fluctuations in the hydroxyl radical concentration and/or residual uncertainties in the calibration of the methods themselves. The amount of data available is too sparse to allow a judgement as to the validity of any single measurement or any set of measurements.

Surface measurements have been made at locations which range from isolated remote areas to polluted urban areas. Hydroxyl radical concentrations which varied between 21 and 46 ppq were measured during April near the crest of an isolated, 1-km tall mountain in New Zealand.[1] On the upwind side of the small, nonindustrial city of Pullman, Washington, the concentrations were between 13 and 145 ppq for measurements which were made between October and July.[1] No seasonal trends were evident in the few values which were reported. These values were approximately equal to those which were obtained in the vicinity of the small, nonindustrial of Julich, Germany which lies in the Ruhr Valley.[2] Between August and November, hydroxyl radical concentrations ranged between less than 85 to 298 ppq. A slight seasonal trend was seen in the reported data with August values averaging 116 ppq, September values averaging 64 ppq, October values averaging 57 ppq and the two November values being 0 ppq. However, the large variability of the data for each month and the large uncertainty which was assigned to each measurement reduces the impact of the trend in the data.

Higher hydroxyl radical concentrations have been observed in more polluted urban areas. In Nashville, Tennessee, values of 85 and 145 ppq were measured during August.[1] Diurnal variations were found for measurements which were made in Dearborn, Michigan during August.[3] On sunny days, daily maximum concentrations varied between 1064 and 2340 ppq and occurred during the afternoon hours. On rainy or cloudy days, the hydroxyl radical concentration was below the minimum detection level of 213 ppq. No data were reported for nighttime measurements.

Very few measurements have been reported concerning the vertical distribution of the hydroxyl radical in the troposphere. However, in situ, airborne measurements have been made which suggest that hydroxyl radical concentrations in the free troposphere are substantially larger than those at the remote surface. Background air measurements have been made in the vicinity of the Four Corners power plant in New Mexico.[4] At an altitude of 2 km, the hydroxyl radical concentration varied between 395 and 536 ppq in the late morning hours during July. A corresponding measurement at an altitude of 7 km yielded a value of 273 ppq. These values are in fair agreement with airborne measurements which were made in the vicinity of El Paso, Texas during October.[5] At an altitude of 7 km, the hydroxyl radical concentration was 290 ppq during the early afternoon hours.

The concentration dropped to below the minimum detection limit of 166 ppq at night.

The hydroxl radical concentration has also been measured in the tropical, marine atmosphere.[5] These measurements were made during October in the Gulf of Mexico approximately 150 km to the east of Tuxpan, Veracruz, Mexico. At an altitude of 7 km, the hydroxyl radical concentration was 671 ppq. This increased slightly to 697 ppq at an altitude of 11.5 km. At night, these concentrations decreased to below the minimum detection limits of 166 and 284 ppq, respectively.

2.8.2 Research or Prototype Instruments. - The basic principle behind the measurement of the hydroxyl radical by resonance fluorescence is the excitation of the hydroxyl radical molecule from its ground electronic state to its first excited electronic state by the absorption of light which is followed by the fluorescence emission of light as the molecule decays back into its ground state. The intensity of light, at the wavelength associated with this decay, which is emitted by a volume of air is proportional to the hydroxyl radical concentration in that volume.

The initial application of this technique was for the measurement of the hydroxyl radical concentration in the mesosphere.[6,7] Resonantly scattered solar radiation under evening twilight conditions produced sufficient quantities of excited molecules to allow measurements to be made without the use of artificial light sources. The fluorescence radiation was measured by an Ebert-Fastie scanning spectrophotometer which was carried into the mesosphere by a sounding rocket. The near-ultraviolet $A^2\Sigma$-$X^2\pi$ transitions at 306.4 and 309.0 nm were monitored. Volume densities which ranged from 3.5×10^6 to 5.5×10^6 hydroxyl radicals/cm^3 were measured between 45 and 70 km altitude.

Because of the strong absorption of ultraviolet light by ozone in the stratosphere, the penetration of the ultraviolet portion of the solar spectrum is attenuated greatly in the stratosphere and troposphere as compared to the mesosphere. This prevents solar radiation from being used as the source of measurable quantities of excited hydroxyl radical molecules in these regions of the atmosphere. Additionally, collisional deactivation ("quenching") of the excited state of the hydroxyl radical by molecular nitrogen and oxygen in the more dense regions of the atmosphere causes reduced fluorescence efficiencies which makes the measurement of the hydroxyl radical concentration more difficult. As a result of these problems, artificial light sources have to be used in the lower portions of the atmosphere to obtain enough fluorescence radiation for measurement. Two types of sources, resonance lamps and dye lasers, have been used in this application.

A plasma discharge resonance lamp has been used in measurement of the hydroxyl radical concentration at altitudes between 29 and 43 km.[8,9] This light source consists of a microwave discharge lamp and a sealed quartz tube which contains helium at a pressure of approximately 2 mm of mercury and a trace amount of water vapor. As microwave energy at 2.4 GHz is pumped into the quartz tube, a plasma is formed and light is emitted from the tube. This light is associated with $A^2\Sigma$-$X^2\pi$ electronic transitions and extends in wavelength from 306.4 to 312.0 nm. As such, it can be used to excite sampled hydroxyl radicals from the ground electronic state ($X^2\pi$) into the first excited electronic state ($A^2\Sigma$).

The instrument for measuring stratospheric hydroxyl radical concentrations consists of an OH resonance lamp and a photon-counting photomultiplier with its associated electronics and optics. These are mounted in an aerodynamically-shaped pod or "nacelle" through which sample airflows. The light from the lamp illuminates a volume of air from a direction which is perpendicular to that of the airflow. The optics of the photomultiplier are focused on this volume along an axis which is perpendicular to both the airflow and the illuminating light. A narrow bandpass interference filter whose transmission maximum is centered at 309.0 nm is included in the optics so that only a single vibrational band of the fluorescence radiation reaches the photomultiplier. The instrument is carried aloft to the stratopause by balloon and then is lowered through the stratosphere by a stabilized parachute. As the instrument descends, air passes through the nacelle and its hydroxyl radical concentration is measured. Periodically, the background countrate of the photomultiplier is measured by releasing gaseous hydrogen chloride at the entry throat of the instrument. This gas rapidly reacts with hydroxyl radicals and eliminates them from the sample air before the sensing volume is reached. The instrument is calibrated on the ground prior to each flight with a fast flow calibration apparatus which introduces known concentrations of hydroxyl radicals under conditions which simulate the stratospheric descent. Additionally, the calibraiton of the instrument during the descent is checked by measuring the lamp flux with a second photomultiplier which is positioned along the axis of illumination.

Using this instrument, hydroxyl radical volume densities which ranged between 4.5×10^6 to 2.8×10^7 molecules/cm^3 were measured at altitudes between 30 and 43 km. It should be noted that the instrument was not capable of performing measurements below an altitude of 29 km because Raleigh-scattered light from the resonance lamp became competitive with the flourescence signal.

Lasers have been the favored excitation source for resonance flourescence measurements of tropospheric hydroxyl radical concentrations. The initial use of this source was for "proof of principle" measurements of the hydroxyl radical concentrations in laboratory air.[10,11] Rhodamine 6G and Rhodamine S dye lasers whose outputs were tuned to a wavelength of 564.4 nm were used as the primary source of the exciting radiation. In order to obtain light in the ultraviolet region, the output of the dye lasers were passed through a frequency-doubling ammonium dihydrogen phosphate crystal which produced second-harmonic light having a wavelength of 282.2 nm. An output energy of 0.1 μJ/pulse at the second-harmonic frequency was obtained for the Rhodamine 6G dye laser while the Rhodamine S dye laser produced energies of up to 6 mJ/pulse at the second-harmonic frequency.

The output of the dye laser was focused on a volume of laboratory air and the flourescence emission at a wavelength of 309.0 nm was measured with a photon-counting photomultiplier and either a single grating spectrometer or two spectrometers which were being operated in tandem. The flourescence radiation was measured in a direction which was perpendicular to the axis of the exciting radiation. Using the Rhodamine S dye laser, the detection limit of this apparatus was 200 ppq.

An important innovation which accompanied the use of lasers as an excitation source was the use of an exciting wavelength which is different from the wavelength of the flourescence radiation. This was made possible because of the monochromatic nature of the laser's output. This eliminated the problem of a high background signal from Raleigh scattering which was seen when a resonance lamp was used as the exciting source. The 282.2-nm wavelength of the laser source is associated with translation from the ν=0 vibrational state of the $^2\pi$ ground electronic state of the hydroxyl radical molecule to the ν=1 vibrational state of the $^2\Sigma^+$ excited electronic state. A portion of the molecules in the $^2\Sigma^+$ (ν=1) state undergo relaxation to the $^2\Sigma^+$ (ν=0) state. The flourescence radiation at 309.0 nm is associated with the transition from the $^2\Sigma^+$ (ν=0) excited state back to the $^2\pi$ (ν=0) ground state.

As part of these experiments, two potential interferences with this measurement technique were discovered. The first of these interferences is the generation of hydroxyl radicals by the exciting radiation via two-photon dissociation of water vapor molecules in the atmosphere.[12] This process involves the production of hydroxyl radicals in the ground state as the direct result of the dissociation of water vapor molecules which have been excited by the absorption of two photons. These artificially generated hydroxyl radicals will then be detected along with the previously existing hydroxyl radicals and will result in a falsely high estimate of atmospheric hydroxyl radical concentration. Because the intensity of the false flourescence signal exhibits a quadratic dependence on the intensity of the exciting radiation, the interference can be reduced to negligible levels by defocusing the beam of the exciting radiation so as to spread the light over a larger volume of air.

The second potential interference involves the production of hydroxyl radicals by the exciting radiation via the dissociation of ozone molecules in the atmosphere.[13,16] The exciting radiation dissociates ozone into molecular oxygen and metastable atomic oxygen. A small fraction of the atomic oxygen will react with water vapor molecules in the atmosphere to form hydroxyl radicals. These hydroxyl radicals will be detected and will lead to a falsely high estimate of the atmospheric hydroxyl radical concentration. Because the intensity of the false flourescence signal varies as a quadratic function of the intensity of the exciting radiation, this interference will also be minimized by reducing the intensity of the exciting radiation. Under surface conditions and with an ambient ozone concentration of 40 ppb, an intensity of less than 7.6 kW/cm^3 must be used to limit the hydroxyl radical concentration which is generated as a result of ozone dissociation to 213 ppq. This restriction on the intensity of excitation is more stringent than that imposed by the process of two-photon dissociation of water. It has also been found that the interference level can also be reduced by narrowing the pulsewidth of the exciting radiation.

The first measurements of tropospheric hydroxyl radical concentrations utilized the Rhotamine 6G dye laser/dual spectrometer apparatus which was described earlier.[3,10,11] The output energy of the second harmonic light was 0.2 mJ. The beam of the exciting radiation was focused to a strip 1 mm x 5 mm in the open atmosphere about 60 cm outside of a laboratory window and about 3 m above the ground. Because of the large focal strip and the resulting reduced intensity of the exciting radiation, the interferences from the dissociation of water vapor and ozone were minimized. The detection limit for this apparatus was 213 ppq.

Resonance fluorescence techniques using lasers as excitation sources have also been used for in situ airborne measurements of tropospheric hydroxyl radical concentrations.[4,5,14] The exciting source for this system is a frequency-doubled dye laser which has an output wavelength of 281.9 nm and an output energy in the range of 0.3 to 0.5 mJ to minimize ozone interference. The exciting radiation from the laser is brought to a focus in a sampling manifold which is located in the interior of the aircraft sampling platform. Tropospheric airflows through the manifold with a transit time of 30 ms to the point of sampling. This minimizes hydroxyl radical losses due to homogeneous reactions with carbon monoxide and methane. Six photomultipliers are located on the perimeter of the sampling manifold for measuring the fluorescence radiation. The light which enters the photomultipliers is filtered by an optical cell which contains a 1:3 mixture of pyridine in water and by an interference filter which has a 5 nm bandpass centered at 309.5 nm. The pyridine filter strongly absorbs the exciting radiation, but has a high transmission at the wavelength of the fluorescence radiation. Instead of using photon-counting techniques as are more typically used, this system utilizes gated charge integrators to accumulate the signals from the photomultipliers. Sampling periods are on the order of 5 to 15 min.[12] This system has a sensitivity of 20 ppq which is approximately an order of magnitude better than the previously described system. A total of approximately 80,000 km has been flown with this system which suggests that it is well-suited for airborne monitoring.

Another in situ technique which has been used to obtain estimates of tropospheric hydroxyl radical concentrations is long-path resonance absorbance. This approach is closely related to the resonance fluorescence technique as $A^2\Sigma^+$ to $X^2\pi$ resonance transitions are measured in both techniques. However, the absorption, rather than the emission, of light by hydroxyl radicals is measured in this technique.

This technique has been used for ground-based spectroscopic studies of the terrestrial hydroxyl radical abundance.[15] The source of radiation was solar Fraunhofer emission lines at approximately 308.0 nm. These emission lines are coincident with hydroxyl radical resonance transmission lines. The intensity of sunlight at this wavelength was measured with an interferometric optical spectrometer which used four Fabry-Perot etalons in series. Over the course of a day, changes in the intensity were attributed to changes in the slant optical path. From these intensity measurements, slant column hydroxyl radical abundances could be calculated.

In an altered form, this technique has been applied to in situ tropospherical measurements of the hydroxyl radical concentration at the surface.[2] A frequency-doubled Rhodamine 6G dye laser is used to provide a source of light with a wavelength of 308.0 nm. This light is directed at a mirror which is located at a distance of 3.9 km from the light source and is then reflected back to the laboratory where it passes through a double grating spectrometer and is then recorded on a photographic plate. After the plate is developed, it is measured by a densitometer and the hydroxyl radical concentration is calculated from the optical density of the absorption line relative to the optical density at nearby wavelengths. Using this technique, a detection limit of 85 ppq is obtainable for a pathlength of 7.8 km. Exposure times vary between 1 and 65 minutes.

The estimates of the tropospheric hydroxyl radical concentration which are obtained by this technique are accompanied by uncertainties which often exceed the estimated value. Much of this uncertainty was due to noise in the densitometer traces arising from the graininess of the photographic plate's emulsion. It was suggested that the sensitivity of the technique could be improved by replacing the photographic plate with an electronic detection system.

This technique could be adapted for airborne in situ measurement by the use of a multiple-traversal White cell. As is described in other sections of this report, kilometer pathlengths have been attained with such cells. Care would have to be taken to vibrationally isolate the entire optical bench from the aircraft platform.

Another technique which has been used to measure tropospheric hydroxyl radical concentrations involves monitoring the oxidation of radioactive carbon monoxide to carbon dioxide.[1] Although there may be some difficulty in adapting this technique to aircraft platforms, it deserves mention because of the outstanding sensitivity which is claimed for this technique.

The basic concept behind this technique lies in the observation that the largest sinks for the hydroxyl radical in the atmosphere are the oxidation of carbon monoxide and methane. Current atmospheric chemistry models indicate that 90 percent of carbon monoxide in the atmosphere is oxidized by the hydroxyl radical. Consequently, the hydroxyl radical concentration in a captive air volume can be determined by measuring the carbon monoxide concentration and the rate at which it is oxidized.

The apparatus which is used to perform this measurement is basically a small irradiation vessel or "smog chamber" which is constructed out of transparent Teflonℓ film. The volume of this vessel is 100 liters. The vessel must be transparent in order for sunlight to maintain a steady-state hydroxyl radical concentration within the vessel as is the case in the atmosphere. The measurement process is begun by filling the vessel with ambient air and then sealing the vessel. Carbon monoxide which has been labeled with carbon-14 is then injected into the vessel. At periodic intervals, a 2 to 5-liter sample of air is withdrawn from the center of the vessel and is passed through freeze-out loops. A portion of the labeled carbon monoxide will have been converted to labeled carbon dioxide by reaction with hydroxyl radicals. This carbon dioxide will be trapped in the freeze-out loops. The loops are then removed and brought to room temperature. The contents of the loops are then flushed into a radiation detector for analysis. The total irradiation period is on the order of 200 seconds. Analysis may take place in the laboratory at a later time.

The sensitivity of this method is approximately 1 ppq with an estimated experimental error of 50 percent.

2.8.3 Hydroperoxy Radical Measurements. - The hydroperoxy radical (HO_2) is another important radical involved in tropospheric photochemistry. Like OH, the HO_2 radical is highly reactive and present in the troposphere at very low concentrations. Therefore, similar problems exist in the sampling and measurement of HO_2 as those discussed for OH. One method for the determination of HO_2 has been reported.[17] The technique is electron paramagnetic resonance (EPR) spectrometry. This involves measuring the response of electron spin to the influence of a strong magnetic field. The analytical capability of this method, however, is not sensitive enough to measure atmospheric concentrations of HO_2 and, therefore, a preconcentration step is required. The preconcentration technique used is matrix isolation. In this technique, a sample is mixed with CO_2 and drawn by a rod, cooled by liquid nitrogen. As the gas mixture comes in contact with the cooled rod the HO_2 molecules in the sample are frozen into a matrix consisting mainly of solid CO_2. The cold temperature and isolation in the matrix keep the HO_2 molecules stable until the measurement can be made. The prototype instrument of this description has been flown on a balloon platform for stratospheric measurements of HO_2. Considerable signal processing is required and calibration procedures are not yet well-defined. The calculated HO_2 concentration from the EPA spectra was 3×10^2 cm^{-3}. Because of calibration problems this figure has an uncertainty of about a factor of 3.

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2.9 Nitric Acid

2.9.1 Tropospheric Concentrations. - Until the past decade, no information had been available on tropospheric concentrations of nitric acid. This changed in the early 1970's as the result of concern which had developed over the hypothesized adverse impact of nitrogen oxides emissions from supersonic transports on stratospheric ozone concentrations. Stratospheric nitric acid acts as a holding reservoir for nitrogen oxides and also as a sink for them via slow transport through the tropopause which is followed by rapid washout in the troposphere. Because of this concern, analytical techniques were developed to measure nitric acid concentrations in the stratosphere. These techniques were subsequently used for tropospheric measurements. In general, a consistent picture has developed from reports of these measurements; however, care should be taken to distinguish real tropospheric measurements from those which may be influenced by anthropogenic pollution sources.

Surface measurements have been made in the equatorial Pacific region between 4°N and 9°S at about 170°W.[1] These may provide the best estimate of the global background nitric acid concentration. Ten (10) filter samples were collected over a period of 20 days. The range of the values was from 0.014 to 0.068 ppb and the mean value was 0.038 ppb.

Similar measurements in marine areas and remote continental areas were made as part of Project Gametag.[2] Filter samples were collected at altitudes between 0.2 and 7 km on flights which ranged from 70°N to 24°S. The measured concentrations, under conditions which were outside of urban influences, varied from less than 0.02 to 0.3 ppb. Most of the values were below 0.15 ppb.

Nitric acid concentrations which were measured in other remote and rural areas fell into the same general range when anthropogenic contamination was not present. In field studies on a mountaintop in rural central Japan, the gaseous nitrate concentration varied between 0.02 and 0.6 ppb.[3] At a remote site in the Rocky Mountains west of Boulder, Colorado, measured values for the nitric acid concentration were commonly around 0.05 ppb and often were below the instrument's detection limit of

0.03 ppb for long periods of time. The nitric acid concentration at this site reached 0.1 ppb only in periods of obvious pollution (i.e., there were concurrent high nitrogen oxide concentrations). While anthropogenic contamination did not occur frequently at this site, it had a much larger impact at a nearby rural site which was to the east of Boulder.[4] Although the nitric acid concentration was frequently below the instrument's detection limit, it was more commonly found to be between 0.5 and 5 ppb. This problem of anthropogenic contamination was also experienced at a rural site on the west coast of Sweden.[5] Although gaseous nitrate concentrations generally were less than 0.5 ppb, values as high as 3.6 ppb were observed. Episodes of such high gaseous nitrate readings were linked to the long-range transport of pollutants from anthropogenic sources. In one episode, maxima in the gaseous nitrate concentration were coincident with maxima for particulate H^+, NH_4^+ and SO_4^{2-}, as well as aerosol number concentration in the 0.4 and 0.6 micrometer-size region. Back-trajectory analysis revealed that the air parcels associated with the maxima had passed over industrial areas in continental Europe or in southern England during the preceding 72 hours.

Although little information has been published concerning the vertical distribution of nitric acid in the troposphere, the data appear to be reasonably consistent. In early flights in Project Gametag, the nitric acid concentration was on the order of 0.08 ppb in the lower 4 km of the troposphere and on the order of 0.12 ppb in the region from 4 to 8 km altitude.[2] Later measurements during Project Gametag were obtained for the equatorial Pacific region between 8°N and 9°S.[1] Nitric acid concentrations ranged from 0.08 to 0.20 ppb in the free troposphere (at 5.5 km altitude) and varied from less than 0.05 to 0.09 ppb within the boundary layer (at 0.27 to 0.37 km altitude). These values can be compared with the previously mentioned surface measurements of 0.014 to 0.068 ppb which were also collected in this region. Total nitrate measurements have also been made in the vicinity of the troposphere as part of NASA's GASP Program.[6] Filter samples were collected at altitudes from 8.8 to 13.7 km. During the winter-spring period, total nitrate concentrations varied from about 0.05 to about 0.15 ppb below the tropopause and from about 0.12 to about 0.3 ppb above the tropopause. Total nitrate concentrations were significantly less during the summer-fall period. Below the tropopause, they were about 0.08 ppb while they ranged between about 0.07 and about 0.016 ppb above the tropopause. From this and other data, it was suggested that the nitrates at this altitude have a predominately stratospheric source.

An acceptable analytical method for measuring tropospheric nitric acid concentrations should have a sensitivity which is on the order of one-half of the expected minimum concentration. In general, these reports suggest that this would correspond to a nitric acid concentration of 0.007 ppb for near-surface measurements. For measurements in the free troposphere (e.g., at an altitude of 5 km), a sensitivity of 0.02 ppb would be required.

2.9.2 Research or Prototype Instruments. - The principle behind the measurement of nitric acid by chemiluminescence is a variation on the technique which is used for the measurement of nitrogen dioxide. Nitrogen dioxide is determined by the subtraction of simultaneous or consecutive measurements of nitric oxide and total oxides of nitrogen in the same chemiluminescence instrument. Nitric oxide is directly measured by the instrument. However, total nitrogen oxides are determined by first passing the sample stream through a heated catalytic converter in which all the nitrogen oxides are converted into nitric oxide. The nitric oxide concentration in the converted sample stream is then measured. The difference between the two measurements is then designated as nitrogen dioxide although it is known that a number of other nitrogenous and chlorine-containing compounds will be positive interferents for the nitrogen dioxide measurements.

In the determination of nitric acid, two oxides of nitrogen measurements are made. However, a chemical filter which selectively removes nitric acid is placed in one of the two sample lines upstream of the converter. This results in a measurement of total oxides of nitrogen and a measurement of total oxides of nitrogen less nitric acid. The subtraction of the two measurements will then yield a value for the nitric acid concentration in the sample stream.

The original application of this technique utilized a commercially-available chemiluminescence nitrogen oxides instrument which has a manufacturer's specified sensitivity of 2.5 ppb and a baseline noise level of 1.2 ppb.[7] Molybdenum catalytic converters, which were maintained at temperatures between 300 and 325 degrees Celsius, were used to convert nitrogen oxides into nitric oxide.[8] Nitric acid and nitrogen dioxide are quantitatively converted at temperatures above 300° C. However, ammonia will not be converted at these temperatures which eliminates this compound from involvement in the nitrogen oxides measurements. Nitric acid was removed from one of the sample streams by a 47-mm nylon membrane filter which has been shown to quantitatively scrub nitric acid while passing nitric oxide and nitrogen dioxide. Peroxyacetyl nitrate will be passed by the nylon filter after an induction period during which approximately 8 ng of the compound is adsorbed by the filter. The observed noise level of the two nitrogen oxide signals was ±4 ppb. This implies that the nitric acid sensitivity for this instrument is approximately 11 ppb.

A more recent application of the chemiluminescence technique has resulted in greatly improved sensitivity.[4] This is largely due to the use of a chemiluminescence NO_x instrument which has a sensitivity of 0.04 ppb.[9] As with the previously mentioned instrument, nitric acid was determined by the difference between a total nitrogen oxides measurement and a nitric acid-free nitrogen oxides measurement. Nitric acid is selectively removed from the sample stream by passage through a trap which is loosely packed with nylon fibers. A Teflon® filter is mounted in the sample inlet of the instrument to remove particulate matter which could harm components of the instrument. A two-stage converter is used in this instrument. A sample stream first passes through a quartz tube which is packed with Pyrex® beads and heated to a temperature between 350 and 400 degrees Celsius. Nitric acid, peroxyacetyl nitrate and other organic nitrates are converted into nitrogen dioxide in the quartz tube. However, ammonia and organic amines are not oxidized in the quartz tube. The nitrogen dioxide is subsequently converted into nitric oxide in a second converter which consists of a bed of granular ferrous sulfate. By alternately placing the nylon wool trap in the sample stream and then removing it, the total nitrogen oxides and the nitric acid-free nitrogen oxides measurements are obtained. For situations in which organic nitrates were not expected to be present in the air being sampled, nitric acid was measured by an alternate method which did not involve the use of the nylon wool trap. Instead, nitric acid was determined by the subtraction of nitrogen dioxide measurements which were made with and without the presence of the quartz tube converter in the sample stream. The detection limit for nitric acid was 0.03 ppb for strip chart recorded data and somewhat less for data which were recorded on magnetic tape by a microprocessor system. This sensitivity is close to what would be required for nitric acid measurements in the free troposphere.

Nitric acid can also be measured by use of a microcoulometric cell. This technique is based on the coulometric titration of iodate and iodide ions with acidic gases in a microcoulometric cell.[10] Iodate and iodide ions are stable in a neutral solution. When acidic gases are bubbled through a neutral solution of potassium iodate and potassium iodide, the solution will become slightly acidic. This permits the iodate and iodide ions to react and form iodine. The iodine then reacts with a thin gaseous hydrogen film on the cathode of the cell to form gaseous hydrogen iodide which is swept from the cell. This hydrogen film is formed on the cathode when a voltage is applied to the cell's electrodes. Normally, the hydrogen generation will cease when the galvanic cell EMF equals the applied EMF; however, it will continue when the hydrogen is being removed by reaction with iodine. A measurable current will exist as the hydrogen is formed. The total charge which passes through the cell will be a linear function of the amount of acidic gas which has been bubbled through the cell.

As described above, the microcoulometric cell method is sensitive to ozone and to total acidic gases which include sulfur dioxide, hydrochloric acid and formic acid, as well as nitric acid. In order to modify the method such that a value is obtainable for the nitric acid concentration alone, two modifications in the method were made.[11,12] The ozone interference was removed by titrating the sample stream with ethylene in a flask preceding the microcoulometric cell. A total acidic gas measurement was obtained by passing the sample stream directly from the titration flask to the microcoulometric cell. The nitric acid-free acidic gas measurement was obtained by rerouting the sample stream from the titration flask through a nylon membrane filter prior to its entering the cell. Nitric acid could then be determined from the difference between the total acidic gas measurement and the nitric acid-free acidic gas measurement. There was good agreement between data which were obtained with this method and those which were obtained with long-path, Fourier transform infrared spectroscopy. This was for both pure gas mixture measurements and smog chamber measurements. Among several possible interferents which were evaluated, only formic acid was found to interfere with a variable response between 0 and 10 percent of the actual formic acid concentration. Because of the slow adsorption and desorption of nitric acid from the interior surfaces of this instrument, at least five minutes were originally needed to obtain a stable reading. This response time was shortened by changing the design of the nylon filter and by using different solenoid valves which decreased the internal volume of the instrument and reduced the effect of surface adsorption. The sensitivity of this technique is about 2 ppb which is not adequate for tropospheric measurements.

The technique of Fourier transform infrared spectroscopy is based on the absorption of infrared radiation at specific spectral frequencies which correspond to vibrational-rotational energy transitions in gaseous molecules. The amount of absorption that a particular molecule will produce in an infrared spectrum is determined by the concentration and absorption coefficient of the molecule and by the optical pathlength that the light has traversed. The functional relationship between these quantities is described by Beer's Law. The absorption coefficient which is dependent on the local atmospheric density, can be determined in the laboratory.[13,14] Additionally, the optical pathlength is easily determined for in situ measurements. As a result, there is a direct functional relationship between a nitric acid concentration and the absorbance which is being measured. This permits this method to be considered as a surrogate reference standard or a basis for comparison of measurements made using other methods. This approach was taken in a recent intercomparison study of various nitric acid methods conducted at Harvey Mudd College and the results of this intercomparison study will be published by the EPA in the near future.

Fourier transform infrared spectroscopy has been used as a remote sensor for stratospheric nitric acid measurements.[13] For such measurements, the Sun is used as the source of the infrared radiation and the entire atmosphere above the spectrometer is the path through which this radiation traverses. A single measurement will yield a value for the atmospheric burden of nitric acid above the spectrometer; however, the vertical distribution of nitric acid can be calculated from multiple measurements which are made at various solar zenith angles.[15]

For tropospheric measurements of the nitric acid concentration, in situ applications of Fourier transform infrared spectroscopy have been more thoroughly investigated than applications which involve the Sun as an infrared source. Typically, a broadband infrared source (e.g., a Nernst glower) is used as a laboratory source of infrared radiation. In order to obtain a sufficiently long pathlength, a multiple-traversal absorption cell (e.g., a White cell) is placed between the infrared source and the spectrometer.

An early attempt at measuring nitric acid using this technique failed because of an inadequate signal-to-noise ratio for the spectrometer.[16] Ten (10) ppb of nitric acid could have gone undetected. A more recent attempt has been successful due to improvements which have been made in the spectrometer and other optical components.[14,17] The Fourier transform spectrometer had a spectral resolution of 0.5 cm^{-1}. Peak-to-peak noise in the recovered infrared spectra was generally about one percent of the ratio plot intensity which corresponds to a signal-to-noise ratio of 100. The multiple-traversal absorption cell was an eight-mirror White cell having a basepath of 23 m. It was adjusted to yield an overall pathlength of approximately 1 km. For the 896 cm^{-1} Q-branch of nitric acid, the detection sensitivity was 6 ppb. During a two-year monitoring program in the polluted atmosphere of Riverside, California, nitric acid concentrations between 6 and 20 ppb were measured on 54 occasions. These values confirm the calculated sensitivity of this instrument.

It should be noted that a signal-to-noise ratio of 2000 to 1 has been observed for a similar instrument.[16] If such a signal-to-noise ratio could be obtained for a nitric acid measurement, this would mean that concentrations on the order of 0.4 ppb should be detectable for a pathlength of 1 km. However, even if this improved signal-to-noise ratio is achieved, the technique does not have adequate sensitivity for measurements of nitric acid in the free troposphere.

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2.10 Peroxyacetyl Nitrates (PAN's)

2.10.1 Tropospheric Concentrations. - In the early studies of photochemical systems, the peroxyacetyl nitrates (PAN's) were commonly observed. Irradiated mixtures of oxides of nitrogen and nonmethane hydrocarbons from gasoline vapors, auto exhaust, pure hydrocarbon and aldehydes produced the photochemical product known as Compound X.[1] Further work identified the structure of these compounds and led to the correct nomenclature now used; peroxyacetyl nitrates. The PAN compounds form a homologous series in which the first commonly observed compound is peroxyacetyl nitrate. The one carbon member of the group which would be called peroxyformyl nitrate has not been measured in ambient or synthesized photochemical systems, and is thought to be too unstable to exist at ambient temperatures. Interest in this group of compounds increased when it was discovered that they are highly toxic to plants and that they are severe eye irritants at concentrations of 10-100 ppb.

