

Monitoring For Ozone



A review for station operators

Donovan Rafferty

Ecology

Ron Cunningham

Oregon DEQ

Anthony Reneau

Tanabyte Engineering

What we will cover

- The Air Monitoring Station
- The Monitoring Equipment
- Performing Quality Control Checks
- Certifying Ozone Standards



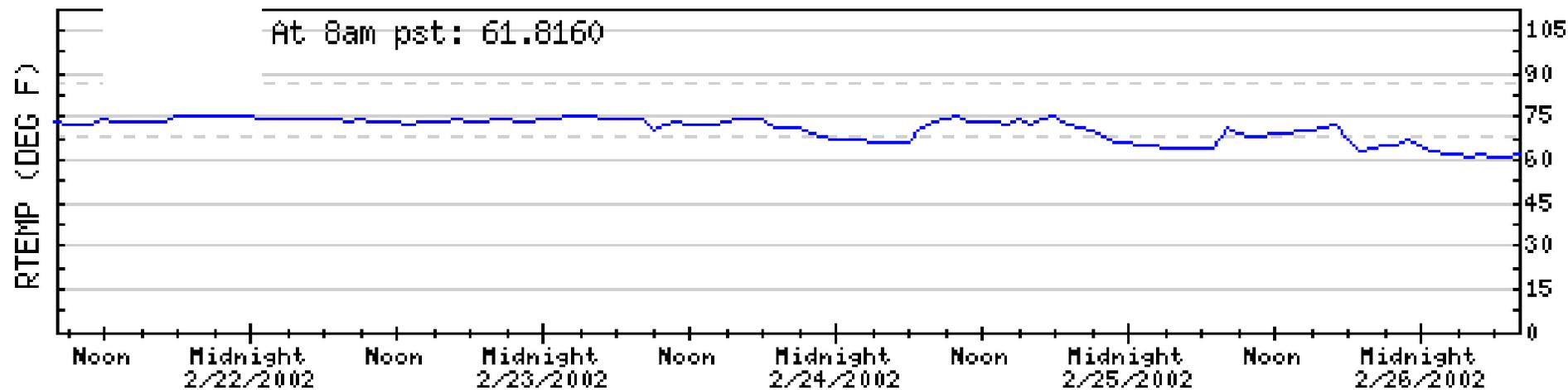
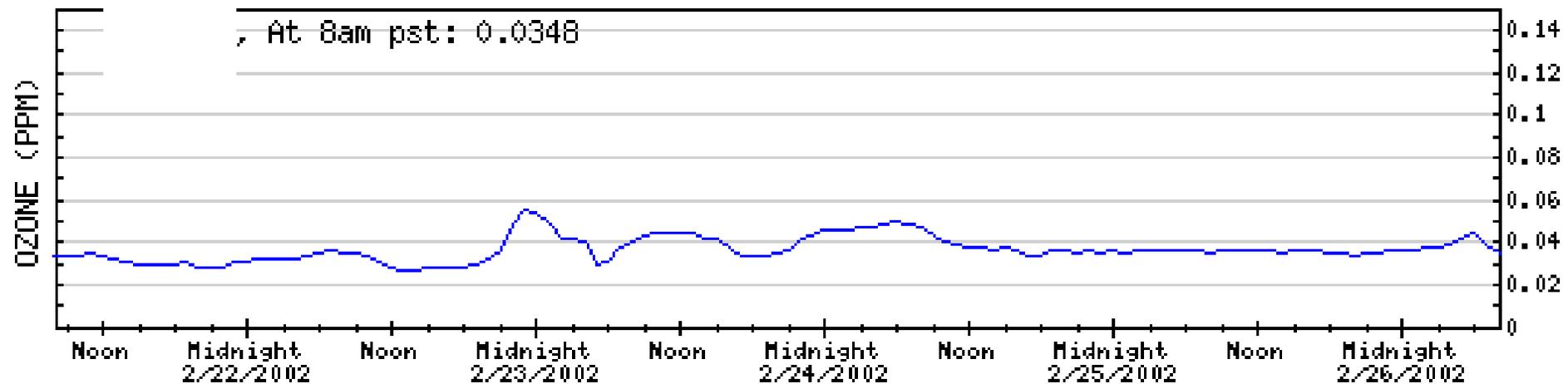
You will learn.....

by making mistakes !

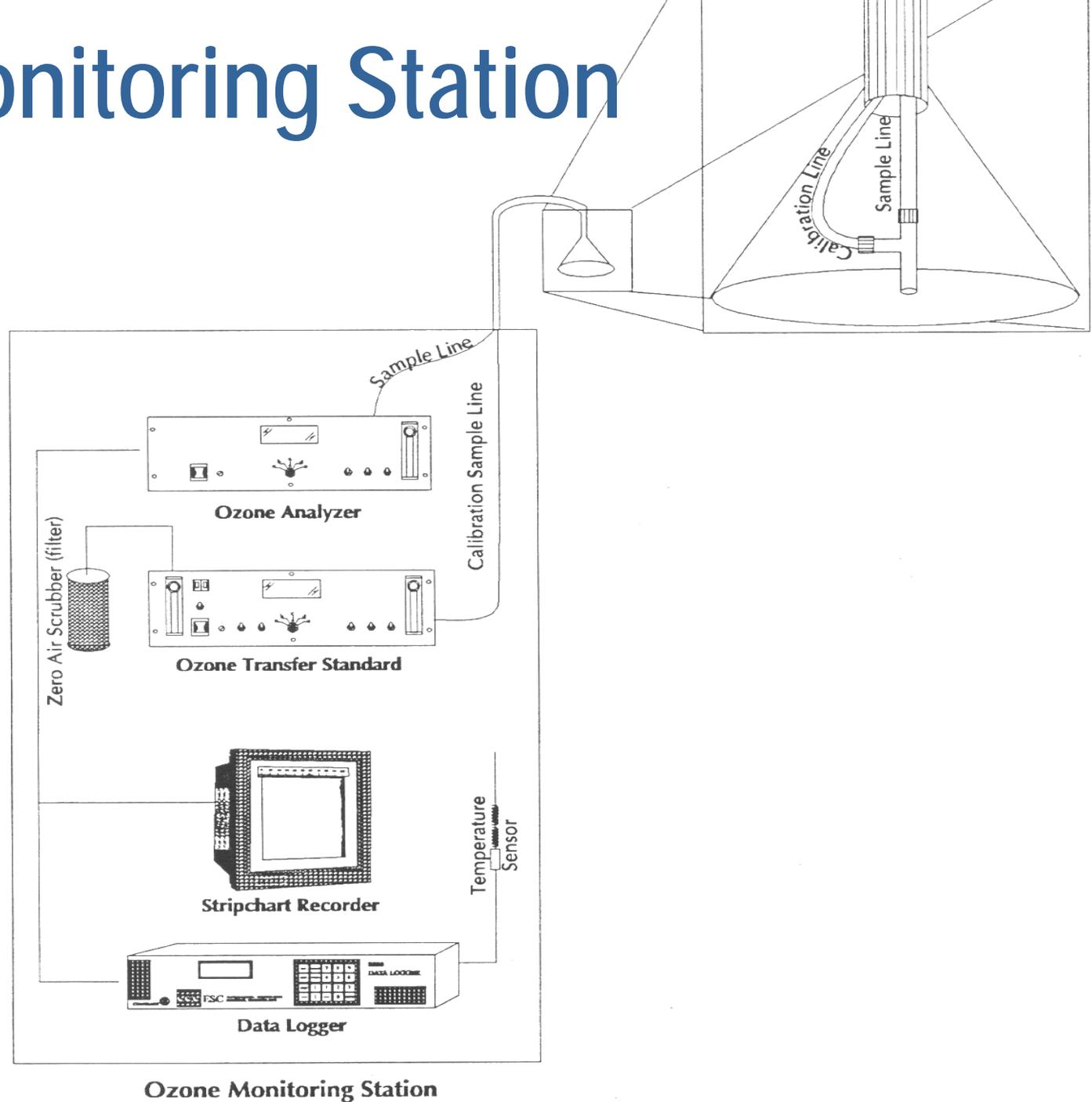
Work Tasks - Ozone 2005	Task Assignment	1-Mar	8-Mar	15-Mar	22-Mar	29-Mar	5-Apr	12-Apr	19-Apr	27-Apr	3-May
Primary bench standard to CARB	RC										
Planning meeting- staff assignments	Staff										
Review of last season	Staff										
Contact with property owners	Alan										
Order supplies	RC										
Site AC's /check w Paula for service	Alan										
Ozone monitors prepped	RC/Lab rat										
Zero air sources prepped	RC/Lab rat										
Confirm Multorpor as site for summer O3	JS/BB										
Training of Aaron and Chris	KS/MH/Staff										
CO equipment down:	STAFF										
Repair recorders	RC/Lab rat										
Program DL's for O3	LH/MH/KS										
Move and configure XMLPusher PCs	Staff/KS/LH										
UPS in place	Staff										
Clean manifold - check fan	Staff										
Replace probes with new teflon	Staff/RC										
Colored exhaust lines	Staff/RC										
Shelter cleanup, general site cleanup	Staff										
Renew Internet Access accounts	JS										
Verify phone line operation	Staff										
Verify temp control operation	Staff										
DAS setup:	KS										
Handling of incoming data	KS/JK										
setup hourly report to AirNow	KS/JK										
Midway meeting and evaluation	STAFF										
Calibrate monitors in lab	RC/Lab rat										
Calibrate transfer-std in lab (6x6)	RC/Lab rat										
Staff training	MH/Staff										
Site Accessories ready for each site	Staff										
Setup at each site	Staff										
Install met at CJHS site	LH/Staff										
Spare monitor & transfer-std	RC										
Chart handling prep- QA sheet prep	BB										
Start up review meeting	Staff										
Celebrate our successes	Staff										
List any problems to avoid in future	Staff										

