REPORT NO. DOT-TSC-0ST-72-4

# SURVEY OF INSTRUMENTATION FOR THE MEASUREMENT OF STRATOSPHERIC TRACE GASES AND PARTICULATES (CIAP)

A. E. O'BRIEN TRANSPORTATION SYSTEMS CENTER 55 BROADWAY CAMBRIDGE, MA. 02142

NOVEMBER 1971 TECHNICAL MEMORANDUM



Approved for U.S. Government only. Transmittal of this document autside the U.S. Government must have prior approval of the Transportation Systems Center

Prepared for. Department of transportation Office of the Secretary Washington, D. C. 20590 The contents of this report reflect the views of the Transportation Systems Center which is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policy of the Department of Transportation. This report does not constitute a standard, specification or regulation.

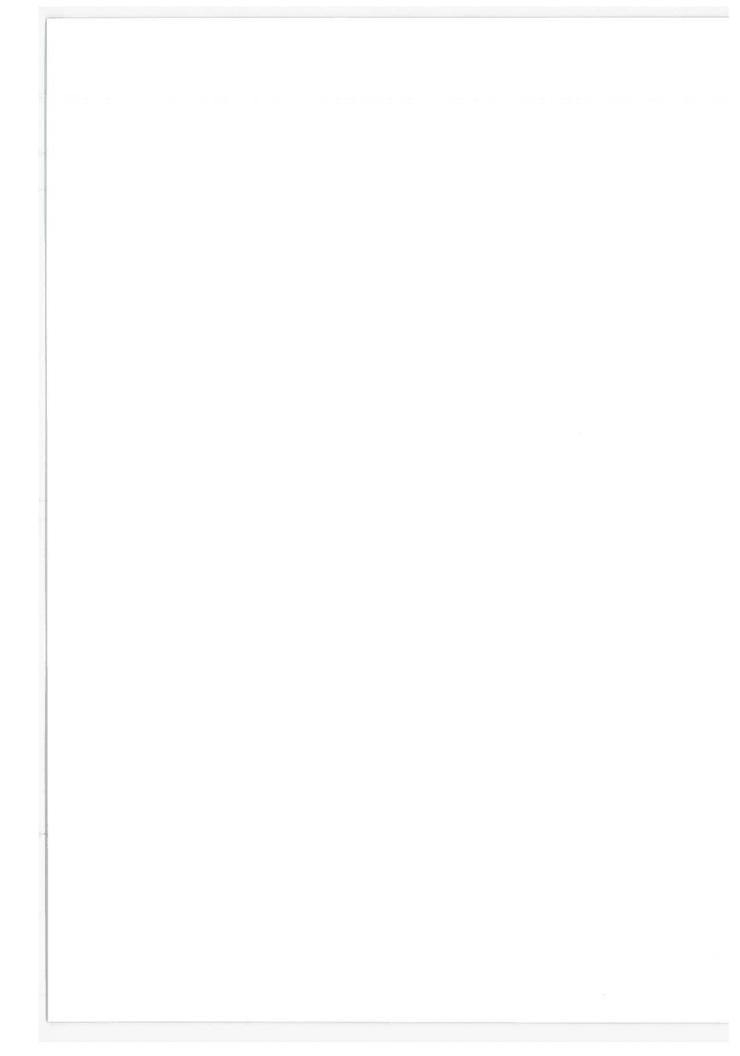
1. Report No. DOT-TSC-OST-72-4	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle SURVEY OF INSTRUMEN	5. Report Date November 1971		
MEASUREMENT OF STRATOSPHERIC TRACE GASES AND PARTICULATES (CIAP)		6. Performing Organization Code	
7. Author(s) A. E. O'Brien		8. Performing Organization Report No.	
9. Performing Organization Name and Address Department of Transportation Transportation Systems Center 55 Broadway		10. Work Unit No. R-2539	
		11. Contract or Grant No. OS-220	
Cambridge, Ma. 02142		13. Type of Report and Period Covered	
12. Sponsoring Agency Name and Address		Technical Memoran-	
Department of Transportation Office of the Secretary Washington, D.C. 20590		dum Sept-Nov 1971	
		14. Sponsoring Agency Code	

15. Supplementary Notes

#### 16. Abstract

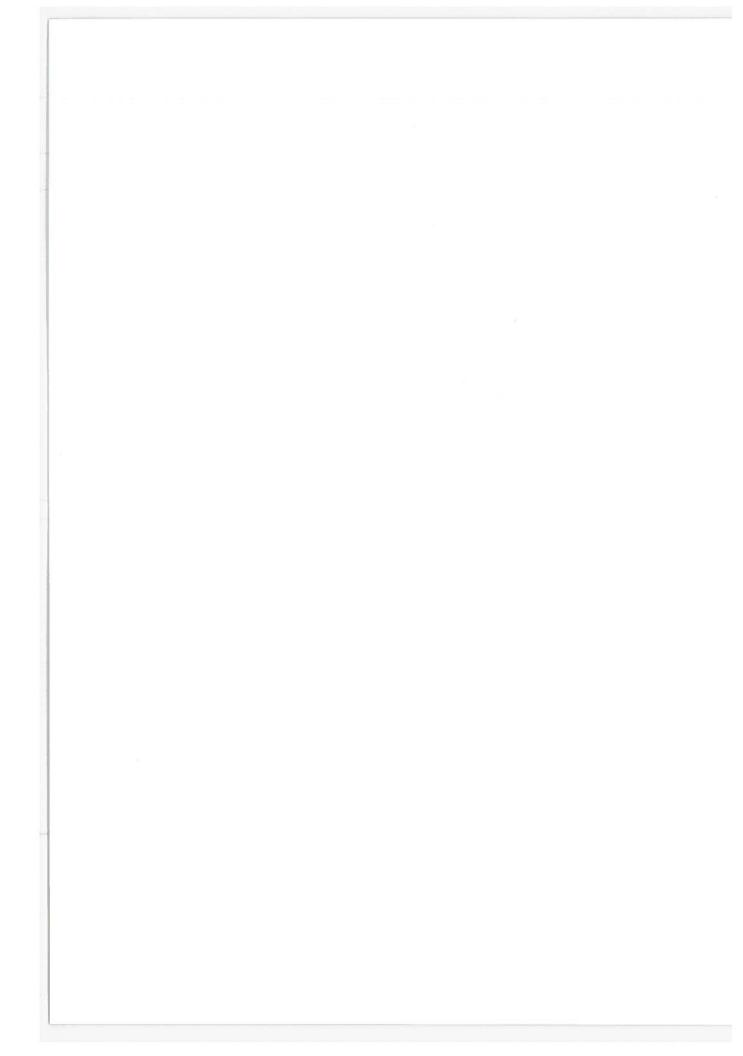
During the period 1 September to 1 November 1971, a survey was conducted for the CIAP Program Office to determine the applicability of presently available instrumentation to the direct and/or remote measure of trace gases and particulates within the stratosphere. Consideration was also given to technique under development where near term applicability could be anticipated. Manufacturers and researchers were queried as to their capability. Details of responses were sifted and, when possible, were tabulated to present the pertinent facts on the performance, electrical, mechanical, environmental and cost factors for instruments which can be considered applicable, either directly or with some modification.