This class of compounds has not been routinely monitored in urban areas so typical tropospheric concentrations are not well known. Measurements of PAN have been made in the Los Angeles Air Basin, however, with concentrations as high as 50 ppb reported in Los Angeles and 10 ppb in Riverside. Very little information exists on the concentrations of PAN compounds in nonurban atmospheres. Rural measurements of peroxyacetyl nitrates in southern England showed a small but persistent background concentration of 1-3 ppb even in clean air masses arriving from the Atlantic Ocean.[2] Measurements were made aboard a research vessel in the Atlantic to try to determine the origin of the background PAN. These background concentrations were detected when glass sampling syringes were used but were not detected when polypropylene syringes were used. When a small amount of glass wool was placed in the polypropylene syringe, however, PAN was once again measured in the sample. It was concluded that in the presence of precursors and sunlight, PAN could be formed at low ppb concentrations by a heterogenous process involving the glass surfaces. This discovery raises some important considerations concerning heterogeneous formation of PAN on aerosols in urban atmospheres, as well as general questions about sampling techniques.

Because of their extreme reactivity and instability, PAN compounds are difficult to work with or store for use as calibration standards.[1,3,4] Three methods are used to produce PAN for calibration purposes. They are:

1. Photolysis of a symmetrical olefin with nitric oxide or nitrogen dioxide in oxygen or dry air.
2. Photolysis of alkyl nitrate in dry oxygen; not useful for the four-carbon homologue.
3. Dark reaction of aldehyde with NO_2 and O_3 in oxygen. In all cases, the PAN's are purified by gas chromatography. Another method utilizes the reaction of chlorine atoms with the appropriate aldehyde.[5] The chlorine atom preferentially abstracts the terminal hydrogen leaving the acyl radical. In the presence of oxygen and NO_2, the formation of the PAN compounds resulted.

2.10.2 Research or Prototype Instruments. - Peroxyacetyl nitrate has a distinctive infrared absorption spectra which can be used as a reference for the determination of PAN on any spectrometer. A colorimetric technique has been used for the detection of PAN compounds.[1] It was discovered that the alkaline hydrolysis of PAN produced nitrite ion on a mole for mole basis. The nitrite ion was then measured colorimetrically by use of Saltzman's reagent. The technique suffers from interference from NO_2 and possibly other nitrogen compounds.

The most common measurement technique used for the determination of PAN compounds is gas chromatography with electron capture detection.[6] At maximum sensitivity, a 2-mL sample responds with 0.017 mV per ppb for both peroxyacetyl nitrate and peroxyproprionyl nitrate. This corresponds to a minimum detectable concentration of approximately 3 to 5 ppb for both compounds.

Holdnen and Rasmussen discovered a severe decrease in the response of the ECD to PAN concentrations between 10-100 ppb in samples with less than 30 percent relative humidity. This effect was noted regardless of the type of ECD used or the type of column used for separation.[7] They concluded that this effect was due to one of three possible causes, including sample interaction with the injection system or container, sample column interaction, or an influence of water on the ECD. Tests of their system lead them to conclude that the problem was in sample column interaction. Shortly afterward, Lonneman tried to reproduce this effect and found no change in the ECD response with variable moisture content in the sample.[8] It was suggested that the column sorbent, Carbowax 400-600, had experienced deterioration. It was noted that at temperatures greater than 100° C, the substrate decomposes and a quantitative elution of PAN could not be accomplished. The possibility of auto-oxidation of the stored substrate at room temperature (leading to measurement unreliability) was suggested. Another possibility was suggested that active sites in the plumbing could be retaining PAN and that the water deactivated these sites leading to their detection at high humidities. The use of glass tubes for the column and glass, Teflon®, or stainless steel only for valves and connecting tubes was recommended. Further work on this problem resulted in a similar change in response with humidity when acid-washed containers were used for PAN sample preparation.[9] Three columns and two electron capture detectors were used with similar results. It was concluded that PAN and water vapor compete for active sites producing the observed change in response with humidity.

The feasibility of a continuous ambient analyzer for PAN based on the detection of chemiluminescence from the reaction of PAN and triethylamine has been investigated.[10] No appreciable interference was found for methylnitrate, ethyl nitrate, ethyl nitrite, NO_2 or NO. Ozone produces a maximum chemiluminescence at a wavelength of only 130 nm from the peak of the chemiluminescence from PAN when reacted with triethylamine. One way of quantifying the PAN concentration, however, was by measuring the ratio of the intensity at the two wavelengths. By accurately determining the ozone concentration independently, the PAN concentration could then be quantified. The possibility of using selective filters to allow only the PAN-triethylamine chemiluminescence to reach the PMT was also investigated. Both ways of determining the sample PAN concentration seem possible. A minimum detectable concentration of this measurement technique of 6 ppb could easily be reached and with improved light detection and filter components, this technique could provide a minimum detection limit of 1 ppb at a continuous sample flow of 10 cm^3/s.

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2.11 Hydrogen Chloride

2.11.1 Tropospheric Concentrations. - The sensitivity which will be needed for an acceptable method for measuring hydrogen chloride in the troposphere is dependent on the concentrations which are expected to be present there. Because hydrogen chloride is an end product of stratospheric halocarbon reactions which have received considerable attention in recent years, numerous measurements of stratospheric hydrogen chloride concentrations have been or are being made. Unfortunately, the literature does not contain as many reports of tropospheric measurements; however, those which do exist appear to yield a consistent picture.

Junge[1,2] made measurements at several coastal locations and found gaseous chlorine concentrations which ranged between 0.5 and 4.1 ppb. In similar maritime areas, Georgii[3] obtained values between 1.1 and 1.3 ppb for gaseous chlorine. In both cases, the gaseous chlorine was assumed to be hydrogen chloride. Georgii measured significantly higher concentrations, on the order of 6.0 ppb, in the vicinity of urban areas. This suggests that there are significant anthropogenic emissions of hydrogen chloride or chemical precursors. Okita et al.[4] concluded that gaseous chloride concentrations are higher in coastal areas, whether they are industrial, residential or seashore resort areas, than those in inland areas.

A better definition of the chemical composition of chlorine in the coastal atmosphere was obtained by Berg and Winchester.[5] On the average, they found that 50 percent of the total chlorine was organic gaseous chlorine, 33 percent was inorganic gaseous chlorine and 17 percent was particulate chlorine. While the proportion of organic gaseous chlorine remained relatively constant from one sample to another, the proportions of inorganic gaseous chlorine and particulate chlorine varied drastically. The results suggest that rapid interchange occurs between inorganic gaseous and particulate chlorine in the atmosphere but that organic gaseous chlorine is relatively decoupled from these forms. This interchange may be actually occurring in the atmosphere or it may take place within the sampling device.

Very little information is available from which the vertical distribution of hydrogen chloride in the troposphere can be inferred. Although there have been numerous measurements of stratospheric hydrogen chloride concentrations, no reports of similar airborne measurements in the troposphere have been found in the literature. However, Junge's and Georgii's measurements on mountains may give some indication of the vertical distribution of hydrogen chloride in the troposphere. On the island of Hawaii, Junge measured a total gaseous chlorine concentration of 1.0 ppb at sea level while at an altitude of 3 km, the concentration declined to 0.4 ppb. Similarly, a concentration of 4.3 ppb was measured by Georgii at an altitude of 0.9 km on Kleiner Feldberg in Germany. At an altitude of 3 km on Zugspitze in Germany, the total gaseous chlorine concentration declined to less than 0.2 ppb.

Some additional information concerning the vertical concentration distribution in the troposphere can be inferred from stratospheric measurements at the tropopause. Lazrus et al.[6] estimated the upper limit for the acidic chlorine (HCl and $ClNO_3$) concentrations to be 0.04 ppb at 1 km below the tropopause.

These findings suggest that tropospheric concentrations of HCl vary by approximately two orders of magnitude and that there is a rapid decrease in the concentration with increasing altitude. In order for tropospheric concentrations to be assessed throughout the expected range of variability, an acceptable analytical method must have a sensitivity which is equal to one-half of the expected minimum tropospheric concentration. This corresponds to a hydrogen chloride concentration of 0.02 ppb.

2.11.2 Commercially-Available Instruments. - The only commercially-available instrument for measuring hydrogen chloride in the atmosphere is the Geomet Model 402-B Hydrogen Chloride Monitor. The basic principle of this technique is the measurement of visible light which is produced from the catalyzed reaction of 5-amino-2, 3-dihydro-1, 4-phthalazinedione (luminol) and hydrogen peroxide. If both luminol and hydrogen peroxide are present in sufficient quantities, the amount of light which is produced will be proportional to the amount of catalyst. For analysis of hydrogen chloride, the sample airstream is passed through an alumina tube which is coated with a film of sodium bromate and sodium bromide.[7] Hydrogen chloride reacts with the film and forms a stoichiometric quantity of bromine which acts as the catalyst for the luminol oxidation.

The basic specifications for this instrument are given in the appendix. The most important specification for applications associated with tropospheric measurements is the sensitivity. The instruction manual for the Model 402-B lists the lower detection limit as less than 20 ppb; however, concentrations of 5 ppb have been accurately measured by the instrument.[7] It is unclear whether or not a lower detection limit for the instrument has been determined. This represents a problem in determining if this instrument is suitable for measuring tropospheric concentrations of hydrogen chloride. As the expected minimum tropospheric concentration is two orders of magnitude lower than 5 ppb, it is not unreasonable to question if the instrument is capable of detecting the low hydrogen chloride concentrations which are present in the troposphere.

A more serious problem with this technique is its lack of specificity. In addition to hydrogen chloride, the instrument will yield a positive response to strong oxidizing agents such as free halogens, ozone and nitrogen dioxide and to acid gases and liquid aerosols. These interferences have not been a problem to date since the use of this instrument has been largely for NASA's Launch Vehicle Effluent Program. In this application, the interferent concentrations equal only about 10 percent of the hydrogen chloride concentration and, therefore, would not introduce substantial error in the measured values. However, the situation is significantly different in the troposphere where interferent concentrations are much larger than the hydrogen chloride concentration. The most noteworthy interferent is ozone. Specificity studies have shown that an ozone concentration of 3 ppm will produce a reading equivalent to 1 ppm of hydrogen chloride. Singh et al.[8] have estimated that the free tropospheric ozone concentration varies between 20 and 80 ppb as a function of the season. This suggests that the instrument will give a false indication of a hydrogen chloride concentration between 7 and 27 ppb as a result of the presence of tropospheric ozone alone. Because tropospheric hydrogen chloride concentrations are actually on the order of 1 ppb or less, this represents an unacceptable level of interference. If this problem cannot be corrected, the technique appears to be unsuited for tropospheric measurements.

2.11.3 Research or Prototype Instruments. - The gas filter correlation monitor uses a variation of the nondispersive infrared (NDIR) absorption method. It represents an improvement over the Luft-cell NDIR instrument which has been a common technique for the analysis of several trace tropospheric species. It is closely related to the dual-isotope absorption NDIR technique which is described elsewhere. The basic principle behind all three approaches is that the amount of infrared light within a given spectral region which is absorbed as it is transmitted through a volume of air is a function of the concentration of an absorbing gaseous species in that volume.

In the Luft-cell, this absorbance is determined by successively measuring the light intensity from a single source which is transmitted through a reference cell and a sample cell. The reference cell is filled with a nonabsorbing gas (e.g., clean air) while the sample cell is filled with the sample air which is to be analyzed. The ratio of the two intensities is a function of the gas concentration.

In contrast to the Luft-cell, the gas filter correlation monitor utilizes only a single cell.[9] After being transmitted through this cell, infrared light passes through a rotating, gas-filled filter before it is detected. One-half of the filter is filled with the absorbing species of interest and is designated as the specifying filter. The other half is filled with a nonabsorbing gas and is designated as the reference filter. When the infrared light passes through the specifying filter, it is strongly attenuated in the spectral region containing the specifying gas's absorption peaks. This does not take place when the infrared light passes through the reference filter. As the filter rotates, the detector produces an AC-modulated signal whose amplitude is a function of the specifying gas in the sample cell.

The instrument which was originally developed for airborne measurements of hydrogen chloride had sensitivity of 50 ppm meters as a result of detector-noise limitations.[10] By mounting the instrument within the aircraft and retroreflector on the wing tip of the aircraft, a sample cell pathlength of 10 m was obtained. This produced a minimum detectable concentration of 5 ppm. Because of this poor sensitivity and other problems, this instrument was judged to be unsatisfactory for airborne measurements.

A second-generation instrument was then built which had improved sensitivity and selectivity.[11,12] These were the result of modifications which were made in the design of the rotating filter and electronic signal processing and by installation of a more sensitive infrared detector and narrower bandwidth interference filter. Additionally, an 8.15-m multiple traversal absorption cell was used as the sample cell.

Because of these changes, the sensitivity was improved by an order of magnitude to 5 ppm-meters. With the sampling cell which was used, this sensitivity corresponds to a minimum detectable concentration of 0.6 ppm. It was noted that lower minimum detectable concentrations could be obtained by using longer optical pathlengths. Currently, a White cell which is adjusted for a 35-m pathlength is being used with the instrument. As a consequence, the minimum detectable concentration is now approximately 140 ppb.

Interferences are minor for the measurement of hydrogen chloride. As a result of the interference filter which was used, the instrument was responsive to infrared radiation only in the narrow spectral region between 3.45 and 3.65 μm. This corresponds to the P-branch absorption peak and part of the R-branch absorption peak for hydrogen chloride. Although methane also absorbs infrared radiation in this spectral region, no interference was found for this species in the hydrogen chloride-measuring version of this instrument. No interference effects were found for water vapor or carbon dioxide. Small but significant interference (approximately 1/18th) were found for ethane, propane and butane.

In its current configuration, the instrument does not have adequate sensitivity to measure the hydrogen concentrations which exist in the troposphere. While some improvements could be obtained through the use of longer pathlengths and more sensitive detectors, it is doubtful that more than about an order of magnitude improvement in sensitivity could be attained.

As was indicated earlier, the dual-isotope absorption technique is closely related to the gas filter correlation approach. The only major difference between the basic principles behind the two approaches lies with the gases which are contained in the rotating filter. The rotating filter in the dual-isotope absorption instrument has one of its cells filled with the stable isotope HCl^{35} while the other cell is filled with the stable isotope HCl^{37}.

In contrast, one cell in the rotating filter for the gas filter correlation monitor is filled with a gas which does not absorb infrared radiation while the other cell contains hydrogen chloride with its natural mixture of isotopes (approximately 75 percent of HCl^{35} and 25 percent of HCl^{37}). Otherwise, the two instruments are identical in principle although there remains significant differences in the design of the optics and electronic signal processing.

The dual-isotope absorption instrument has existed only as a prototype unit which has been evaluated in the laboratory.[13] In this configuration, the instrument had a minimum detectable concentration of 0.3 ppm. Interferences from other gaseous species are small and appear to be approximately of the same magnitude as was seen for the gas filter correlation instrument. The instrument has not been developed past the prototype because of difficulties which were encountered during measurements of hydrogen chloride in moist air. Condensation on the walls of the sample cell resulted in zero stability problems. These problems appear to have been circumvented in the development of the gas filter correlation monitor.

As with the gas filter correlation monitor, the dual-isotope absorption instrument is not sensitive enough to measure tropospheric concentrations of hydrogen chloride. It does not appear that the instrument could be modified in such a manner that it would be capable of doing so.

Work is beginning at the National Bureau of Standard's Center for Analytical Chemistry on a laser/opto-acoustic technique for measuring hydrogen chloride. The basic principle behind this approach is that a pressure increase in a sample of air will accompany the absorption of laser-generated light by hydrogen chloride molecules in the sample. This pressure increase can be detected by a sensitive microphone which is located in the sample cell. In order to minimize wall losses, the sample cell will be of a high-flowrate, open-cell design. The microphone will be oriented on an axis which is perpendicular to the mutually perpendicular axes of the flow and the laser beam. A pulsed, dye laser with 5 harmonics in the visible region will be used to excite the hydrogen chloride molecules. The target sensitivity for this technique is 1 ppb although it is questionable whether or not this can be attained. The largest potential limitation on the sensitivity is the noise which will be generated by the flow of gas through the sample cell and by the heating of the windows of the cell.

The microcoulometric cell technique is based on the coulometric titration of silver ions with chlorine ions in a microcoulometric cell. When hydrogen chloride is bubbled through the electrolyte, silver ions react with the chlorine ions to form a silver chloride precipitate. The resulting decrease in the silver ion concentration from a pre-established level is detected by sensing electrodes. This causes replacement silver ions to be electrochemically produced from a metallic silver-generating electrode. When the desired silver ion concentration has been regained, the total charge (i.e., current X time) which has passed through the generating electrode will be a function of the hydrogen chloride concentration and can be measured.

An instrument which is based on this principle was developed for the measurement of hydrogen chloride, organic chlorides and chlorine in ambient air.[14] The standard microcoulometric cell was modified by the installation of a pyrolysis furnace at the inlet of the cell. Ambient air samples are drawn into the furnace and chlorine-containing compounds are converted in an oxidizing atmosphere into hydrogen chloride. For the measurement of volatile inorganic chlorides alone, ambient air can be drawn directly into the cell without passing through the pyrolysis furnace. The minimum detectable hydrogen chloride concentration for this instrument is 8 ppb. When hydrogen chloride alone is being measured, hydrogen sulfide and mercaptans are potential interferences since these compounds will react with silver ions to form a silver sulfide percipitate. Bromides and iodides are also interferents.

This technique was also used in a similar instrument for airborne monitoring of hydrogen chloride emitted from solid propellant launch vehicles.[15] Ambient air is drawn directly into the microcoulometric cell. The minimum detectable concentration for hydrogen chloride was

80 ppb. As the result of coastal ambient air measurements, it was confirmed that the instrument did not have sufficient sensitivity to detect tropospheric concentrations of hydrogen chloride. The concentrations were found to be in the range of from 1 to 50 ppb as determined by an impinger method.

In general, it appears that microcoulometric cell methods do not have sufficient sensitivity to directly measure tropospheric concentrations. However, improved sensitivity can be obtained via a manual microcoulometric cell method which is used in conjunction with a solid-coated sampling tube. This technique is described in Section 3.3.

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2.12 Particulate Measurements

Commercially-available particulate measurement devices that are aircraft-compatible and that provide real-time information are few. The recent interest in the distribution of particulates has resulted in development tasks designed to provide real-time size distribution and composition measurements but no instruments for these measurements are currently proven and available.

Condensation nuclei counters have been flown aboard airborne platforms to measure both horizontal and vertical distributions up to 6.1 km MSL of the number of particles larger than 0.0025 microns in diameter.[1] The manufacturers' measurement specifications of a typical condensation nuclei counter, the Environment One Rich 100, are listed below:

Particle Size	0.0025 micron and larger diameter
Concentration Range	300 x 10^7 particles/cc
Range Selection	0-1k, 0-3k, 0-10k, 0-30k, 0-100k, 0-300k linear. 0-300k x 10^7 non-linear
Accuracy	±20% for points 30% or more of full scale on linear range
Repeatability	±3% of full-scale linear range
Recorder Output	0-10 mVdc; 0-1 mAdc
Sample Flow	30-70 mL/s
Response Time	5 sec at 50 mL/s
Physical Characteristics	
Dimensions (H/W/D)	20.3 x 35.5 x 38.1 cm
Power Requirements	115 Vac, 50/60 Hz, 80 watts
Weight	17.7 kg

The condensation nuclei counter is small and light, and requires no additional support devices and therefore is applicable to aircraft platforms.

Integrating nephelometers have also been used extensively on aircraft platforms. The manufacturer's operational characteristics of the MRI 1550B integrating nephelometer are listed below:

Sensitivity	0.1 to 100 x $10^{-4}m^{-1}$ or ∞ to 0.3 miles visual distance
Accuracy	±10% of full scale
Output	0 to 5 Vdc; 0 to 1 mA
Sample Flow	Approx. 140 L/min
Averaging Time	5, 10, 20, 50, 100 or 200 seconds
Physical Characteristics	
Power Requirements	105-125 Vac, 60 Hz, 70 watts
Dimensions	
Optical assembly	10 cm - diameter 100 cm - length
Electronics control panel(HWD)	18 x 48 x 28 cm
Blower filter assembly (HWD)	23 x 20 x 41 cm
Weight	
Optical assembly	7.7 kg
Electronics control panel(HWD)	10.9 kg
Blower filter assembly	5 kg

The inlet line in this system was not heated and, therefore, the instrument will respond to high concentration water vapor or small water droplets as are found in clouds. When the inlet line is unheated the integrating nephelometer requires no additional equipment and the unit is capable of continuous operation aboard an aircraft platform to 4270-m altitude.

While condensation nuclei counters and nephelometers are easily mounted and operated on aircraft platforms, they do not provide mass concentration data. One real-time mass concentration device, the piezoelectric microbalance, has been operated on an aircraft platform.[2] The piezoelectric method can provide a continuous measure of mass concentration. This instrument has been mounted in a Cessna 402 aircraft although the specification, size, weight characteristics and power requirements are not available at this time. Operation in a Cessna 402 indicates that its requirements are suitable for mounting it in any light aircraft.

Another advantage of the piezoelectric technique is that several crystals can be operated in a cascade impactor-type of size separation device or some other size separation technique to provide real-time size distribution information. Samples can also be collected on some other substrate and elemental composition determined by laboratory analysis at a later time.

These instruments are sensitive to particle mass in the range of 1.0 to 10,000 $\mu g/m^3$, in a size range of 0.01 to 10.0 microns in diameter with an efficiency of 98%. Electrostatic precipitation is used to collect the particles. If inertial impaction is used to collect the particles, greater than 10 $\mu g/m^3$ can be detected in the size range 0.1 to 100 microns in diameter. Such instruments cost approximately $15,000.

Another technique that can provide mass concentration data in nearly real time is beta ray attenuation.[3] An air sample is drawn through a paper tape and the particulate material is collected on the tape. After sufficient sample is drawn, the tape is moved to a location between a beta ray source and a beta ray detector. As the beam of beta rays passes through the sample, some of the rays are attenuated and the decrease in counts as the sample is encountered is proportional to the mass of particles collected.

An air sample pump, tape drive and beta ray source, and detector and some means of recording the detector output are all that is required so the technique could be easily fitted into an aircraft. The disadvantages are that it is not a real-time technique, and at high aircraft speed, the resolution may not be sufficient for some applications. These monitors can also be expensive - $12,000 to $15,000 plus $10,000 to $20,000 for the automatic tape advancing mechanism.

Commercially-available FPD sulfur analyzers have been used to make real-time measurements of particulate sulfate concentrations in ambient air. The only addition to a standard FPD sulfur gas analyzer required is some means of eliminating sulfur gases from the sample air. Two techniques to accomplish this have been suggested and operated. One is a sulfur gas denuder that removes sulfur-containing gases by diffusion to the interior coated walls of a tube.[4] The particulate sulfur penetrates the denuder due to much slower diffusion of particles than the diffusion of the gases. Pulsed electrostatic precipitation has also been used to distinguish between total sulfur (including particles) and sulfur gases.[5] Extensive laboratory work has demonstrated the sensitivity of the particulate sulfate system to be $\pm < 1.0$ ppb aerosol sulfur (< 4 μg/m^3 sulfate). The system has also been characterized for altitude corrections and therefore could be operated in an aircraft. The characteristics of the FPD sulfur gas analyzer would apply to particulate sulfate measurement.

2.12.1 Electrical Aerosol Analyzer and Optical Particle Counter. - The combination of Electrical Analyzer (EAA) and Optical Particle Counter (OPC) are frequently used together to obtain size distribution information in laboratory and ambient measurement programs. The EAA is responsive to size ranges of approximately 0.0056μ to 1μ in nine discrete measurement intervals and the OPC provides size distribution information from approximately 0.4μ to 6μ.

The EAA associated equipment and mounting stands nearly 1.5 m tall, weighs approximately 34 kg and requires a 50 L/min flow. For the actual sample, it only requires 5 L/min; however, the 45 L/min excess is used as a sheath to prevent particle deposition on the walls of the sample inlet and within the charging section of the instrument. These characteristics may limit the choices of aircraft that could be used to house the instrument. The power requirements of a pump to produce the large flow may also be large enough to require special considerations. The OPC is smaller, weighs only 16 kg and has no special power requirements. The vibration in an aircraft may have effects on the optical system within the instrument.

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2.13 Hydrogen Peroxide

2.13.1 Tropospheric Concentrations. - Hydrogen peroxide is an oxidation product of photochemical atmospheric systems. At present, the only evidence available for its occurrence in the ambient troposphere is its detection in urban areas during photochemical activity. It is important, especially to photochemical modelers, because its concentration is related to the concentration of hydroperoxy (HO_2) and hydroxyl radicals (HO). Presently, H_2O_2 is a molecule that is difficult to detect; however, it is much more stable than either the HO_2 or OH radical. Therefore, a technique for detecting reliably of the H_2O_2 concentration is desirable to understand the role of other photochemical species and to aid in the understanding of photochemical systems from a kinetics viewpoint.

Ambient measurements of H_2O_2 have not been reported in rural locations where concentrations are expected to be very low. Measurements have been made, however, in urban ambient air at Riverside, California and in New Jersey.[1,2] At a site in Hoboken, New Jersey, on a day with photochemical activity, a maximum H_2O_2 concentration of 0.04 ppm was reported, however, no H_2O_2 was detected on an overcast day with minimal photochemistry.[1] During a more severe smog episode in Riverside, California, when 0.65 ppm of total oxidant was measured, the H_2O_2 concentration reached a maximum of 0.18 ppm. While the relationship between total oxidant and H_2O_2 concentration is complex, a trend relating the two measurements was apparent. Presently, there are no commercially-available instruments for the measurement of hydrogen peroxide.

2.13.2 Research or Prototype Instruments. - A spectrophotometric method which is specific for H_2O_2 and sensitive enough to measure ambient concentrations has been described by Cohen and Purcell.[3] In this technique, the ambient sample is bubbled through a solution containing $TiSO_4/(NH_4)_2SO_4/H_2SO_4$. A sample flow of 0.5 L/min is desirable since a single bubbler can achieve 100% collection efficiency. Typically, a 45-60 minute sample is required. A complex of $Ti(IV)/H_2O_2$ is formed in solution. The sample is shaken with 10 mL of 8-quinolinol in the presence of a sodium acetate buffer. The complex and color are sensitive to pH and the buffer is added to maintain a pH of 4.2 ± 0.2. The color is determined by a spectrophotometer at 450 nm.

A similar colorimetric technique using a $TiCl_4/HCl$ solution has also been described.[4] In this method, sample air is drawn through the solution and a complex of $Ti(IV)/H_2O_2$ is formed. Samples were collected for 40 min but no flowrate was given. The absorbance of the complex was measured directly at 410 nm. For concentrations of H_2O_2 less than 0.1 ppm, a 5-cm cell and 0.05 absorbance full-scale range were used. No details on sensitivity or minimum detectability were given. A fine precipitate was formed in this technique which served to scatter some of the light confusing the measurements. The precipitate resulted from either atmospheric particles or TiO_2 formed in solution.

A chemiluminescent method with a sensitivity of 1 ppb for ambient H_2O_2 analysis has also been described.[5] The technique is based on the chemiluminescent reaction of 5-amino, 2,3-dihydro, 1,4-phthalazinedione (luminol) with H_2O_2 in the presence of a metal catalyst. Aqueous H_2O_2 samples are collected by bubbling sample air through midget impingers at a flowrate of 1 L/min for 30 min. The sample and luminol source are mixed in a reaction cell before a photomultiplier selected to detect the chemiluminescence centered at 450 nm. Flow of reagents is carefully controlled by a peristaltic pump. This technique has also been used to sample gas phase H_2O_2 concentrations continuously. Water and sample air are continuously drawn through an absorbing column where the H_2O_2 is concentrated in the aqueous solution. The chemiluminescent reaction is dependent upon pH; therefore, the luminol and solution containing a copper catalyst are made basic by the addition of NaOH. The pH is kept at 12.8 where the maximum response is observed. The response was found to be linear from 0-100 ppb of H_2O_2 and no interferences were found. For the preconcentration technique, the minimum detectable concentration was found to be 0.5 ppb while for the continuous gas phase method, the limit of detection was approximately 1 ppb.

The three methods described above for detection of H_2O_2 have been compared.[4] The sample averaging times were slightly different and while there was relative agreement between the methods, the comparisons were lacking in precision. These results reflect the difficulty in quantifying the ambient H_2O_2 concentrations. In all cases, the three methods yielded values between 4 and 20 ppb. The relative agreement of the methods implies that the order of magnitude of ambient concentrations of H_2O_2 in photochemical systems is 10-20 ppb.

This same technique has also been used to make measurements of H_2O_2 in rain water.[6] The rain water was collected in beakers maintained at a temperature of 0° C to minimize decomposition of H_2O_2. The samples were collected for periods of about one-hour duration and were analyzed immediately by the chemiluminescent method.

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2.14 Aldehydes

2.14.1 Tropospheric Concentrations. - The importance of ambient aldehyde concentrations is primarily related to their role in photochemistry. Hydroxyl radical attack on aldehydes, primarily acetaldehyde, result in the formation of peroxyacyl radicals. These radicals can be effective in oxidizing NO to NO_2 thus propogating the cyclic chain leading to ozone formation. They can also react with NO_2 to form nitrates such as peroxyacetyl nitrate (PAN), which has been identified as one of the major eye irritants in photochemical smog. The major source of aldehydes is from auto and diesel exhaust; therefore, tropospheric concentrations of aldehydes vary with traffic patterns in urban areas. There is also a large variation in ambient concentrations between urban and rural areas. Junge estimated ground level ambient concentrations to be between 0 and 10 ppb.[1] Measurements of urban formaldehyde concentrations at four sites in New Jersey during the months of May through September ranged between 3.8 and 6.6 ppb for 24-hr averages.[2] The upper decile one-hour average concentrations at the same sites ranged between 14 and 20 ppb. In Los Angeles, maximum one-hour formaldehyde concentrations of 40 to 150 ppb were reported,[3,4] reflecting the importance of formaldehyde in urban areas with high traffic density. Twenty-four hour maximum concentrations of total aldehydes in Houston were approximately 40 ppb.[5]

2.14.2 Commercially-Available Instruments. - There is one commercially-available continuous analyzer for ambient formaldehyde concentrations. It is manufactured by CEA Instruments, Inc. The system is a colorimetric technique which employs continuous flow of reagents to provide the continuous measurements. Sample air is drawn through a bubbler with the flow of collection reagent controlled by a peristaltic pump. The flow of the other reagents is likewise controlled by the peristaltic pump and the color of the reagent mixture is continuously monitored. Due to the flow system, the instrument has a lag time of 330 seconds and a rise time to 90% of the input signal of 180 seconds. The minimum detection limit is 10 ppb on a 0-1 ppm scale. The power requirements are 35 watts at 120 Vac, but the system is also available as a battery-powered unit. The dimensions of the instrument are 50.8 cm by 14.0 cm and 30.5 cm high and it weighs 11.8 kg. Its cost is approximately $4875. A full list of the operating specifications is included in the appendix.

2.14.3 Research or Prototype Instruments. - Most of the methods that have been described for the measurement of ambient aldehydes utilize wet chemical analysis and require one hour of sampling by drawing sample air through a bubbler or impinger. Since these techniques are so important as ambient measurement methods, they will be discussed in a special section to follow.

An in situ microwave spectrometer has been developed to detect the microwave rotational absorption transition of formaldehyde molecules.[6] Without preconcentration of the sample, the minimum detectable concentration was only 1-4 ppm. Enrichment of the sample by using a two-stage dimethyl silicon membrane was employed to reach a minimum detectability of 0.030 ppm but averaging time is increased. No interferences were discovered; however, a serious problem with long response times was observed. The problem with response time was thought to be due to wall effects resulting from membrane response and polymerization of formaldehyde on inlet walls. Heating the inlet system may provide better response.

A laser fluorescence technique has also been investigated as a monitor for various aldehydes.[7] Aldehydes in the sample were excited by a frequency-doubled tunable dye laser covering the 320-345 nm range. Concentrations of 0.04 ppm were detected, and the sensitivity could be increased by increasing the pathlength and using a curved mirror to focus the fluorescence on the photomultiplier.

Aldehydes can also be monitored by Fourier Transform Infrared Spectroscopy. A limitation of both the laser fluorescence and FTIS methods is the high cost of the equipment and the technical personnel required for operation.

A semicontinuous gas chromatographic technique has been designed to distinguish aldehyde species in ambient samples. In this technique the aldehydes are concentrated on a precolumn of Porapak Q. The column is backflushed to a separation column then diverted through a methanizer.

Formaldehyde and the carboxyl group of acetaldehyde are then measured in an FID as methane. Twenty minutes are required for an analysis and concentrations of 20 ppbC can be measured.