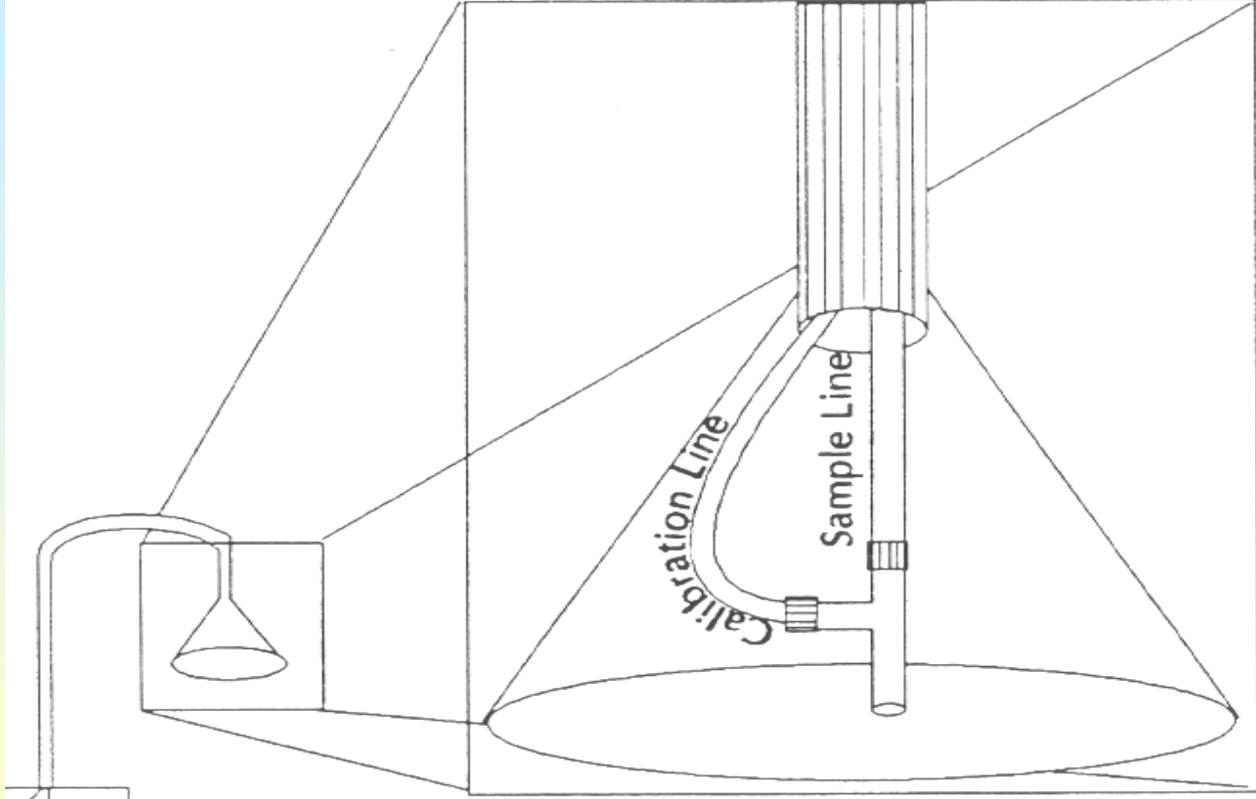
Ozone sites include:	3 letter	LASAR #	Network
Spangler Rd., Canby	SPR	10093	South
Lotspeich residence, Talent	TAL	10109	Medford
Cascade Jr. High, Turner	CJH	10130	South
SE Lafayette, Portland	SEL	10139	North
Sauvie's Island, Portland	SIS	14152	North
St. John's Church, Milwaukie	MSJ	23306	South
plus a possible visibility site at Multorpor			

Air Quality Site Operator's Page



The Monitoring Station





The Probe

- Probe is made of Teflon®.
- The residence time is critical.
- EPA requires a sample residence time of less than 20 seconds.
- At 2.0 LPM the maximum probe length should be less than 170 ft.
- For 10 seconds the maximum probe length should be 84 ft.

When you arrive at the site.....

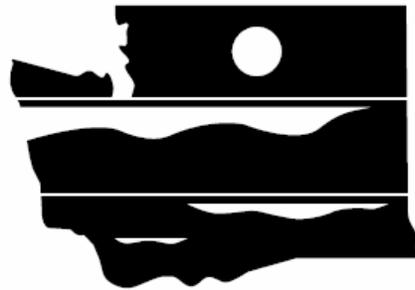
- Survey the structure housing the equipment for weather leaks, safety, and security.
- Perform routine maintenance.
- If you find a problem, you are responsible for seeing it is corrected.
- Record the actions that you took.

Environmental Controls for Monitoring Equipment

- Instrument vibration (Never “stack instruments”)
- Keep sunlight from “shining” on instruments.
- Electrical voltage
- Temperature
- Security
- Cleanliness

Standard Operating Procedures

- Data collected using fully documented procedures have much higher credibility.
- Developed using the CFR's and technical assistance documents.



WASHINGTON STATE
DEPARTMENT OF
E C O L O G Y

Ozone Monitoring Procedure

Air Quality Program

July 2004

95-201G (rev. 7/04)



*If you didn't record it
you didn't do it.*

Monitoring Checklist

- Developed to help the first time operator or one that does it infrequently.

STATION CHECKLIST

Site name

Site number

Operator

Record the time the station was entered.

PST

Record the date the station inspection.

THE MONITORING STATION

2. Has any damaged occurred to the station since the last inspection?

Are there any unusual noises or odors?

THE ANALYZER

Is the power on?

Is the sample flow set to 2.0 LPM?

Is the selector switch in the "operate" mode?

Is the solenoid valve cycling every 10 seconds?

Has channel 03 on the data logger been disabled?

Has it been noted on the strip chart?

Record the sample chamber temperature.

°C

Record the unadjusted sample frequency.

KHz

Record the sample chamber pressure.

Atm

Is the control frequency 50.000?

Do the analyzer, recorder and data logger all read the same?

Record the analyzer span setting.

THE TRANSFER STANDARD

Is the ozone adjust thumbwheels set to 000?

Is the auto/man switch in the "auto" position?

Is the ozone switch in the "off" position?

Is the generator pump switch in the "on" position?

Is the selector switch in the "operate" position?

Is the T/P switch in the "on" position?

Is the valve switch in the "on" position?

Is the sample pump switch in the "on" position?