17. Key Words		18. Distribution State	ement	
•Instrumentation •Stratosphere •Trace Gases •Particulates		Approved for Transmittal side the U.S prior approv	of this docu	ment out-
19. Security Classif. (of this report)	20. Security Classif. (of this page) UNCLASSIFIED			22. Price
UNCLASSIFIED	UNCLASS	PILIED	25	



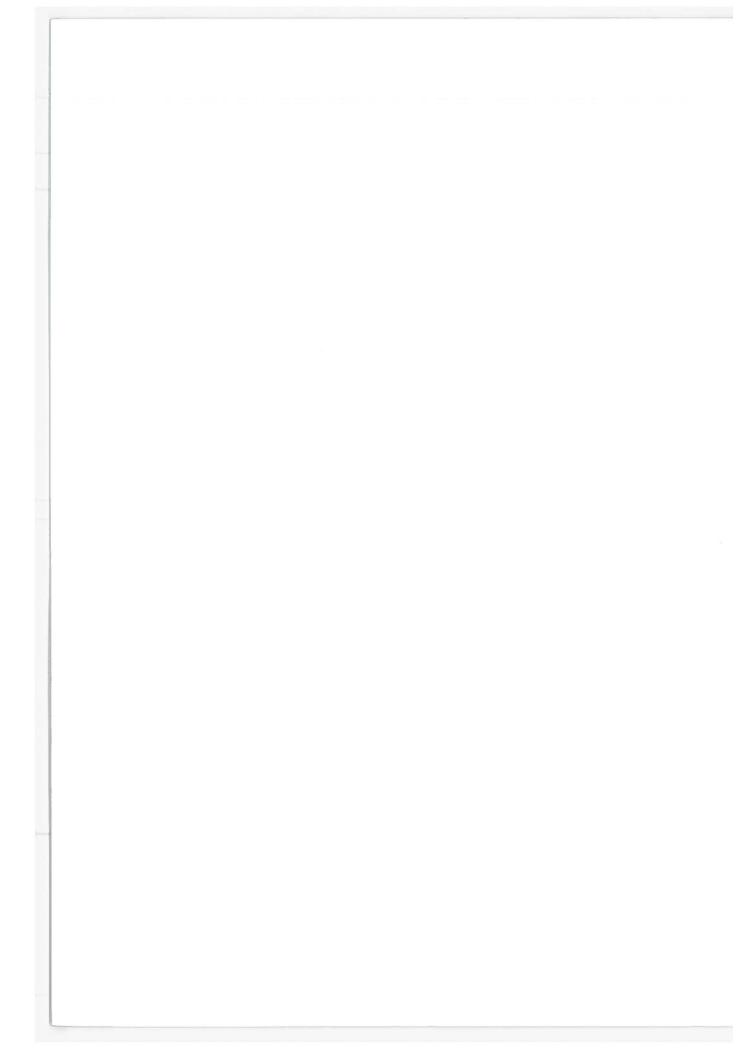
# TABLE OF CONTENTS

	Page
SECTION 1 INTRODUCTION	
Purpose	$\frac{1}{1}$
Scope	i
Approach	_
SECTION 11 INSTRUMENTATION	
Trace Gases	
Direct Measure of Trace Gases	4
Direct Measurement-Non-Real Time	
Indirect Measurements	
Particulates	16
SECTION 111 CONCLUSIONS	21
SECTION IV RECOMMENDATIONS	23
SECTION V MANUFACTURERS QUERIED	24



# LIST OF TABLES

		Page
I.	Water Vapor Sensors	6
II.	Ozone Sensors	8
III.	NO <sub>X</sub> Sensors	10
IV.	Sulfur Dioxide Sensors	12
V.	Indirect Sensors	17



## SECTION I INTRODUCTION

During the period 1 September to 1 November 1971, a survey was conducted to determine the availability and characteristics of instrumentation for the remote and in situ measurement of trace gases and particulates which reside in the lower stratosphere. This effort was conducted in support of CIAP. Details as to the purpose, scope, and approach to the effort are summarized below.

### 1.1 PURPOSE

The primary purpose of this effort was to conduct a comprehensive survey of presently available instruments applicable to the direct and/or remote measure of trace gases such as water vapor, NO, NO2, O3, CO, CO2,  $\rm H_{X}C_{Y}$  and particulates which reside in the stratosphere. The concentrations of the trace gases (in PPM) were estimated to be: CO2 485, H2O 2-40, CO 0.001-0.01,  $\rm H_{X}C_{Y}$  0.01, NO<sub>X</sub> 0.001-0.04, SO2 0.0001-0.001. Particulates were estimated to be in the size range from 0.001 to 2 microns and in the concentration range from 1 to  $10^{4}/\rm cc$ .