2.14.4 Wet Chemical Methods. - Aldehydes, as a group, represent a unique measurement problem in atmospheric applications. Their importance in atmospheric studies is critical and yet their typical concentrations and extreme reactivity make them very difficult to quantify. For these reasons, many wet chemical methods have been developed which provide the advantage of integrating the sample over a time period of one hour or more. The methods described previously are promising; however, none have yet surpassed the sensitivity or minimum detection limits offered by the wet chemical techniques. Because the wet chemical methods still represent the methods of choice for both technical and economic reasons for ground level measurements, a brief summary of the well-used methods is included here. Table 2-6 is a list of the important operating parameters and the references for further information considering these techniques.

One technique that uses a wet chemical sample concentration that shows promise as an effective measurement method for aliphatic and aromatic aldehydes in ambient air has received much attention recently.[16,17] Ambient air is drawn through two bubblers in series at 0.5 L/min for 60 min. The aldehydes in the ambient sample are complexed in the sampling solution, 2,4-dinitrophenyelhydrazone (2,4-DNPH). After some simple extractions, the sample is routed through a high-pressure liquid chromatograph where the components representing the aldehydes in the sample are separated and detected by a UV detector, based on their known molar absorptivities at various wavelengths. There are small potential interferences by aromatics in the sample but the response of the detector to benzene, toluene and xylenes is estimated to be only 1/25 of the response to 2,4-DNPH. The detection limit extends down to 0.1 ng for formaldehyde.

A method for formaldehyde based on the liquid-phase chemiluminescent reaction of gallic acid (I) (3,4,5-trihydroxylbenzoic acid) and formaldehyde is being developed by G. L. Kok. Atmospheric samples are obtained by drawing sample air through specially designed bubblers. A peristaltic pump

Table 2-6.

SUMMARY OF SELECTED METHODS FOR ALDEHYDE ANALYSIS

Impinger Spectroscopic Methods	Aerometric Applications	λ Maximum (if applicable nm	Range 5/mL of Solution	Estimate of Min. Detectability at 0.05 Absorbance Units for One Hr. Sample, ppm	Interferences	References
Chromotrophic Acid	Formaldehyde	580	0.24-4.0	0.05	High Conc. of NO_2, Alkenes. Acetaldehydes Phenols	8
Chromotrophic Acid	Formaldehyde	580	0.1-4.0	0.005-0.01	Same as Above	9
MBTH	Formaldehyde Total Aldehydes	628	0.05-2.5	0.03	Aerometric Amines Schiff Bases Azo-dyes	10
MBTH	Same as Above	628-680	0.005-2.5	0.002-0.004	Same as Above	11
Pararosaniline	Formaldehyde	560		0.01-0.02	High Conc. of Acetaldehyde and Propionaldehyde	12
J-acid	Formaldehyde	470	0.001	0.03	Acrolein	13
P-Phenylenediamine	Formaldehyde	485	0.05-2.5	0.035-0.07	High Conc. of Acetaldehyde or Benzaldehydes	14
4-hexylresorcinol	Acrolein	605	1-30 μg	0.01	Dienes	15

is used to control reagent flow during analysis. The reaction cell-photomultiplier housing is integrated and the flow of reagents is introduced to maximize the detection of the chemiluminescence. The sampling time is between 30 and 60 minutes to achieve a sensitivity of 1 ppb or less.

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3.0 INTEGRATED IN SITU COLLECTION AND OFF-LINE ANALYSIS

3.1 Hydrocarbons

Hydrocarbons in the ambient air are often collectively referred to as either nonmethane hydrocarbons (NMHC) or nonmethane organic carbons (NMOC). The term NMHC refers principally to the summation of all compounds composed solely of carbon and hydrogen other than methane while NMOC includes the compounds that have hydrocarbon structures with attached functional groups such as aldehyde, ketone, hydroxyl, or halogen. The need for measurement of hydrocarbons is closely linked to their role in photochemical reactions that lead to the production of ozone and other oxidants. It is these secondary pollutants that manifest toxicological effects and cause damage to plants and materials. High molecular weight hydrocarbons are also involved in the production of aerosol.

Ambient concentrations of individual hydrocarbons vary greatly. Automobile emissions and industrial processes of all sorts are principal sources of many hydrocarbons; and therefore, the concentrations of hydrocarbons in urban areas are much higher than in remote rural locations. However, there are also natural processes that release hydrocarbons to the air. The current national ambient air quality standards for nonmethane hydrocarbons is 0.24 ppmC. The primary measurement method for hydrocarbons is the flame ionization detector (FID). The FID responds to individual carbon atoms when hydrocarbons are burned in a hydrogen-rich flame. The flame ionization detector alone cannot distinguish the individual species from which the carbon atoms originated; therefore, to selectively quantify the concentrations of individual hydrocarbons in a sample, the compounds must first be separated from one another before detection. This is accomplished by gas chromatography; a process whereby a sample is routed through a column packed with various materials that selectively pass individual species at different rates. By the time the sample has passed through the column, the individual species have separated and they elute individually; and therefore, the detector response can be associated with individual compounds.

Gas chromatographs and the detectors used to measure the species concentrations are quite sensitive and often require special support features (carrier gas, heating systems, cryogenic systems), and therefore, are operated under controlled laboratory conditions. This necessitates a means of obtaining a representative sample from some remote area, storage space and transportation of the sample while maintaining stability of the individual compounds in the sample, and a method of introducing the sample into the gas chromatograph.

The choice of what hydrocarbon species to identify and quantify lies with the analyst and is closely linked to the separation capabilities of the chromatographic column and the detail necessary for the particular study. Some measurements are made only of hydrocarbon compounds in the molecular weight range C_1-C_5, while others are much more extensive. Lonneman[1] reports sixty-seven (67) individual known and unknown NMOC peaks in the analysis of ambient air hydrocarbon concentrations in Florida. In another study in and near Houston, Texas, Westburg[2] lists the individual hydrocarbon species most often present as:

Paraffins	Olefins	Aromatics
ethane	ethylene	benzene
propane	acetylene	toluene
i-butane	propene	ethylpenzene
n-butane	1-butene	p- and m-xylene
i-pentane	i-butene	o-xylene
n-pentane	t-2 butene	1,3,5 trimethylbenzene
2-methylpentane	c-2 butene	1,2,-1 trimethylbenzene
3-methylpentane	1-pentene	1,2,3 trimethylbenzene
n-hexane		
2,4-dimethylpentane		

This section of the report discusses the collection and storage techniques for hydrocarbon samples and the separation and analysis techniques used to quantify individual hydrocarbons.

3.1.1 Methods of Sample Collection. - The collection of samples for the measurement of individual hydrocarbons is influenced by several factors. First of all, the concentrations of most individual hydrocarbon compounds in the ambient atmosphere are very low and the sensitivity of the detection techniques are such that an integrated sample is necessary to achieve a sample volume large enough for its components to be accurately measured. In addition, the container in which the sample is collected must also be used to store the sample until it is analyzed. This presents problems related to sample stability. The container must have properties that insure that degradation or enhancement of some species does not occur.

Many different containers have been described and tested for their characteristics regarding sample collection for hydrocarbons. One report describes a study that evaluated the four primary containers used to obtain ambient air samples for hydrocarbon analysis.[3] The four containers evaluated in this study were Teflon® bags, Tedlar bags, glass containers and stainless steel containers. These containers were evaluated for their performance with respect to both contamination and sample integrity.

Each container was filled with zero air to evaluate the effects of contamination over a storage period of 18 days. Teflon® bags showed significant contamination for C_1-C_5 hydrocarbons but by the 18th day, concentrations of FID responsive species in the C_5-C_{10} group were measured in the range of 1-2 ppmC. Both the stainless steel and glass containers showed virtually no contamination of the zero air after 18 days. The glass containers were more difficult to work with, however, since they could not be pressurized to any great extent. This complicated retrieval of the sample for analysis purposes.

Tests of sample integrity with combinations of NO + hydrocarbons were made to simulate the conditions likely to be present in early morning urban samples. Stainless steel cannisters and Tedlar bags maintained sample integrity quite well. Teflon® bags showed a steady increase in concentration of all compounds with time while the glass containers showed a steady decrease of all compounds in the sample. A long-term stability study using the stainless steel cannisters was performed. Of these four containers, stainless steel cannisters were found to be the best sample collection device for subsequent ambient hydrocarbon analysis.

A similar study was performed to evaluate bags made from aluminized Scotch Pak in addition to Teflon® and Tedlar bags and stainless steel cannisters.[4] Similar results were found for the Tedlar, Teflon® and steel containers and a much larger contamination was observed using the aluminized Scotch Pak bags. The contamination was attributed to the release of organic species from the bag material itself.

While the sampling containers are useful for obtaining whole air samples for the analysis of the principal hydrocarbon species in urban atmospheres, other important and interesting compounds are present at much lower concentrations in the atmosphere. To collect a sample of sufficient magnitude to allow quantification of these very low concentration species, a method is required to concentrate the sample from a large volume of air. Many materials have been used for trapping particular species of interest. The primary techniques used for trace organic species are cryogenic, absorption and adsorption.

Highly volatile substances are effectively trapped in cryogenic systems employing liquid nitrogen, liquid oxygen, or dry ice in acetone. However, large amounts of water can also be trapped. The presence of water in the sample causes problems in chromatographic analysis.

A number of solid or liquid sorbents have been shown to be effective in trapping specific compounds.[5] These materials can be chosen to be highly selective for particular species and the choice of sorbent is dependent on the particular need of the study. The list of materials which can be used as sorbents for trapping trace organics is extensive and all of the possibilities cannot be mentioned here. The widely used sorbents used for atmospheric sampling are: Tenax GC, Porapak Q, Chromosorb 101, Chromosorb 104, Carbonwax 600, Carbowax 400, oxypropionitrile,[5] Porapak N, Carbosieve 13, Porapak R, 20% DC-200 silicone oil[6] and graphitized carbon black.[7] Any of these substances require that a large volume of sample air be drawn through a tube containing the sorbent. While any of these techniques could easily be incorporated on an aircraft platform, the necessary integration time for the collection of the sample would make spatial resolution very limited. For this reason, detailed discussion of this sampling strategy was not included in this report.

3.1.2 Separation and Analysis Techniques. - Just as there are many sorbents used for sample concentration of organic materials, there are also many sorbent materials used for the separation of species within the sample. All of the materials mentioned as collection media previously are also routinely used in gas chromatographic columns for separation. A small volume of the concentrated sample is introduced to the separation column and flushed through the column with an inert carrier gas. The sorbent material in the column selectively retains individual species so that they are eluted at characteristic times. In this way, the individual species within a sample can be identified by accurately measuring their time of appearance in the detector at the outlet side of the gas chromatographic column.

The list of materials used for chromatographic packing is extensive and cannot be detailed here. The choice of packing materials is a decision that must be made depending on what specific information is required of a particular study. Individual hydrocarbon species are also numerous and any program of hydrocarbon analysis by chromatography must consider the information desired from the study as a first step. Only then can an appropriate chromatographic separation column be selected to best achieve program goals.

There are also many available techniques that can be used for hydrocarbon analysis. The two primary analytical methods used in quantifying individual hydrocarbon compounds separated by gas chromatography are flame ionization detection[8] and mass spectrometry.[9] In flame ionization detection, the materials that elute from the separation column are introduced to a hydrogen-rich flame. The carbon atoms within the hydrocarbon molecule are ionized by the heat in the flame and then enter an electric field. The ion current produced is measured and is proportional to the number of carbon atoms. The retention time (elapsed time between sample injection into the separation column and detector response) allows the individual species to be identified with a modest degree of certainty by comparison to retention times of known compounds. In mass spectrometry, the eluting sample components are introduced into a charging space and later detected by observing their mobility through an electromagnetic field which is dependent on their mass. Mass spectrometry is highly selective and the identity of the compound is more certain than by gas chromatography alone, but the technique is costly.

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3.2 Halogenated Organic Compounds

3.2.1 Collection Techniques. - Recent interest in the interaction between chlorine atoms and stratospheric ozone has brought attention to the measurement of flourochloromethanes in the upper troposphere and lower stratosphere. These compounds are very stable in the troposphere but undergo photolysis in the stratosphere producing free chlorine atoms which are suspected to cause depletion of the protective stratospheric ozone layer which filters solar ultraviolet wavelengths. An aircraft system for collecting samples for the measurement of halocarbons, principally CCl_3F and CCl_2F_2 has been described.[1] The system was flown at stratospheric altitudes in a Lear jet 24D. The system is similar to the stainless steel canister collection method described for tropospheric hydrocarbons. The samples are obtained by pumping ambient air into the stainless steel cans and analysis is carried out later in a laboratory.

More complex halogenated hydrocarbons, such as perchloroethylene and trichloroethylene, which are widely used in dry cleaning and in industrial metal degreasing, as well as many other halogenated organics, are receiving attention as potential carcinogens.[2] Sampling for these species is accomplished by concentration on activated charcoal scrubbers, tenax GC or other widely used chromatographic materials.

3.2.2 Separation and Analysis Techniques. - Separation of fourteen (14) different halocarbons of interest in atmospheric samples was obtained using 10% SF-96 on Chromosorb W. The column was temperature programmed from -10° to 70° C at 8° C/min.[1] Detection of these compounds is accomplished by either electron capture detection or mass spectrometry. The higher molecular weight halocarbons were separated on a column with 0.1% SP-1000 on Carbopack C. The analysis was completed with electron capture detection.

As was the case with the discussion of hydrocarbon species identification procedures, there are many separation columns and several detection methods available for separating and verifying atmospheric halocarbons. In each case, the use of any particular method is always dependent on the goals of the specific program as well as the resources available to the laboratory.

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3.3 Filter Collection of Gaseous Species

The technique of filter collection of gaseous species involves passing a known volume of sample air through either a treated filter or a sorbent column. The sorbent that is impregnated on the filter or placed in a column selectively retains the compound of interest. Analytical techniques that are not sensitive enough to directly measure ambient concentrations can then be used since a detectable amount of the compound can be concentrated on the filter medium.

A common problem to all sorbent sampling methods is that a sample mass above the detectability of the analytical technique must be collected before saturation of the sorbent occurs. At saturation, the condition known as breakthrough occurs and additional sample will pass through the sorbent without being trapped. Other limitations of this sampling technique, particularly in aircraft applications, is that the collection properties of the sorbent material may be temperature and/or pressure dependent.

Advantages of filter collection techniques, in addition to concentration enhancement, is that collection efficiencies are easily determined by arranging filters in series. Experimental artifacts can also be eliminated or minimized by masking a portion of the filter and using it as a control.

Filters made of natural cellulose material and treated with dibutoxyethylpthalate and Kronisol™ oil can be used for the collection of small particles. By dividing a filter into two sections treated with Kronisol oil, it is possible to distinguish between gaseous or particulate origins of the compound measured. The two sections of the filter can be divided by a chemically inert silicone rubber strip. Some of the specific materials used as filter or column sorbents and the species they effectively collect will be described below. Many such techniques exist or are possible and only the major atmospheric species that have been quantified in this way will be discussed.

3.3.1 Methods for Ammonia Sampling and Analysis. - The Oxalic acid/ring over technique[1,2] appears to be the most sensitive of the integrative methods for the determination of ammonia in ambient air. It consists of passing a known volume of sample air through a filter or filter tape (Whatman Nos. 1, 41 or 542) which has been impregnated with oxalic acid. The collection efficiency is essentially 100 percent. A heated Teflon® (TFE) prefilter is used to prevent the collection of ammonium salts on the impregnated filter. Subsequently, the sampled filter is placed in a ring oven[3] where it is sequentially washed with a 5% solution of o-phthaldicarboxylaldehyde, ethanol, 0.1 M sodium hydroxide and further distilled water. As a result of these washings, the reaction product is transported to and concentrated at a narrow ring on the perimeter of the filter which is adjacent to the heated zone of the ring oven. The determination of the ammonia concentration is based on the visual observation of the intensity of the colored ring and, by comparison, with the intensity of standard rings.

The technique is currently being used at the National Center for Atmospheric Research for their measurements of tropospheric ammonia levels. The sensitivity of this technique was estimated to be on the order of 0.1 ppb for these measurements. This estimate is supported by another estimate of 0.07 ppb sensitivity for a 200-min sampling period at a flow-rate of 5 L/min.[2] In field tests over the South Pacific, concentrations of approximately 0.14 ppb have been measured often.

Preliminary work has indicated that it is feasible to analyze oxalic-acid-impregnated filters by ion chromatography.[4] The reacted ammonia on the filter is extracted into solution where it can be measured as ammonium ion. Solution concentrations as low as 0.09 micrograms per liter have been analyzed with good precision. If it is assumed that 20 mL of liquid is required for the extraction and, if the filter sample volume is 30 m^3, this would correspond to a gaseous ammonia concentration of 0.1 ppb. This suggests that this analytical technique has the potential capability for tropospheric ammonia measurements; however, there has been no further development of this technique.

Another integrative technique, which has been recently developed, involves the collection of ammonia on a solid sorbent and subsequent analysis by any one of a number of techniques.[5] The sample air is drawn through a Pyrex® tube which is packed with 5 g of Chromosorb T (i.e., 30/60 mesh TFE Teflon® beads). This collection occurs at ambient temperature. At the time of analysis, the ammonia is thermally desorbed by heating the beads to a temperature of 100° C while passing purified air over the beads. The release of the ammonia occurs over a much shorter period (e.g., 6 min for 95% release) than the sampling period. As a result, the ammonia concentration in the purified air is many times larger than the original ammonia concentration. This permits much lower atmospheric concentrations to be measured than would be indicated by an analytical technique's intrinsic sensitivity.

Two analytical techniques were used in conjunction with this method: chemiluminescence and laser opto-acoustic detection. Both techniques yielded comparable results for ambient air ammonia concentrations between 0.2 and 0.5 ppb. It was also suggested that the thermally desorbed ammonia could be collected as ammonium ions in an acidic solution and then analyzed by ion chromatography.

The sensitivity of the overall method is limited by the sensitivity of the analytical technique and by the amount of sample volume which may be passed through the sorbent before breakthrough. The time until breakthrough was found to be a function of the ammonia concentration. The authors indicate that the sampling period must be no more than 40 min at a 1 L/min flowrate. They also estimate the method has a sensitivity of 0.5 ppb. However, reanalysis of the data which was presented in the paper suggests that much longer sampling periods should be possible for ammonia concentrations on the order of those which are found in the troposphere (e.g., 7 1/2 hrs at 1 ppb). This would permit much lower ammonia concentrations to be detected than is indicated in the paper.

This method has been recently used by NASA for the comparison of simultaneous remote ammonia measurements by an infrared heterodyne radiometer to in situ measurements using this method.[6] Tropospheric ammonia concentrations in the 1-2 ppb range were obtained at altitudes between 1.6 and 3.0 km.

3.3.2 Methods for Hydrogen Chloride Sampling and Analysis. - Although continuous in situ methods have been or are being developed for the measurement of hydrogen chloride in the troposphere, these methods do not appear to have yet attained adequate sensitivity to measure the low concentrations which exist in the troposphere. As a result, there has been heavy reliance on integrative methods of performing these measurements. The technique which has been used most frequently for the collection of hydrogen chloride samples in the troposphere and stratosphere is that of chemical-impregnated filters. However, there also exist other collection techniques which are still potentially useful. The most common technique which has been used for the analysis of such samples is spectrophotometry. The choice of this analytical technique has been primarily for reasons of accessibility and cost rather than because of the technique's sensitivity. Other analytical techniques have been developed which are as sensitive as or more sensitive than spectrophotometry. In the following paragraphs, several of these sampling and analysis methods will be discussed.

The tetrabutylammonium hydroxide (TBAH)-impregnated filter was developed for use in stratospheric measurements of acidic gases (e.g., hydrogen chloride, nitric acid and sulfur dioxide). TBAH was found to have the highest collection efficiency (virtually 100 percent) for hydrogen chloride among several impregnating agents which were tested.[7] TBAH also has the advantage of remaining viscous at the low temperatures (-70° C) which can be encountered in the stratosphere. Because of the low acidic gas concentrations which exist in the stratosphere, sample volumes on the order of 3,000 m^3 to 4,000 m^3 were needed in order to collect enough material for analysis.[8] Institute of Paper Chemistry Type 1478 cellulose filters were used because of their low airflow resistance. The filters were also coated with dibutoxyethylpthalate (also known as Kronisol™ oil) to improve the filter's collection efficiency for small aerosol particles and to improve the collection efficiency for sulfur dioxide.[9] In order to distinguish between acidic gases and particulate material, each filter is segmented into impregnated and unimpregnated halves. The acidic gas concentration can be determined by difference because the acidic gas can be collected only on the TBAH-impregnated half of the filter.

Until recently, statospheric acid chlorine vapor was assumed to be solely hydrogen chloride. It is now known that a significant fraction of stratospheric chlorine exists as chlorine nitrate.[10] The collection efficiency for chlorine nitrate on TBAH-impregnated filters has been found to be approximately 80 percent.[11] This means that the technique is not specific for hydrogen chloride but rather measures total acidic chlorine.

The TBAH-impregnated filter technique has been adapted for use in the measurement of tropospheric acidic gases.[9] The sampling apparatus was modified from that which is used for stratospheric measurements. A fluoropore membrane prefilter was used to collect aerosols. The acidic gases were then collected on a TBAH-impregnated Whatman 41 filter. Because this filter had a much higher airflow resistance than the IPC 1478 filter, only much smaller sample volumes could be passed through it. Typically, 30 m^3 of air was drawn through the filter over a 13-min exposure period. It was found that nitric acid vapor concentrations as low as 0.02 ppb could be measured with this sampling system.[12] Although the sampling system had been estimated to have a minimum detectable concentration of hydrogen chloride of 0.11 ppb, difficulties were encountered with background contamination which prevented measurement of tropospheric hydrogen chloride concentrations. Firstly, it is difficult to remove chlorine from the TBAH which had been introduced during the synthesis of TBAH. Secondly, TBAH seems to release a large and variable amount of chlorine contamination from the filter media itself. These problems were enhanced by the relatively small sample volumes which were used and the very low tropospheric hydrogen chloride concentrations.

Other impregnating agents have also been used for measurements of tropospheric inorganic chlorine concentrations. Whatman 41 cellulose filters which had been impregnated with 1.0 N lithium hydroxide in a 10 percent glycerol-water mixture have been used for surface measurements at remote, semiremote and coastal locations.[13,14] These filters were part of a three-stage sampling system for determining the distribution of tropospheric halogens among particulate and organic and inorganic gaseous fractions. The lithium hydroxide-impregnated filter was preceded in the sampling train by a Nucleopore membrane filter for particulate chlorine collection and was followed in the sampling train by activated charcoal beds for organic gaseous chlorine collection. Laboratory tests demonstrated that 100 percent of gaseous hydrogen chloride was trapped by a series of two lithium hydroxide-impregnated filters while virtually 100 percent of an organic chlorine compound, carbon tetrachloride, passed through the filters and was collected on the activated charcoal. The average sample volume which was passed through the sampling train was 100 m^3. Two to three days of sampling were needed to attain this sample volume. It appears that TBAH-impregnated filters are now favored over lithium hydroxide-impregnated filters. Although TBAH has a somewhat higher collection efficiency, the main reason for the choice of TBAH is that it remains tacky at the low temperatures which are encountered in the stratosphere.[15] Nevertheless, lithium hydroxide has been used successfully in remote atmospheric measurement programs.

Sodium carbonate-impregnated cellulose nitrate filters have also been used for the collection of inorganic chloride and fluoride gases.[16] The collection efficiency for hydrogen chloride ranges between 95 and 90 percent. The impregnated filter was preceded in the sampling train by a heated Teflon® filter which collected particulate chlorides. The penetration of hydrogen chloride through the membrane filter ranged between 90 and 97 percent. The sample volume ranged between 2.4 m^3 and 4.8 m^3 for sampling periods which varied from 2 to 4 hrs in length.

There appear to be two preferred methods for the analysis of chemical-impregnated filters: spectrophotometric techniques and neutron activation analysis. Each technique has desirable features which are not present in the other technique. The spectrophotometric techniques are relatively simple and do not require the expensive and uncommon nuclear reactor which is used in neutron activation analysis. However, neutron activation analysis has much greater sensitivity than does spectrophotometric techniques and is not subject to the minor interferences which are present for spectrophotometric techniques.

Two spectrophotometric techniques have been used in the analysis of chemical-impregnated filters. The mercury thiocyanate method[17] has been used with TBAH- and sodium carbonate-impregnated filters while the iron (III) perchlorate method[18] has been used with lithium hydroxide-impregnated filters. The mecury thiocyanate method has a sensitivity of 0.05 micrograms of chloride per milliliter of solution while the iron (III) perchlorate method has a sensitivity of 4 micrograms of chloride per millimeter of solution. Clearly, the mercury thiocyanate method is more sensitive by two orders of magnitude. The corresponding minimum detectable hydrogen chloride concentration in the atmosphere will be dependent on the sample volume and the details of the analytical procedure. For example, a TBAH-impregnated filter will have a minimum detectable hydrogen chloride concentration of 0.03 ppb when the sample volume is 3500 m^3 and it is analyzed by the mercuric thiocyanate method.

Both spectrophotometric methods suffer from slight to moderate interferences from various compounds. However, the only interferring compounds which are collected on the impregnated filters are inorganic bromine and iodine compounds. Because the tropospheric concentrations of these species are at least an order of magnitude less than that of hydrogen chloride, this should not represent a serious problem with these analytical techniques.[13]

The analysis of chemical-impregnated filters by neutron activation analysis offers greater sensitivity and specificity than spectrophotometric methods. An additional advantage of neutron activation analysis is that the filters can be analyzed directly without sample preparation being required. However, this technique requires access to a nuclear reactor and gamma-ray counting instrumentation. As a result, the instrumental requirements of neutron activation analysis are considerably more sophisticated and expensive than the spectrophotometric methods. Current detection limits for chlorine are on the order of 50-100 ng for filter samples although a sensitivity of 1.4 ng has been reported in the earlier literature for chemically-concentrated liquid samples.[13,15,19,20] If a conservative estimate of 100-ng detection limit is used and if a sample volume of 30 m^3 is assumed, then tropospheric concentrations on the order of 0.002 ppb can be measured using chemical-impregnated filters and neutron activation analysis.

The microcoulometric cell technique has been used in conjunction with sodium nitrate-coated Pyrex® sampling tubes for the analysis of hydrogen chloride in moist air.[21] Ambient air can be drawn through the tubes at a flowrate of 100 mL/min for the duration of the sampling period. The tubes are then capped and are taken into the laboratory for analysis. The tubes are washed with distilled water which is then directly injected into the microcoulometric cell. The sensitivity of the technique is limited by a 15 ± 8 ng chlorine background which is obtained from the coated tubes. Although some efforts had been taken to reduce the magnitude of this background chlorine level, this value represents the best which had been attained. However, it is possible that further reductions could be made. If one assumes that 16 ng (i.e., two times the standard deviation of the background level) represents a minimum quantification level and if the sampling period is on the order of three hours, then the minimum quantifiable concentration for this technique is 0.6 ppb. This could be improved by increasing the sampling period or increasing the bore of the sampling tube which could allow higher sample flowrates. This method was found to have high collection and recovery efficiencies and good reproducibility. No information is available concerning the effect of relative humidity on the collection efficiency.

A laboratory technique has been described for measuring hydrogen chloride in acetone-water solutions by derivatization of hydrogen chloride with epoxides which is followed by analysis with gas chromotography.[22] The epoxide (7-oxabicyclo [4.1.0] heptane) will be converted into 2-chlorocyclohexanol by reaction with hydrogen chloride. A small volume of the 2-chloroalcohol is injected into a gas chromatograph which is equipped with a flame ionization detector and either a packed or a capillary column. The minimum detectable aqueous concentration was determined to be about 20-40 ng of 2-chloroalcohol per gram of sample. This is believed to be sufficient for stratospheric measurements of hydrogen chloride. However, the method has not yet been used for actual atmospheric measurements. Several important details, such as the method of atmospheric sampling, must still be developed. It remains to be seen whether or not this analytical technique will prove itself.

3.3.3 Methods for Nitric Acid Sampling and Analysis.

- Although continuous methods for the measurement on nitric acid concentrations have recently been developed which appear to have adequate sensitivity for tropospheric measurements, their accuracy, precision and long-term reliability still has to be proven. In contrast, filter methods for the measurement of nitric acid have been used reliably in the field for a number of years. They have been shown to have adequate sensitivity for tropospheric measurements. As a result, they are competitive methods for nitric acid measurements in the immediate future although they may be eventually supplanted by continuous methods. In the following paragraphs, several filter methods of sampling for nitric acid and their associated analytical techniques will be discussed.

The most common filter methods for the measurement of nitric acid are those which involve chemical-impregnated filters. Two different impregnating agents have been developed. These are tetra-N-butylammonium hydroxide (TBAH) and sodium chloride.

The TBAH-impregnated filter was developed for use in stratospheric measurements of acidic gases (e.g., nitric acid, hydrogen chloride and sulfur dioxide).[8] For such measurements, Institute of Paper Chemistry Type 1478 filters were used because of their low airflow resistance. In addition to being impregnated with TBAH, these filters were also coated with dibutoxyethylpthalate (also known as Kronisol™ to improve their collection efficiency for small particles. In order to distinguish between acidic gases and particulate material, each filter is segmented into impregnated and unimpregnated halves. The acidic gas concentration is determined by difference because the acidic gas is collected only on the TBAH-impregnated half of the filter. In order to measure the very low nitric acid concentrations which exist in the stratosphere, sample volumes on the order of 3,500 m^3 to 4,000 m^3 are passed through the filters. The range of detection limits was 3 to 7 x 10^{-9} g/m^3 ambient, depending on altitude and sampling time, for balloon sampling.[23] At standard conditions, this corresponds to a sensitivity between 0.001 and 0.003 ppb. At an altitude of 11 km, the sensitivity would be between 0.008 and 0.019 ppb.

TBAH-impregnated filters have recently been used for measurements of nitric acid in the troposphere.[12,24] Whatman 41 cellulose filters which have been impregnated with TBAH and Kronisol™ oil have been used to collect nitric acid.[9] Two of these filters are used in series. These filters are preceded in the sample stream by fluoropore prefilter (Teflon®, 1 micrometer maximum pore size) which collects particulate nitrates in an attempt to eliminate a particulate nitrate interference with the nitric acid measurement. (Note that problems with this approach will be discussed in a later paragraph.) For airborne measurements at altitudes of up to 8 km, sample volumes on the order of 30 m^3 were passed through the filters during a 13-min sampling period. With these measurements, the nitric acid sensitivity was 0.06 ppb. TBAH-impregnated Whatman 41 filters have also been used for surface measurements of nitric acid.[24] Sample volumes on the order of 17 m^3 were passed through the filters during two-hour sampling periods. In this case, the nitric acid sensitivity was 0.008 ppb.

It should be noted that a slight interference from nitrogen dioxide has been seen for TBAH-impregnated filters.[12] Nitrogen dioxide reacts with TBAH to form a nitrate salt on the filter. Laboratory measurements indicate that the nitrogen dioxide collection efficiency is less than 5 percent. Because nitrogen oxides concentrations in the remote troposphere are on the order of 0.1 ppb, this interference should have a negligible effect on measurements of nitric acid in the troposphere. It was suggested that peroxyacetyl nitrate would cause a significant interference. However, no laboratory results were presented which confirm or refute this hypothesis.

For both stratopheric and tropospheric measurements, the preferred method for analysis of the TBAH-impregnated filters is the idophenol blue ammonia test.[25,26,27] After sampling has been completed, the filters are removed from the filter holders and are sealed in small microclean bags in which extraction takes place. The extractant is water which contains 20 ppm of disodium ethylenediamine-tetraacetate (EDTA) and 120 ppm of a nonionic wetting agent (BRIJ-35). This was added to the bag through a small slit which is then resealed. The bag is ultrasolicated to aid the extraction process. The extract is pressure-filtered through a millipore filter to remove particles. The extract is then transferred to the sampler of a Techicon Auto-Analyzer II in which the analysis takes place. After an electrolyte solution has been added, the extract is passed through a column which contains a granular copper-zinc alloy and in which nitrate and nitrite ions are reduced to ammonium ions. Sequentially, EDTA tetrasodium salt solution, sodium phenate solution, sodium hypochlorite solution, and finally, sodium nitroprusside solution are added. The optical density of the resulting indophenol blue solution is determined spectrophotometrically at a wavelength of 610 nm. The detection limit of the indophenol method is 5 ppb total inorganic fixed nitrogen in water.