Quality Control Checks

- Should be performed at least once every two weeks.
- Inspection of the shelter and instruments.
- Zero, Precision and Span Checks
- Adjustments

Never perform a calibration check on days forecasted to be above 90° F. unless there appears to be a problem with the ozone analyzer.

The current ozone standard is 80 ppb/eight hour average.

Calibrations should never be performed when ozone values are elevated.

The Monitoring Equipment

- Ozone analyzers must meet reference method or equivalent method specified by the EPA in Appendix D of 40 CFR Part 50.
- Dasibi 1008PC

Dasibi Ozone Analyzers

- Meet EPA designated equivalent method requirements when operated under the following conditions:
 - ◆ Concentration range of 0 - .5 ppm
 - ◆ Line voltage of 105 -125 vac
 - ◆ Temperature of 68°- 86° F
- The analyzers must be operated and maintained according to the Operating and Maintenance Manual to conform to the EPA Designation requirements.



O₃ ADJUST

0 0 0

 **U.S.E.P.A.**
DESIGNATED
EQUIVALENT METHOD
EQQA-0383-056
MARCH 10, 1983
APPROVED RANGES:
0.5, 1.0 ppm

ALTS



MANUAL



ANALOG



SPAN

ON



OFF

OZONE

ON

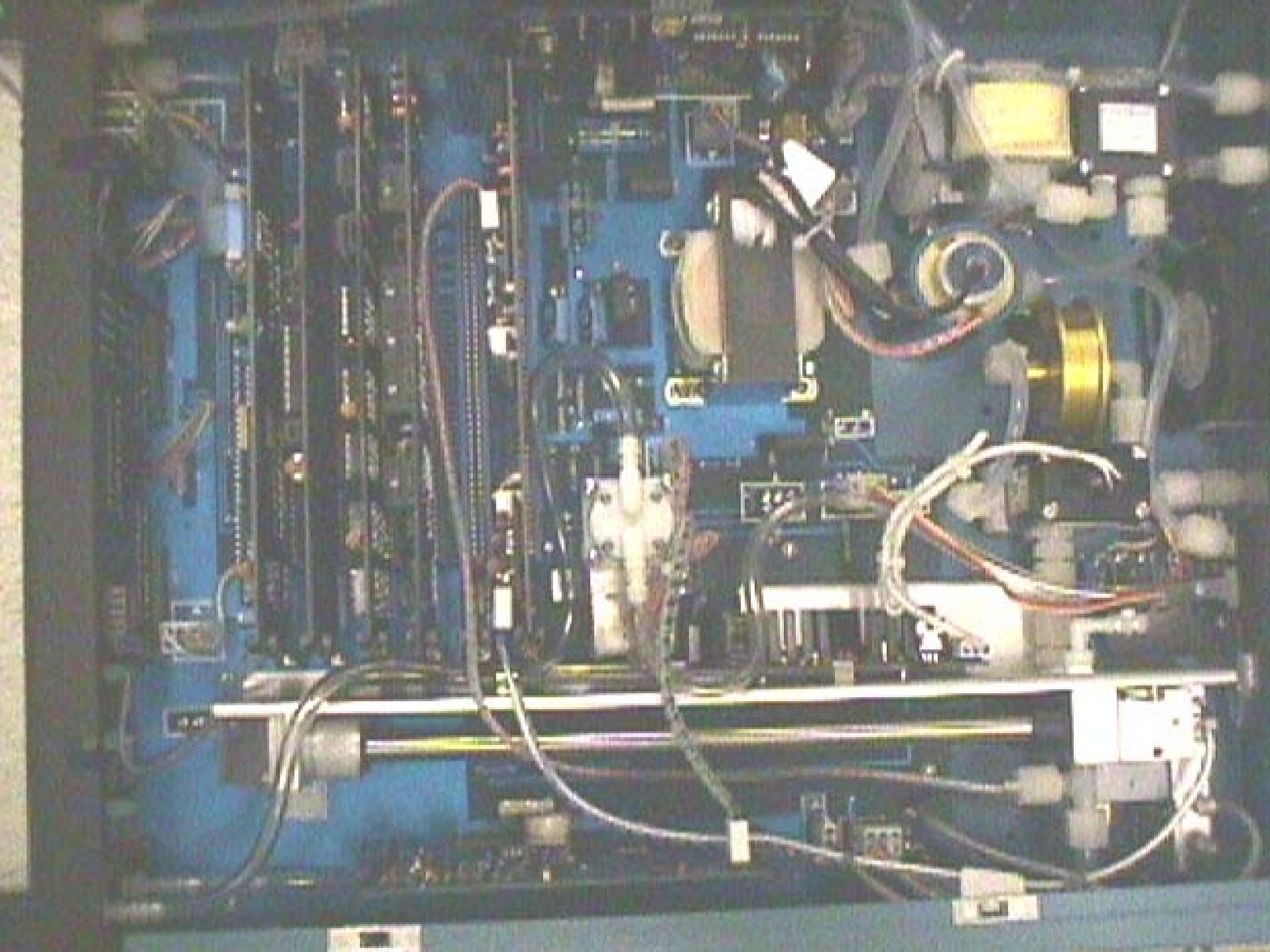


OFF

PUMP

OZONE G

5
ZERO





*Think of the instrument
as being divided into
two components.....*

The Analyzer (Photometer).