### 1.2 SCOPE

In keeping with program direction, the survey was conducted over a two month period and is summarized in this report. Initial efforts were directed exclusively to presently available instruments; however, it later appeared prudent to expand the scope to include instruments and techniques in various stages of development which show promise of availability and applicability consonent with the requirements of CIAP. Consideration was given to the fact that the instrument platforms for direct measurements would be balloons and/or RB 57 type aircraft, that the platform for remote sensing would be Boeing 707 type aircraft, and that certain measurements would be made from the ground. The survey sought to provide information on each applicable instrument as to operational characteristics, availability, price and cost of modification, if necessary, for adaptation to aircraft and/or balloon platforms.

### 1.3 APPROACH

Upon initiating the survey it was recognized that it would be virtually impossible for any single individual to survey every manufacturer and/or researcher in as broad a field as this in a two month period. It was further recognized that other governmental agencies, particularly EPA, NASA, NSF and DOD have conducted or sponsored measurement programs in this general area in the past and that many of these programs are continuing. An initial probe indicated that little formal documentation was available on these programs; however, it soon became obvious that, despite the lack of formal documentation, a considerable body of knowledge existed with those active in the field. It thus appeared that the only approach offering any reasonable assurance of completing the required "comprehensive survey" in the time available was that of supplementing an individual effort with direct contact with those having an intimate knowledge of and direct involvement in current activities and contemplated programs.

To implement this approach, initial contact with identifiable organizations was made by phone or by mail and where deemed appropriate follow-on contact was made by personal visit. To this end, contact was made early in the program with, among others, EPA, MITRE, AFCRL and the Mass. Public Health Department. Following initial contact, visits were made to these organizations. These visits were invaluable in establishing the state of the art of commercially available instrumentation and in identifying sources of potentially applicable instrumentation. These sources were then queried as to the applicability of their product lines to the needs of CIAP.

Contact was also made with such organizations as DRI, NCAR, LASL, JPL, NRL, A. D. Little, Utah State University, NASA Ames and NASA Lewis. A visit was made to DRI to determine the characteristics and capabilities of their remote sensing instruments and to NCAR to cover the subject of particulates in more detail than possible by other means of communication. Discussions with the other organizations listed above determined varying degrees of involvement with upper atmospheric measurements, with NASA Ames and NASA Lewis the most active.

During discussions with NASA Lewis it was learned that they have been involved in a similar survey for over 6 months, that they have purchased potentially applicable instrumentation for comparative evaluations, and that they contemplate a continuing survey/evaluation program for instrumentation operable at the tropopause and in the lower stratosphere. To date, little documentation exists on their efforts, however it appears that they are doing in greater detail the very task that was commissioned here.

## SECTION II INSTRUMENTATION

After discussing the requirements of the CIAP program with those versed in the field of instrumentation for trace gas and/ or particulate measurements, it became abundantly clear that no available instrumentation was specifically designed to operate under stratospheric conditions. It was further determined that the possibility of uncovering off-the-shelf instruments operable under such conditions with the sensitivities required by CIAP would, except for a few specifics, be quite remote; however, the possibility of re-designing available instrumentation bore some promise in many instances. Upon reviewing program requirements and manufacturers capabilities, some 30 companies prominent in the manufacture of instrumentation for the measure of trace gases and/or particulates were identified as having the potential to provide or develop suitable equipment. These manufacturers were then queried as to the applicability of their product lines to the needs of CIAP.

To facilitate the evaluation of applicable candidates, instrument fact sheets were prepared to summarize the source responses in the categories of direct and remote measures of trace gases. These fact sheets detail the performance characteristics of the instruments and the electrical, mechanical, environmental and cost factors needed to evaluate their overall potential. Fact sheets for the measure of particulates were considered but discarded because of the unique relationship of the sensor to the instrument platform.

Only sensors or instruments which have demonstrated a degree of applicability to CIAP, or a definite potential of such applicability are reported here. No definitive analysis is presented nor are specific instruments recommended.

It should be noted that since not all possible sources were queried there is the possibility of omission in a given area. It is hoped that this report can serve as a vehicle to uncover any such omissions so that they may be properly evaluated as this program continues.

### 2.1 TRACE GASES

Trace gases in the lower stratosphere can be monitored either by direct measure or by inference. Direct measure here includes the in situ measurements on a real-time or quasi-real-time basis of collected or flowing samples or the non-real-time evaluation of samples collected in situ and returned to the laboratory for detailed analysis. Measurement by inference means the quantitative interpretation of the data obtained by

remote or indirect measure of the constituent of interest based upon its interaction with or effect upon a known phenomenon.

### 2.1.1 Direct Measure of Trace Gases

The direct measure of trace gases within the lower stratosphere has received little attention to date, primarily because of the lack of suitable measurement platforms and appropriate instrumentation. The limiting factor, according to researchers and instrument manufacturers, is the lack of suitable platforms rather than the development of appropriate instrumentation. Instruments can and have been developed to measure the various trace gases in the concentrations anticipated in stratospheric environment; however, for the most part, they have not been designed to operate under ambient stratospheric conditions. Some have been so designed and others could be re-designed to do so, either by modifying the instrument, by providing a suitable environmental chamber to house it, or by determining a functional altitude-response relationship for data interpretation using available designs.

In the following sub-section data is given based upon the response of those manufacturers queried as to the applicability of their instruments to the direct measure of specific trace gases within the stratosphere. The presentation here is by specific trace gas, listing the manufacturers queried and then tabulating the responses of those which appear applicable on the aforementioned instrument fact sheets.

### 2.1.1.1 Water Vapor

Water vapor in the stratosphere has been the subject of more attention than any other trace gas, yet little, if any, substantiated data exists on the quantity, variability, or transport of this constituent, nor is much known as to its basic role in stratospheric chemistry.

Several sensor technologies have been "perfected" and instruments have been deployed to ambient stratospheric environments. These have produced differing and sometimes contradictory measurements of stratospheric humidity with resultant impact on theoretical postures. On the surface it appears that the basic difficulty is a questionable basis of calibration compounded by sensor/vehicle interaction. The resolution of this difficulty is far from simple and has been the subject of much investigation over the past several years.