Sodium chloride is the other impregnating agent which has been used for the collection of nitric acid vapor on filters. This method was developed for air pollution measurements in urban and rural areas[28,29,30] and in power plant plumes.[31] Cellulose filters (Toya 51A, Whatman 40 and 41 and Schleicher and Schuell 2W Fast Flow) were used for these measurements. Because of the relatively high airflow resistance of these filters, the sample flowrates were correspondingly low and ranged between 1.2 m^3/hr and 34 m^3/hr. The sampling periods ranged between 2 and 8 hours. Typically, Teflon® or quartz prefilters were used upstream of the impregnated filter to prevent the collection of particulate nitrates on the impregnated filter (see below for a discussion of problems associated with this approach). One investigator estimated the minimum detectable nitric acid concentration to be approximately 0.1 ppb.[31] However, others have reported measured concentrations as low as 0.02 ppb of gaseous nitrates.[28]

One problem which exists with sodium cloride-impregnated filters is a variable collection efficiency which is a function of the relative humidity. The collection efficiency of single sodium chloride-impregnated filters was 80 to 90 percent in the 50 to 95 percent relative humidity range. However, the efficiency dropped to approximately 50 percent at 25 percent relative humidity.[31] In order to achieve greater than 95 percent collection efficiency, it is standard practice to use two of the sodium chloride-impregnated filters in series when sampling. While this appears to have solved the problem for surface measurements of air which is relatively moist, there still may be a serious collection efficiency problem under the dryer conditions which exist in the middle and upper troposphere.

A slight interference from nitrogen dioxide has been observed for sodium chloride-impregnated filters. Nitrogen dioxide collection efficiencies varied between 0.4 and 0.5 percent.[28,30] Since remote tropospheric nitrogen oxides concentrations are on the order of 0.1 ppb, this interference should not significantly alter the values which are obtained for tropospheric nitric acid concentrations. Only a very slight interference was found for peroxyacetyl nitrate (approximately a 0.03 percent collection efficiency) and no interference was found for n-propyl nitrate.[28]

Two related spectrophotometric methods have been used for the analysis of sodium chloride-impregnated filters. The first of these methods is a hydrazine reduction-diazotization auto-analyzer technique.[32,33] Nitrate is extracted from the filter with hot water. The extract is transferred to the sampler of a Technicon Auto-Analyzer II. After a sodium hydroxide solution has been added to increase the pH, the extract is reacted with a hydrazine sulfate solution which reduces the nitrate ions in the extract to nitrite ions. This is done in the presence of a copper sulfate solution which acted as a catalyst for the reduction. The extract is then mixed with a color developing reagent which contains sulfanilamide to diazotize the nitrite ions and N-(1-naptha)-ethylenediamine dihydrochloride which reacts with the nitrite ions to form a highly colored Azo dye. The optical density of the dye solution is measured spectrophotometrically at a wavelength of 529 nm. The applicable range of this method is from 0.01 to 10 mg of nitrate per liter of extract. The nitrate ion concentraction by analyzing the same sample with and without the reduction step.

The second spectrophotometric method for the analysis of sodium chloride-impregnated filters is a cadmium reduction-diazotization autoanalyzer technique and is rather similar to the first method.[34,35] After the extract has been transferred to the sampler of the Technicon Auto-Analyzer II, a solution is added which contains ammonium chloride, disodium EDTA and BRIJ-35. The extract is then passed through a column which contains a granular copper-cadmium alloy and in which the nitrate ions in the extract are reduced to nitrite ions. The subsequent diazotization step and dye formation step are the same as in the first method. The optical density of the dye solution is measured spectrophotometrically at a wavelength of 540 nm. The applicable range of this method is from 0.05 to 10.0 mg of nitrate per liter of extract. The nitrate ion concentration is distinguished from the nitrite ion concentration by analyzing the same sample with and without the reduction step.

In the early stages of stratospheric monitoring for nitric acid, Institute of Paper Chemistry Type 1478 filters were used without impregnation. They were coated only with dibutoxyethylpthalate. It was found that gaseous stratospheric nitric acid was absorbed rather efficiently on these unimpregnated filters.[8,23,36] This method has more recently been used for total nitrate measurements which were made near the tropopause as part of NASA's Global Atmospheric Sampling Program (GASP).[37,38] These measurements were made from both research and commercial aircraft. For the sampling which was done from commercial aircraft, the sample flowrate was nominally 3.6 m^3/min (ambient) at an altitude of 10.7 km. The routine filter exposure time was 120 min. The standard deviation of the background nitrate level in the filters was 3.1 micrograms. If the minimum detectable nitrate mass is assumed to be equal to twice this standard deviation, then the minimum detectable total nitrate concentration is 0.018 ppb. This sensitivity is adequate for measurements in the free troposphere. However, it should be noted that this sampling was done without the presence of a prefilter in front of the impregnated filter to remove particulate nitrates. Consequently, this method yields nitrate values rather than nitric acid values.

The analytical technique which was used to analyze these unimpregnated filters is ion chromatography.[39] Nitrate which had been collected on the filters was extracted with a solution containing sodium carbonate and sodium bicarbonate. An anion exchange resin was used to separate ions in the filter extract. This was followed by an eluent suppression stripper column which neutralized background ions in the eluent. The ions were measured with a continuous conductivity detector. The sensitivity of the analytical technique was near one microgram.

Nitric acid has also been collected for analysis on unimpregnated filters which are composed of nylon and other fibers. As has been discussed in Section 2.9.2, nylon has frequently been used in continuous nitric acid instruments as a chemical filter which would selectively remove nitric acid from a sample stream. Nitric acid is determined by the subtraction of values from measurements which are made with and without the use of the nylon filter. Following such an application of nylon filters, it is not unexpected for someone to measure nitric acid by analysis of the filters.

A method which employs nylon wool as a filter has been tested in both the laboratory and the field.[40,41] One-hundred milligrams (100 mg) of nylon fiber was loosely packed into a sampling tube. A Teflon® membrane filter was located upstream of the sampling tube to remove particulate nitrates (see below for a discussion of problems associated with this approach). Sampling flowrates were up to 4.9 L/min for up to 65 min duration. The collection of nitric acid by the filter appears to be highly efficient as only a statistically insignificant amount of nitric acid was measured to pass through the filter. Insignificant amounts of nitrogen dioxide in both dry and humid air are collected by the filter. Although the analytical technique associated with this method is quite sensitive, the sensitivity of the overall method is limited by relatively high filter blanks (0.1 to 0.5 micrograms). The lowest measured nitric acid concentration which has been reported using this method is 0.8 ppb. It is unclear whether or not this method could be modified to attain the sensitivity which is required for tropospheric measurements.

Cotton fiber filters have also been used to collect nitric acid samples for analysis.[42] These fibers are loosely packed to a depth of 3 cm inside glass sampling tubes of 0.8-mm diameter. A Teflon® membrane filter is placed upstream of the sampling tube to prevent the collection of particulate nitrates on the fibers. Sampling flowrates vary from 8 to 15 L/min. Typically, 1 m^3 of sample is passed through the fibers. Cotton fibers were found to have as high a nitric acid collection efficiency as nylon fibers (95 to 100 percent) and were more efficient than Institute of Paper Chemistry Type 1478 filters (89 to 94 percent). Little or no detectable retention (less than 5 percent) was observed for nitrogen dioxide or nitric oxide which were passed through the cotton fibers. No data were presented concerning background nitrate levels or their variability on the fibers. The lowest measured value for an atmospheric nitric acid concentration have been measured with this method at a remote continental site (Fritz Peak, Colorado) which are approximately an order of magnitude lower than those which were reported (see supporting information in reference 13). This suggests that this method may have adequate sensitivity for measurements of nitric acid in the free troposphere.

For both nylon and cotton fiber filters, the preferred method of analysis for nitric acid is liquid extraction which is followed by conversion of the nitrate ions into nitrobenzene and the subsequent measurement of the nitrobenzene by gas chromatography.[43,44,45] The nitrates on the filter may be extracted with a sodium hydroxide solution prior to conversion or they may be converted directly without the extraction step. The desorption efficiency of the sodium hydroxide solution is essentially 100 percent. Nitrate ions are converted into nitrobenzene in a reaction vial which contains equal amounts of benzene and concentrated sulfuric acid and a lesser quantity of extract or water. The vial is then agitated for 10 to 15 min. The efficiency of the conversion of nitrate ions into nitrobenzene was essentially 100 percent. A 1 to 10 microliter sample is removed from the benzene layer for injection into the gas chromatograph. This should take place within 15 min after the completion of the reaction in order to prevent the loss of the reacted nitrate into the aqueous phase and to prevent the formation of benzene sulfonic acid which is a potential interferring peak in the chromatogram. Analysis is performed with a gas chromatograph which is equipped with an electron capture detector. The detection limit is approximately 10^{-12} grams for a one-microliter sample. A precision of 4 percent relative standard deviation is obtainable with the use of an internal standard in the benzene to correct for differences in injection size, detector sensitivity, fluctuation, etc.

It should be noted that a spectrophotometric method has also been used for the analysis of nitric acid which has been collected on nylon filters.[46] The previously described indophenol blue ammonia method has been used in conjunction with a Technicon Auto-Analyzer II. The filters are extracted with a sodium hydroxide and BRIJ-35 solution. The detection limit of the method is 5 ppb of nitrate in the extract.

A potential problem in the filter methods for the collection of nitric acid which have been discussed is their ability to distinguish nitric acid from particulate nitrate. Each of these methods utilize a Teflon® prefilter which is located upstream of the nitric acid-collecting filter to remove particulate nitrates from the sample stream. It is assumed that particulate nitrates will be permanently trapped on the prefilter and that only nitric acid will be collected on the downstream filter. Substantial evidence now indicates that these assumptions are at least partially incorrect. This problem has been discussed in the literature in terms of "artifact nitrate."

Initial research into this problem concerned the collection of nitric acid and nitrogen dioxide on glass fiber filters which were being used for particulate nitrate measurements.[47,48] It was found that nitric acid and, to a less extent, nitrogen dioxide would be converted into nitrates on the filters. It was estimated that roughly 90 percent of the nitrate which was extracted from polluted ambient air filter samples was due to artifact nitrate. However, the problem does not extend to Teflon® prefilters. Numerous investigators have shown that Teflon® filters do not absorb nitric acid or nitrogen dioxide.[28,30,42,47,48] This indicates that nitric acid measurements using filter methods will not have a low bias as the result of the use of Teflon® prefilters.

However, Teflon® prefilters may cause a high bias in such nitric acid measurements due to the volatilization of nitric acid from particulate nitrates which have been collected on the prefilters. Nitrate levels on glass fiber filters have been found to decrease during storage and during extended sampling.[49,50] Similar results have been seen for quartz and Teflon® filters.[30,31] When clean air at 50 and 80 percent relative humidity was passed through Teflon® filters bearing ammonium nitrate aerosol, 40 and 50 percent of the nitrate was lost respectively. Approximately the same amount of nitrate was collected on sodium chloride-impregnated filters which were located immediately downstream of the Teflon® filters. Ammonium nitrate is considered to constitute a significant fraction of particulate nitrate in the atmosphere. It has been shown directly and indirectly that particulate ammonium nitrate exists in equilibrium with gaseous nitric acid and ammonia.[51,52,53] Consequently, ammonium nitrate which has been collected on filters will volatize and release nitric acid if the gaseous nitric acid and ammonia concentrations or the temperature are altered from when the ammonium nitrate was collected. The presence of water vapor, sulfuric acid aerosol and particulate ammonium sulfate also influence the equilibrium relationship in a complex fashion.

These results suggest that it may be difficult to obtain an entirely accurate value for the tropospheric nitric acid concentration when filter methods are used in conjunction with Teflon® filters. It may be difficult to distinguish between gaseous and particulate nitrate concentrations in the troposphere. As these results were obtained for surface conditions, it is difficult to extrapolate to conditions in the free troposphere. Additional research is needed in this area before firm conclusions are reached.

It should be noted that research is in progress on an alternate method to measure nitric acid via filter methods. This is the diffusion denuder difference approach which was originally applied to the measurement of total sulfur in submicrometric aerosols suspended in air containing sulfur dioxide.[54] This approach has subsequently been used to determine gaseous nitric acid concentrations.[55] The basic principle behind the diffusion denuder is the difference in the diffusivities of gaseous nitric acid and particulate nitrates. The diffusion coefficients of gases are several orders of magnitudes higher than those of aerosols. Consequently, if a dilute mixture of gaseous nitric acid and particulate nitrate flows laminarly through a long, narrow tube whose wall is a perfect sink for nitric acid, the nitric acid will be completely absorbed within the tube while most of the particulate nitrate will emerge from the exit of the tube. Nitric acid can then be measured by the difference between the total nitrate which has been collected on two nylon membrane filters; one of which has a nitric acid diffusion denuder upstream. Experiments have been conducted which show that this method has excellent precision and yields values for nitric acid concentrations which are consistent with those which were obtained from long-path infrared Fourier transform spectroscopy. The results of these experiments are due to be published in the near future.

3.3.4 Other Filter Methods. - Filters impregnated with triethanolamine have been used to collect samples of NO_2.[56] The filters treated in the same way can also be used to collect NO by first reacting the sample air O_3 to convert NO to NO_2. The analysis is completed using a modified Saltzman reagent. A solid absorbent coated with triethanolamine was also used to collect ambient samples of NO_2.[57] The technique was expanded to include the collection of NO by first producing an oxidizing reaction with CrO_3. The determination of NO_2 concentration was made spectrophotometrically following a color producing reaction with sulfanilomide and N-1-napthylethylene diamine dihydrochloride.

A filter collection technique for SO_2 has been reported.[58,59] In this method cellulose filters are impregnated with a solution of 0.5N KOH. The filter collection efficiency was greater than 90% for linear velocities of 50 to 90 cm/s. At relative humidities below 30%, the collection efficiency dropped sharply.

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3.4 Particulate Filter Collection

An excellent review of particulate filter collection principles has been given by D. F. Leahy. There are a number of filter materials available and the selection of any one of them is ultimately dependent on application. The most basic use of filter collection is to make determination of total particulate mass. This is usually accomplished in HiVol samplers with glass fiber filters. In this approach, a large flowrate of air is drawn through a sheltered filter for a period of 24 hrs. Obviously, the time resolution of such a measurement eliminates any analysis involving diurnal distributions. Also, total mass of particulate is not very meaningful since no size distribution or composition information is provided. The trend in particulate sampling is toward size fractionated elemental, or compound composition, analysis. The principal compounds of interest in ambient particulate measurement are ammonium, nitrate, sulfate, acidity and sulfuric acid. Aircraft-mounted particulate filters collected over a sampling time of approximately 30 min have been analyzed successfully for nitrate and sulfate. After the total mass has been determined by gravimetry, the sample is extracted into a buffer solution, and analyzed by ion chromatography.

Sensitive analysis techniques are possible so that exposures of approximately 30 min yield sufficient collected material for quantification. Therefore, it is important that the filter material have low consistent blank values with respect to the compounds that are measured. In addition, the filter material itself must be strong, inert and efficient under conditions of high linear flowrates. Some filter materials can also collect gaseous compounds such as NO_2 or SO_2. These compounds can sometimes be oxidized producing artifact nitrate or sulfate formation on the filter material itself. Many filter materials can be pretreated to remove background concentrations of materials that will interfere with the measurements or give rise to chemical reactions on the filter that can result in artifact particulate formation.

There are several measurement methods applicable to the determination of elemental analysis of filter collected particulate samples. Some of the possible analyses and the elements determined are listed below. This list is by no means exhaustive but merely provides a guide to the types of analysis that are possible. Flameless atomic absorption spectrometry is used to determine the elemental composition of cadmium, lead and manganese in size-fractionated aerosol samples.[1] Energy dispersive x-ray fluorescence spectrometry has been used for the determination of 27 elemental constituents in particulate samples.[2] The elements measured are: Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Hg, Pb, Cd, Sn, Sb and Ba.

The minimum detectable limits range from 2.6 ng/cm^2 for selenium to 200 ng/cm^2 for aluminum. Membrane filters of 0.45 μm pore size were used to collect particle samples for analysis by neutron activation.[3] The filters were 99% efficient for collection of particles larger than 0.1 μm in diameter. The system was used to collect 10 m^3 of sample aboard an aircraft. The filters were analyzed by neutron activation for mercury, arsenic and bromine. The detected concentrations were 0.7-10 ng Hg/m^3, 0.05-20 ng As/m^3 and 1-90 ng Br/m^3. Samples for the determination of inorganic particulate nitrate were collected on a sample train consisting of a millipore FHLP filter and a Toyo 51A filter treated with NaCl.[4] The nitrate determination was made colorimetrically. Interference due to NO_2, PAN and organic nitrate were negligible.

A system for the collection of size fractionated aerosol has been devised and operated aboard an aircraft.[5] In this particular arrangement a four-stage cascade impactor was mounted on the wing of a Queen Air research aircraft. Operating with a flow of approximately 5 L/min for a sampling period of one hour allowed samples to be acquired that were suitable for analysis by proton induced x-ray emission (PIXE). Although PIXE analysis can be achieved for virtually any element, the work described here was united to the quantification of sulfur and iron.

The cascade impactors were housed in a specially designed streamline pod which was mounted to the wing of the aircraft. The system was designed to optimize the collection of a representative sample. The particle size fractions collected on these flights was <0.4, 0.4 - 0.8, 0.8 - 1.6, and >1.6 μm aerodynamic diameter. Since cascade impactors can be arranged to suit the needs of a variety of analysis methods, this system appears to represent a means of obtaining size distribution information as well as mass and composition information from aircraft platforms.

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4.0 METEOROLOGICAL SENSORS

In situ meteorological sensors are used for the routine acquisition of meteorological data both at the Earth's surface and at altitudes up to 30,000 m. Measurements are made on surface-based platforms, tower-mounted platforms, and airborne platforms (either by aircraft or balloon). Rugged and reliable meteorological instrumentation has been developed and operated for many years to provide data for weather forecasting and recording climatology. Since accuracy requirements were not stringent for these applications, the emphasis was placed on developing instrumentation which was relatively inexpensive, maintenance-free and reliable. These instruments have been in service for many years and because of their satisfactory performance, little has been done toward the development of radically new instruments. Recent advances in technology have made possible more accurate, sensitive meteorological instrumentation which has been used for special research programs, model verification studies, or remote sensor verifications where more sensitive or more accurate data were needed. Many of these instruments are still in the experimental or developmental stages with improvements expected as the development process continues. These newer instruments offer increased sensitivity, faster response, and decreased susceptability to interferences. However, increased requirements for attention, maintenance and calibration are often necessary for these instruments.

Four meteorological variables are routinely measured at the surface by the National Weather Service. These measurements are made at a large number of locations which make up a network from which the synoptic meteorological systems can be tracked, for the purpose of local weather forecasts. A brief description of these variables and the reason for measuring them is given below.

Wind velocity is the instantaneous rate of air movement at a point, and may be expressed as a three-component vector quantity. In many cases only the horizontal components are necessary for determining transport rates or simply defining meteorological conditions. Wind speed and direction are usually reported as an average over a period of time to facilitate data handling for synoptic forecasting and pollution dispersion calculations.

Wind direction is also important in defining frontal zones, predicting storm movement, and anticipating orographic influences on local weather. In an air pollution sense, the wind direction and wind speeds control where the major impacts of sources will be.

Aside from their function of furnishing a comfort index for humans, temperature measurements furnish valuable information for modeling of atmospheric phenomena. The atmospheric mixing depth, stability characteristics, and chemical reaction rates are some important temperature dependent features of chemical dispersion models.

Humidity is a general term for the water vapor content of the air. Relative humidity and dew point are specific measures which are related to humidity. Relative humidity is the dimensionless percentage ratio of the partial pressure of water to the maximum vapor pressure attainable before saturation at the given temperature. Dew point is the temperature to which the air must be cooled before moisture condenses. Of the three terms, ambient temperature, dew point and relative humidity, if any two are known, the third may be computed through use of psychrometric charts or tables.

Pressure measurements are made for two purposes. In fixed locations, pressure measurements are made to monitor variations in atmospheric pressure for the purpose of locating regional weather systems (when a network of such measurements are made). Pressure sensors used for this purpose must be stable since the observable changes are small compared to the pressure being monitored. The second application of pressure sensors is to keep track of the altitude at which other variables are measured aboard airborne platforms to determine vertical profiles.

The various sensor techniques commonly used to obtain measurements of these meteorological variables are discussed in Section 4.1 of this report. The advantages and disadvantages of each sensor type are discussed in terms of accuracy, stability and precision.

The importance of atmospheric mixing, and both short- and long-range transport at altitudes above the surface have been identified as significant factors for determining accurately the fate and impacts of atmospheric pollutants. Therefore, upper air winds, and vertical temperature and humidity profiles are being monitored with higher frequency than ever before. In Section 4.2 some of the considerations applied to in situ sensor systems for obtaining such information are discussed. Instrument operation under conditions of changing pressure and temperature (such as those encountered in altitude profile measurements) or of high speed (such as those on an aircraft platform) presents problems in addition to those encountered at a fixed surface station.

The remainder of Section 4 describes the capabilities and limitations of improved technology and remote measurement systems for various meteorological features. The systems discussed include acoustic sounder systems, radio acoustic sounder systems, and systems utilizing radiometers and radars.

4.1 In Situ Measurement Techniques

4.1.1 Wind Speed and Direction. Horizontal winds may be measured by one of two techniques. The first technique consists of measurement of air motion over a period of time by use of balloons or parachutes whose horizontal velocity component is assumed to be equal to that of the wind. The second technique is the direct measurement of the wind with fixed sensors.

The technique of tracking air movement with balloons is routinely used by the National Weather Service (NWS) to determine upper air movement by recording the trajectory of ascending balloons. Constant pressure altitude balloons, dropsondes and aircraft may also be used to measure winds by this technique.

A variety of techniques are available for the measurement of wind speed and direction at a fixed location. The most frequent technique is the rotational anemometer. In this technique, the speed of the wind is measured by the rate at which it rotates a set of cups or a propeller. The cup anemometer responds equally to wind from any direction in the plane of the cups, while the propeller must be oriented in the direction of the wind (if total wind speed is to be measured). This orientation may be maintained by wind vanes if a single propeller is used; however multiple propellers may be mounted orthogonally to determine each component of the wind. The vertical component is only measured where estimates are to be made of turbulence. When propeller anemometers are used to measure winds which are not parallel with the rotational axis, a small correction may be necessary to compensate for slight discrepancies between actual response and the ideal cosine (vectoral) response. Within the sensor, rotation rate may be sensed by a generator or photochopper; the latter yielding thresholds as low as 0.1 m/s (0.2 mi/hr). However, low threshold units generally have high maintenance requirements and limited durability when compared to the more durable, less sensitive units.[1]

The pressure anemometer is one in which the wind is measured by the force it exerts on a plate or tube. Commercial instruments using strain gauges to make these measurements are available for one- or two-dimensional flow. These units have the advantage of no moving parts but require more elaborate electronics for signal processing than other techniques.

Hot wire anemometers determine scaler wind speed by measuring the rate of cooling of heated elements. These sensors are primarily used as portable sensors for point measurement of airflow inside buildings since the sensors would be susceptable to errors from precipitation.

Sonic anemometers consist of sound transmitter/receiver pairs which measure acoustic velocity in both directions along a line. The vector component of the wind along that line may be determined from the difference in the two speeds. Typically, the velocity is measured by measuring the pulse travel time over short distances on the order of 0.2 m. Experimental instruments have been made with accuracies of 1% and thresholds of 0.005 m/s.[2]

The frequency at which vortices are shed from a fixed strut in moving air is directly related to the velocity of air across the strut. Wind sensors have been fabricated based on this principle but generally have limited use because most configurations have to be oriented with the wind in order to make meaningful measurements. The vortex-shedding frequency is not dependent on density of the air which makes the sensor useful as a true airspeed sensor on aircraft (no compensation is necessary for temperature or altitude).

Wind direction is usually sensed by either a vane coupled to potentiometers to provide electrical output, or as mentioned earlier, by vectorial measurement of wind speed using fixed axis anemometers. Vane-type sensors typically provide accuracies of ±2°. Optional configurations for vane-type units are usually available which allow the units to track wind directions continuously over 540° to reduce errors which are frequently encountered when averaging wind direction data when wind direction fluctuates about 0°. An alternative solution is to use processors which vectorally average the speed and direction data.

4.1.2 *Temperature*. - A variety of sensor types have been used for the measurement of temperature. Those which are appropriate for atmospheric measurements are as follows:

Thermometers
Thermistors
Resistance Temperature Devices
Thermocouples
Deformation-type Thermometers

Liquid in glass thermometers usually contain an alcohol/dye mixture or mercury (alcohol used below -38° C where mercury freezes). This type of sensor is frequently used as a transfer standard but is not usually acceptable for routine monitoring because of the lack of an electrical output. NBS traceable units are available with resolution of better than 0.1° C.

Linear thermistors are composites of two or more thermistors configured to give a voltage which is linear to a fine tolerance over a given range (i.e., within 0.1° C for -5 to +45° C). When used in the proper circuit, linear thermistors provide the largest unamplified voltage change of any of the common temperature sensors for a given change in temperature.

Resistance temperature detectors are wire resistance elements (e.g., platinum) whose resistance changes with temperature. These provide the best stability of temperature sensors but because of small resistance temperature coefficient (0.39 Ω/°C for a 100° sensor) require very stable circuitry for conversion of resistance to a voltage form suitable for recording. Also, RTD's are inherenty nonlinear and must be compensated if the full accuracy potential is to be realized.

Thermocouples are sensors which produce a small voltage from the peltier effect at the junction of two dissimilar metals. Thermocouple signals require considerable amplification and must be linearized. Lead wire to the sensor is usually made from the same dissimilar metals which comprise the thermocouple to minimize the number of junctions in the system. Because of the sensitivity of this technique to temperatures in other parts of the circuit and the requirement for some form of ice point reference, this technique is usually reserved for high temperature measurements where other techniques are unsuitable.

Deformation-type thermometers are sensors which rely on thermal expansion (deformation) of a bimetalic strip or a gas-filled bellows for sensing of temperature. Mechanical movement is amplified through levers or gears and coupled to a dial or strip-chart mechanism.

Quartz oscillators are crystal-controlled oscillators whose frequency varies with temperature. These are usually not used for ambient measurements because of self-heating characteristics due to power consumed. The frequency dependence on temperature is highly repeatable, and these sensors perform well as high resolution transfer standards when used in well-stirred constant temperature baths.

4.1.3 Humidity. - A number of techniques are currently available for measurement of humidity. Those which are suitable for routine use are as follows:

- Psychrometers
- Hygrographs
- Cooled-mirror hygrometers
- Lithium chloride hygrometers
- Hygristors

Psychrometers consist of a pair of thermometers one of which is covered with a wick wetted with water. The depression in temperature arising from evaporation may be used to compute relative humidity (or dew point) through psychrometric tables. These devices require a moisture source and some form of aspiration to bring the evaporative process to equilibrium. This technique is usually used for manual observations.

Hygrographs measure relative humidity by indicating the change in the physical dimensions of a hygroscopic material (human hair, gold beaters skin) in response to changes in the moisture content of ambient air. These instruments which usually give only a mechanical-type readout have a range of operation from 20% to 80%. Electric hygrometer elements have electrical properties (e.g., resistance) which change directly as a result of changes in moisture content of the air. Example sensors of this category are the carbon hygristors used in radiosondes where the simplicity of these devices is most beneficial.

Cooled-mirror hygrometers sense dew point directly by cooling a reflective surface to the point where condensation forms on the surface. The presence of condensation is sensed photo-optically and the cooling of the mirror is continuously adjusted to maintain equilibrium. Although initial instruments were not noted for reliability this principle has been successfully used in a number of commercial instruments. Claimed accuracy for some commercial versions are 0.2 to 0.4° C.

Lithium chloride dewcell sensors utilize a bobbin saturated with lithium chloride solution. This bobbin is heated by electricity flowing through the solution to the point where the water is driven off and conductivity decreases. The temperature at which this equilibrium is maintained is proportional to dew-point temperature. These sensors must be kept in operation to prevent washout of the LiCl salt with water absorbed from the air, and as such, are not suitable for unattended operation.

Other humidity sensor systems which are used in research applications and have not yet reached widespread usage are the diffusion hygrometer, microwave cavity refractometer and Lyman-Alpha hygrometer. The diffusion hygrometer measures the diffusion of moisture through porous membranes. The microwave cavity device measures changes in the humidity-related dielectric constant of air by microwave techniques. The Lyman-Alpha hygrometer measures the absorption of ultraviolet radiation by water vapor in the air and is used where fast response is necessary, such as on aircraft.[3] All these techniques have been used in research programs but are still in the developmental stage.

4.1.4 Pressure Sensors. - Common sensing techniques which are used to measure pressure are as follows:

Mercury Barometers
Expansion Bellows
Strain Gauge Pressure Transducers

Mercury barometers have a column of mercury held in an evacuated glass tube by atmospheric pressure. The height of the column may be accurately measured by optical or mechanical means providing a direct measure of atmospheric pressure. This technique is inherently accurate and simple; however, it is suitable only for fixed laboratory environment.

Expansion bellows are configured such that changes in atmospheric pressure produce a deformation in temperature-compensated bellows. The mechanical movement produced may be linked either to a potentiometer for electrical readout or to a dial indicator for visual indication. In radiosonde applications, the bellows are linked to a commutator which multiplexes various sensors and references at a rate indicative of ascent rate.

Strain gauge pressure transducers measure differential pressure between two sides of a diaphragm by measurement of deformation of the diaphragm with strain gauges. Absolute pressure measurements may be made by placing a sealed vacuum against one side of the diaphragm and applying the atmosphere to be measured to the other. Transducers fabricated in this manner are rugged and give accurate results in comparison to their full scale; however, they are not as accurate as either the bellows or mercury barometer units. The system complexity is also higher for these units because of the circuitry necessary to convert small resistance changes to output voltages.

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4.2 Meteorological Sensor Systems

The application of meteorological sensors for making measurements at the Earth's surface is generally straightforward if certain guidelines are followed to ensure the measurements are representative of the observed meteorological conditions.[1] The conditions at the surface are greatly influenced by conditions which occur above the surface. In order to study and characterize some meteorological processes, measurements must be made throughout the troposphere. In situ instrumentation has been used for these measurements by operating it on fixed or mobile platforms which can be elevated above the surface. This section describes some of the systems which have been used for this purpose.

A particular problem associated with temperature measurements on any meteorological sensing system is to avoid erroneous air temperature measurements due to radiative heating. Care must be taken to totally shield the ambient temperature sensor from effects of both solar and terrestrial radiation. Power-ventilated aspirators with baffled inlets preventing radiation from entering the intake are used for fixed ambient measurements where power is available and weight is not a premium. A variety of self-ventilated designs have been produced for use on other applications such as tethered balloons and remote locations where power is not available. To avoid radiative heating of temperature sensors on radiosondes, the sensor thermal mass to surface area ratio is reduced by making the sensor as small as possible. In addition to providing shielding for radiation effects, housings for use in high velocity environments (such as in an aircraft) must be designed to eliminate errors (or provide for their correction) due to frictional or compression heating effects (see Section 4.2.6).

4.2.1 Tower-mounted Systems. - Tower-mounted meteorological systems are the most common source of meteorological data for those variables which vary significantly with altitude near the surface. Variables in this category include winds (speed and direction, vertical and horizontal) and temperature.

Towers provide direct and rigid mounting of in situ meteorological sensors. Since cabling can be routed to each sensor, bulky electronics which do not have to be collocated with the sensor can be mounted in a shelter near the base of the tower.

The economic feasibility diminishes as the altitude of measurement increases. Ten-meter (10-m) towers are commonly used for low-level meteorological monitoring. Towers of this height are easily installed with ordinary hand tools and can be easily relocated. Taller towers become necessary when measurements of temperature lapse rate are to be made or when upper air wind measurements are required continuously. Towers of 100-m height are frequently used in applications such as compliance monitoring and special field studies involving dispersion from elevated pollution sources.