000
CONCENTRATION PPM

dasibi
MODEL 4000 P1

OPERATE
SAME/TIME
CONT/PRESS

T/P
ON
OFF

VALVE
ON
OFF

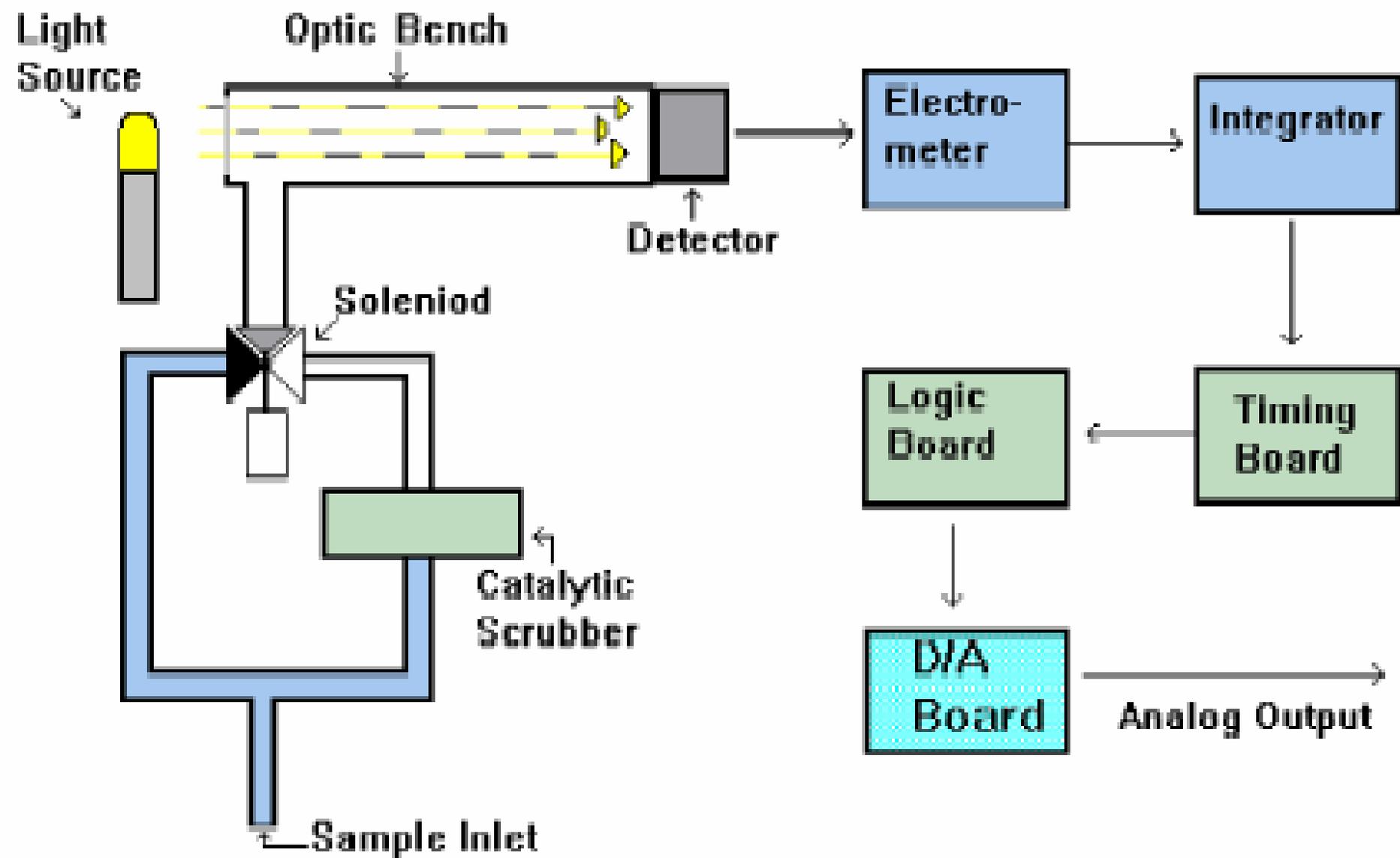
PUMP
ON
OFF



Flow set to 2.0 LPM.

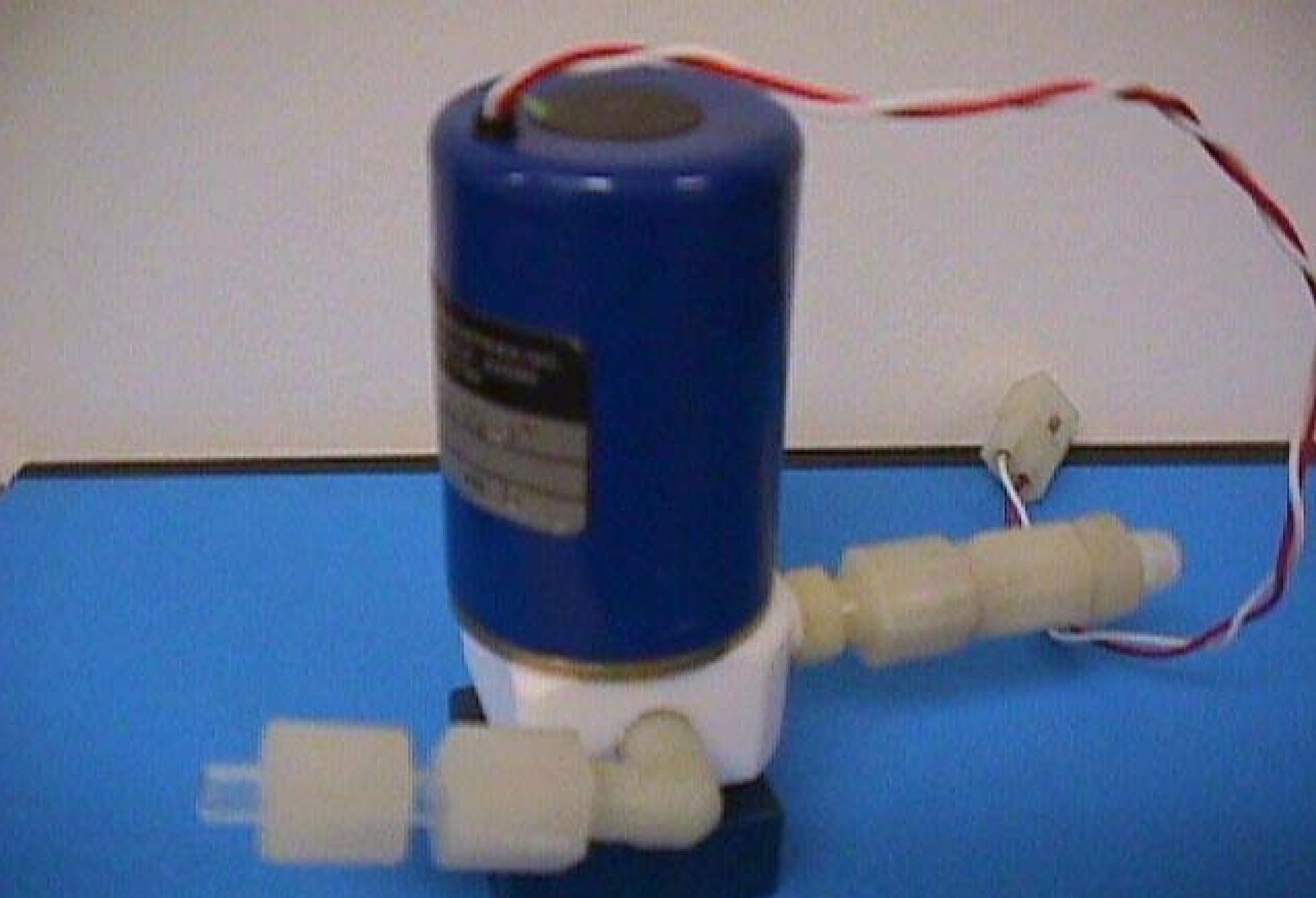
The Ozone Analyzer Technique

- Based on the principle that ozone molecules absorb UV light (254 nanometers wavelength).
- A column of air is illuminated at one end by an ultraviolet lamp.
- The intensity of the lamp is measured at the opposite end by a detector.
- The measurement is performed within the sample tubes (absorption tubes) of the analyzer.



Critical Components of an Ozone Analyzer (Photometer)

- Solenoid valve
- Ozone to oxygen converter
- Absorption tubes
- Sample pump
- UV lamp source
- Detector