The manufacturers queried as to their capability of supplying and/or designing an appropriate water vapor sensor are the following:

DuPont EG&G Mine Safety Appliances Panametrics

Of these, all but Mine Safety Appliances responded with details which indicated that their instruments were adaptable to the needs of CIAP. The EG&G and Panametrics instruments have operated in ambient stratospheric environments, the DuPont instrument has not but could be modified to do so. Characteristics of the applicable instruments are given in Table I.

### 2.1.1.2 Ozone

Ozone is the only stratospheric trace gas other than water vapor to have received concerted attention. Balloon borne sensors have operated and obtained meaningful data in the ambient stratospheric environment and other sensors have been operated in high altitude, pressurized, temperature controlled aircraft.

The anticipated concentrations in the altitude region of concern to CIAP is from 0.01 to 10 PPM. This range is within the capability of sensors utilizing UV absorption, or the chemiluminiscent reaction between ozone and ethelyne, and of those using an absorbing reagent of potasium iodide.

The manufacturers queried as to their capability of providing an appropriate ozone monitor are as follows:

Beckman
Bendix
Dasibi
Mast
Meloy
\*REM
Spectrometrics
Technicon

Of these all but Beckman and Technicon responded with instrument characteristics compatible with CIAP requirements. The Bendix instrument has been flown to altitudes in excess of 60 kft. in an Air Force program, the details of which are unavailable.

<sup>\*</sup>Not directly queried. Data received via telecon from NASA/ Lewis.

TABLE I. WATER VAPOR SENSORS

H <sub>2</sub> O	DU PONT MODEL 26-303	PANAMETRICS MODEL 1000	EG & G EXPENDABLE MODEI
PERFORMANCE			
Technique	ELECTROLYTIC CELL	ALUMINUM OXIDE HYGROMETER	CYROGENIC HYGROMETER
Range (PPB)	1-1000 PPM	DEW POINT +60 to -110°C	DEW POINT +50 to -70°C
Resolution (PPB)	1 PPM	0.1% of SCALE	~ 1°C
Accuracy	5%	2%	~ 1°C
Response Time	4 30 SEC		5°C/SEC
Drift		NOT DETECTABLE	NA
Calibration Method/Freq.			
Interferences	NH3,F,HF,P2O5	NONE	NONE
Sample Flow Rate	100 CC/MIN		ADJUSTABLE
Reagent Flow Rate			
Other Const Measured			1
FLECTRICAL CHARACTERISTICS			
Output	0-100 mV dc	0-100 mV	RADIOSONDE TELEMETRY
Display	PANEL METER	PANEL METER	NONE
Power Requirements		105-125/210-250 V @ 48-68H Z OR BATTERY PACK	8 "C" CELLS
MECHANICAL CHARACTERISTICS			
Size (in)	11 x 5 1/2 x 7 1/2	12 3/8 x 10 1/8 x 6 1/2	5 x 5 x 15
Weight (lb)	15	11.5	2
ENVIRONMENTAL FACTORS			
Temperature/Pressure		+60 to -110 C/	+50 to -80° C/
Flight Qual/Altitude	NO /	YES / 100 KFT	YES / > 45 KFT
COST FACTORS			
Cost			~\$300
Availability			30-60 DAYS
Maintenance & Service			EXPENDABLE

None of the other sensors have operated under ambient stratospheric conditions but they do have the potential of doing so. Ozone sensor characteristics are listed in Table II.

# 2.1.1.3 NO-NO<sub>x</sub>

Nitric oxide and nitrogen dioxide sensors have been the subject of much attention of late with most of the effort being expended in the development of instruments operating on the chemilumenescent reaction of nitric oxide and ozone. Other instruments use the UV absorption characteristics of NO and NO $_2$  as the measurement principle. Both techniques are capable of providing detection capabilities on the order of parts per billion, and thus are compatible with CIAP sensitivity requirements.

The manufacturers queried for these gases are the following:

Aero Chem Research
Bendix
DuPont
Scott Research
Spectrometrics
Technicon
Thermo Electron

Only Spectrometrics and Thermo Electron responded with equipment details which indicated that their instruments were adaptable to the needs of CIAP. The Spectrometrics instrument operates on the principle of UV absorption and has been flown to altitudes of the order of 10 kft. in pressurized aircraft. The Thermo Electron instrument is not designed to operate under stratospheric conditions but could be modified for such application. The characteristics of these two sensors are detailed in Table III.

## 2.1.1.4 Sulfur Dioxide

Sulfur dioxide has been of concern primarily as a combustion by-product pollutant in the ground level environment where the nominal concentration is orders of magnitude greater than the part per billion or less expected in the stratosphere.

Although a number of manufacturers market instruments to satisfy the needs of ground level measurements, it was held highly improbable that any would be capable of stratospheric measurement. Because of this a relatively large group of instrument manufacturers was sampled for this constituent:

TABLE II. OZONE SENSORS

03	DASIBI MODEL 1003	BENDIX FRIEZ OZONE MONITOR	MELOY LABS MODEL OA 330
	PIODES 1000		
ERFORMANCE	UV ABSORPTION	CHEMILUMINESCENT	CHEMILUMINESCEN
Technique	10-1000	0-10 to 0-10 <sup>4</sup>	0-10 to 0-10 <sup>4</sup>
Range (PPB)		0.1	<1
Resolution (PPB)	10	± 3%	2.%
Accuracy	.13%	7.74	5 sec
Response Time	8 or 30 sec		3 300
Drift	<1 PPB/WEEK	-0.2 PPB/°F	
Calibration Method/Freq.	INTERNAL REF CELL	INTERNAL O <sub>3</sub> GEN	
Interferences	NONE		NONE
Sample Flow Rate	7 1/MIN FOR 8 SEC 1 1/MIN FOR 30 SEC	INTERNAL	
Reagent Flow Rate		CONTROL	
Other Const Measured			
ELECTRICAL CHARACTERISTICS			
Output	0-10V	0-100 mVdc	0-100 mV, 0-1V
Display	DIGITAL PANEL METER	PANEL METER	PANEL METER
Power Requirements	115 V @ 60Hz	115 V @ 60 Hz, 250W	115 V @ 60Hz
MECHANICAL CHARACTERISTICS			
Size (in)	BENCH 15x15 1/4x18 5/8 RACK 19x5 1/4x18 5/8	7x17 1/4x22 1/2	12x12x20
Weight (1b)	45	55	40
ENVIRONMENTAL FACTORS			
Temperature/Pressure	32-120°F /		10 to -40°C /
Flight Qual/Altitude	YES / 3KFT	NO/FUNCTIONAL CALIB TO 60 KFT	NO /
COST FACTORS			
Cost	\$4200	\$4950	\$3825
Availability	60 DAYS		
Maintenance & Service	1000 HR MTBM		

TABLE II. OZONE SENSORS (Cont.)