Towers taller than 100 m for meteorological monitoring are seldom encountered except in special purpose meteorological research installations. The most elaborate installation in the United States is the Boulder Atmospheric Observatory jointly operated by the Wave Propagation Laboratory (a part of the National Oceanographic and Atmospheric Administration) and the National Center for Atmospheric Research located near Boulder, Colorado.[2] This facility includes a 300-m tower instrumented at eight levels for the measurement of winds (including turbulence), temperature and dew point. Additional measurement capability is located at the site by acoustic sounders, optical anemometers, conventional anemometers and sensitive pressure transducers, to provide additional data to complement data from the tower-mounted sensors. A 1000-kg capacity carriage is provided on one side of the tower for obtaining 0 to 300-m profile data with a single set of instruments. A two-man elevator provides ready access to all instrumented levels.

Television towers have been used in some cases for mounting of meteorological instrumentation. Towers generally exist near urban centers which may be instrumented up to heights of 300 to 500 m. The use of existing television towers obviously saves the expense of erecting towers especially for making meteorological measurements.

4.2.2 Tethered Systems. - Tethered systems refer to those systems which rely on buoyant forces to maintain the measurement platform at some altitude and utilize rope or cable to maintain the platform at a relatively stable location. The platforms may be subdivided into two classifications: 1) balloons (lighter than air), and 2) kites which require wind in order to remain aloft. Balloons of many different sizes have been used for tethered meteorological monitoring purposes. The British Meteorological Office has operated one of the largest balloons used for this purpose, having a volume of 1300 m^3 and a payload capability of 800 kg at an altitude of 900 m. More common balloon volumes described in literature are around 7 m^3. The lift capacity of the balloons varies with the volume and weight of the balloon; therefore, the size of the balloon may be selected based on the sensor package desired.

For balloons which fly at significant heights (greater than 100 m), it is generally easier to provide on board energy storage (batteries) in the instrument package than to provide additional wiring for carrying power from the ground simply because of the additional weight necessary for the power cable. For the same reason, radio telemetry is also used to transmit the data to the ground thus saving the weight of signal cable.

Since the balloons are tied to the ground, they remain relatively stationary in the wind field and therefore provide a suitable platform for monitoring the average wind velocity. However, tethered balloons are susceptable to local movement due to wind changes, and may even oscillate about their tethered point under certain conditions (lightweight tethers and some balloon configurations). These motions would make the platform unusuable for the mounting of turbulence or fast response wind sensors. Attempts to alleviate this problem by the use of multiple tethers result in increased operational difficulty in control of the tethers.[3]

Tethered balloons offer the operator the choice of altitude where measurements are to be made within the maximum limitations of the balloon. Vertical soundings may be taken by raising and lowering the balloon at a rate governed by the winch which reels in the cable. Ascension/descension rates from 1 to 3 m/s are typical for most systems reviewed, allowing 600-m profiles to be obtained in 3.3 to 10 minutes.

Tethered balloons are operational during most weather conditions except for 1) a condition of sufficient turbulence to cause damage to the balloon or instrument package, and 2) sustained high winds which push the balloon laterally and prevent it from reaching its intended altitude. The maximum winds which may be withstood vary with the construction of the balloon. Some balloons are specified as operable only at ground wind speeds of 4 m/s and up to 10 m/s once airborne,[4] while other units will tolerate winds to 25 m/s.[5]

Almost any type of sensor or instrument may be operated on a balloon so long as sufficient power and support (gases, etc.) can be provided in a self-contained package or from the ground with a reasonably lightweight umbilical cord. In some cases, multiple packages may be installed along the tether so that the balloon does not need to be completely lowered to make a sounding. The inexpensive, rugged and reliable radiosonde-type instrument packages are most commonly used (see Section 4.2.3). The tethered balloon may also be used for applications which require the sensor package to maintain a known orientation if special provisions are made for measuring the orientation. Such packages have been produced using a remote reading compass to determine the package orientation.[5,6,7,8]

It is possible to utilize lifting forces provided by heavier-than-air kites to lift instrument packages to altitudes. However, the more common application is to use the kite as a sensor of wind speed by measuring the stress on the tether line, and direction by sensing the heading of the tether line. Commercial implementations of this concept are available which indicate the measured values or record them on a strip-chart recorder.[9] This system operates at wind speeds of 3 to 50 m/s.

The system may be used when ground level winds are less than 3 m/s by attachment of a balloon with thread that will allow the balloon to break away once the kite encounters winds above 4 m/s. This generally occurs once the kite gets above surrounding trees, etc. Advantages of this system include low cost and ease of installation compared to other systems for obtaining wind speed and directions at altitudes up to 300 m.

4.2.3 <u>Balloons - Untethered</u>. - Untethered balloons, with or without instrument packages, are used for one of two purposes: 1) to obtain a single vertical profile of some meteorological parameter(s), or 2) to obtain data including location of a constant pressure altitude airparcel as it is carried through a region. The balloons used for a vertical profile are by far the more common as exhibited by the number of daily radiosonde soundings taken by the NWS and others.

The instantaneous position of a free flight balloon is specified as an altitude and a lateral position vector. The altitude is always required in order to determine a point in the vertical profile where the measured data are to be placed. The measurement of horizontal position is somewhat more complex and is required only when upper winds are to be determined. There are a variety of methods available for both of these measurements (some techniques yield both altitude and lateral position). The selection of specific methods is dependent on required accuracy of data, training of available personnel and economics.

Altitude is usually measured by one of three basic methods: 1) time elapsed since the launch, 2) measurement of pressure, and 3) triangulation from ground. The elapsed time method is the simplest method in terms of equipment and operator skill required. The balloon is inflated until its buoyancy is sufficient to lift a known weight. With proper care during this process, the balloon should exhibit an empirically determined constant rate of ascent, particularly over a low altitude range. This rise rate may be periodically verified by triangulation sitings from the ground.

The second method is measurement of pressure on board the radiosonde and telemetering the information back to the ground. Usually an aneroid barometer is coupled to a switch arrangement which causes the telemetry transmitter to alternate between different measured parameters and reference signals at a rate which is dependent on pressure change. Therefore, the pressure altitude of a given data point may be determined directly by its location in the known commutation sequence. Other arrangements are utilized, including units with dual-aneroid pressure transducers, one for low altitudes (1060 to 60 mbar) and a second for higher altitudes (100 to 3 mbar). Typical errors for aneroid pressure sensors range from 2 mbar at near full-scale pressure of 1000 mbar (adjustable to lesser value during preflight procedure), to fractions of a mbar at lower pressures.

Other pressure measuring techniques include the monitoring of the temperature of a liquid with a boiling point below ambient temperatures (such as Freon 11). This device is called a hypsometer. Although such measurements are a more repeatable physical characteristic (and therefore not subject to unit-to-unit variation), the required accuracy of the temperature measurement restricts the available precision of the measurement. The sensitivity coefficient is 0.03° C/mbar at 1000 mbar rising to 0.36° C/mbar at 50 mbar. Such devices are useful at higher altitudes (lower pressures), and are sometimes used to supplement aneroid-type commutators to provide additional high altitude data.

The last altitude measurement technique is triangulation. This technique consists of the measurement of angular elevation and heading to the balloon from two separate points by visual sighting. This method is generally referred to as the double-theodolite method named for the telescopic instrument used to measure the angles. The attainable accuracies vary substantially with measurement conditions; decreasing with altitude, winds and visibility. The accuracy functions are well-tabulated.[10]

The measurement of lateral position is essential for the accurate determination of winds. Winds are determined from changes in position of the balloon. The more accurately the position can be determined, the shorter time period necessary for confidently determining winds to the required accuracy. Therefore, there is a tradeoff involving vertical resolution of the wind measurements at the expense of accuracy of the reported measurements.

Techniques for the measurement of lateral position for the purpose of obtaining wind information include radio tracking, radio tracking with ranging radar, visual tracking (manual) and processing of navigational signals.

Visual tracking is performed by the same techniques described for altitude measurement. Position and altitude information may be determined from triangulation from dual-theodolite measurements. If altitude information is known, either from direct radiosonde pressure measurements or from an assumed ascent rate, then lateral position can be computed from azimuth elevation measurements made at a single observation point.

The tracking of the balloon requires that the operator keep the image of the balloon centered in a telescope, periodically stopping every 30 seconds or every minute to read angles of heading and elevation from the theodolite scales. This method, like all manual techniques, is dependent on the care and ability of the operator to make the measurements accurately. Modifications have been made to some theodolites to provide automatic recording of the data to allow the operator to concentrate entirely on the tracking process and not take his eye off the balloon to make readings.

Theodolites generally provide azimuth and elevation data accurate to typically 0.1°, although newer units with shaft encoders reduce this error to approximately 0.03° to 0.05°, and perhaps more importantly, reduce chances of erroneously read data.[11] Errors occur in the latter units, or in those of the same magnitude as the radio theodolites.

The first method involves the use of a highly directional tracking antenna and receivers to determine the direction from which radiosonde signals are transmitted. These receivers track the radiosonde by scanning a circular pattern about the radiosonde and reorienting the central axis when the signal is detected to be off axis. These systems when used with 403-MHz radiosondes provide measurement of azimuth and elevation angles within 0.15°. Winds computed from angular measurements made with this degree of accuracy have accuracies which vary with altitude and average wind speed. The following table lists the typical errors for various altitudes and wind speeds:

Table 4-1. ACCURACY OF WIND MEASUREMENTS[12]

Altitude (km)	Mean Wind Speed 15 m/s	15-30 m/s	30-45 m/s
3	.5 m/s	1.5 m/s	3.0 m/s
6	1.0	2.5	5.5
12	1.5	5.0	10.5
18	1.0	3.5	7.5
24	1.5	5.0	10.5
30	2.0	6.0	13.0

Two systems which operate on the radio tracking principle and are used for tracking 1680-MHz radiosondes are the AN/GMD-1 (a military version) and a Weather Bureau Radio Theodolite (WBRT). Both units are used by the National Weather Service and have similar capabilities, specifically as follows:[12]

- Accuracy of azimuth and elevation - 0.05°
- Minimum Elevation Angle - 6° above horizon
- Tracking range with 0.5w radiosonde - 125 km

The radio-tracking units do not yield satisfactory results when high winds carry the balloon far from the station at low elevation angles. Small changes in elevation result in large computed errors in lateral position. To improve the accuracy under these conditions, systems utilizing transponder-type radiosondes are used. These radiosondes receive 403-MHz signals from the tracking station and retransmit them on the 1680-MHz channel. The distance to the radiosonde may be determined by the time differential between the time the signal leaves and returns to the tracking station. The transponder enhancement improves the accuracy to 2.5 m/s for all conditions quoted in Table 4-1 for nontransponder radiosondes. Note that the transponding radiosonde is more expensive so their use is generally limited to cases of high winds where data might otherwise be lost.

Extremely cloudy conditions, showers, or scattered thunderstorms would eliminate the possibility of tracking balloons with radar since some radars return an echo from clouds with sufficient water content to produce rain. Radars can track a 1-m^2 target in an atmosphere with up to 98% relative humidity. Obviously, the cost of setting up a radar tracking system for each radiosonde release site would be prohibitive; however, for special purpose studies that require a high degree of accuracy and resolution, existing radar facilities could be used to plot the motion of radiosondes or dropsondes.

Typical specifications for a sophisticated radar tracking facility include the following:

Accuracy of range	2 m
Accuracy of elevation angle	0.1 milliradian
Range	2700 km

Retransmission of Navaid Signals. Navaid (Navigational Aid) radio transmitters are installed worldwide to provide radio signals which can be used for location determination by the receiver. Two such systems in operation are LORAN-C and OMEGA which provide either broad North American coverage (LORAN-C) or worldwide coverage (OMEGA). Other Navaid systems are in use particularly for aircraft; however, their coverage is more localized, and in many locations, nonexistent at low altitudes.

The receivers and decoders used for determining position are relatively expensive and complex when compared to radiosonde packages. Therefore, the radiosonde package consists of a receiver-transmitter package which receives the low frequency navigational signal and retransmits it to a base station for processing.

This configuration possesses a number of advantages over tracking the radiosonde from a central location. In these systems, location is determined from phase relationships of received signals; therefore, as long as the retransmitted signals can be received at the base station, the accuracy of the derived location is independent of range. (This is in contrast to large tracking errors which arise in azimuth-elevation tracking systems under low elevation angles and long-range conditions.) The azimuth elevation errors are most significant at low angles (high wind conditions) because of the presence of ground reflections which increase the value of uncertainty in the measured angles. These errors are also significant at long ranges since the error in position is proportional to the product of the range and the error in the measured angle.

A second advantage of this system is that large, mechanically complex tracking antennas are not required. Instead, a small, nondirectional receiving antenna is used for receiving the retransmitted signals and telemetry data. These data are usually processed on a small computer to determine position and change in position due to winds.

Accuracy specifications are different for LORAN-C or OMEGA systems. Accuracy specifications for a commercially-available LORAN-C-based system (Beaukers LO-CATE system) are 0.2 m/s. An accuracy of 2 m/s is given for the OMEGA-based system for averaging time of 2 min. The error may be reduced by increasing the average time. In one analysis of errors associated with OMEGA-based wind-finding systems, an improvement of 1.56 was noted for increasing the sample time from 2 min to 4 min.[13]

In situ measurement techniques applicable to radiosonde systems are necessarily restricted to those which are inexpensive (since the equipment is seldom recovered) and lightweight (because of the limited lift of balloons and the FAA restrictions on airborne objects). Presently, radiosondes are routinely used to measure temperature, humidity and pressure. Special purpose sensors are available for ozone.

A t-sonde is a small thermistor sensor package which transmits temperature information to a receiver to provide temperature profile on a continuous basis usually to altitudes of 2 km. Altitude is determined by assuming a constant rate of ascent, and may be verified by a double-theodolite test. Wind data may be obtained by tracking the balloon with theodolite.

The most commonly-encountered radiosonde units in the United States are those which are used for routine soundings by the National Weather Service. These radiosondes use a thermistor for temperature sensing, a carbon hygristor for humidity sensing and a mechanical aneroid pressure sensor for obtaining altitude information. The mechanical output of the aneroid altimeter is linked to a commutator to provide a multiplexed transmission of temperature, humidity and reference level information. Altitude or ascent rate information is determined from the multiplex rate. According to National Weather Service procurement specifications,[14] the commutator shall consist of a minimum of 150 contacts (alternate design which is specified has 180 contacts) most of which are swept by a movable arm during a pressure change from approximately 1050 mb to zero. The contacts cause interruption of the normally transmitted temperature signal with signals containing either humidity or one or two references. The spacing of contacts is such that the temperature signal is interrupted for every 20 mb change in ambient pressure at 1000 mb, 10 mb change at 150 mb ambient and 4 mb change at 50 mb. Specified values for acceptance tests for the pressure sensing units are ±4 mb up to 50 mb ambient pressure and ±3 mb over the remainder of the range. Specifications for temperature measurements made by the device are ±1° from 20 to -60° C with an rms average error of 0.45° C. Time response for the temperature sensor is 5 seconds. The humidity sensor is selected to yield measurements of ±5% accuracy with a response time of 2 seconds (between 90% and 40% relative humidity at 25° C).

In addition to the standard configuration which is specified, optional configurations are also specified to allow expanded measurement capabilities or to allow utilization of improvements in the state of the art. The optional configurations include:

- Addition of a hypsometer to provide increased ambient pressure measurement accuracy at low pressures (below 50 mb). The hypsometer which measures the boiling temperature of Freon 11 yields an accuracy of approximately 3% of the reading.
- Addition of a 403-MHz super-regenerative receiver to allow the retransmission of time pulses from ground-tracking units. The resulting transponder configuration allows improved slant range measurement capability resulting in improved wind computations.
- Replacement of amplitude modulation by frequency modulation or pulse modulation.
- Replacement of relay with solid state circuitry.
- Replacement of pressure driven commutation with time commutation. Signals representing reference, temperature, humidity and pressure are time-multiplexed or commutated such that all parameters are transmitted for 0.25 seconds each with the entire sequence repeated once per second.

The National Weather Service operates a sounding network in the United States consisting of 69 stations in the continental United States, 14 in Alaska, 2 in Hawaii, 10 on islands in the Pacific and Caribbean.[15] Two soundings are made at each of these sites each day with the exception that only one sounding is made at five of the island sites. Thirty-four (34) additional stations which are operated by agencies other than the NWS participate in the upper Air Observational Network to extend coverage in Mexico, in the Caribbean, and in central and South America. Half of these stations also make soundings twice per day with the remaining stations making only one sounding. There are 129 stations participating in the network making 236 soundings each day.[15]

Soundings taken at 0000 and 1200 GMT are found at the stations which take two soundings per day. The sounding data generally range from near ground level to 30,000 m at the various pressure-altitudes listed below:

1000 mbar
950
900
850
800
750
700
650
600
550
500
450
400
350
300
250

200 mbar
175
150
125
100
80
70
60
50
40
30
25
20
15
10
7

Individual values are determined by interpolation between values reported by the radiosonde to provide uniformity of altitudes of reported data.

4.2.4 Dropsondes. - Dropsondes are very similar to normal radiosondes except that the instrument package is dropped through the atmosphere to be measured rather than pulled through the atmosphere with a balloon. Parachutes are used to slow descents of dropsondes to reasonable rates of

5 m/s[16] (25 m/s for AMT-13 used by Air Weather Service[17]) so typical radiosonde sensors may be used without excessive errors due to instrument lag time. Dropsondes are generally launched from aircraft which usually contain the necessary equipment for receiving the encoded signals from the sonde. This system is useful for obtaining several atmospheric soundings over an area within the flight range of a high altitude aircraft. Operation of the airborne sonde launching/tracking system is significantly more expensive when compared to ground-based radiosonde systems. Therefore, their application is limited to situations where ground-based launch sites are impractical or where maximum flexibility must be retained in the selection of launch sites. Dropsondes are best suited to applications where numerous soundings are required over a short period of time within a regional area of the country. The selection of sounding locations may be varied as the flight progresses making this system appropriate where sampling locations must be selected based on information which becomes available during the flight (such as tracking air parcels). Minimum separation of soundings is determined by the number of dropsondes which may be tracking simultaneously. Existing systems developed by NCAR use 3 separate frequencies for telemetry data allowing up to 3 sondes to be in the air simultaneously without interference.[16]

Measurements telemetered from dropsondes typically include temperature, humidity and pressure. Sensors are similar and in some cases identical to those used in radiosondes for the same measurements. The AMT-13 dropsonde uses the same basic sensors as the JOOX series radiosondes used for routine soundings by the National Weather Service. Thermistors are used for sensing temperature and carbon hygristors are used for humidity. Altitude is sensed by a mechanical aneroid pressure sensor which is coupled to a variable resistor. The commutation between these measurements is linked to a meter rather than directly to the pressure sensor as in the radiosonde possibly because of the greater speed at which the sonde is in motion (25 m/s for the dropsonde versus 5 m/s for the radiosonde). The sensors for this unit are not especially designed for any faster response to minimize errors due to sensor lag time and consequently the error due to thermal lag where the temperature lapse rate is high will be greater for the dropsonde. Wind tunnel tests of this unit indicate the error to be less than 1°C.[17]

Dropsondes may also be used to gather wind data by retransmission of OMEGA signals received by the sonde. This technique is implemented in the NCAR unit where the retransmitted signals are processed by computer on board the dropsonde launching aircraft. The quoted rms error for vectoral wind measurements made by the system is 1 m/s when an averaging time of 4 min is used (corresponds to a vertical range of 1200 m).[16]

4.2.5 Remotely-Piloted Aircraft. - The classification of Remotely Piloted Aircraft (RPA) includes all aircraft which may be remotely controlled from ground position usually by a radio telemetry link. There are many types of RPA's which have been developed and produced in small quantities. A recent summary of world aircraft lists approximately 80 different RPA's manufactured in the United States alone.[18] These systems vary in size and scope from units slightly larger than hobbiest model airplanes to military fighter jets which are modified for remote control. The majority of these aircraft are intended for military applications such as target drones, hostile area surveillance and enemy radar harrassment. The remaining listed RPA included prototypes of experimental aircraft and sensing aircraft.

The payloads which may be transported by RPA vary with the size of the aircraft. The largest drones actually are capable of carrying more than equivalent piloted aircraft since human conveniences may be omitted. Many of the medium units' 4-m wing span have payload capabilities of 11-22 kg. (25 to 50 lb), while model airplane size units were only capable of 0.8 kg.[19]

If properly equipped, the RPA meteorological sensing of nearly any variables which may be monitored by unattended mobile sensors. However, operational units for this application at this time are generally custom prototypes and are not commercially-available. Small RPA's could be used to transport radiosonde-type instrument packages to altitudes above 3000 m (10,000 ft) if visual contact can be maintained. Larger drones could be used for more sophisticated instrument packages for measuring variables such as turbulence.

Two aspects of remotely-piloted aircraft fall under regulation by government bodies. These aspects include allocation of radio telemetry frequencies and control of airspace the aircraft is operating in. The actual frequencies and bandwidths required for control of the aircraft and transmission of data depends on a number of factors including:

- Magnitude of control signals passed to aircraft,
- Bandwidth requirements of returned data, and
- Range over which the RPA is to be operated.

Approval is required for use of frequencies although, in some cases, existing approved frequencies might be available for the data telemetry function.

The regulation of airspace has a far more critical impact on operation of RPA. In the United States, the FAA is responsible for regulating the usage of airspace and certification of aircraft which operate within it. All aircraft operating in controlled airspace must do so under control of Air Traffic Controllers. By 1982, controlled airspace will consist of all airspace from 365 m (1200 ft) above ground to 5500 m (18,000 ft) above sea level with the lower limit reduced to 200 m (700 ft) in traffic controlled areas near airports. Aircraft operating in these regions must have a navigational capability sufficient to maintain from other aircraft which may be directed as close as 2.5 nm horizontally or 300 m (1000 ft) vertically. The knowledge of the RPA location must be maintained in real time for coordination with Air Traffic Controllers, necessitating data transmission of location to the remotely-located pilot who must then maintain contact with aircraft traffic control. Aircraft operating below the minimum of 365 m (1200 ft) might avoid the requirement of active navigational equipment although safety features such as xenon flashers would be required. A larger configuration using standard commercially-available radio control equipment was fielded by John Hopkins University. This unit weighed 5 kg (11 pounds) at takeoff and was capable of flying to well above 3000 m (10,000 ft). The 1.3-kg instrument package used on this aircraft monitors temperature (wet and dry bulb), relative humidity, pressure, airspeed and vertical velocity. Data were telemetered to the groundbased recorder in real time.

Many of the technological problems of RPA design and operation have been solved with a great sophistication for military applications. The RPA's were constructed for environmental monitoring, and the RPA's designed specifically for this application have been developed by Elablissement d'Etudes et de Rechercher Meteorologiques (EERM) in France and by NASA in the United States. The EERM produced several different configurations including a circular wing, classic airplane and delta wing capable of carrying payloads of 0.6 kg, 1.8 kg and 0.8 kg, respectively.[19] The delta wing unit is capable of climbing to 5000 m at an initial climb rate of 7 m/s using a 10-cm^3 1.5-hp diesel engine. These RPA's have been employed for telemetry of temperature humidity and pressure information to ground-based stations, and collection of gas samples for laboratory analysis. They have participated in research programs associated with volcanic impact on local meteorological environment in Sicily and for monitoring thermal profiles for support in glider competitions.

A more sophisticated RPA development of effort was launched by NASA in 1975 to produce an RPA capable of carrying a 27-kg payload in addition to on board telemetry equipment. The design goals for the developing aircraft were to develop an RPA capable of making turbulence and pollutant measurements at altitudes up to 27,500 m (90,000 ft). Several versions have been produced in this development process including two models powered by aviation fuel-powered go cart engines. The third model utilizes a hydrazine engine specially designed to deliver 30 hp, but the engine usually runs at a maximum of 17 hp to extend its engine life. Both the gasoline and hydrazine versions of this aircraft have operated at altitudes in excess of 6000 m (20,000 ft). One of the plans for the aircraft include sampling of chemical species such as ozone and NO_x, as well as measurement of meteorological variables. The hydrazine version of the mini-sniffer is viewed as a potential research vehicle for use on Mars.[20]

4.2.6 Manned Airborne Platforms. - Aircraft have been used for a number of years as a mobilization platform to allow special purpose meteorological measurements and observations above the surface. Although aircraft can never compete economically with radiosonde techniques for obtaining routine sounding data, they do offer advantageous capabilities of: 1) horizontal profiling of measured variables, in addition to vertical profiling, 2) visual observation from a perspective other than a surface perspective, 3) larger instrument payload, and 4) presence of an operator to insure instrumentation is functioning correctly.

Airborne systems may be assembled to measure nearly all meteorological variables which are measured at the ground. Measurements of temperature are routinely made (although not usually recorded) on all aircraft for the purpose of applying temperature corrections to other measurements. Other meteorological variable measurements which can be easily instrumented include dew point and turbulence.

The largest problem with the use of aircraft for meteorological measurements stems from the velocity of the aircraft through the medium being studied. Temperature sensors must be designed to be free from or compensate for the effects of frictional or stagnational heating. If dew point is measured by an instrument inside the aircraft then the sample delivered to it must be representative of the air around it. If winds are to be measured by the aircraft, accurate measurements must be made of the aircraft velocity relative to the ground and relative to the surrounding air. The wind measurement is the difference in those two velocities. Sensor systems which are used on aircraft to overcome the problems unique to airborne measurements are described in the following sections.

Nearly all small aircraft provide temperature information to the pilot with a windshield thermometer, usually a bimetal dial thermometer with the sensitive stem protruding through the cabin wall into the passing airstream. A protective baffle surrounds it for protection and reduction of radiation effects.

Temperature sensor configurations which have been designed to reduce errors from high airflow are the vortex housing, flat plate and total temperature sensors.

A vortex housing is a sensor housing designed to reduce pressure surrounding the temperature sensor to such a degree that adiabatic cooling offsets the effects of compression heating. Such sensor configurations are necessarily designed for proper operation only over a limited range of airspeeds.

A flat plate senses temperature at locations where air moves parallel to sensing surface, and therefore minimizes errors due to compression. Remaining errors are due to frictional heating.

A total temperature sensor consists of a small chamber which has an opening oriented in the direction of flight. Air is compressed in the chamber by ram pressure which causes slight adiabatic heating. A small leak is provided for a slow exchange of air thus providing a slow airflow across a sensor located in the chamber. The sensed temperature is called total temperature which is equal to ambient temperature and includes an additional predictable correction due to the compression. The magnitude of this correction is computed from the known true airspeed of the aircraft.

Conventional wet bulb thermometers have been used in a housing along with dry bulb thermometers for humidity monitoring. Corrections for wet bulb thermometers due to frictional or partial heating will differ from corrections for dry bulb thermometers because of increased surface area of the sensor covered with wick. Continuous readings are difficult because frequent rewetting of the wick is required. Since freezing temperatures are frequently encountered, ice buildup in supply lines is a problem for this type of sensor.

Dew point sensors, such as the self-heated lithium chloride unit or the cooled-mirror dew-point hygrometer, offer the advantage that they may be operated in the cabin of the aircraft with sample air piped to them. Small changes in ambient temperature of the sample do not affect the measurement.

Pressure measurements are made for the recording of altitude information along with other meteorological measurements. Standard pressures sensing techniques are used such as strain gauge transducers and standard aneroid altimeters modified to provide automatic recording of the measured altitude.

Average measurements of wind speed and direction may be vectoral comparisons of distance traveled computed from airspeed and heading with actual ground distance covered. The distance traveled on the ground may be determined from visual observation of landmarks or navigational fixes of the end points. Point measurements of winds may be made by coincident measurement of airspeed and heading (while aircraft is in straight and level flight) and measurement of true aircraft velocity by doppler radar.

Atmospheric turbulence may be measured by observing the high frequency variations in true airspeed. One commercial instrument manufactured by Meteorology Research Incorporated (MRI) consists of a sensitive, fast response pressure transducer coupled to a pitot static airspeed probe. The ac-component of the output voltage is detected and compensated because of the nonlinear relationship between pressure and airspeed.

Numerous airborne air sampling systems have been assembled which measure a limited number of meteorological parameters such as temperature, and dew point in conjunction with atmospheric pollutants. However, aircraft especially for meteorological monitoring include specially instrumented research aircraft and aircraft used in weather modification experiments. The National Center for Atmospheric Research (NCAR) operates a number of aircraft which have been instrumented for meteorological monitoring with state-of-the-art instrumentation. Aircraft range from a two-seat single-engine aircraft to a four-engine Electra.[21] One aircraft is the Queen Air. This unit measures wind (3 components), air and surface temperature, and humidity. Wind is sensed by airplane velocity detected by an inertial navigation system and air velocity detected by sensors on the nose of the aircraft. Tower comparison tests show this system to agree with conventional measurements within 0.6 m/s (average difference). Temperature sensors agreed within 0.4° C.[22]

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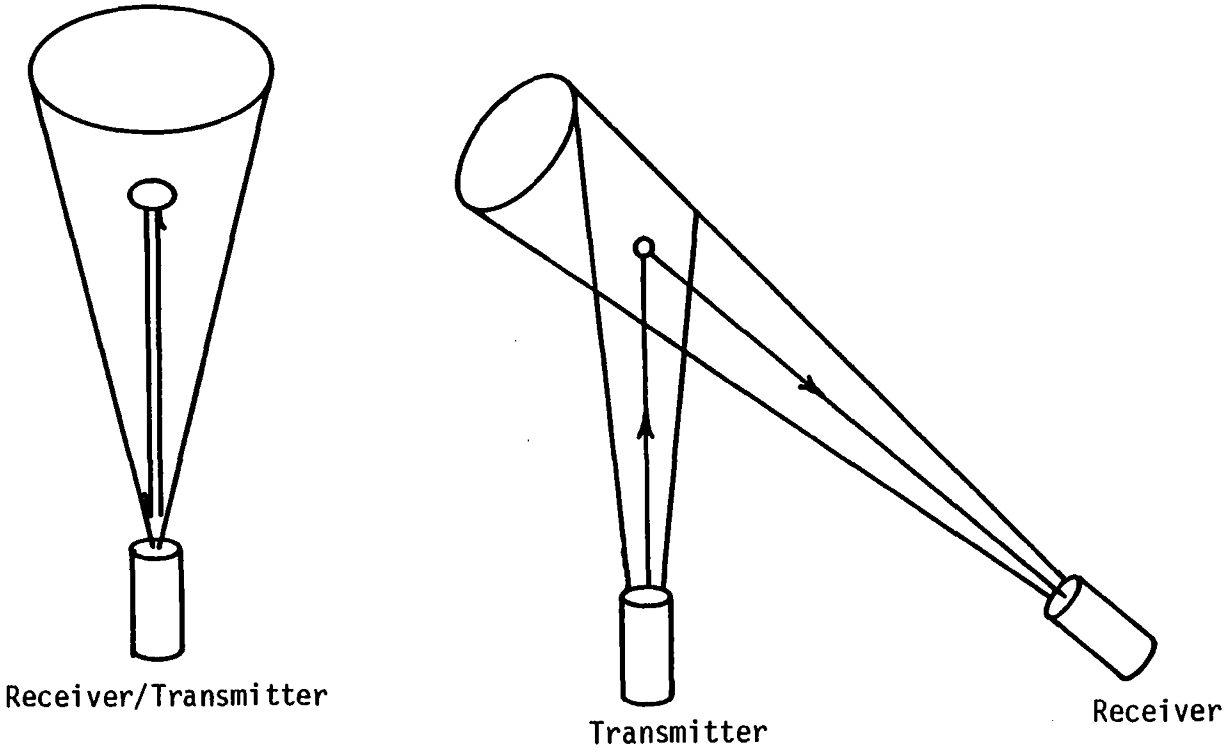
4.3 Acoustic Sounders

4.3.1 Operating Principle. - Acoustic sounders operate on the principle that sound waves are scattered when passing through inhomogeneous regions in the atmosphere where those inhomogeneities are significant compared to the acoustic wavelength. Sources of these inhomogeneities are the thermal gradients and local velocity variations. The instruments are composed of two parts: a transmitter which emits short duration acoustic pulses (typically 900 to 2000 Hz with a duration of 50 to 200 ms), and a sensitive receiver for detecting the scattered acoustic energy. The transmitted energy is focused to a beam width of 2 to 10°[1] usually by means of parabolic reflectors, although multiple-phased acoustic sources have been used.[2] Typical acoustic sounders detect scattering features in the atmosphere up to a distance of 1 km. The altitude of the scattering volume may be determined from the length of time between the emission and reception of the acoustic tone burst. The strength of the echo is proportional to many factors including transmitted beam power, attenuation of the beam, scattering angle, strength of atmospheric target inhomogeneity, and attenuation along the path. Because of the dependence of the strength on so many variables, the absolute value is not usually processed, rather the relative variations in signal strength versus time are examined to locate features in the atmosphere. Velocity information about the scattering feature relative to the receiving antenna may be obtained by processing the echo return to determine the amount of frequency shift due to the doppler effect. Velocity of both thermal gradients and local velocity gradients may be determined in this manner.