Gas Valve: actuated by a solenoid



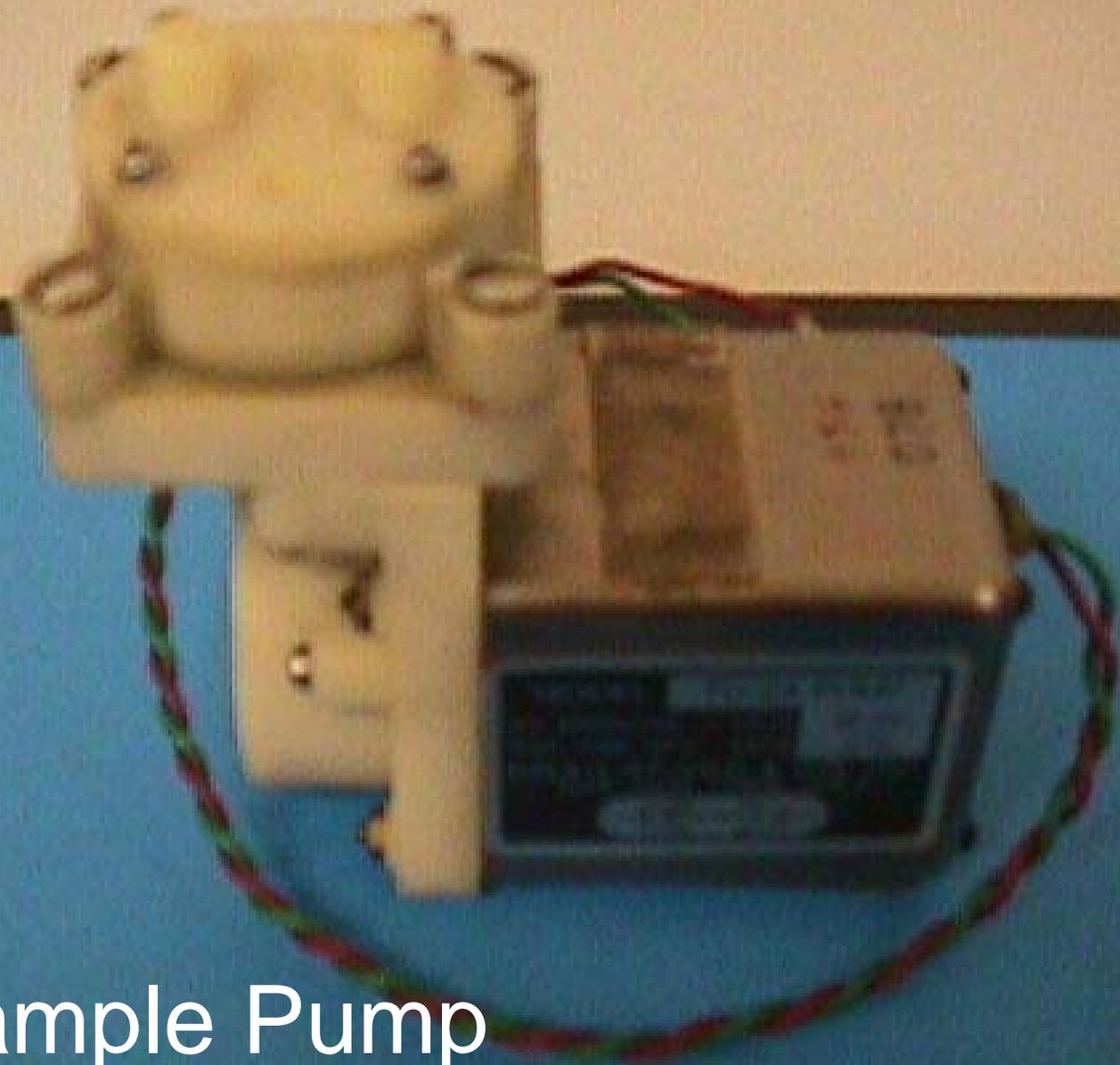
Ozone Scrubber



Scrubber Cartridge

copper screens coated with manganese dioxide

- 
- The MnO_2 catalyzes the reaction of ozone to diatomic oxygen.
 - The sample entering the absorption cell after passing through the filter is preserved intact except for the ozone.



The Sample Pump

UV Lamp with
output
concentrated at
253.7 nm where
absorption of
ozone is
maximized





Detector: Measures the intensity
of the lamp

The Measurement

- Each measurement cycle is completed within 10 to 20 seconds.
- Each measurement contains two half cycles.

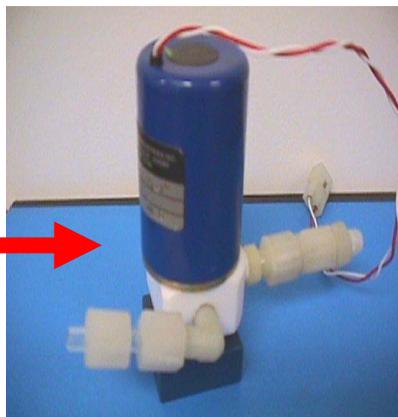
The First Measurement Half-Cycle

- Ambient air is directed by the analyzer's solenoid valve to the scrubber where any ozone present is converted to oxygen.
- The ozone-free sample is directed through the absorption tubes.

- 
- The UV source lamp illuminates the sample and the transmitted intensity is measured by the detector.
 - The analyzer stores the intensity value.

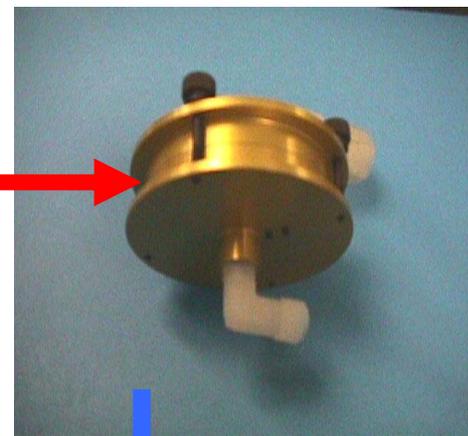
The First Measurement Half Cycle

Sample



Solenoid

Scrubber



Absorption Tubes



Zero (reference) gas with the ozone “scrubbed”

Absorption Tubes

- The optical path length through the sample.
- Transmittance of the sample at a wavelength of 253.7 nm



- The temperature and pressure of the sample

The Second Measurement Half-Cycle

- The sample is directed to the absorption tubes.
- The UV source lamp illuminates the sample.
- The detector measures the transmitted intensity.

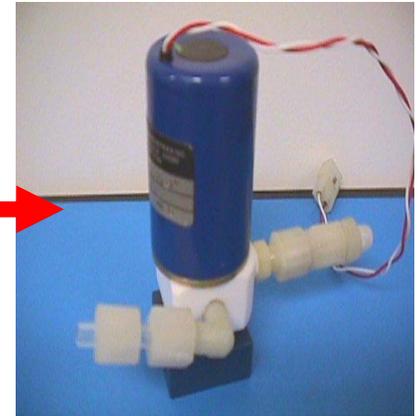
The Second Measurement Half-Cycle

- Any ozone present in the sample absorbs some UV light resulting in a lower intensity value as measured by the detector.
- This value is subtracted from the previously stored value and the resulting difference is the amount of ozone in the ambient sample.

The Second Measurement Half Cycle

Sample

Solenoid



Absorption Tubes



Sample without the ozone "scrubbed"

At the end of The Measurement Cycle

- The measured result is displayed on the instrument as a concentration.
- Presented as an electrical signal to the data logger and the strip chart recorder.

Since ozone is a highly reactive gas, accurate concentration of the gas cannot be made and stored for any length of time.

To calibrate the analyzer, various concentrations of ozone must be made and measured on site.

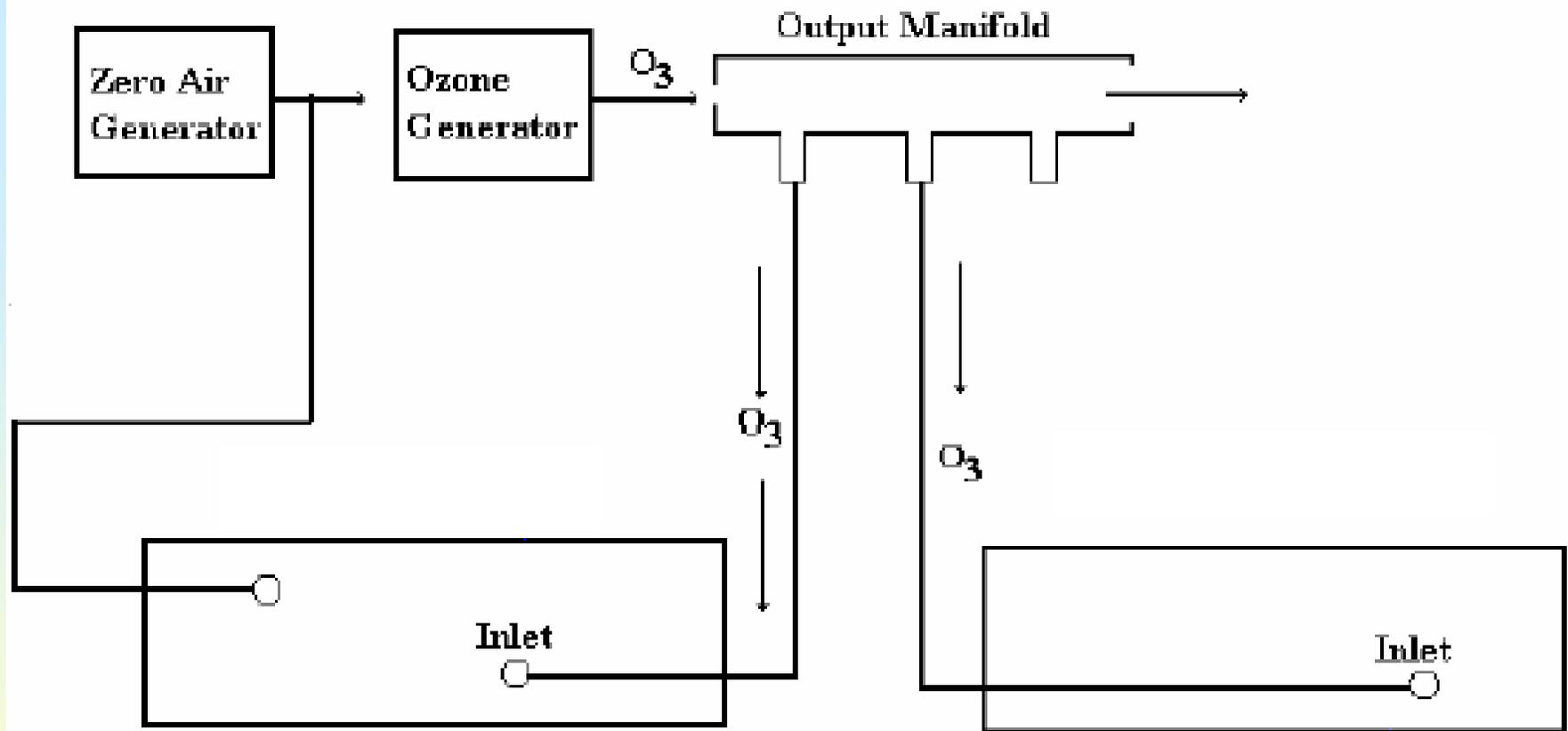
Specific protocols have been developed to generate and measure accurate concentrations of ozone on site.