03	SPECTROMETRICS NON STANDARD MODEL III d <sup>2</sup>	MAST MODEL 742
PERFORMANCE		
Technique	U.V ABSORPTION	COULOMETRIC
Range (PPB)	0-30000	0-1000
Resolution (PPB)	6	2%
Accuracy		
Response Time	45	30
Drift		
Calibration Method/Freq.	INTERNAL SELF TEST	
Interferences	NONE	
Sample Flow Rate	1.5 SCFM	140 cc/MIN
Reagent Flow Rate	-	1.25 ml/hr
Other Const Measured	NO,NO2,SO2,NH3,HxCy	
ELECTRICAL CHARACTERISTICS		·
Output	ANALOG AND/OR DIGITAL	
Display	PANEL METER 6" CHART RECORDER	PANEL METER
Power Requirements	115V @ 60Hz 125W	115V @ 60Hz 12W
MECHANICAL CHARACTERISTICS		•
Size (in)	56 x 22 x 14 1/2	7 1/2 x 6 x 11 1/2
Weight (1b)	123	10 1/2
ENVIRONMENTAL FACTORS		
Temperature/Pressure	-55 to +55°C/	35-120°F/
Flight Qual/Altitude	YES/10KFT	YES/10KFT
COST FACTORS		
Cost	~ 15000	~ 1000
Availability	~ 90 DAYS	30 DAYS
Maintenance & Service	FIELD USE	

TABLE III.  $NO_X$  SENSORS

	THERMO-ELECTRON	SPECTROMETRICS NON STANDARD
NONO <sub>X</sub>	MODEL 12A	MODEL III d <sup>2</sup>
PERFORMANCE		
Techniqu <b>e</b>	CHEMILUMINESCENT	UV ABSORPTION
Range (PPB)	0-10 to 0-10 <sup>6</sup>	0-4800 (NO) 0-19800 (NO <sub>2</sub> )
Resolution (PPB)	2	1 (NO) 4 (NO <sub>2</sub> )
Accuracy	±3%	
Response Time	7 (NO) 10 (N) <sub>2</sub> )	45 sec
Drift	2%/8 HRS	
Calibration Method/Freq.		INTERNAL SELF TEST
Interferences	NONE	NONE
Sample Flow Rate	0.1 cu ft/HR	1. < SCFM
Reagent Flow Rate		-
Other Const Measured		so <sub>2</sub> ,o <sub>3</sub> ,NH <sub>3</sub> ,H <sub>x</sub> C <sub>y</sub>
FLECTRICAL CHARACTERISTICS		
Output	0-10 mV, 0-10V	ANALOG AND/OR DIGITAL
Display	PANEL METER	PANEL METER 6" CHART RECORDER
Power Requirements	115V @ 60Hz	115V @ 60Hz 125W
MECHANICAL CHARACTERISTICS		
Size (in)	22 1/2x26 3/4x16 1/4	56x22x14 1/2
Weight(lb)	145	123
ENVIRONMENTAL FACTORS		
Temperature/Pressure		-55 to +55°c/
Flight Qual/Altitude	NO /	YES/10KFT
COST FACTORS		
Cost	7250 <sup>+</sup>	~ 15000
Availability	90 DAYS	~ 90 DAYS
Maintenance		FIELD USE

American Optical
Baird Atomic
Barringer Research
Beckman
Bendix
Combustion Equipment
Intertech
Meloy
Mine Safety Appliances
Phillips
Spectrometrics
Technicon

Only Spectrometrics responded with instrument details which indicated that their product could measure concentrations on the order of parts per billion or less. This is the same instrument reported in Section 2.1.1.3. Its characteristics re  $\mathrm{SO}_2$  are given in Table IV.

### 2.1.1.5 Carbon Monoxide

Carbon monoxide is expected to be present in the stratesphere in concentrations of from 1 to 10 parts per billion, considerably less than at ground level.

The following manufacturers were queried as to their capability of providing real or quasi-real time measurement capability for this constituent.

Barringer
Beckman
Bendix
Byron
Intertech
Mine Safety Appliances
Stanford Research Institute

No replies responsive to the needs of CIAP were received from those queried; however, responses were obtained which are pertinent to non-real time measurements. This subject is treated in Section 3.1.3.

### NOTE:

Somewhat late in the conduct of this survey it was learned that NASA is sponsoring the development of a carbon monoxide monitor that may meet the needs of CIAP. Details are forthcoming.

TABLE IV. SULFUR DIOXIDE SENSORS

so <sub>2</sub>	SPECTROMETRICS NON STANDARD MODEL III d <sup>2</sup>	
PERFORMANCE		
Technique	UV ABSORPTION	
Range (PPB)	0-3600	
Resolution (PPB)	0.75	
Accuracy		
Response Time	45 sec	
Drift		
Calibration Method/Freq.	INTERNAL SELF TEST	
Interferences	NONE	
Sample Flow Rate	1.5 SCFM	
Reagent Flow Rate	-	
Other Const Measured	NO,NO <sub>2</sub> ,O <sub>3</sub> ,NH <sub>3</sub> ,H <sub>x</sub> C <sub>y</sub>	
ELECTRICAL CHARACTERISTICS		
Output	ANALOG AND/OR DIGITAL	
Display	PANEL METER 6" CHART RECORDER	
Power Requirements	120V, 60Hz, 125W	
MECHANICAL CHARACTERISTICS		
Size (in)	56 x 22 x 14 1/2	
Weight (lb)	123	
FNVIRONMENTAL FACTORS		
Temperature/Pressure	-55 to +55°C/	
Flight Qual/Altitude	YES/10KFT	
COST FACTORS		
Cost	~ 15000	
Availability	~ 90 DAYS	
Maintenance & Service	FIELD USE	

### 2.1.1.6 Carbon Dioxide

Carbon dioxide was estimated to be present in the stratosphere at a concentration level of some 485 PPM. This is a considerably greater concentration than that expected for any other trace constituent.