Two basic configurations are used for obtaining acoustic sounding data: monostatic systems and bistatic systems. Monostatic systems utilize collocated transmitter and receivers, so only waves which are scattered back along the transmitted axis (180° scattering) are received (see Figure 4-1a). The monostatic system offers the advantage that a transmitting beam is automatically aligned with the field of view directional receiver, throughout the entire range.

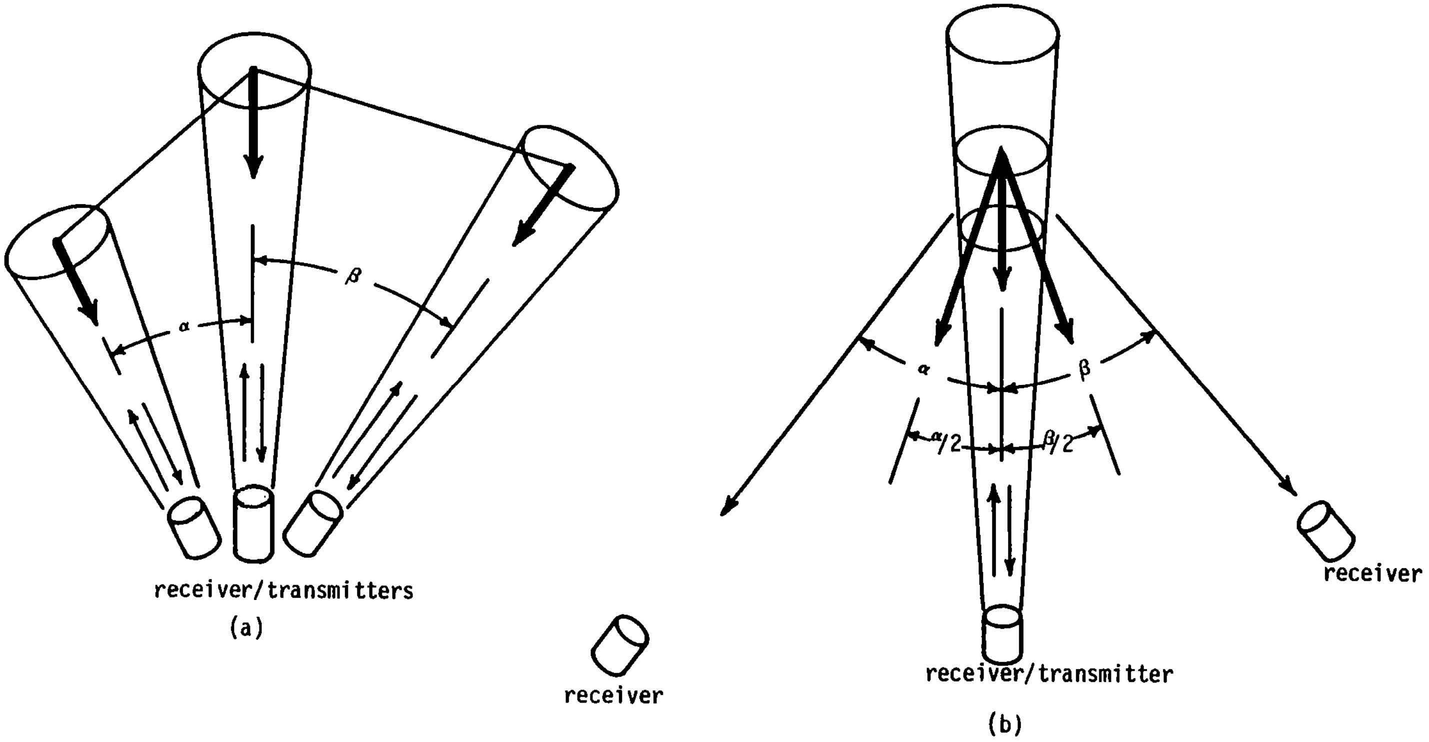


a) Monostatic Configuration b) Bistatic Configuration

Figure 4-1. Basic Acoustic Sounder Configurations, a) Monostatic Configuration and b) Bistatic Configuration

The bistatic system (Figure 4-1b) differs in that separate transmitting and receiving antennas are used allowing detection of energy at scattering angles other than 180°. The antennas are aligned such that the transmitted beam intersects the receiving antenna field of view. The actual scattering angle of the detected energy depends on the transmitter-receiver antenna separation and the altitude of the scattering point. Scattered energy is received only from the region where the transmitted beam intersects the receiver field of view. To illuminate a substantial portion of the receiver field of view, the transmitting power must be spread vertically resulting in a lower power density and signal-to-noise ratio for a given transmitted power. The bistatic configuration, however, offers the advantage of detecting signals scattered from both temperature and velocity inhomogeneities. However, a distinct disadvantage to the monostatic system is that only scattering from thermal gradient features can be detected since scattering from velocity inhomogeneities is minimal at 180°. Therefore, the monostatic systems will not receive reflections from neutral layers of the atmosphere making monostatic systems somewhat less desirable for determining the velocity of the atmosphere within those layers.

Velocity information may be determined through processing of echo returns for doppler frequency shift in either the monostatic or bistatic configurations. For the monostatic configuration, the component detected is along the axis of the transmitted/reflected beam. For the bistatic units, the measured component lies along the vector which bisects the angle formed by the intersecting transmitted beam and receiver field of view. For detection of multiple components of wind (i.e., U,V,W), multiple systems may be installed at the same location. For economy, transducers may be time-shared between these systems such that a complete three-component system may be assembled from three transducers, either a triple monostatic unit or a single monostatic unit with two additional bistatic receiver units (see Figure 4-2). The magnitudes of the three-orthogonal vector components of winds may be determined from the three directly measured nonorthogonal components. The three-monostatic unit configuration can give better accuracy because the component measured is closer to horizontal (difference from horizontal is 90°-β for monostatic and 90°-$\beta/2$ for



(a)

(b)

Figure 4-2. Three Dimensional Wind Velocity Acoustic Sounder Systems: a) three monostatic systems and b) monostatic vertical system with two additional receivers to form bistatic systems bistatic for a given elevation angle β). However, the bistatic unit yields more consistent results due to stronger returns typical of angular scatter.[3] The bistatic unit also has the advantage in that sensed scattering volume may be the same for all three measured components. This is not true for monostatic units unless the beams are oriented so the beams intersect, and then can only be true at the point of intersection. Even though all data are not acquired from the same volume, valid wind and turbulence information may be statistically computed if the assumption holds that winds at a given altitude exhibit the same mean velocity and variability over the entire area of observation. However, this technique requires that multiple data points from each altitude be processed to compute the mean and variance data at each altitude for each component.[4]

There are a number of operational parameters which may be varied to taylor the acoustic sounder for specific measurement objectives. Included are pulse frequency, pulse duration, antenna directivity, transmitted power and a number of factors which affect system gain. Signal-to-noise ratio of the system can be increased by either increases in transmitted power level or by the implementation of integration to average out random variations (noise) which mask the desired signal. Appropriate techniques of integration may be divided into two categories: coherent and incoherent.[5] Coherent integration includes integration over portions of an individual set of echo returns resulting from a single acoustic tone burst to average the noise at the sacrifice of spatial resolution. Electrical filtering of the signal (including narrowing of receiver bandwidth) and lengthening the transmitted pulse duration are examples of coherent integration.

Incoherent integration refers to the averaging of several sets of echo returns. This concept is most easily implemented in sounders which use computers for processing of data where digital values corresponding to each range are averaged over time up to 30 min. The obvious tradeoff in this technique is the loss of information regarding short-term changes in atmospheric structure.

Other parameters which can be varied for the specific measurements include the frequency of the acoustic pulse. Tones near 1000 Hz are typically used as a compromise between higher frequencies for detection of smaller scattering features and lower frequencies for reduced atmospheric attenuation. In applications requiring short range data, such as stack plume tracking, higher frequencies of 5 kHz have been used to reduce transducer ranging and obtain data at closer range.

4.3.2 Available Units. - Acoustic sounder units are commercially-available in a variety of configurations. The simplest systems consist of a single monostatic unit which use a facimile recorder for displaying the altitude distribution of scattering features versus time. The single monostatic units typically cover a range of ground to 1000 m. However, the reception of echo over the entire range depends on the quantity and strength of thermal structures at the upper altitudes. Resolution is essentially continuous for those systems using the facsimile chart recorder although the altitude of structures cannot be resolved to greater than 10 m on the chart.

The doppler acoustic sounders yield three-dimensional wind speed information typically within 0.5 m/s for speed and 5 to 10° for direction.[6] There are presently several such systems available including units from AeroVironment,[7] Xonics[8] and Radian.[9] All of these manufacturers produce units capable of measuring wind speeds by means of doppler techniques at a minimum of six altitudes. Characteristics of a typical system such as the AeroVironment unit are as follows:

Altitude range - 30 to 600 m
    (Actual upper limit of data range as restricted by signal-to-noise ratio is 300 to 1000 m dependent on meteorological conditions.)

Velocity range (each component) - 0 - 25 m/s

Vertical resolution - 30 m

Wind speed range - 0 - 25 m/s
    Accuracy - 0.5 m/s
    Precision - 0.2 m/s for high signal to raise ratio

Computed variables -
    Three components of wind speed - (U, V and W)
    Turbulence estimator
    Wind direction vector; direction and magnitude

Averaging period - 5 to 30 minutes (selectable)

Transmitted pulse - 1500 Hz, 100 watts (electrical at driver)
    Duration is 180 ms

4.3.3 Application of Acoustic Sounders. - The remote sensing capability of acoustic sounders in the simplest monostatic configuration makes possible the identification of atmospheric layers continuously. The facimile trace has yielded mixing depth information supporting a number of studies.[10,11] Data from this type of study are usually reduced from the facsimile-type records to take advantage of human eye pattern recognition capabilities for the identification of the atmospheric layers. Quantitative measurements are made along the altitude and time axes of the chart; however, only the relative magnitude is observed (from the dark areas of the chart) for locating altitudes of maximum return.

Acoustic sounders with doppler processors (either analog comb filters or digital spectral estimating processors) can be used to measure vertical winds with measurements made by a single monostatic transducer. Winds in three dimensions may be measured by two additional transducers: either two complete monostatic units oriented tilted from the vertical by angles of about 30° in two directions separated by 90°. Alternately, two acoustic transmitters could be placed on the ground some distance from the vertical transducer oriented such that the field of view of the central transducer is illuminated. From the variability of the individual wind vectors, estimates may be made of turbulence at all altitudes. The parameter, ϵ, the rate of dissipation of kinetic energy, may be determined as well. This technique is implemented in at least one commercial unit.[4] Other acoustical techniques have been suggested[12] for measurement of turbulence by processing of simultaneous monostatic and bistatic measurements for scattering due to velocity fluctuations alone. For measurement of humidity, a technique has been proposed where two separate frequencies are used with a backscatter sounder and the returns compared for differences in absorbed energy.[13] This technique is not commonly used.

Processing the amplitude of the echo return quantitatively is not performed frequently due to the inherent variability of the return signal level due to turbulence.[14] This variability is a function of many factors including beam geometry, orientation, as well as the atmospheric parameters which cause scattering. In order to make amplitude measurements meaningful, some reference measurements must be made simultaneously. Such a scheme has been proposed by Little.[13]

4.3.4 System Advantages and Problems. - The acoustic sounder offers the advantage of simplicity in concept and implementation. Transducers utilized are similar to those used in audio transmission. Data processing is done at speeds within reach of microprocessors and small computers. Total systems could be produced at reasonable costs if they become a mass-produced item. Installation and operation of acoustic sounders for the acquisition of wind data may be far more economical than the operation of a tower equipped with in situ instrumentation. Routine calibration and maintenance are performed at ground level.

There are some problems inherent in the measurement technique. Acoustic sounders necessarily respond to weak audio signals at the frequency of the transmitted pulse and are therefore susceptable to noise from a variety of sources including birds, crickets, wind, traffic or any other source of acoustic energy containing energy near the transmitted frequency. Several techniques have been successfully utilized to reduce the interferences including mounting receiving antennas in baffles and burial of sensors. Acoustic sounders have been successfully operated in noisy urban environments using lead-lined plywood baffles.[5,15] In cases where the inherent sources are sporadic, their effect may be minimized by averaging several echo returns. Noise due to wind and rain mask data at times when such data are desirable. The mechanical impact of raindrops on sensitive receiver surfaces and the noise set up by wind across the housing may overload the receiver. Techniques to reduce wind noise have been suggested including diffusing fringes around the top of baffles[4] or the placement of receivers in bunkers flush with the Earth.[16] The bunker configuration also includes offsetting the opening to prevent precipitation from reaching sensitive surfaces of the receiver.

Acoustic sounders presently available are only suitable for operation in fixed locations in a fixed orientation. Mechanically-generated noise would be generated by mobilizing platforms or tracking mechanisms which would mask the desired echo returns or else be mistakenly identified as echoes. Another restriction which makes scanning or mobilization difficult is the necessity of maintaining the receiving antenna stationary for a period of approximately 10 seconds (dependent on range) after each pulse.

Although the acoustic sounder is not suitable for mobilization, it is a rugged portable instrument which can readily be deployed in a field environment. Unlike laser or microwave systems, no extensive alignment, stringent environment control or manned operation is required. Although the transponders for receiving and transmitting are bulky, trailer-mounted versions are currently produced which may be towed to a site, connected to line power and operate in a short period of time.

4.3.5 Future System Enhancements. - In 1972, Little[5] stated nine (9) areas where an improvement in sensitivity could be realized. Most of his suggestions simply called for either an increase in signal level due to increased power or gain, or a tradeoff in the amount of resolution for increased sensitivity through averaging. Since that writing many ideas from both suggestions have been implemented. As an example, the concept of incoherent integration (averaging over sets of echo returns) has been implemented with small computers to provide averaging. Efforts are forthcoming to increase the reliability of acoustic sounder data through a data validation process that accepts only wind data which are compatible with data from adjacent levels and selects between several processing algorithms to find the most reliable technique whose result meets the data validation criteria.

The opportunity exists for further research in the application of digital signal processing to the detection and recovery of signals from the received signal, in an effort to increase the range of reliable operation of the acoustic sounder. Improved processing techniques are needed for detection of the return signal and the accurate determination of its doppler shift frequency. Also, the computer data might be expanded to include more parameters describing turbulence.[7]

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4.4 Radio-Acoustic Sounding System

4.4.1 Basic Operating Principle. - An extension of the use of acoustic sounders for lower atmosphere temperature sensing has been made available by combining an acoustic sounder, radar transmitter and receiver. The radio acoustic sounding system (RASS) is the product of this work. The operation of the system relies on the fact that the local density variation produced by the propogating acoustic wave causes a variation in the index of refraction. This change in index of refraction causes a small amount of the radio wave energy to be reflected back to the receiver.[1] The basic concept of the RASS is that the propogation of the acoustic pulse can be doppler tracked by receiving the fraction of the radio energy reflected from the propogating acoustic wave. The speed of sound (U_s) is temperature dependent according to the following relationship:

$$U_s = AT^{1/2}$$

where A is a function of relative humidity, and T is temperature. Therefore, the doppler tracking of the acoustic pulse can be used to develop a real-time temperature profile.

The intensity of the reflected radio signal is very low, but two important considerations serve to make the signal strong enough to track the acoustic pulse to as high as 2.5 km from the surface. The first consideration is that the acoustic wave propogates spherically in an unpreturbed atmosphere making a spherical reflecting surface for the radio signal. The second consideration is that if the acoustic and radio frequencies are chosen such that the acoustic wavelength (λ_a) is equal to one-half the RF wavelength (λ_e), then the condition known as Bragg scattering occurs and the reflected signals from each acoustic wavefront add coherently at the surface.

In the configuration described above the RASS is operated in a monostatic mode; that is, the acoustic source, radar transmitter and receiver are collocated. When operated in this mode, the intensity of the reflected radio signal is dependent only on the strength of the acoustic wave which varies by H^{-2}, where H is the height above the surface. This relationship is for the "ideal" case where turbulence and horizontal winds are negligible.

In conditions of strong turbulence, the sphericity of the acoustic wave is altered and, therefore, so is the coherency of the reflected signal.[2] The impact of turbulence on the returned signal strength will be discussed later. Horizontal wind speeds of greater than approximately 4 ms^{-1} require that the RASS be operated with a bistatic radar.[2] That is, the radar antennas are aligned in the direction of the wind. The atmospheric motion also moves the focus of the spherical acoustic pulse downwind. However, signal returns near those predicted for the monostatic ideal situation can be achieved if the configuration of the apparatus is such that the transmitting radar antenna is located upwind of the acoustic source and the receiving antenna is located downwind of the source. Because the focus of the acoustic pulse shifts in the downwind direction, a phase error occurs at each wavefront and the received signal is decreased. By locating space-diversified receiving antennas in the direction of the wind, the received signals can be used to determine the vertical profile of winds as well as the temperature profile.

4.4.2 Applications of RASS. - The principle of RASS was demonstrated using a 22-Khz acoustic pulse. However, the range at which the acoustic pulse could be tracked was limited to approximately 33 m. It was later shown both theoretically and experimentally that the tracking range could be greatly increased if a much lower acoustic frequency was used.[3] Use of an 85-Hz acoustic pulse and a 36.8-Mhz radar extended the observable range to 1.7 km. Later, a stationary RASS was constructed that tracked an acoustic pulse to an altitude of 2.5 km.

Presently, Stanford University operates a RASS routinely from a fixed location using an 85-Hz acoustic pulse. Since the range is dependent only on the intensity of the acoustic pulse in the absence of turbulence, a range array of acoustic drivers are used. The Stanford RASS acoustic source measures 8 x 8 m^2 and contains nine (9) horns which are each 1.8 m high and 1.6 m across at the openings. The large size and weight prevent this configuration from becoming a mobile unit. Sufficient acoustic intensity could be produced at a high frequency using a smaller unit; however, the range would then be limited due to the frequency itself. This tradeoff of the acoustic frequency limitations creates a serious problem for the construction of a mobile RASS. A smaller acoustic source measuring 7 x 7 m^2 which produces an acoustic frequency at 360 Hz has been operated in conjunction with a radar frequency of 159 Mhz.[4] This system has been used to track the acoustic pulse to 1500 m. The weight is less than two tons and it is claimed that the system could be transported to obtain measurements at various locations.

4.4.3 Advantages and Limitations. - The obvious advantage of the RASS over the conventional pure acoustic sounding system (PASS) is that real-time temperature profiles are possible with RASS whereas only the thermal structure of the lower troposphere can be obtained with the PASS. In addition, by properly arranging the transmitting and receiving antennas, vertical profiles of wind speed in a layer with nondirectional shear can also be determined. Continuing progress in the development of high frequency acoustic sources may ultimately yield a mobile RASS capable of operation at virtually any location. Development work is proceeding on a RASS using a 1-Khz acoustic source.[5] This sytem is capable of tracking the acoustic pulse up to 1 km even during periods of moderate to strong turbulence.

In all cases, the range of RASS operation can be severely limited by the influence of strong turbulence. The effective range of RASS operation under ideal conditions is dependent on the intensity of the acoustic pulse which varies as H^{-2}. Detailed theoretical treatment of the influence of turbulence on the propogating acoustic wave, however, reveals a new dependence on height.[6] Turbulence causes irregularities in the sphericity of the acoustic wave. Any variation of the sphericity weakens the focussing effect and therefore weakens the reflected radio signal. As a result strong turbulence can change the range dependence from H^{-2} to $H^{-18/5}$.

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4.5 Meteorological Radars

4.5.1 Operating Principle. - During the early development of radars there were many studies of radar and point-to-point radio propagation. These studies were designed to determine the properties of radar and radio wave propagation in the atmosphere. It was soon discovered that radars operating at frequencies of a few megahertz were reflected by the significant concentrations of electrons in the ionosphere with sufficient strength to study some characteristics of the ionosphere from ground-based radars. During subsequent experiments designed to probe the ionosphere, investigators also discovered radar echoes from the troposphere and stratosphere. The initial explanation of these echoes postulated that there were also regions of ionization in the troposphere and stratosphere that were capable of reflecting radar energy. The specific details of the nature of the reflection of radar waves from the troposphere and stratosphere are not yet completely understood. It is now known, however, that the echoes result from scattering by isotropic irregularities in the refractive index, and from partial reflection from horizontally stratified layers in the atmosphere. The isotropic irregularities in the refractive index result from small variations in the atmospheric density produced by turbulence. The stratified layers that produce partial scattering of radar signals are stable layers characterized by temperature inversions. The discovery of clear air echoes, first referred to as angles, in the troposphere and stratosphere was followed by several studies of the morphology of the scattering areas. Some radars were then altered and new units designed to include the capability of coherently analyzing the return signal so that the doppler shift in the return signal could be determined. The addition of doppler capabilities made the radars able to provide nearly real-time profiles of the radial velocity of the scattering regions, relative to the radar location.[1] These doppler radars are pulsed and require some signal averaging to minimize error due to noisy returns.

Microwave, FM-CW, VHF, and UHF radars were all studied to determine their properties for probing the structure of refractivity irregularities in the troposphere and stratosphere. The refractivity structures that are responsible for the echoes are considered isotropic when they are on a scale approximately one-half of the radar wavelength. The scale lengths of turbulence features can be divided into three rough categories. Large eddies are anisotropic and are invisible to radar scattering. Very small eddies that are severely damped by molecular viscosity, known as the viscous subrange, are also ineffective in scattering. The intermediate range of eddy size, called the inertial subrange, is viewed as isotropic by the radar and causes the reflection of radar signals. The influence of decreasing density with altitude causes the transition region between the viscous and inertial subranges to shift to longer scale lengths. Therefore, the maximum height that can be probed in this manner is dependent on the radar wavelength used.[2]

The scale lengths of turbulence viewed as isotropic by VHF radars extends into the mesosphere. Since the VHF radars can obtain information in the mesosphere, stratosphere and troposphere they are sometimes referred to as MST radars. The shorter wavelength UHF radars are only capable of probing into the lower to mid-stratosphere and are therefore sometimes called ST radars.[3] VHF radars can be constructed of large-phased dipole arrays at a much lower expense than the dish-type antennas for UHF radars. For these reasons most radars designed specifically for meteorological research are VHF radars. The advantage of increased maximum range of the VHF radars is obtained at the expense of range resolution. Typically, VHF radars operate with a range resolution on the order of 1 km, while UHF radars provide range resolution of 30-300 m in the lower to mid-troposphere.[4] FM-CW radars with doppler capabilities can be used to obtain very fine resolution measurements of 1-30 m, but have a maximum range of only 1-2 km.

4.5.2 Examples of Meteorological Radar Facilities. - Table 4-2 is a list of some radars that has been used to study the clear atmosphere, along with some important characteristics and appropriate references for further information. The phased array antenna configurations used for the VHF radars are constructed of rectangular array of coaxial cable. By phase shifting the input signal to the sequential lines of the antenna the signal can be directed through a vertical plane perpendicular to the antenna

Table 4-2. SOME RADARS USED FOR CLEAR AIR METEOROLOGICAL STUDIES

Radar Facility	Location	Frequency (MHz)	Wavelength (m)	Average Power Aperture ($W \times m^2$)	Beam Width (degrees)	Antenna Configuration	Reference
Jicamarca	Peru	49.9	6.01	2×10^{10}	1.0	Phased Dipole Array	5
Poker Flat	Alaska	49.9	6.01	5×10^{9}	1.5	Phased Dipole Array	6
Urbana	Illinois	40.9	7.33	4×10^{8}	3.6 x 4.8	Phased Dipole Array	7
SOUSY	Germany	53.95	5.61	9×10^{7}	10	Phased Yagi Array	8
Platteville	Colorado	49.9	6.01	4×10^{6}	3 x 3	Phased Dipole Array	9
Sunset	Colorado	40.5	7.41	9×10^{6}	5 x 9	Phased Dipole Array	10
Arecibo	Puerto Rico	430	0.75	7×10^{9}	0.17	Fixed Dish/Steerable Feed	11
Chatanika	Alaska	1290	0.23	2.6×10^{7}	0.6	Steerable Dish	12
Wallops	Virginia	430	0.75	3.1×10^{6}	2.9	Steerable Dish	13
Defford	England	2800	0.107	1.9×10^{6}	0.33	Steerable Dish	14
FM-CW	Colorado	3000	0.1	1.06×10^{3}	2.8	Twin Dish Steerable	15

elements. This phase shift steering feature can be effective through a large range of zenith angles. Steerable dish antennas can be rotated to allow virtual hemispheric coverage. At large zenith angles near the horizon the signal may be masked by ground clutter.

4.5.3 Applications of Meteorological Radars. - Pulsed doppler radars can be used to obtain measurements of a variety of features important in meteorological research. Some of these features are closely related to the transport and dilution of both primary and secondary air pollutants. In some cases radar-generated meteorological information may even be helpful in the study of atmospheric conversion of air pollutants. A partial list of the measurement capabilities of pulsed doppler radars is given below.[2,16]

1. A determination of the three-dimensional wind profile.
2. Estimates of turbulence as a function of height by a variety of means.
3. The identification and time development of stable stratified layers including the tropopause.
4. The identifications of air mass boundaries.
5. The study of atmospheric wave (gravity wave) and atmospheric tide phenomena.

Of the measurement capabilities included in the list, the determination of three-dimensional wind profiles is the most important measurement capability. The different types of antenna configurations can be used in different ways to obtain a measure of the profiles of wind speeds.

Since most radars committed to meteorological research are phased dipole array VHF radars, a description of the Sunset VHF radar will be used as an example of the wind measurement technique. All other VHF antennas use a similar technique, and even steerable dish UHF antennas sometimes use this technique.[17]

The sunset radar antenna is divided into six identical but independent sections. The six sections are operated as three independent transmit-receive pairs. Two pairs are aligned in the east-west verical plane and the other in the north-south plane. Each pair can be steered to within ±45° of zenith. The system can be sequenced to obtain measurements at three independent beam positions by computer control in 8 minutes. At each beam position information is obtained for 16 altitude ranges. The return signals are processed by computer with a Fast Fourier Transform algorithm and are transformed into radial velocity spectra with a resolution of 37 cm seconds^{-1}. This is done by evaluating the doppler shift of the returned signals resulting from the refractivity echoes. It is assumed that the refractivity features are advected by the wind motion.

A typical orientation sequence of the beam positions is 3° from zenith toward the east, 27° from zenith toward the west, and 30° from zenith toward the north. The three independent radial vectors can then be resolved into the orthogonal wind components. The additional important assumption is that a uniform wind field exists over the region including the three scattering volumes. In this case measurements made up to an altitude of 19 km were from scattering volumes separated by a maximum of 10 km. In tests of this system, measurements were in good agreement with simultaneous radar tracked rawinsonde measurements.

Dish-type antennas are sometimes rotated through 360° at some fixed zenith angle.[18] The resulting distribution of radial velocity as a function of azimuth is called a velocity azimuth display (VAD). The display appears as a sinusoidal variation through the 360° of azimuth angle. From this VAD the magnitude and direction of the wind vector can be obtained.

Estimates of the intensity of atmospheric turbulence at the various measurement altitudes can also be made by analyzing the return signals.[19] The eddy dissipation rate, ε, is often used to parameterize atmospheric turbulence. There are three methods available to estimate the eddy dissipation rate from doppler radar observations. They are:

1. The refractivity turbulence structure constant $\bar{C}_n^2$ observed in the radar scattering volume.

2. The width of the observed doppler spectra.

3. Time series analysis of observed mean winds.

Numerical descriptions of turbulence spectra have been presented which yield estimates of the intensity of turbulence by the use of each of these features provided by doppler radar observations. Several references are available giving the details of these processes.[19,20,21]

As mentioned earlier enhanced clear air echoes are also produced by stratified layers within the atmosphere. Use of VHF radars continuously over time can be useful in studying the time development of stably stratified layers, which are key factors controlling the atmospheric mixing volume. The details are not to be discussed here; however, they can be found in the literature.[22] The same technique can also be used to develop time histories of the behavior of the tropopause. This capability of radars may prove valuable in studying the dynamics of stratospheric intrusion events. This same technique may also be useful to identify and chart airmass boundaries as a function of time.

Orographically-induced gravity waves and atmospheric tides can also create target features for radar signals.[4] Information concerning these features will be important in meteorological research in terms of energy balance, global circulation, and troposphere-stratosphere exchange mechanisms.

4.5.4 Potential Improvements in Meteorological Radars. Radars have been shown to be useful for detecting and measuring atmospheric features in addition to those discussed above. These techniques are not routine but as the number of measurements increase some of these uses will also become reliable and may have capabilities that make them advantageous. Wind variability can be measured by time series radar observations and by utilizing spaced antenna systems.[23] Measurement of pressure and density fluctuations obtained from radar observations are feasible.[24]

Measurements have also been made of jet streams in the middle atmosphere by use of doppler radar.[25] The ability to study the development of convective cells in storm formation has also been demonstrated using radar systems.[4]

As radar measurements continue, the understanding of the processes causing the spectral structure of returned doppler signals may provide additional measurement capabilities. Data processing software will likely key the development of additional capabilities. Techniques to increase the power and signal-to-noise ratios of doppler radars may allow improved height resolution.

With a worldwide network of meteorological radars it would be possible to obtain continuous measurements of global circulation patterns, greatly improving the knowledge of upper air winds possible with twice daily radiosonde releases.[26] Satellite platforms in geostationary orbit with surface receivers could also have significant advantages. The use of radars to study cloud development and precipitation dynamics, as well as local circulation patterns (i.e., land-sea breeze), may also become routine in the future. Obviously all of the possibilities concerning developments and improvements of radar systems for meteorological measurements have not been discussed. However, the possibilities for detailed and high time and altitude resolution measurements by radars of many meteorological features is clearly evident.

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5.0 SUMMARY

This report outlines some of the instrumentation methods that have been described in literature for the in situ detection and quantification of various atmospheric trace species and meteorological variables. The section on meteorological sensors also includes some recently developed remote measurement techniques that show promise and versatility for making rapid vertical profile measurements of some important meteorological characteristics of the atmosphere. The content of this report is admittedly incomplete and does not mention every technique or capability of techniques that have been proposed for the measurement of the pollutant species or meteorological parameters mentioned. In most cases the discussion of in situ techniques has been limited to methods that have been or could be mounted on airborne platforms.

A list of those species that have been identified by NASA as important to their overall global tropospheric program and the preliminary measurement requirements for those species are listed in Table 5-1. Some of the meteorological variables important to the NASA global tropospheric program are also listed in the table. In all cases these measurements are described for a global sampling strategy. Other routine meteorological measurements, specifically humidity and wind direction, are also discussed in the report although the requirements for the instrumentation are not given in the table. In this summary, the specific requirements for instrumentation requested by NASA that have not yet been achieved will be identified and discussed. In all cases the spatial and temporal requirements are achievable with instrumentation described in the report, provided of course that suitable instrumentation packages can be mounted and operated on an airborne platform.

Airborne sampling presents problems in addition to those encountered when sampling from a fixed surface-based platform. Temperature and pressure vary rapidly with altitude and on powered aircraft platforms, aircraft vibration can lead to stability problems, and high speed motion can influence the smooth introduction of a sample to the instrument. Each of these influences can affect the accuracy and precision of the measurement. Another important consideration is that the measurement of some of the

Table 5-1.