The Ozone Transfer Standard

- Think of as two instruments.
- One half makes ozone.
- The other half measures the sample.
- Capable of generating and measuring accurate ozone concentrations.

Critical Components of an Ozone Transfer Standard

- Zero air source.
- Pump
- Flow controller
- Ozone generator
- Manifold



Ozone transfer
standard

Ozone
analyzer

Charcoal Column



Used to absorb ozone in ambient air while performing a zero check

Generator Pump





O₃ ADJUST

0 0 0

AUTO

MANUAL



ANALOG

SPAN

ON

OFF

OZONE

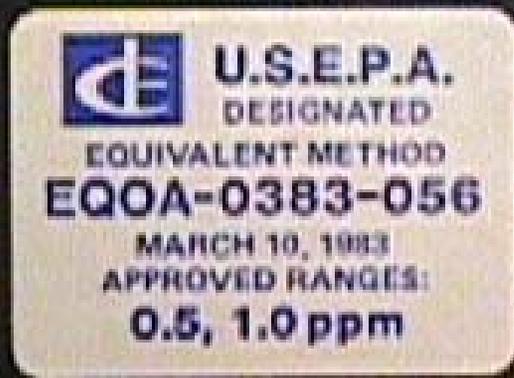
ON

OFF

PUMP

OZONE G

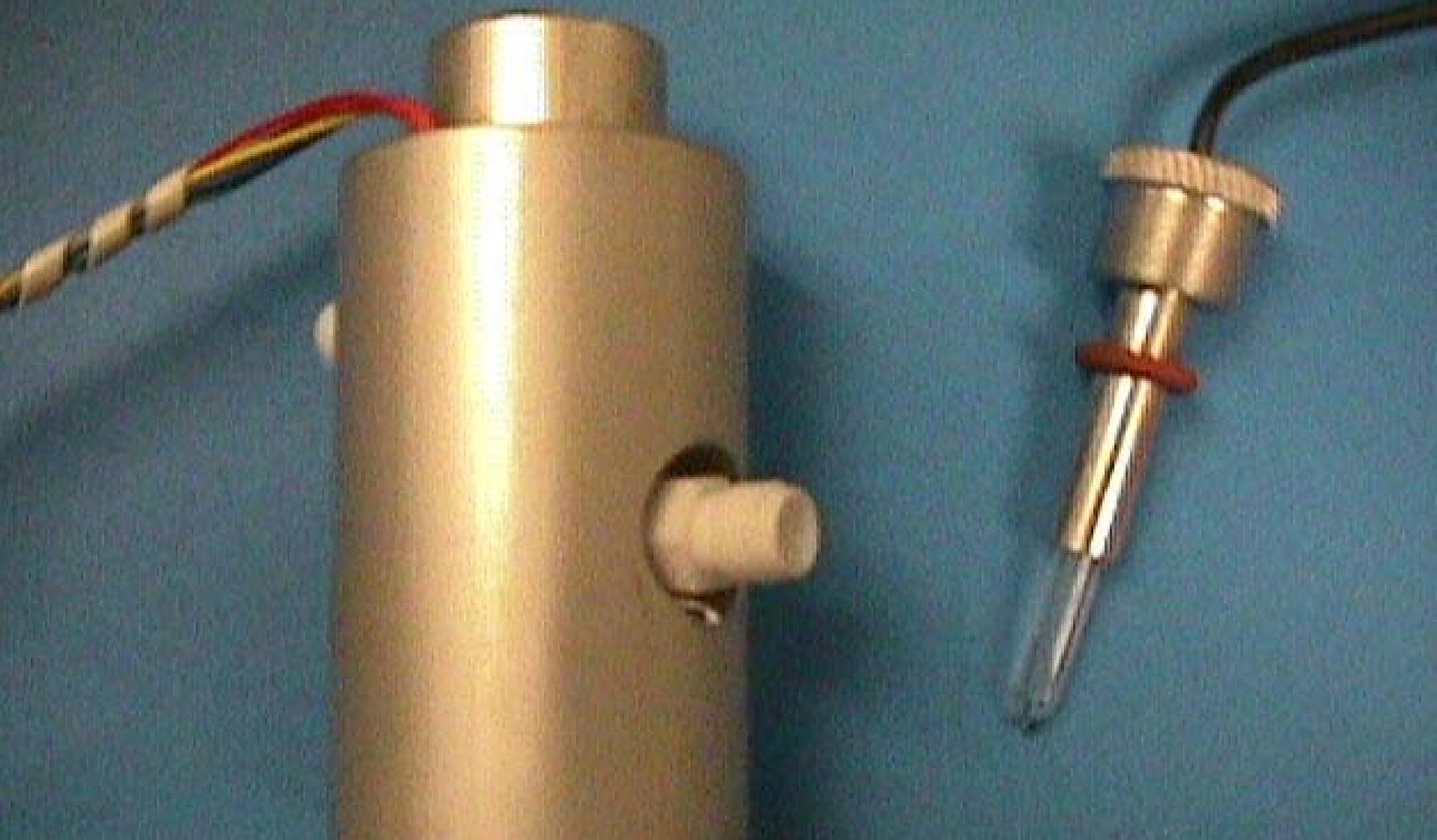
5
ZERO



Flow Controller for ozone generator (5 LPM)

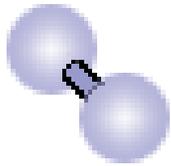


Ozone Generator:
produces ozone for calibration check

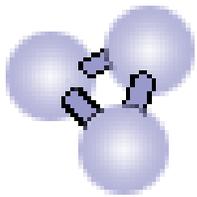


Ozone Generator with
Ultraviolet (UV) Lamp

The Ozone Generator



Oxygen molecules have two oxygen atoms.



Ozone molecules have three oxygen atoms.

- Incoming air is subjected to ultraviolet radiation from a mercury vapor lamp.
- The oxygen absorbs the UV light.
- To dissipate the resulting gain in energy, the irradiated O_2 molecules split into two negatively charged oxygen atoms.
- These atoms combine with unsplit oxygen to form O_3 .

The Manifold

- A specific volume of ozone or zero air enters the manifold.
- The calibrator pulls a “sample” from the manifold.
- The instrument that is being check also pulls a “sample” from the manifold.
- The excess is allowed to vent.

The Manifold

5 LPM

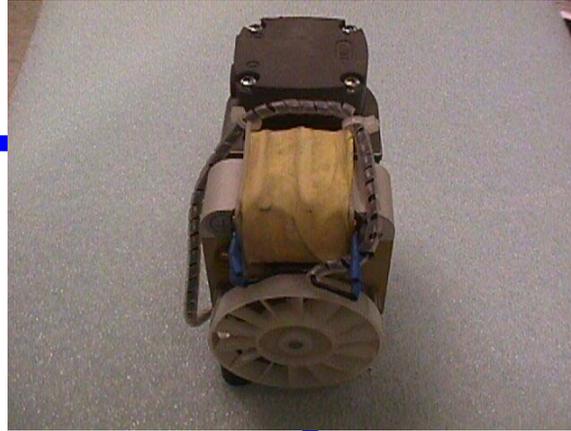


Capped

2 LPM for
transfer standard

2 LPM + excess to analyzer

Ozone Scrubber



Flow Controller



Ozone Generator



The Ozone Generator

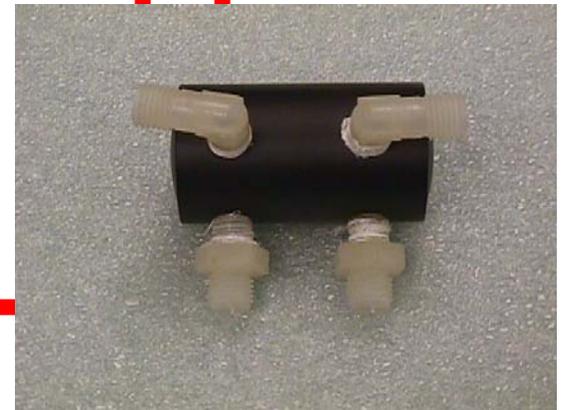
Analyzer



To transfer standard



capped



Manifold

Primary Standards and Transfer Standards

- Are used to verify the accuracy of the instrument.
- Primary Standards have the highest authority.