It was anticipated that this would be relatively easy measurement task and the following manufacturers were contacted:

Beckman
Bendix
Intertech
Mine Safety Appliances

None replied in a manner responsive to the needs of CIAP for real time direct measuring sensors. Although a Beckman instrument (Model IR-315A) has been flown in a high altitude temperature controlled pressurized aircraft (NASA 990), it does not appear that this instrument could be modified to operate under ambient stratospheric conditions.

### 2.1.1.7 Hydrocarbons

Hydrocarbons are expected in concentrations of the order of 10 parts per billion. No evidence of current programs relating to stratospheric measurements were uncovered.

The following manufacturers were queried as to their capability of providing instrumentation for the measure of stratospheric hydrocarbons:

Beckman
Bendix
Mine Safety Appliance
Spectrometrics

Only Spectrometrics replied in the affirmative for real time direct measuring sensor capability. Their approach is to use the UV absorption instrument reported in Section 2.1.1.3; however, details of sensitivity and dynamic range are not available at this time.

## 2.1.2 Direct Measurement-Non-Real Time

The non-real-time approach to the direct measure of trace gases within the stratosphere employs the use of specially constructed vessels for the collection of samples of the ambient stratosphere coupled with analysis of such samples after they have been returned to the laboratory.

This technique has been successfully employed in the past for upper stratospheric soundings obtained with rocket probes. In such instances post flight analysis has been conducted through the use of gas chromatography or mass spectrometry. Proponents of this method of measurement off several plusses for is application to CIAP:

- (1) Sensor/vehicle problems are lessened or obviated
- (2) Sensor/environment problems are lessened or obviated
- (3) Multi-constituent analysis is possible in the laboratory
- (4) Sensitivities far beyond those of other measurements are attainable
- (5) Laboratory standards are applicable to processed results

Opponents offer such counter arguments as:

- (1) The sample could easily be contaminated
- (2) The sample represents an average measure over the collection volume
- (3) The method does not permit derivation of the shortterm variations that may occur and may be of significance.

Although this technique has most often been applied to rocket probes of the upper stratosphere, there is no technological reason that it could not be extended to apply to balloon and/or aircraft sampling of the lower stratosphere.

With judicious treatment of the factors involved this could well be a most powerful tool for the immediate exploration of stratospheric parameters and could also serve as vehicle for assessing the chemical dynamics of that region of the atmosphere since the collection techniques are approachable and the analysis techniques available.

Several manufacturers market the analytical equipment necessary for the resolution of sample constitution. Notable among these are Beckman and Varian Aerograph. The details of these equipments are not presented here since they are not actually what one would define as stratospheric sensors. The

collection elements themselves—the evacuated bottles—generally stainless steel, are not unique in design and could be procured at a nominal cost.

It should be noted here with respect to Section 2.1.1 that all the gases listed in that section plus many others are determinable by this technique. It should further be noted that the sensitivities afforded by this technique far exceed those offered by real time direct measurement techniques. It should be cautioned, however, that the cost could become prohibitive for multi-gas analysis.

Although time consuming and in some cases cumbersome, the collection of ambient samples coupled with the non-real-time laboratory analysis of such samples offers much in support of the basic needs of CIAP. The actual value must, of course, be weighted in light of the data obtainable compared to that of other techniques referenced to the time, complexity and cost involved.

### 2.1.3 Indirect Measurements

As noted previously, indirect measurement of trace gases is in effect measurement by inference based on the effect of the gas on known phenomena. The principal phenomena presently utilized are the emission and the absorption of infrared energy. Laboratory-type instrumentation operating on one or both of these principles exist at JPL, Denver Research Institute and Utah State University.

The JPL instrument operates on the principle of absorption at fixed wavelengths in the 1.4 $\mu$  water vapor band using the sun as the source. This instrument was designed to probe the Martian atmosphere but could be adapted to stratospheric water vapor measurements.

The Utah State instrument operates on the principle of emission and scans the spectral region from 6 to  $20\mu$ . This instrument is responsive to water vapor, HNO3 and possibly NO and NO2, and has been used to make measurements on parachute drops from rocket vehicles. Its greatest accuracy is in the range from 70 km down to 40 km, data is of questionable value below 30 km.

Denver Research Institute has two instruments, one working on each principle. The absorption sensor scans the spectral region from 5 to  $20\mu$  in octave steps while the other scans the spectral region from 5 to  $12\mu$ . These instruments were designed as balloon borne packages and have operated in the altitude region up to 100 kft. Water vapor, O3, HNO3 and NO2 have been

detected in absorption and there is a possibility of detecting NO. Water vapor and O3 have been detected in emission.

An instrument fact sheet was prepared to detail the characteristics of these instruments. That sheet is included here as Table V.

### 2.2 PARTICULATES

During the past several years interest in the atmospheric particulate population has fostered the promulgation of a myriad of techniques offering the potential of determining size distribution, composition, and/or mass concentration of such entities.

A summary of the current state-of-the-art re size distribution analysis is given in reference (1) which contains a concise appraisal of the current situation. No such summary exists on the subjects of composition or mass concentration.

To augment information published in the trade literature and to gather information directly related to CIAP, several manufacturers identified in the above referenced report as primary instrument sources were contacted as to their capability for stratospheric measurement of particles in the 0.001 to  $2\mu$  range. These included:

- (1) American Optical
- (2) Altantic Research
- (3) Environment/One
- (4) Meteorology Research
- (5) Mini Safety Appliance
- (6) Research Appliance

These inquiries brought no positive responses for the application in question and attention was then re-directed from manufacturers to researchers.