PRELIMINARY INSTRUMENTAL REQUIREMENTS FOR VARIOUS ATMOSPHERIC TRACE SPECIES

Measurement Parameters	Concentration	Vertical Resolution (km)	Horizontal Resolution (km)	Temporal Resolution
O_3	5 - 200 ppb	0.1 - 1.0	5 - 100	Hourly to Weekly
NO	0.002- 1 ppb	0.2 - 1.0	5 - 100	Hourly to Weekly
NO_2	0.002- 1 ppb	0.2 - 1.0	5 - 100	Hourly to Weekly
HNO_3	0.01 - 3 ppb	0.2 - 1.0	5 - 100	Hourly to Weekly
NH_3	0.01 - 3 ppb	0.2 - 2.0	5 - 100	Hourly to Monthly
N_2O	330 ppb	3	1000	Monthly
CO	30 - 250 ppb	0.2 - 1.0	5 - 100	Hourly to Daily
CH_4	1 - 2 ppm	10	1000	Seasonal
H_2CO	0.02 - 5 ppb	0.2 - 1.0	5 - 100	Hourly
NMHC	0.01 - 2 ppb	0.2 - 1.0	5 - 100	Hourly
CO_2	330 ppm	3 - 5	200	Seasonal
SO_2	0.01 - 1 ppb	0.2 - 1.0	5 - 100	Daily to Weekly
H_2S	0.2 ppb	0.2 - 1.0	5 - 100	Daily to Weekly
OCS	0.5 ppb	1 - 3	100	Monthly
OH	10^5-10^9 cm^{-3}	0.2 - 1.0	5 - 100	Hourly
HO_2	10^5-10^9 cm^{-3}	0.2 - 1.0	5 - 100	Hourly
H_2O_2	0.01 - 10 ppb	0.2 - 1.0	5 - 100	Hourly
CH_3Cl	0.3 - 1 ppb	0.2 - 1.0	5 - 1000	Daily to Weekly
HCl	0.01 - 3 ppb	0.2 - 1.0	5 - 1000	Daily to Weekly
Pressure	1%	1.0	5 - 100	Hourly
Temperature	2-4° K	1.0	5 - 100	Hourly
Wind Speed	2-4 m/sec	1.0 - 5.0	5 - 100	Hourly
Inversion Height	N/A	1 km	5 - 100	Hourly
Aerosol Loading	0.1 - 20 g/m^3	1 km	5 - 100	Hourly

chemical species at very low concentrations are subject to uncertainty of 50% or more due to small interferrents and/or calibration difficulties. Therefore, reported minimum detectable concentrations based on signal-to-noise ratios or established in controlled laboratory settings may be misleading in some cases when the instruments are operated on airborne platforms in complex chemical atmospheres.

5.1 In Situ Pollutant Species Measurements

The commercially-available NO_x analyzers cannot meet the minimum detectability requirements of 2 ppt for NO and NO_2. However, an instrument which uses an improved design for the chemiluminescent detection of NO has been operated aboard a ship with a reported minimum detectable concentration of 1 ppt, when the signal was averaged for 3 minutes. This instrument, when operated on ship or on an aircraft, produced an artifact NO signal which is thought to be due to O_3 luminescence with some other interferring species. The problem was more pronounced at night. This instrument was also subject to erroneous signals when sampling in an environment with rapidly changing water vapor concentration such as when entering or leaving a cloud. Several modifications of the basic commercial chemiluminescent NO_x analyzer, however, can provide reasonably stable and accurate measurements of NO and NO_2 in the range of 20-50 ppt. Nitric acid in the gas phase can be measured by the principle of chemiluminescence in a way very similar to the measurement technique for NO_2. In one sample line, nitric acid is removed by a nylon trap or filter. A second sample line passes through a quartz tube packed with Pyrex® beads and heated to 400° C. The nitric acid is converted to NO_2 in the quartz tube. This differencing technique can detect nitric acid at a minimum detectable concentration of 0.03 ppb; however, interferrents such as PAN and some other organic nitrates are also converted to NO_2 in the quartz tube. Although several techniques exist for the measurement of ammonia in ambient air, so far none have achieved minimum detectable concentrations requested by NASA. A laser/opto acoustic technique has potential to achieve 0.01 ppb sensitivity; however, it is subject to severe interference due to typical tropospheric concentrations of CO_2 and H_2O.

The basic instrumentation available for the detection of sulfur-containing species, specifically SO_2, H_2S, and COS, is limited to flame photometric detection and pulsed UV flourescence. Commercial instruments for SO_2 detection are available that can measure a minimum detectable concentration of 1 ppb. By first passing a sample through a chromatograph column, H_2S and COS can also be separated and detected by flame photometric detection down to low ppb concentrations. No improved measurement techniques for the in situ detection of sulfur species were discovered in the literature although several new remote measurement methods were discussed. A sensitive filter collection method for SO_2 detection has been used effectively aboard airborne platforms and is promising as a method for ambient SO_2 analysis in remote regions where SO_2 concentrations are very low. The inherent problem associated with filter collection is the lack of temporal and spatial resolution that is made necessary by the requirement of integrated sample collection. The greatest need for in situ instrumental development work clearly lies in the detection of sulfur-containing species. The complex relationship between sulfur species and acid rain is now being investigated and although it is likely that improvements in analytical methods will be developed to aid in these efforts, presently the capabilities of SO_2 in situ detection are seriously lacking.

Another group of chemical species listed by NASA for which reliable analytical methods are not yet available is the HO_x group. Three separate molecules within this group were identified as important to NASA in their Global Tropospheric Program. They are H_2O_2, OH, and HO_2. Each of these species are active in photochemical ozone systems. While the ambient concentrations of H_2O_2 can exceed 0.1 ppm in photochemically active urban atmospheres, the ambient concentrations of each of these species are typically very low.

The methods for H_2O_2 detection are all based on absorption of H_2O_2 in sample air in an aqueous solution containing corrosive or caustic chemicals. Therefore, operation of these techniques aboard airborne platforms necessitates special considerations. The best performance of any of these methods was reported to have a minimum detection limit of 1 ppb. This particular method which relies on detecting the chemiluminescence of a reaction in solution is adequate for measuring peak H_2O_2

concentrations in photochemically active atmospheric systems but is not sensitive enough to measure rural concentrations and is an order of magnitude from NASA's requested values.

The measurement of hydroxyl radical (OH) and hydroperoxy radical (HO_2) offer some additional problems. Even in active photochemical systems they are so reactive that their concentrations are rarely above the parts per trillion (ppt) level. Concentrations of these two species are believed to be often in the range of 10^5 to 10^7 molecules/cm^3 at sea level pressures. These very low concentrations coupled with the extreme reactivity of these species make it very difficult to obtain a sample that is representative of ambient air and to accurately measure the concentrations of OH and HO_2. These two species, however, are so important, particularly to modelers of photochemical kinetics, that several methods have been discussed to measure ambient OH and HO_2 concentrations.

Hydroxyl radical can be measured at altitudes above 45 km by measuring resonance flourescence of the decay to ground state after excitation by solar radiation. In the troposphere, however, the solar wavelengths required for exciting the molecules are filtered so an artificial light source is used. Rhodamine S dye lasers passed through a frequency doubling cavity to produce second harmonic radiation, and photon counting photomultipliers were able to achieve minimum detection limit of 2×10^6 cm^{-3} while minimizing the water vapor interference and an interference caused by O^3. Airborne sampling was accomplished with a similar instrument which integrated the measurement for 5 to 15 minutes. This instrument achieved minimum concentration measurements of 2.5×10^5 cm^{-3}.

Only one technique for HO_2 was found in the literature. It relied on freezing the HO_2 in a solid matrix of CO_2 and measuring the influence of a strong magnetic field on electron spin. This system, called electron paramagnetic resonance spectrometry, was operated in a balloon platform in the stratosphere and measured 3×10^7 cm^{-3}.

The techniques described for the measurement of H_2O_2, OH, and HO_2 are not commonly used in ambient monitoring and therefore are specialty methods that have not benefited from the experience of wide use. Calibration difficulties which introduce uncertainty, and sample loss due to chemical reaction in the sample system are likely in some of these systems. These techniques suffer from uncertainties ranging from 50% to a factor of 3 or more.

Aldehydes have also been discussed to be important intermediaries in photochemical systems. In the atmosphere, these species (particularly formaldehyde, acetaldehyde, and proprionaldehyde) are present in the atmosphere principally as a result of secondary chemical generation rather than as primary emissions. For this reason they are typically associated with polluted urban atmospheres and are present at very low concentrations in rural areas.

The well established analytical methods for aldehyde measurement are wet chemical techniques with colorimetric detection or absorption spectroscopy. These techniques require a sampling period of one hour or more which limits their usefulness for airborne applications. One wet chemical collection technique followed by liquid chromatography and UV detection achieved measurement sensitivity of 1 ng for formaldehyde and can detect several aliphatic and aromatic aldehydes after appropriate column separation. A wet chemical sampling technique that measures formaldehyde by detecting chemiluminescence with Gallic acid (I) can measure a minimum detectable concentration of 1 ppb or less for a 30 to 60 minute sample integration.

In situ measurement methods are being developed for the measurement of aldehydes that do not require preconcentration of the sample. These will increase the utility of aldehyde measurements on airborne platforms if sufficient sensitivity and specificity can be achieved. A semicontinuous chromatographic technique requiring 20 minutes per measurement has a minimum detection limit of 20 ppbC. Initial work has been done on instruments using microwave spectrometry and laser flourescence. So far, minimum detectable concentrations of 30-40 ppb have been achieved and improvements have been forecast.

Atmospheric distribution of HCl particularly in the stratosphere have received attention recently because HCl is believed to be the end product of $Cl-O_3$ reactions in the stratosphere. The measurement of HCl is difficult, however, because many techniques respond to total gaseous chlorine or all acidic chlorine.

Although the measurement of HCl has received considerable attention recently, the analytical techniques are not adequate for ambient measurements. A commercial instrument has been developed and has been used by NASA in its Launch Vehicle Effluent Program to map the dispersion plume of rocket launch effluents. For the relatively high HCl concentrations associated with rocket launches this system has worked well; however, the sensitivity and specificity are inadequate for ambient measurements. Of the various techniques proposed for HCl measurement, the best performance with respect to minimum detectable concentration is 1 ppb. From best estimates of the typical atmospheric loadings of HCl, a minimum detectability of at least 20 ppt is required for ambient monitors. Significant improvements in measurement techniques for HCl are required.

Hydrocarbon measurements are often made by collecting an in situ grab sample which is later analyzed by gas chromatography and flame ionization detection. This procedure, however, is time consuming; and in some cases, the measurements are subject to contamination or chemical alteration, and the information available from such systems is dependent on the type of chromatographic columns used. In addition, a large amount of species-specific information is generated some of which is not extremely useful. Typical commercial hydrocarbon analyzers provide a measurement of total nonmethane hydrocarbons. The principal use of hydrocarbon data is for input to photochemical models. The measurement of total nonmethane hydrocarbon has limited use in chemical models since various classes of hydrocarbons making up the nonmethane hydrocarbon measurement vary considerably in their photochemical reactivity.

Several instruments are now being developed that provide a direct measure of hydrocarbons based on their reactivity. An in situ chemiluminescent monitor based on the reaction of alkenes and O_3, which can be operated on an aircraft, provides good resolution and is highly specific for the alkenes, the most photochemically active hydrocarbon class. A similar instrument which measures the chemiluminescence of oxygen atoms and alkenes has also been described. These systems offer the advantage of providing a direct measure of the reactive fraction of hydrocarbons and therefore is useful for input to photochemical models.

Other systems which can provide in situ measurements of reactive hydrocarbons have also been described. In most cases, the tests conducted on these systems indicate that they will be able to provide resolution at least as good as flame ionization detection and therefore offer a significant improvement over other kinds of commonly used hydrocarbon analysis. Since the chemiluminescent instruments have been made by modifying existing ozone chemiluminescence monitors they are highly suited for aircraft use.

Instrumentation methods that are currently available or in the developmental stages for a variety of compounds have been summarized and reference lists have been provided. Although the lower limits of detection requested by NASA have not been met in all cases, the current and projected capabilities of instrumentation are promising. It is likely that the use of sophisticated electronics and improvements in laser technology will contribute to improved instrument design. The development of aircraft-compatible in situ instrumental methods will certainly continue. This summary of available methods provides a conservative evaluation of the current and near future state of the art in instrument development. Published work that was not reviewed in this document and research efforts that are as yet unpublished may already be able to provide capabilities representing significant advancements over the descriptions summarized in this report.

5.2 Meteorological Measurements

The ultimate impact of anthropogenically emitted air pollutants is highly related to physical atmospheric processes. To develop a complete understanding of air pollution systems, chemical concentration data must be integrated with information concerning atmospheric dispersion and advection in a logical manner. This report discusses some measurement techniques of important meteorological parameters that must be considered to explain the movement of pollutant species from source to receptor areas.

Meteorological measurement systems to obtain vertical profile measurements of various meteorological variables are receiving a lot of attention at the present time. The basic weather service radiosonde and rawinsonde balloon releases are being complemented by measurements obtained on more sophisticated airborne platforms. A review of measurement strategies and sampling systems for altitude profile measurements is included in this report ranging from tower-mounted systems to manned aircraft instrument platforms. The versatility of powered aircraft measurement systems provide obvious advantages over the other systems available for vertical profile measurements. The costs involved in the operation and maintenance of such systems, however, can be prohibitive for some applications.

The routine measurement methods for meteorological parameters are well known and widely used. In most cases the accuracies, and spatial and temporal resolution capabilities are also well known. Refinements in numerical modeling efforts require improved input data of both chemical species information and meteorological information. Remote measurement methods show promise for obtaining improved input data for both chemical and physical parameters. Some remote measurement systems for meteorological measurements have been tested and have been used on a routine basis. These systems include acoustic sounding systems for temperature structure to 1 km, radio acoustic sounding systems for temperature profiles to 2 km, and doppler radars, that can provide wind measurements up to the mesosphere. These remote measurement systems for obtaining information on meteorological parameters have been shown to be very effective. Because of the importance of these systems and the promising improvements that are likely to be made, the basics of their operation have also been discussed in this report.

Microwave radiometers are also being developed. These systems were not discussed in the report since their importance to air pollution transport and dispersion is not presently as clear as for the other remote meteorological measurement systems. They are being developed to provide vertical profile information on temperature and water vapor. Some of these systems will have the ability to provide information on water vapor and cloud water content as a function of time. This information is important to the understanding of cloud development, severe storm formation, and precipitation dynamics. As these processes become more completely understood the role of clouds in chemical conversion processes may also be more completely understood. It is possible that these radiometer systems will aid in the explanation of gas to particle conversion mechanisms in clouds. For systems such as SO_2 to $SO_4^=$ conversion this mechanism may provide an important atmospheric sink for SO_2, and may also lead to a better understanding of the acid rain problem.

APPENDIX

OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS AMBIENT AIR QUALITY MONITORS

APPENDIX

OPERATIONAL CHARACTERISTICS FOR COMMERCIALLY-AVAILABLE CONTINUOUS AMBIENT AIR QUALITY MONITORS

A.1 Sources of Information

The primary sources of the operational characteristics which are listed on the attached tables are the vendors' sales literature and operating manuals for the monitors. As an example, sales literature specifications for the Monitor Labs Model 8410E ozone monitor are presented on an attached sheet. Prices and additional information were obtained from telephone conversations with the vendors. As a result, the operational characteristics may be optimistic in some cases. In the cases of several ozone and sulfur dioxide monitors, more objective data were obtained from the test results which the vendors submitted to EPA as part of the equivalency procedure (see References 1 through 3).

As part of EPA's equivalency designation protocol, RTI has performed post-designation testing of various ozone and sulfur dioxide monitors to verify the vendor's results. In general, the results of these post-designation tests have been in good agreement with those of the vendors. As an example, the test data for the Bendix Model 8002 ozone monitor are presented on an attached sheet.

A.2 Explanation of Operational Characteristics

For consistency, the performance parameters which are specified in EPA's equivalency designation protocol were used to compare the commercially-available ambient air quality monitors. While it is obvious that some of EPA's specifications are incompatible with airborne monitoring applications (e.g., rise times), this set of data nevertheless allows some objective basis for comparing the monitors.

The following description of the performance parameters that are listed in the attached tables was taken from Reference 3.

Noise is produced by short-term deviations in the analyzer output not caused by changes in the input concentration. Noise is measured at both 0 percent and 80 percent of the upper range limit (URL) and is the standard deviation of 25 readings taken at 2-min intervals. Normally, this value will be slightly less than the average deviation from the mean value and usually much less than the peak-to-peak noise.

The Lower Detectable Limit (LDL) is the smallest pollutant concentration that produces an output change at least twice the noise level.

The total interference equivalent is the relative degree of (unwanted) response due to various other compounds that may be present in the ambient air sample. The reported values should not be interpreted as the actual error to be expected in the measurements because the test concentrations of most of the interferents are higher than those normally encountered in ambient air. Note that a list of interferent test concentrations is included on an attached sheet. For each type of analyzer, EPA has designated a number of gaseous compounds which may interfere with the measurement method. EPA has set performance specifications for the maximum amount of interference which may exist due to the presence of individual or multiple interferents. The total interference equivalent is the sum of the absolute values of the interference equivalents for individual interferents.

The zero drift (12-hr) is the maximum change in continuous output response to zero input concentration over a 12-hr period of unadjusted operation. Twelve-hour (12-hr) drift includes any peak-to-peak noise component, so it may be higher than the 24-hr zero drift.

The zero drift (24-hr) is the (net) change in response to zero input concentration between two points in time approximately 24 hours apart during unadjusted analyzer operation and including changes in ambient temperature, line voltage, or both. Twenty-four-hour (24-hr) zero drift tends to be sometimes positive, sometimes negative; hence, the average would be misleadingly low. Therefore, the average of the absolute values of individual daily drift is reported in Table 1 as a more meaningful value.

Span drift (20% URL) is the (net) change in response to an input concentration of about 20 percent of the upper range limit between two points in time approximately 24 hours apart, during unadjusted analyzer operation and including changes in ambient temperature, line voltage, or both. Because of the 20 percent URL concentration level, the reported value represents a combination of both zero and span drift over the period. The average of the absolute values is reported.

Span drift (80% URL) is similar to span drift at 20 percent URL, but an input concentration of approximately 80 percent URL is used. The 80 percent URL span drift is calculated without a correction for zero drift; therefore, it may be somewhat higher or lower than the actual change in the slope of the calibration curve. Again, the average of the absolute values of the individual daily results is reported.

Lag time is the time required for the first observable change in response to a sudden change in input concentration.

Rise time is the time (not including lag time) required for the response to reach 95 percent of its final value after a sudden increase in the input concentration.

Fall time is the time (excluding lag time) for the response to decrease to 5 percent of its previous value when the input concentration is suddenly changed to 0 ppm.

Long lag, rise, or fall times do not necessarily adversely affect measurements expressed as hourly averages; however, long response times may be a source of error during calibration and zero and span adjustment.

Precision is the variation in the response to repeated measurements (at 20 percent and 80 percent of the upper range limit) of the same upscale pollutant concentration, reported as the standard deviation. The reported precision is a measure of the repeatability of an analyzer's reading when approached alternately from lower and higher concentrations.

EXAMPLE SALES LITERATURE SPECIFICATIONS FOR MONITOR LABS 8410E OZONE MONITOR (TAKEN FROM A MONITOR LAB BROCHURE)

Ranges	0.2, 0.5, 1.0, 2.0, 5.0 ppm full scale standard. Others available.
Precision	±0.5%
Zero Noise	0.5 ppb (20 second time constant)
Minimum Detectable Conc.	1 ppb (20 second time constant)
Zero Stability	±0.5%/24 hours ±0.5%/7 days
Span Stability @ 25°C	±2%/24 hours ±3%/7 days
Temperature Coefficient 20°C to 30°C	0.4% of reading/°C
Interference	Total interference equivalent < 4 ppb, per USEPA Reference Method designation.
Linearity	±1% of full scale
Lag Time (from step change at input)	4 seconds
Rise or Fall Time, step change in sample conc.	90 seconds to 95% of reading on 20 second time constant
Operating Temperature	10°C to 40°C
Humidity Tolerance	0-95%
Sample Flowrate(Nominal)	300 cc/min
Support Gas	Ethylene
Support Gas Flowrate	30 cc/min
Data Outputs	Separately buffered DAS and RECORDER outputs. Standard outputs: DAS = 0-1V Recorder = 0-100 mV Others available to 0-10V
Time Constant	Frong panel selectable; 1, 5, 20 and 60 seconds
Status Outputs (options)	Range, Time Constant, Function, Warning, Power Fail
Unattended Operation	30 days
Power Requirements	115V ± 10V, 50/60Hz Standard, 100V to 240V Optional
Weight	21 kg (45 lbs)
Dimensions	25 cm x 50 cm x 47 cm (HxDxW) (9 7/8" x 19 3/4" x 18 1/2")

SAMPLE EQUIVALENCY TEST RESULTS FOR BENDIX MODEL 8002 OZONE MONITOR (TAKEN FROM REFERENCE 3)

Performance parameters	Units	EPA specs.[a]	Manufacturer's test results[b]	RTI test results[c]
Noise - 0% URL	ppm	0.005	0.000	0.000
Noise - 80% URL	ppm	0.005	0.001	0.001
Lower detectable limit	ppm	0.010	0.010	0.013
Interferents	ppm			
H_2O		±0.020	<0.001	<0.001
H_2S		±0.020	<0.001	0.000
CO_2		±0.020	0.006	0.000
Total		≤0.060	0.007[d]	<0.001[d]
Zero drift - 12 hr	ppm	±0.020	0.001[d]	0.001[d]
Zero drift - 24 hr	ppm	±0.020	0.001[d]	0.001[d]
Span drift - 20% URL	%	±20.000	2.450[d]	2.800[d]
Span drift - 80% URL	%	±5.000	2.330[d]	2.590[d]
Lag time	min	20	0.3	0.1
Rise time	min	15	2.0	1.1
Fall time	min	15	2.0	1.5
Precision - 20% URL	ppm	0.010	0.001	0.000
Precision - 80% URL	ppm	0.010	0.001	0.001

[a] From EPA equivalency regulations, 40 CFR Part 53.

[b] Average, from manufacturer's application for equivalency determination.

[c] Average, from RTI Phase I postdesignation tests.

[d] Average of absolute values.

INTERFERENT TEST CONCENTRATION IN PARTS PER MILLION
(TAKEN FROM REFERENCE 1)

Pollutant	Analyzer type	Hydrochloric Acid	Ammonia	Hydrogen Sulfide	Sulfur Dioxide	Nitrogen Dioxide	Nitric Oxide	Carbon Dioxide	Ethylene	Ozone	M-Xylene	Water Vapor	Carbon Monoxide	Methane	Ethane
SO_2	Flame photometric (FPD)			0.1	0.14^d			750				$20,000^c$	50		
SO_2	Gas chromatography (FPD)			0.1	0.14^d			750				$20,000^c$	50		
SO_2	Spectrophotometric-wet chemical (paro-sanlline reaction)	0.2	0.1^c	0.1	0.14^d	0.5		750		0.50					
SO_2	Electrochemical	0.2	0.1^c	0.1	0.14^d	0.5	0.5		0.2	0.50		$20,000^c$			
SO_2	Conductivity	0.2	0.1^c		0.14^d	0.5		750							
SO_2	Spectrophotometric gas phase				0.14^d	0.5	0.5			0.50	0.2				
O_3	Chemiluminescent			0.1^c				750		0.08^d		$20,000^c$			
O_3	Electrochemical		0.1^c		0.50	0.5				0.08^d		$20,000^c$			
O_3	Spectrophotometric-wet chemical (potassium reaction)		0.1^c		0.50	0.5	0.5^c			0.08^d					
O_3	Spectrophotometric-gas phase				0.50	0.5	0.5^c			0.08^d					
CO	Infrared							750				20,000	10^d		
CO	Gas chromatography with flame photometric detector											20,000	10^d		0.5
CO	Electrochemical						0.5		0.2			20,000	10^d		
CO	Catalytic combustion thermal detection		0.1					750	0.2			20,000	10^d	5.0	0.5
CO	IR fluorescence							750				20,000	10^d		0.5
CO	Mercury replacement-UV photometric								0.2				10^d		0.5

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[a] Concentrations of interferent listed must be prepared and controlled to ±10% of the stated value.

[b] Analyzer types not listed will be considered by the Adminstrator as special cases.

[c] Do not mix with pollutant.

[d] Concentration of pollutant used for test. These pollutant concentrations must be prepared to ±10% of the stated value.

NOTE: The interference equivalent for an individual interferent is the shift in an analyzers response caused by the measurement of the interferent at the above concentrations specified above.

REFERENCES

1. Hauser, T. R. and S. D. Shearer, "Air Monitoring Equivalency Regs," Environmental Science and Technology, Vol. 9, No. 6, pp. 539-544, June 1975.

2. U. S. Environmental Protection Agency, "Summary of Performance Test Results and Comparative Data for Designated Equivalent Methods for SO_2," U. S. EPA Publication No. QAD/M-79.12, December 1979.

3. U. S. Environmental Protection Agency, "Summary of Performance Test Results and Comparative Data for Designated Reference and Equivalent Methods for Ozone," U. S. EPA Publication No. QAD/M-80.06, June 1980.

A.3 Ozone Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR
COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Bendix 8002	Mast 727 - 2(a)
EPA Designation	---	Reference	None
Measurement Principle	---	Chemiluminescent	UV Absorb.
Max. Detection Range	ppm	0 - 1	0 - 10
Individual Range(s)	ppm	0.01, 0.02, 0.05, 0.10, 0.20, 0.50, 1.00	10.0
Noise (0% URL)	ppm	0.000	-----
Noise (80% URL)	ppm	0.001	-----
Lower Detection Limit	ppm	0.010	0.010
Total Interf. Equiv.	ppm	0.007	-----
Zero Drift (12-hr)	ppm	0.001	-----
Zero Drift (24-hr)	ppm	0.001	1% of Cal. Level
Span Drift (20% URL)	%FS	2.45	-----
Span Drift (80% URL)	%FS	2.33	1% of Cal. Level
Lag Time	seconds	18	5
Rise Time	seconds	120	5 (90%)
Fall Time	seconds	120	5 (90%)
Precision (20% URL)	ppm	0.001	0.010
Precision (80% URL)	ppm	0.001	0.010
Temperature Range	deg. C	5 - 40	0 - 50
Power Required	watts	350	20
Voltage	volts ac	105 - 125	115
Height	cm	21.5	15
Width	cm	42	28
Depth	cm	47	58
Weight	kg	20.4	7
Cost	$	4225 (GSA)	2750 (LIST)
Comments:		Flight Tests by RTI, Flown by RTI	

VENDOR TEST RESULTS OR SPECIFICATIONS FOR
COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Columbia Scientific Industries MEC. 1100-2	Columbia Scientific Industries 2000
EPA Designation	---	Reference	Reference
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 1	0 - 1
Individual Range(s)	ppm	0.05, 0.10, 0.50 1.00	0.10, 0.20, 0.50 1.00
Noise (0% URL)	ppm	0.001	0.000
Noise (80% URL)	ppm	0.002	0.002
Lower Detection Limit	ppm	0.011	0.010
Total Interf. Equiv.	ppm	0.002	0.002
Zero Drift (12-hr)	ppm	<0.001	0.004
Zero Drift (24-hr)	ppm	0.001	0.003
Span Drift (20% URL)	%FS	1.62	2.71
Span Drift (80% URL)	%FS	1.21	1.37
Lag Time	seconds	6	<6
Rise Time	seconds	12	<30
Fall Time	seconds	18	<30
Precision (20% URL)	ppm	0.001	0.001
Precision (80% URL)	ppm	0.001	0.001
Temperature Range	deg. C	10 - 40	10 - 40
Power Required	watts	250	10
Voltage	volts ac	105 - 125	105 - 125
Height	cm	26.5	17.8
Width	cm	48.3	20.3
Depth	cm	45.7	45.7
Weight	kg	25	9.9
Cost	$	3795 (GSA)	4740 (GSA)
Comments:		Higher Ranges Available	Portable: 8-hr Lifetime Flown by FAA

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Anal. Instru. Develop. 560	Beckman 950-A
EPA Designation	---	None	Reference
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 10	0 - 25
Individual Range(s)	ppm	0.01, 0.10, 1.00 10.00	0.025, 0.05, 0.10 0.25, 0.50, 1.00, 2.50
Noise (0% URL)	ppm	0.0005	0.000
Noise (80% URL)	ppm	0.0005	0.001
Lower Detection Limit	ppm	0.001	0.009
Total Interf. Equiv.	ppm	None Found	0.002
Zero Drift (12-hr)	ppm	-----	0.003
Zero Drift (24-hr)	ppm	0.002	<0.001
Span Drift (20% URL)	%FS	2 (8 hr)	3.41
Span Drift (80% URL)	%FS	2 (8 hr)	1.29
Lag Time	seconds	<2	18
Rise Time	seconds	3 (90%)	72
Fall Time	seconds	3 (90%)	72
Precision (20% URL)	ppm	-----	0.002
Precision (80% URL)	ppm	-----	0.002
Temperature Range	deg. C	10 - 40	4 - 43
Power Required	watts	8	250
Voltage	volts ac	115	105 - 125
Height	cm	29.2	22.9
Width	cm	19.0	45.1
Depth	cm	38.3	55.9
Weight	kg	9	31.8
Cost	$	3560 (LIST)	3600 (GSA)
Comments:		Portable (Battery/C_2H_4 Lasts 8 hr) RTI Evaluation Study Has Been Flown	

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Dasibi 1003-AH, -PC, -RS	Dasibi 1008-AH, -PC
EPA Designation	---	Equivalent	None
Measurement Principle	---	UV Absorb.	UV Absorb.
Max. Detection Range	ppm	0 - 1	0 - 1
Individual Range(s)	ppm	1.0	
Noise (0% URL)	ppm	0.002	
Noise (80% URL)	ppm	0.002	
Lower Detection Limit	ppm	0.009	0.001
Total Interf. Equiv.	ppm	0.002	
Zero Drift (12-hr)	ppm	0.007	
Zero Drift (24-hr)	ppm	0.001	
Span Drift (20% URL)	%FS	0.89	
Span Drift (80% URL)	%FS	1.09	
Lag Time	seconds	36	
Rise Time	seconds	36	50 (99%)
Fall Time	seconds	18	50 (99%)
Precision (20% URL)	ppm	<0.001	0.005
Precision (80% URL)	ppm	0.002	0.005
Temperature Range	deg. C	0 - 50	0 - 45
Power Required	watts	110	
Voltage	volts ac	105 - 125	
Height	cm	13	13
Width	cm	38	43
Depth	cm	56	57
Weight	kg	14	12.7
Cost	$	4004-5170 (GSA)	5170-5626 (GSA)
Comments:		1003-AN Used in NASA's GASP Program	Temperature and Pressure-Compensated Custom Order Could Be Built With a 2-3 second Response Time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Meloy Labs OA 325-2R and OA 350-2R	Monitor Labs 8410E
EPA Designation	---	Reference	Reference
Measurement Principle	---	Chemiluminescence	Chemiluminescence
Max. Detection Range	ppm	0 - 10	0 - 10
Individual Range(s)	ppm	0.01, 0.10, 0.50, 1.00, 5.00, 10.00	0.05, 0.10, 0.50, 1.00, 2.00, 10.00
Noise (0% URL)	ppm	<0.001	0.001
Noise (80% URL)	ppm	0.001	0.002
Lower Detection Limit	ppm	0.010	0.009
Total Interf. Equiv.	ppm	0.001	0.002
Zero Drift (12-hr)	ppm	0.001	0.001
Zero Drift (24-hr)	ppm	<0.001	<0.001
Span Drift (20% URL)	%FS	0.48	2.26
Span Drift (80% URL)	%FS	1.25	2.87
Lag Time	seconds	6	<60
Rise Time	seconds	24	<60*
Fall Time	seconds	24	<60*
Precision (20% URL)	ppm	<0.001	0.001
Precision (80% URL)	ppm	0.001	0.001
Temperature Range	deg. C	10 - 40	10 - 40
Power Required	watts	250	250
Voltage	volts ac	105 - 125	105 - 125
Height	cm	31	24.2
Width	cm	48	46
Depth	cm	51	43.2
Weight	kg	18	21
Cost	$	3455-4025 (LIST)	3372 (GSA)
Comments:			RTI Altitude Data *2.3-s response time on 1-second time constant

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS OZONE MONITORS.