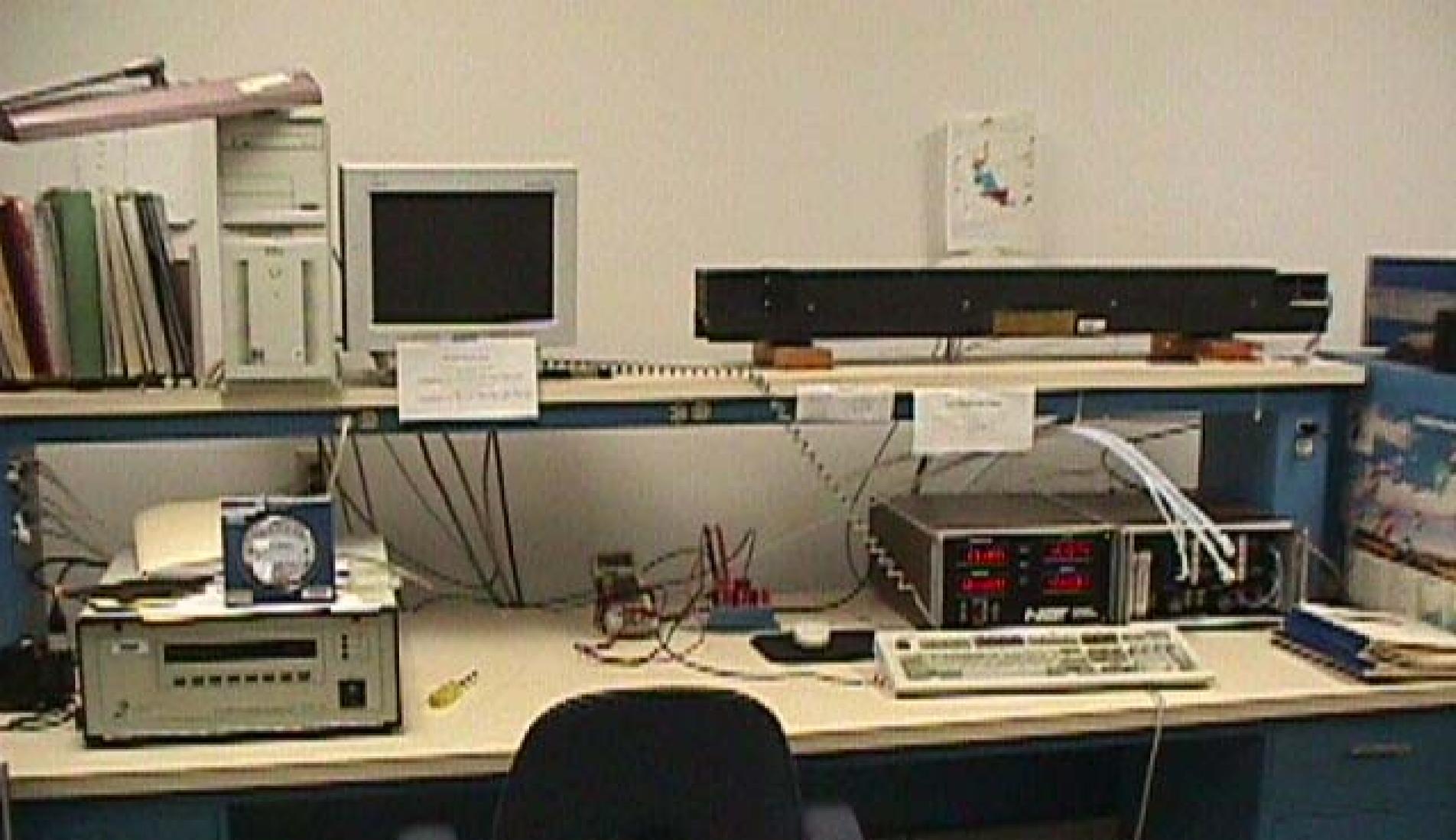
Primary Standards

- Located at a central laboratory where it can remain stationary, protected from the physical shocks of transportation, operated by an experienced analyst under optimum conditions.
- Serves as a common standard for all analyzers in a network.
- Compared against other primary standards.

STATE OF CALIFORNIA

AIR RESOURCES BOARD

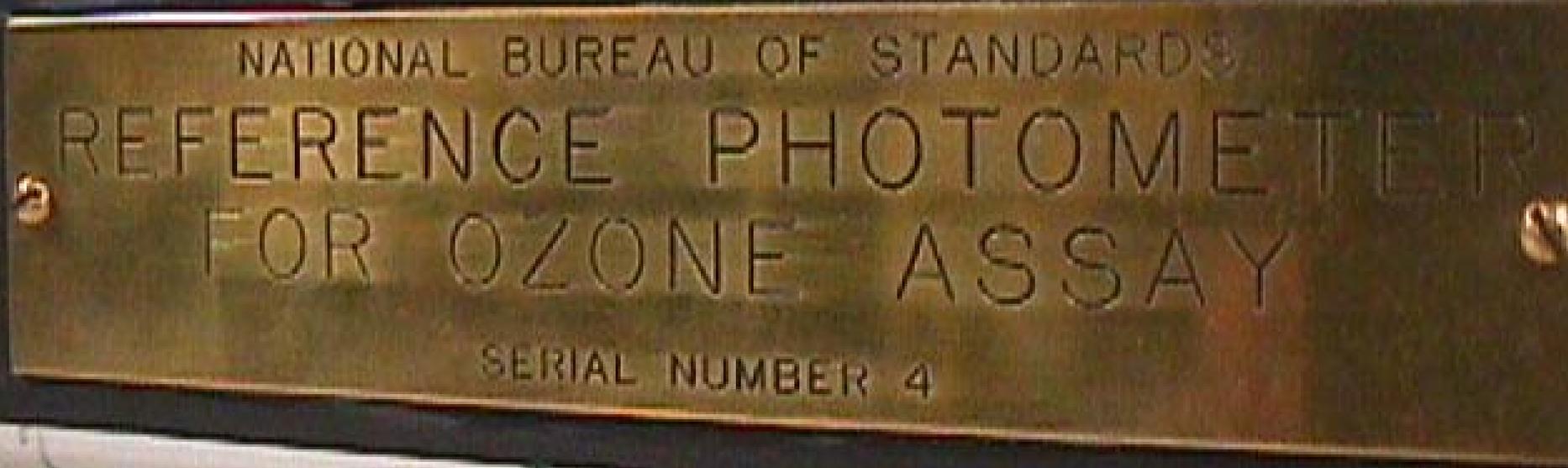




Compared against the Standard Reference Photometer (SRP)



Primary standards have the highest authority.



Participants of the SRP Program (SRP #4)

- Arizona DEQ
- Ecotech LTD (Australia)
- California, Arizona, Hawaii, Utah
- EMPAC (China)
- Alaska, Oregon, Wash, Idaho
- Lawrence Livermore Labs
- National Park Service
- Vandenberg AFB
- Westinghouse Hanford Company

Ozone Transfer Standards

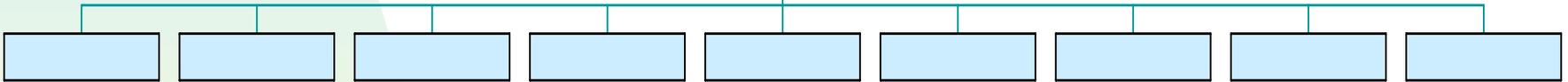
- Transportable instrument
- Contains an ozone analyzer and generator.
- Together with the associated operational procedures, can accurately reproduce ozone concentration standards that are related to an authoritative primary or master standard.