Responses from the researchers queried have indicated that the subject is fraught with problems, most notably those of:

- (1) Collection of sub-micron particles
- (2) Contamination of collection systems
- (3) Lack of standardized quantizing criteria

Despite these problems a number of efforts have been undertaken in this area of atmospheric particulates.

<sup>(1)</sup> Particle Size Analysis, L.D. Carver, Industrial Research, Aug. 1971, pp. 40-43.

TABLE V. INDIRECT SENSORS

INDIRECT SENSORS	DRI	DRI	UTAH STATE
Technique	IR ABSORPTION	IR EMISSION	IR EMISSION
Spectral Range	OCTAVE WITHIN 5-20µ BAND	5-12µ	6-20µ
Spectral Resolution	0.3 cm <sup>-1</sup>	2-5 cm <sup>-1</sup>	BANDWIDTH 0.4µ
Sensitivity	1% TRANSMITTANCE	10-10 w/cm <sup>2</sup> /STR	10-10 w/cm <sup>2</sup> /STR
Minimum Detectable Concer	10 <sup>-9</sup> GM/GM	10 <sup>-11</sup> GM/GM	a
Accuracy	20-30%	20-30%	
Repose Time	10-15 SEC	~ 2 MIN	
Calibration Method/Freq.	RELATIVE MEAS.		
Interferences	COMPLEX SPECTRA	COMPLEX SPECTRA	COMPLE SPECTRA
Constituents Meas.	NO2, NO(?) H <sub>2</sub> O,O3,HNO3,CH <sub>4</sub>	POSSIBLY NO, NO2, HNO H2O, O3DEFINITE	POSSIBLY NO,NO2 O3,H2O,HNO3 DEFINITE
ELECTRICAL CHARACTERISTICS			
Output	TELEMETRY MAG TAPE	])	EL.
Display		SAME	
Power Requirements	INTERNAL POWER PACK	])	28 VDC @ 1 AMP
MECHANICAL CHARACTERISTICS			
Size	8' x 3' x 3'	8' x 3' x 3'	5." DIA x 6"
Weight (1b)	800	800	
ENVIRONMENTAL FACTORS			
Temperature/Pressure	CRYOGENIC/AMBIENT	CRYOGENIC/AMBIENT	CRYOGENIC/AMBIENT
Flight Qualified/ Altitude	YES/100 KFT	YES/100 KFT	YES/40-70 KM
COST FACTORS			
Cost			~ 100K
Availability	~ 6 MO	~ 6 MO	6-9 MOS.
Maintenance & Service			

TABLE V. INDIRECT SENSORS (Cont.)

INDIRECT SENSORS	JPL	
PERFORMANCE		
Technique	IR ABSORPTION	
Spectral Range	1.4µ (5 CHANNEL)	
Spectral Resolution	1 cm <sup>-1</sup>	
Sensitivity		
Minimum Detectable Concen	~ 0.1 PRµ	
Accuracy	50%	
Response Time	0.25 SEC	
Calibration Method/Freq.	ZERO CHECK	
Interferences	NONE	
Constituents Meas.	H <sub>2</sub> O	
ELECTRICAL CHARACTERISTICS		
Output TELEMETR		
Display		
Power Requirements		
MECHANICAL CHARACTERISTICS		
Size (in)	OPTICS 28x8x11 POWER 14x6x2	
Weight (lb) 45		
ENVIRONMENTAL FACTORS		
Temperature/Pressure	DESIGNED TO PROBE	
Flight Qualified/ Altitude	MARTIAN ENVIRONMENT	
COST FACTORS		
Cost		
Availability	~ 6 MOS	
Maintenance & Service		

As one would assume, most current efforts are directed to the immediate problem of pollution in the lower atmosphere; however, the upper atmospheric problem has not been totally neglected.

Measurement programs sponsored primarily by the AEC have continued since the onset of atmospheric nuclear testing to collect radioactive particles in the lower stratosphere and have led, directly or indirectly, to the current status of stratospheric measurement capability. Much of the work in establishing this capability was done by groups at LASL and at NCAR in support of the AEC. Other work has been performed indendently at lower levels by EPA and NCAR, this work being altitude limited at about 45 kft. by the availability of research aircraft and by the level of available support. EPA efforts have been and continue to be limited to an altitude of 45 kft. by aircraft capability--prime interest has been in the determination of combustion by-product presence in the traposphere. NCAR efforts are also currently altitude limited to 45 kft. by aircraft capability and their interest is primarily in the determination of soil particle population in that altitude region.

Aircraft rather than instrument capability limits measurements to the 45 kft. altitude noted above; however, experience has set the lower limit of reliability of sampled particle size Although some samples having dimensions less than 0.1µ at 0.1µ. have been collected, the collection process is not considered reliable below that level and no confidence is placed in the population density of smaller particles. The exclusion of such sub-micron finite particles does not, of course, measurably affect the measure of mass concentration but could lead to an erroneous measure of sample composition and size distribution. Particles of dimensions less than 0.1 have been reliably analyzed by various laboratory techniques. The basic problem lies not with the analysis of such particles but the question of the collection of representative samples of sub-micron particles since current techniques are decidely biased toward the larger particles.

The characteristics of particle sampling equipment uncovered here defied the definition of equipment fact sheets such as those given in the preceding section. Representative instruments employ elaborate ducting and collection systems which are designed in singular fashion for each research platform. The collection system itself is generally a compact unit (filter or impactor surface) within the platform. The analysis facility is most often a laboratory set-up capable of providing in-depth treatment of collected samples by a variety of techniques in a clean environment. As noted in reference 1, size determination

of collected samples to the order of milli-microns is possible with currently available equipment. The basic problem, however, is the reliable collection of such samples and development is needed in this area.

## SECTION III CONCLUSIONS

The basic conclusion to emerge from this survey is that instrumentation directly applicable to the needs of CIAP is conspicuous by its absence. Although some instruments have been applied to stratospheric measurements, these were either not specifically designed for such application or have not yet gained the general confidence of the research community. Continued experience, more reliable calibration, and attention to the sensor/vehicle interaction problem could alter this situation.