	Units	Thermo-Electron 49
EPA Designation	---	Tentative
Measurement Principle	---	UV Absorb.
Max. Detection Range	ppm	0 - 1
Individual Range(s)	ppm	1.0
Noise (0% URL)	ppm	0.001
Noise (80% URL)	ppm	0.001
Lower Detection Limit	ppm	0.002
Total Interf. Equiv.	ppm	
Zero Drift (12-hr)	ppm	
Zero Drift (24-hr)	ppm	<1/2%/month
Span Drift (20% URL)	%FS	
Span Drift (80% URL)	%FS	<1%/month
Lag Time	seconds	10
Rise Time	seconds	20
Fall Time	seconds	20
Precision (20% URL)	ppm	0.002
Precision (80% URL)	ppm	0.002
Temperature Range	deg. C	0 - 50
Power Required	watts	150
Voltage	volts ac	115
Height	cm	22.2
Width	cm	43.2
Depth	cm	58.4
Weight	kg	15.9
Cost	$	6175 (LIST)
Comments:		Temperature and Pressure-Compensated Flown by EPA-LV in 1980 Northeast Corridor Study

A.4 Nitrogen Dioxide Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NITROGEN DIOXIDE MONITORS.

	Units	Thermo-Electron 14 B/E	Thermo-Electron 14 D/E
EPA Designation	---	Reference	Reference
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 10	0 - 10
Individual Range(s)	ppm	0.05, 0.10, 0.20, 0.50, 1.00, 2.00, 5.00, 10.00	0.20, 0.50, 1.00, 2.00, 5.00, 10.00
Noise (0% URL)	ppm	0.001	0.0012
Noise (80% URL)	ppm	0.001	0.0012
Lower Detection Limit	ppm	0.002	0.0025
Total Interf. Equiv.	ppm	<0.025	<0.040
Zero Drift (12-hr)	ppm		
Zero Drift (24-hr)	ppm	0.001	0.002
Span Drift (20% URL)	%FS	1	1
Span Drift (80% URL)	%FS	1	1
Lag Time	seconds	30	3
Rise Time	seconds	120	60
Fall Time	seconds	150	60
Precision (20% URL)	ppm	0.0005	0.001
Precision (80% URL)	ppm	0.001	0.0015
Temperature Range	deg. C		10 - 40
Power Required	watts	475	475
Voltage	volts ac	105 - 125	115
Height	cm	43.2	43.2
Width	cm	48.3	48.3
Depth	cm	46.0	50.1
Weight	kg	34.0	34.0
Cost	$	6128 (GSA)	6631 (GSA)
Comments:		Flown by EPA Single Chamber: 60-s cycle time External Pump	Flown by EPA Dual Chamber External Pump

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NITROGEN DIOXIDE MONITORS.

	Units	Beckman 952-A	Bendix 8101-C
EPA Designation	---	Reference	Reference
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 25	0 - 2
Individual Range(s)	ppm	0.24, 0.50, 1.00 2.50, 5.00, 10.00	0.20, 0.50, 1.00, 2.00
Noise (0% URL)	ppm	0.002	0.002
Noise (80% URL)	ppm	0.003	0.005
Lower Detection Limit	ppm	0.010	0.004
Total Interf. Equiv.	ppm	0.010	<0.040
Zero Drift (12-hr)	ppm	0.020	0.005
Zero Drift (24-hr)	ppm	0.005	0.005
Span Drift (20% URL)	%FS	2	
Span Drift (80% URL)	%FS	2	
Lag Time	seconds	30	30
Rise Time	seconds	90	60
Fall Time	seconds	60	60
Precision (20% URL)	ppm	0.005	0.005
Precision (80% URL)	ppm	0.005	0.010
Temperature Range	deg. C	4 - 43	5 - 40
Power Required	watts	600	500
Voltage	volts ac	105 - 125	115
Height	cm	22.9	21.5
Width	cm	45.1	42.0
Depth	cm	55.9	43.0
Weight	kg	34.5	22.7
Cost	$	5819 (GSA)	6430 (GSA)
Comments:		Single Chamber: 60-s cycle time	Single Chamber: 30-s cycle time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NITROGEN DIOXIDE MONITORS.

	Units	Columbia Scientific Industries 1600	Columbia Scientific Industries 2200
EPA Designation	---	Reference	None
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 5	0 - 5
Individual Range(s)	ppm	0.5, 0.10, 0.20, 0.50, 1.00, 2.00, 5.00	0.50, 1.00, 2.00, 5.00
Noise (0% URL)	ppm	0.001	0.005
Noise (80% URL)	ppm	0.001	0.005
Lower Detection Limit	ppm	0.002	0.010
Total Interf. Equiv.	ppm	0.010	0.010
Zero Drift (12-hr)	ppm	0.001	0.005
Zero Drift (24-hr)	ppm	0.001	----
Span Drift (20% URL)	%FS	1.000	2.0/12-hours
Span Drift (80% URL)	%FS	1.000	2.0/12-hours
Lag Time	seconds	8	5
Rise Time	seconds	90*	20*
Fall Time	seconds	90*	20*
Precision (20% URL)	ppm	0.005	0.010
Precision (80% URL)	ppm	0.005	0.010
Temperature Range	deg. C	10 - 40	10 - 40
Power Required	watts	500	
Voltage	volts ac	105 - 125	115
Height	cm	27.7	20.3
Width	cm	48.3	17.8
Depth	cm	68.6	45.7
Weight	kg	34.0	8.7
Cost	$	6650 (GSA)	5875 (GSA)
Comments:		Single Chamber: 15-s cycle time External Pump *with 5-s time constant	Single Chamber: 10-s cycle time, Portable (4-5 hrs. on batteries), Ferrous Sulfate Converter *with 5-s time constant

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NITROGEN DIOXIDE MONITORS.

	Units	Meloy Labs NA530-R	Monitor Labs 8440E
EPA Designation	---	Reference	Reference
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 5	0 - 5
Individual Range(s)	ppm	0.10, 0.25, 0.50 1.00, 5.00	0.20, 0.50, 1.00, 2.00, 5.00
Noise (0% URL)	ppm	0.002	0.001
Noise (80% URL)	ppm	0.004	
Lower Detection Limit	ppm	0.004	0.002
Total Interf. Equiv.	ppm	0.015	<0.008
Zero Drift (12-hr)	ppm	-----	
Zero Drift (24-hr)	ppm	0.007	0.002
Span Drift (20% URL)	%FS	-----	2.00
Span Drift (80% URL)	%FS	0.013 ppm	2.00
Lag Time	seconds	<5	1
Rise Time	seconds	5 - 300 (95%)	90
Fall Time	seconds	5 - 300 (95%)	90
Precision (20% URL)	ppm	0.002	0.050
Precision (80% URL)	ppm	0.003	0.050
Temperature Range	deg. C	10 - 40	10 - 40
Power Required	watts	300	
Voltage	volts ac	115	105 - 125
Height	cm	31	See Below
Width	cm	48	See Below
Depth	cm	51	See Below
Weight	kg	27	34.5
Cost	$	7700 (LIST)	6300 (LIST)
Comments:		Dual PM Tube External Pump Proprioratory (copper) Converter	Dual PM Tube Analyzer: 25 x 47 x 50 Signal Processor: 25 x 47 x 50 Airborne Option has 10-s response time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR
COMMERCIALLY-AVAILABLE, CONTINUOUS NITROGEN DIOXIDE MONITORS.

	Units	Monitor Labs 8840	Thermo-Electron 14A
EPA Designation	---	Reference	None
Measurement Principle	---	Chemiluminescent	Chemiluminescent
Max. Detection Range	ppm	0 - 10	0 - 2500
Individual Range(s)	ppm	0.05, 0.10 0.20, 0.50, 1.00, 5.00, 10.00	0.01, 0.025, 0.10, 0.25, 1.00, 10, 100, 1000, 2500
Noise (0% URL)	ppm	0.001	
Noise (80% URL)	ppm		
Lower Detection Limit	ppm	0.002	0.0002
Total Interf. Equiv.	ppm	0.002	
Zero Drift (12-hr)	ppm		
Zero Drift (24-hr)	ppm	0.002	0.001
Span Drift (20% URL)	%FS	1	1
Span Drift (80% URL)	%FS	1	1
Lag Time	seconds	3	
Rise Time	seconds	180	1 - 30 (90%)
Fall Time	seconds	180	1 - 30 (90%)
Precision (20% URL)	ppm	0.050	
Precision (80% URL)	ppm	0.050	
Temperature Range	deg. C	10 - 40	
Power Required	watts	320	1100
Voltage	volts ac	105 - 125	105 - 125
Height	cm	22.2	43
Width	cm	43.2	48
Depth	cm	61.0	46
Weight	kg	26.8	74.8 (?)
Cost	$	6200 (LIST)	8425 (LIST)
Comments:		Dual PM Tubes External Pump High Performance Option has 3 times better signal-to-noise ratio	Single Channel: Manual Switching Stock, Optional Auto. Switching with 60-s cycle time

A.5 Sulfur Dioxide Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS.

	Units	Beckman 953	Bendix 8303
EPA Designation	---	Equivalent	Equivalent
Measurement Principle	---	UV Fluorescent	Flame Photometric
Max. Detection Range	ppm	0 - 2	0 - 1
Individual Range(s)	ppm	0.25, 0.50 1.00, 2.00	0.50, 1.00
Noise (0% URL)	ppm	0.001	0.001
Noise (80% URL)	ppm	0.002	<0.001
Lower Detection Limit	ppm	0.010	0.009
Total Interf. Equiv.	ppm	0.023	0.010
Zero Drift (12-hr)	ppm	0.003	0.001
Zero Drift (24-hr)	ppm	0.001	0.001
Span Drift (20% URL)	%FS	1.05	1.73
Span Drift (80% URL)	%FS	0.58	0.71
Lag Time	seconds	18	18
Rise Time	seconds	372	18
Fall Time	seconds	306	18
Precision (20% URL)	ppm	0.001	<0.001
Precision (80% URL)	ppm	0.002	0.001
Temperature Range	deg. C	20 - 30	5 - 40
Power Required	watts	900	300
Voltage	volts ac	105 - 125	105 - 125
Height	cm	31.1	21.5
Width	cm	48.3	42
Depth	cm	56	45.7
Weight	kg	41	27.2
Cost	$	6763 (GSA)	6295 (GSA)

Comments:

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS.

	Units	Lear Siegler SM 1000	Meloy Labs SA 185-2A
EPA Designation	---	Equivalent	Equivalent
Measurement Principle	---	2nd Deriv. Spectro.	Flame Photometric
Max. Detection Range	ppm	0 - 2	0 - 1
Individual Range(s)	ppm	0.50, 2.00	0.50, 1.00
Noise (0% URL)	ppm	0.003	<0.001
Noise (80% URL)	ppm	0.003	<0.001
Lower Detection Limit	ppm	0.013	0.007
Total Interf. Equiv.	ppm	0.006	0.020
Zero Drift (12-hr)	ppm	0.018	0.001
Zero Drift (24-hr)	ppm	0.004	<0.001
Span Drift (20% URL)	%FS	3.98	3.23
Span Drift (80% URL)	%FS	0.86	2.99
Lag Time	seconds	54	6
Rise Time	seconds	504	66
Fall Time	seconds	480	30
Precision (20% URL)	ppm	0.002	<0.001
Precision (80% URL)	ppm	0.002	0.002
Temperature Range	deg. C	0 - 35	10 - 40
Power Required	watts	150	250
Voltage	volts ac	105 - 125	105 - 125
Height	cm	See Below	31.1
Width	cm	See Below	43.2
Depth	cm	See Below	50.8
Weight	kg	37	18 - 22
Cost	$	11,620 (LIST)	4735 (LIST)
Comments:		Analyzer: 28 x 28 x 41 Optics: 20 x 86 x 38	RTI Altitude Data

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS.

	Units	Meloy Labs SA 285 E	Meloy Labs SA 700
EPA Designation	---	Equivalent	Equivalent
Measurement Principle	---	Flame Photometric	Flame Photometric
Max. Detection Range	ppm	0 - 1	0 - 10
Individual Range(s)	ppm	0.05, 0.10, 0.50, 1.00	0.25, 0.50, 1.00 5.00, 10.00
Noise (0% URL)	ppm	<0.001	0.001
Noise (80% URL)	ppm	0.001	-----
Lower Detection Limit	ppm	0.009	0.002
Total Interf. Equiv.	ppm	0.022	0.020
Zero Drift (12-hr)	ppm	0.001	0.005
Zero Drift (24-hr)	ppm	0.002	0.003
Span Drift (20% URL)	%FS	2.25	0.60
Span Drift (80% URL)	%FS	1.25	0.80
Lag Time	seconds	<6	<60
Rise Time	seconds	48*	90
Fall Time	seconds	24*	90
Precision (20% URL)	ppm	<0.001	0.001
Precision (80% URL)	ppm	0.002	0.001
Temperature Range	deg. C	10 - 40	0 - 45
Power Required	watts	250	300
Voltage	volts ac	105 - 130	105 - 130
Height	cm	31	31
Width	cm	43	43
Depth	cm	51	51
Weight	kg	18 - 23	18 - 22
Cost	$	5450 (LIST)	6300 (LIST)
Comments:		*3 - 10 seconds with Fast Response Option Tested and flown by RTI	

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS.

	Units	Monitor Labs 8450 E	Monitor Labs 8850
EPA Designation	---	Equivalent	Equivalent
Measurement Principle	---	Flame Photometric	UV Fluorescent
Max. Detection Range	ppm	0 - 1	0 - 10
Individual Range(s)	ppm	0.10, 0.50, 1.00	0.25, 0.50, 1.00 5.00, 10.00
Noise (0% URL)	ppm	0.001	<0.001
Noise (80% URL)	ppm	0.001	0.001
Lower Detection Limit	ppm	0.002	0.001
Total Interf. Equiv.	ppm	0.035	0.011
Zero Drift (12-hr)	ppm	0.001	0.001
Zero Drift (24-hr)	ppm	0.001	0.001
Span Drift (20% URL)	%FS	0.5	1.38
Span Drift (80% URL)	%FS	0.5	1.41
Lag Time	seconds	<1	18
Rise Time	seconds	90	204
Fall Time	seconds	90	204
Precision (20% URL)	ppm	0.001	0.001
Precision (80% URL)	ppm	0.001	0.001
Temperature Range	deg. C	10 - 40	10 - 40
Power Required	watts	500	700
Voltage	volts ac	105 - 125	105 - 125
Height	cm	See Below	23.5
Width	cm	See Below	48.3
Depth	cm	See Below	57.2
Weight	kg	45.5	27
Cost	$	5208 (GSA)	6487 (GSA)
Comments:		Analyzer: 24 x 46 x 58 Signal Processor: 24 x 46 x 58	External Pump High Performance Unit Available with 120-s Rise Time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS SULFUR DIOXIDE MONITORS.

	Units	Thermo-Electron 43
EPA Designation	---	Equivalent
Measurement Principle	---	UV Fluorescent
Max. Detection Range	ppm	0 - 5
Individual Range(s)	ppm	0.50, 1.00, 5.00
Noise (0% URL)	ppm	0.001
Noise (80% URL)	ppm	0.001
Lower Detection Limit	ppm	0.003
Total Interf. Equiv.	ppm	0.005
Zero Drift (12-hr)	ppm	0.005
Zero Drift (24-hr)	ppm	0.001
Span Drift (20% URL)	%FS	0.52
Span Drift (80% URL)	%FS	0.46
Lag Time	seconds	12
Rise Time	seconds	234
Fall Time	seconds	282
Precision (20% URL)	ppm	0.001
Precision (80% URL)	ppm	0.001
Temperature Range	deg. C	5 - 45
Power Required	watts	150
Voltage	volts ac	105 - 125
Height	cm	22.3
Width	cm	43.2
Depth	cm	58.4
Weight	kg	25
Cost	$	7101 (GSA)
Comments:		Fast Response Option Available (About 10-s Response Time)

A.6 Carbon Monoxide Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS CARBON MONOXIDE MONITORS.

	Units	Thermo-Electron 48	Dasibi 3003
EPA Designation	---	None	None
Measurement Principle	---	Gas Filter Corr.	Gas Filter Corr.
Max. Detection Range	ppm	0 - 200	0 - 50
Individual Range(s)	ppm	10, 20, 50, 100, 200	.50
Noise (0% URL)	ppm	----	----
Noise (80% URL)	ppm	0.05	0.10
Lower Detection Limit	ppm	0.20	0.20
Total Interf. Equiv.	ppm		
Zero Drift (12-hr)	ppm	----	
Zero Drift (24-hr)	ppm	0.30	1.00
Span Drift (20% URL)	%FS	----	
Span Drift (80% URL)	%FS	1.00	0.5
Lag Time	seconds		
Rise Time	seconds	120	30
Fall Time	seconds	120	30
Precision (20% URL)	ppm		
Precision (80% URL)	ppm	0.5% FS	0.2
Temperature Range	deg. C	5 - 45	15 - 35
Power Required	watts		
Voltage	volts ac	115	105 - 125
Height	cm	22.2	13.3
Width	cm	43.2	43.7
Depth	cm	58.4	57.2
Weight	kg	24.9	13.6
Cost	$	6650 (LIST)	6750 (LIST)

Comments:

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS CARBON MONOXIDE MONITORS.

	Units	Beckman 866	Bendix 8501-5CA
EPA Designation	---	Reference	Reference
Measurement Principle	---	NDIR (Luft)	NDIR (Luft)
Max. Detection Range	ppm	0 - 50	0 - 1000
Individual Range(s)	ppm	50	50, 250, 500, 1000
Noise (0% URL)	ppm	0.2	0.5 (%FS)
Noise (80% URL)	ppm	0.2	0.5 (%FS)
Lower Detection Limit	ppm	0.2	0.5
Total Interf. Equiv.	ppm	1.5	1.0
Zero Drift (12-hr)	ppm	0.5	1 (%FS)
Zero Drift (24-hr)	ppm	0.5	1 (%FS)
Span Drift (20% URL)	%FS	1	----
Span Drift (80% URL)	%FS	1	1.0
Lag Time	seconds	----	----
Rise Time	seconds	13 (90%)	
Fall Time	seconds	13 (90%)	
Precision (20% URL)	ppm	0.2	----
Precision (80% URL)	ppm	0.2	1 (%FS)
Temperature Range	deg. C	0 - 50	20 - 30
Power Required	watts	500	300
Voltage	volts ac	105 - 125	105 - 125
Height	cm	47.6	76
Width	cm	34.3	48
Depth	cm	72.1	27
Weight	kg	40.8	27.2
Cost	$	5602 (GSA)	7315 (GSA)
Comments:		External Pump	Vibration - Sensitive

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS CARBON MONOXIDE MONITORS.

	Units	Horiba AQM-10	Horiba APMA-300 E/SE
EPA Designation	---	Reference	Under Testing
Measurement Principle	---	NDIR (Luft)	NDIR (Cross-FLow-Mod.)
Max. Detection Range	ppm	0 - 50	0 - 500
Individual Range(s)	ppm	50	50, 100, 250, 500
Noise (0% URL)	ppm	0.15	0.10
Noise (80% URL)	ppm	0.15	0.10
Lower Detection Limit	ppm	0.30	0.10
Total Interf. Equiv.	ppm	1.50	1.00
Zero Drift (12-hr)	ppm	----	----
Zero Drift (24-hr)	ppm	0.5	0.50 (%FS)
Span Drift (20% URL)	%FS	2.0	----
Span Drift (80% URL)	%FS	2.0	1.00 (%FS)
Lag Time	seconds	18	
Rise Time	seconds	60	15
Fall Time	seconds	60	15
Precision (20% URL)	ppm	0.2	----
Precision (80% URL)	ppm	0.2	1.00 (%FS)
Temperature Range	deg. C	20 - 30	0 - 40
Power Required	watts	300	340
Voltage	volts ac	105 - 125	105 - 125
Height	cm	See Below	See Below
Width	cm	See Below	See Below
Depth	cm	See Below	See Below
Weight	kg	34	48
Cost	$	5337 (GSA)	7690 (LIST)
Comments:		Vibration-Sensitive Control Panel: 49 x 48 x 10, Analyzer: 15 x 10 x 86	Analyzer: 22 x 48 x 27 Sampling System: 22 x 48 x 27

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS CARBON MONOXIDE MONITORS.

	Units	Monitor Labs 8310	MSA/LIRA 202S
EPA Designation	---	Reference	Reference
Measurement Principle	---	NDIR (Micro-Flow Sensor)	NDIR (Luft)
Max. Detection Range	ppm	0 - 100	0 - 50
Individual Range(s)	ppm	50, 100	50
Noise (0% URL)	ppm	<0.05	0.06
Noise (80% URL)	ppm	<0.05	0.06
Lower Detection Limit	ppm	<0.10	1.00
Total Interf. Equiv.	ppm	<0.50	0.50
Zero Drift (12-hr)	ppm	<0.50	0.50
Zero Drift (24-hr)	ppm	<0.50	0.50
Span Drift (20% URL)	%FS	<2.00	0.4
Span Drift (80% URL)	%FS	<2.00	1.25
Lag Time	seconds		30
Rise Time	seconds	<45	36
Fall Time	seconds	<45	48
Precision (20% URL)	ppm	0.10	0.05
Precision (80% URL)	ppm	0.10	0.05
Temperature Range	deg. C	-5 - 40	0 - 50
Power Required	watts	400 (VA)	500
Voltage	volts ac	105 - 125	115
Height	cm	114.3	110
Width	cm	48.3	47
Depth	cm	35.6	50
Weight	kg	30	
Cost	$	7268 (GSA)	5748 (GSA)
Comments:			Possible Vibration Problems

A.7 Nonmethane Hydrocarbon Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NONMETHANE HYDROCARBON MONITORS.

	Units	HNU Systems PI-201-250	Meloy HC500-2C
EPA Designation	---	None	None
Measurement Principle	---	Continuous PID (UV)	Catalytic Oxidation-FID
Max. Detection Range	ppm	0 - 20	0 - 1000
Individual Range(s)	ppm	5, 10, 20	10, 50, 100, 500 1000
Noise (0% URL)	ppm	----	----
Noise (80% URL)	ppm	0.050*	0.05
Lower Detection Limit	ppm	0.050	0.10
Total Interf. Equiv.	ppm	See Comments	----
Zero Drift (12-hr)	ppm	----	----
Zero Drift (24-hr)	ppm	<1% FS	1% FS
Span Drift (20% URL)	%FS	----	----
Span Drift (80% URL)	%FS	<0.5	2% FS
Lag Time	seconds		<15
Rise Time	seconds	<20 (90%)	<30 (90%)
Fall Time	seconds	<20 (90%)	<30 (90%)
Precision (20% URL)	ppm	----	----
Precision (80% URL)	ppm	1% FS	1% FS
Temperature Range	deg. C	5 - 40	10 - 40
Power Required	watts	200	250
Voltage	volts ac	115	105 - 125
Height	cm	24.5	31.1
Width	cm	50.2	43.2
Depth	cm	63.5	50.8
Weight	kg	24.9	18.1
Cost	$	5445 (LIST)	4170 (LIST)
Comments:		Interferences from Nonorganic Compounds *ppm Carbon Rather than ppm Volume	

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NONMETHANE HYDROCARBON MONITORS.

	Units	Baseline 1030A	Bendix 8202
EPA Designation	---	None	None
Measurement Principle	---	Backflush GS-FID	Direct GC-FID
Max. Detection Range	ppm		0 - 50
Individual Range(s)	ppm		10, 20, 50
Noise (0% URL)	ppm		----
Noise (80% URL)	ppm		1% FS
Lower Detection Limit	ppm		0.005
Total Interf. Equiv.	ppm		<0.010
Zero Drift (12-hr)	ppm		----
Zero Drift (24-hr)	ppm		±1% FS
Span Drift (20% URL)	%FS		
Span Drift (80% URL)	%FS		1
Lag Time	seconds		Not Applicable
Rise Time	seconds		Not Applicable
Fall Time	seconds		Not Applicable
Precision (20% URL)	ppm		----
Precision (80% URL)	ppm		1% FS
Temperature Range	deg. C		5 - 40
Power Required	watts	100	700
Voltage	volts ac	115	105 - 125
Height	cm	18.4	23.4
Width	cm	31.1	42.2
Depth	cm	39.4	44.7
Weight	kg	9.1	27.2
Cost	$	4449 (LIST)	5875 (GSA)
Comments:		General-Purpose Gas Chromatograph Rather Than an Instrument That Was Specifically Designed for NMHC Measurements	Three-minute Cycle Time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NONMETHANE HYDROCARBON MONITORS.

	Units	Byron 301	Byron 404
EPA Designation	---	None	None
Measurement Principle	---	Backflush GC-FID	Oxidation/Reduction FID
Max. Detection Range	ppm	0 - 100	0 - 500
Individual Range(s)	ppm	2, 5, 10, 20, 50, 100	1, 5, 10, 20, 50, 100, 200, 500
Noise (0% URL)	ppm	----	----
Noise (80% URL)	ppm	<1%FS	<0.5% FS
Lower Detection Limit	ppm	0.005	----
Total Interf. Equiv.	ppm	"None"	"None"
Zero Drift (12-hr)	ppm	"None"	"None"
Zero Drift (24-hr)	ppm	"None"	"None"
Span Drift (20% URL)	%FS	----	----
Span Drift (80% URL)	%FS	<1	<0.5
Lag Time	seconds	Not Applicable	Not Applicable
Rise Time	seconds	Not Applicable	Not Applicable
Fall Time	seconds	Not Applicable	Not Applicable
Precision (20% URL)	ppm	----	----
Precision (80% URL)	ppm	<1% FS	1% FS
Temperature Range	deg. C	5 - 40	5 - 40
Power Required	watts	200	200
Voltage	volts ac	105 - 125	105 - 125
Height	cm	26.7	26.7
Width	cm	50.8	50.8
Depth	cm	47.0	47.0
Weight	kg	24.9	27.2
Cost	$	6690 (LIST)	9575 (LIST)
Comments:		Three-Minute Cycle Time	Twelve-Minute Cycle Time

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS NONMETHANE HYDROCARBON MONITORS.

	Units	MSA 11-2
EPA Designation	---	None
Measurement Principle	---	Catalytic Oxidation-FID
Max. Detection Range	ppm	0 - 20
Individual Range(s)	ppm	5, 20
Noise (0% URL)	ppm	<0.050
Noise (80% URL)	ppm	<0.050
Lower Detection Limit	ppm	0.040
Total Interf. Equiv.	ppm	----
Zero Drift (12-hr)	ppm	----
Zero Drift (24-hr)	ppm	<1% FS
Span Drift (20% URL)	%FS	
Span Drift (80% URL)	%FS	<1
Lag Time	seconds	
Rise Time	seconds	<15 (100%)
Fall Time	seconds	<15 (100%)
Precision (20% URL)	ppm	----
Precision (80% URL)	ppm	1% FS
Temperature Range	deg. C	0 - 40
Power Required	watts	1000
Voltage	volts ac	115
Height	cm	84
Width	cm	33
Depth	cm	51
Weight	kg	28
Cost	$	6460 (GSA)
Comments:		Flown in EPA's RAPS Study Fast Response Option Possible

A.8 Ammonia Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS AMMONIA MONITORS.

	Units	Thermo-Electron 14T	Fuji Electric Model ZSF
EPA Designation	---	None	None
Measurement Principle	---	Chemiluminescence	NDIR (Micro-Flow Sensor)
Max. Detection Range	ppm	0 - 10	0 - 50
Individual Range(s)	ppm	0.05, 0.10, 0.20, 0.50, 1.00, 2.00 5.00, 10.00	2.00, 10.00, 50.00
Noise (0% URL)	ppm	----	
Noise (80% URL)	ppm	0.002*	
Lower Detection Limit	ppm	0.004*	<0.060
Total Interf. Equiv.	ppm	0.010	"Negligible"
Zero Drift (12-hr)	ppm	0.001*	
Zero Drift (24-hr)	ppm	0.001*	"None"
Span Drift (20% URL)	%FS	----	
Span Drift (80% URL)	%FS	1	<2.5% FS/Week
Lag Time	seconds	1	----
Rise Time	seconds	120	150
Fall Time	seconds	120	150
Precision (20% URL)	ppm	0.002	
Precision (80% URL)	ppm	0.002	±2% FS
Temperature Range	deg. C		0 - 40
Power Required	watts	625	
Voltage	volts ac		90 - 110
Height	cm	43.2	159.0
Width	cm	48.3	54.1
Depth	cm	45.7	75.0
Weight	kg	34.0	
Cost	$	9935 (LIST)	Price is Being Established
Comments:		*On 0-0.05 ppm range Range Triple Chamber Instrument/Dual Converters Outputs: NO, NO_2, NO_x, NH_3, Total Nitrogen	NH_3 is Converted into NO which is Measured

A.9 Formaldehyde Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR
COMMERCIALLY-AVAILABLE, CONTINUOUS FORMALDEHYDE MONITORS.

	Units	CEA Instruments 555
EPA Designation	---	None
Measurement Principle	---	Colorimetric
Max. Detection Range	ppm	0 - 10
Individual Range(s)	ppm	0.5 Variable Up to 10
Noise (0% URL)	ppm	0.3% FS
Noise (80% URL)	ppm	
Lower Detection Limit	ppm	0.010*
Total Interf. Equiv.	ppm	No Known Interferents
Zero Drift (12-hr)	ppm	
Zero Drift (24-hr)	ppm	<2% FS
Span Drift (20% URL)	%FS	
Span Drift (80% URL)	%FS	<2
Lag Time	seconds	330
Rise Time	seconds	180 (90%)
Fall Time	seconds	210 (90%)
Precision (20% URL)	ppm	
Precision (80% URL)	ppm	
Temperature Range	deg. C	4 - 49
Power Required	watts	35
Voltage	volts ac	120
Height	cm	30.5
Width	cm	50.8
Depth	cm	14.0
Weight	kg	11.8
Cost	$	4875
Comments:		*For a 0.1 ppm FS Range Utilizes the Modified Schiff Reaction Battery-Powered A General-Purpose Automated Wet Chemistry Instrument Set Up to Measure HCHO

A.10 Hydrogen Chloride Monitors

VENDOR TEST RESULTS OR SPECIFICATIONS FOR COMMERCIALLY-AVAILABLE, CONTINUOUS HYDROGEN CHLORIDE MONITORS.

	Units	Geomet 402-B
EPA Designation	---	None
Measurement Principle	---	Luminol Chemiluminescent
Max. Detection Range	ppm	0 - 200
Individual Range(s)	ppm	0.2, 2.0, 20, 200
Noise (0% URL)	ppm	
Noise (80% URL)	ppm	<1% FS
Lower Detection Limit	ppm	<0.02
Total Interf. Equiv.	ppm	----
Zero Drift (12-hr)	ppm	1% FS (8-hours)
Zero Drift (24-hr)	ppm	----
Span Drift (20% URL)	%FS	----
Span Drift (80% URL)	%FS	2 (8-hours)
Lag Time	seconds	
Rise Time	seconds	1 (90%)
Fall Time	seconds	1 (90%)
Precision (20% URL)	ppm	----
Precision (80% URL)	ppm	5% FS
Temperature Range	deg. C	0 - 40
Power Required	watts	75
Voltage	volts ac	28 VDC
Height	cm	See Below
Width	cm	See Below
Depth	cm	See Below
Weight	kg	18.1
Cost	$	12,000 (LIST)
Comments:		Airborne Version Sensor: 20 x 25 x 46 Control: 10 x 40 x 23 Interference Problems

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15. Supplementary Notes

Langley Technical Monitor: Gerald L. Gregory
Final Report

16. Abstract

The current techniques available for the in situ measurement of ambient trace gas species, particulate composition and particulate size distribution are reviewed. The operational specifications of the various techniques are also described. In most cases the techniques described are limited to those that have been used in airborne applications or show promise of being adaptable to airborne applications. Some of the instruments described are specialty items that are not commercially-available.

The report also includes a discussion of in situ measurement techniques for several meteorological parameters important in the study of the distribution and transport of ambient air pollutants. Some remote measurement techniques for meteorological parameters are also discussed.

A summary is also presented which compares the state-of-the-art measurement capabilities with a list of capabilities and specifications desired by NASA for ambient measurements in the global troposphere.

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