No specific instrumentation or techniques are recommended in this preliminary report primarily because it is just that --preliminary. The identified candidates should be subjected to more detailed investigation and comparative evaluation before committments are made to specific techniques or instruments.

In many instances commercially available techniques for direct real time measurement of trace gases were uncovered which are applicable to the needs of CIAP and instruments designed to operate on such principles for ground level measurements could be redesigned, modified, or adapted in some way for stratospheric application with the requisite sensitivities. Cost factors for such extensions of current capability are not readily discernible for most instruments nor are the time factors involved; however some, notably the multi-constituent sensor of Spectrometrics, could be developed in less than 6 months for a cost in the range of 15-20K.

Non-real time direct measurements could utilize the basic techniques of sample collection perfected in the past for rocket sondes of the upper stratosphere with later analysis by gas chromatographic or mass spectrometric techniques in the laboratory. Specific collection systems would have to be perfected for aircraft and/or balloon platforms; however, and there is the continued question as to the contamination of the samples. These problems are not considered insurmountable and this technique appears to hold the most promise for ready application.

The indirect measure of trace gases within the stratosphere is based on inference from the remote measure of the effect of such gases on known phenomena. The phenomena employed in current research projects are the absorption and emission of infrared energy. The term research projects must be stressed here since measurements to date have been performed with unique laboratory type equipment tailored to specific measurements, as such they are not readily available nor have they proven their usefulness to this program. Continued effort in this area could prove quite fruitful.

Particulate measuring techniques currently available do not approach the needs of CIAP. The primary problem is with the collection process, particularly where sub-micron particles are involved and new techniques are needed to alleviate this situation. Particulate collection systems are designed into specific instrument platforms and considerable lead time is required to resolve the problems of sensor-platform interface. The design of an instrument appropriate to CIAP and its incorporation into a suitable platform would be no mean task; the cost in time and money would most certainly be considerable.

From the foregoing it can only be concluded that there is very little readily available instrumentation appropriate to the needs of CIAP. This is so primarily because there has been no real support for the development of such instrumentation. The potential does exist however, and it appears that the development of the potential must be sponsored by those seeking the data the resultant capability could provide. The "those" refered to above include NASA/Ames, NASA/Lewis and the CIAP Program Office. Close coordination should be maintained between these groups to ensure that individual efforts are complemented and not duplicated.

## SECTION IV RECOMMENDATIONS

After exposure to the myriad of manufacturers, researchers, experimenters, etc., involved with various aspects of atmospheric measurements it is recommended that a survey of this subject matter be conducted on a continuing basis not bounded by a finite time interval such as that encountered here. It is further recommended that contact with others involved in like programs be encouraged to maximize cooperation and minimize duplication of effort. Full advantage should be taken of ongoing or contemplated efforts which could be of value to CIAP. Reciprocal cooperation to support other activities is an assumed by-product of DOT activities.

It should be recognized that this is a preliminary report subject to sins of omission and commission. It is therefore recommended that this document serve as a vehicle to solicit constructive criticism on the subject matter.

## SECTION V MANUFACTURERS QUERIED

Discussions with those active in the field of trace gas measurements led to the early conclusion that no available instrumentation was specifically designed for operation under stratospheric condition and that few off-the-shelf instruments were likely to be applicable without some modification. A similar conclusion was reached on the subject of particulates primarily where the particle sizes of interest are less than o.lu. As a result of these discussions, some 30 companies prominent in the manufacture of instrumentation for the measure of trace gases and/or particulates were identified as having the potential to provide or develop suitable equipment. These manufacturers were given the needs of the CIAP program and were queried as to the characteristics of their product lines and the cost, if any, to adapt to the needs of CIAP. The manufacturers so contacted are listed below.

Aero Chem Research Princeton, New Jersey

American Optical Co. Central Research Lab Southbridge, MA 01550

Baird Atomic Inc. 125 Middlesex Turnpike Bedford, MA 01730

Barringer Research Ltd. 304 Carlingview Drive Rexdale, Ontario, Canada

Beckman Instruments % Process Instrument Corp. 599 North Avenue Wakefield, MA

Bendix Corporation Environmental Science Div. 1400 Taylor Avenue Baltimore, Maryland 21204

Byron Instruments
Raleigh, North Carolina

Combustion Equipment Assoc. 555 Madison Avenue
New York, New York 10022

Dasibi Corporation 3223 North Verdugo Rd. Glendale, California 91208

DuPont Instrument and Equipment Div. Wilmington, Delaware 19898

E G & G Environmental Equipment Div. 151 Bear Hill Rd. Waltham, MA 02154

Environment/One Corp. 2773 Balltown Rd. Schnectady, New York 12309

Intertech Corp. 262 Alexander Street Princeton, New Jersey 08540

Mast Development Corp. Davenport, Ohio

Mee Industries Inc. 1973 Mendocino P.O. Box 365 Altadena, California 91001 Meloy Labs 6631 Iron Place Springfield, VA 22151

Meteorology Research Inc. 464 W. Woodbury Drive Altadena, California 91001

Mine Safety Appliance 201 North Braddock Ave Pittsburg, PA 15208

Panametrics 221 Crescent Street Waltham, MA 02154

Peerless Instrument Co. 90-15 Corona Ave Elmhurst, New York 11373

Phillips Industries %LICO
Burlington, MA

REM Inc. Santa Monica, California

Research Appliance Co. Allison Park, PA

Scott Research
Plumsteadville
Bucks County, PA 18949

Spectrometrics of Florida, Inc. P.O. Box 517
Penellas Park, Florida 33565

Stanford Research Institute Menlo Park, California 94025

Technicon Industrial Systems Tarrytown, New York 10591

Thermo Electron Corp. 85 First Ave Waltham, MA

Trapelo West 2030 Wright Ave Richmond, California 94804

Varian Aerograph 2700 Mitchell Drive Walnut Creek, California 94598