Primary Photometer
Research Triangle Park

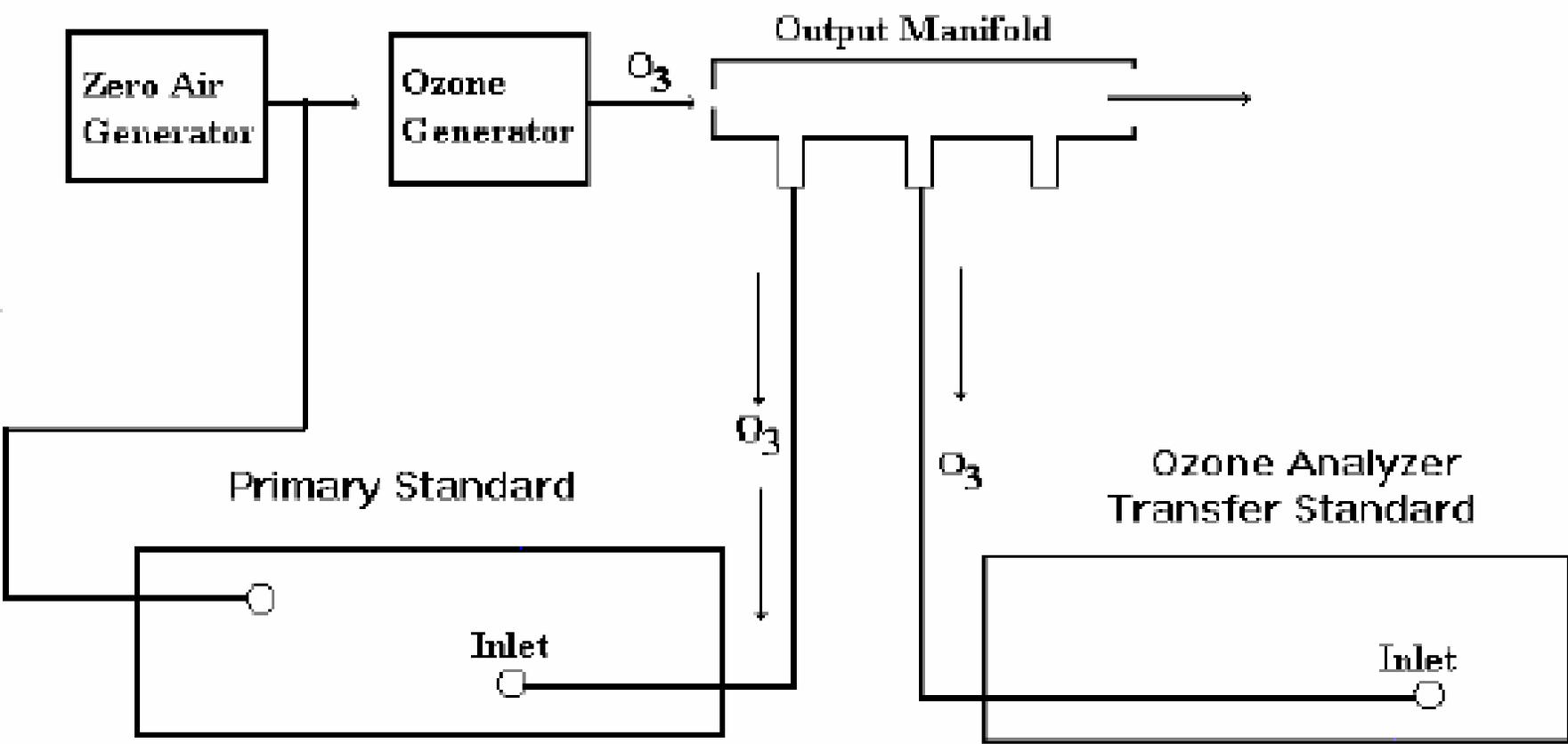
Standard Reference Photometer
California Air Resources Board

Primary Standard
Ecology

**Primary
Standards**

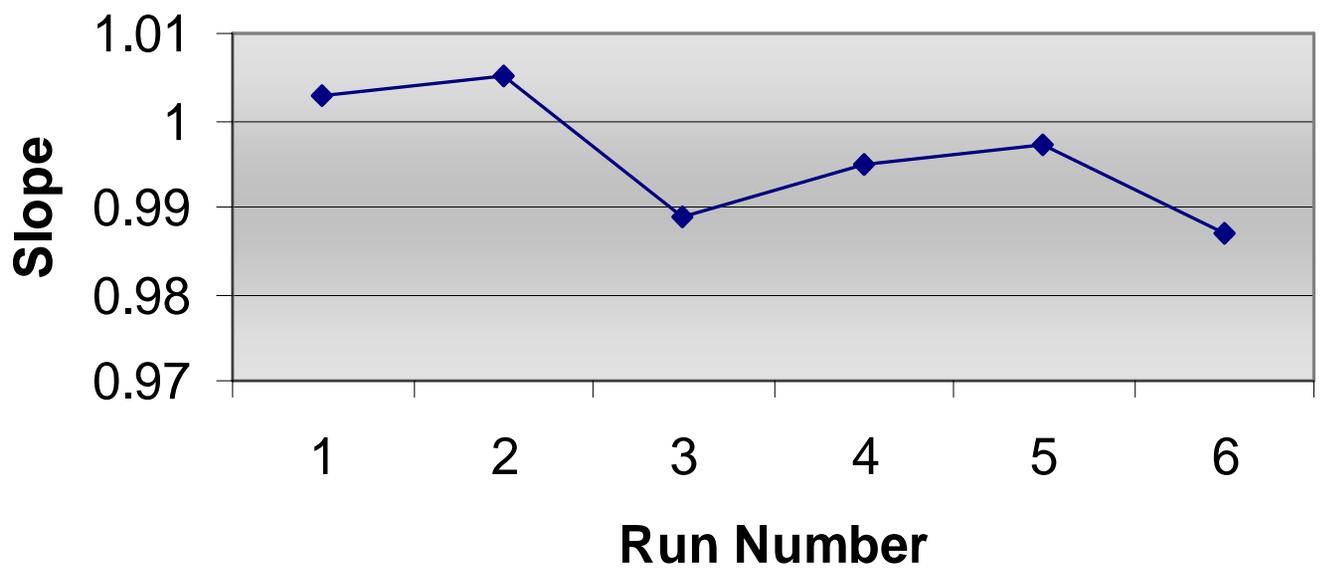


Transfer Standards



1.035	11/2/1999
1.036	1/30/2000
1.036	3/20/2000
1.042	6/20/2000
1.04	9/4/2000
1.04	11/2/2000
1.039	1/20/2001
1.012	4/20/2001
1.017	4/26/2001
1.014	7/17/2001
1.015	4/15/2002
0.993	4/24/2002
1.009	7/15/2002
1.003	4/7/2003
1.005	8/2/2003
0.989	4/27/2004
0.995	4/28/2004
0.997	8/30/2004
0.987	12/6/2004

Ozone Transfer Standard #6452
True ozone = display x 1.00 - zero
12/06/2004



Data Loggers and Telemetry

- Before performing any calibration checks, disable the ozone channel.
- Joan Kiely (360) 407-6839

Performing the Zero Check

- Make sure the Transfer Standard has warmed up.
- Set the ozone adjust thumbwheels to 000.
- Set the ozone switch to the off position.
- Turn the generator pump on.

Zero Check

- Record the values using the form provided.
- Check the data logger and recorder to make sure they are reading zero.
- Allow @15 minutes to sample zero air.
- Record the values using the ten count.
- Remember to subtract the zero offset from all readings to obtain the true ozone reading.

The Precision Check

- Turn the ozone lamp switch on.
- Set the lamp to AUTO.
- Set the thumbwheels to 090.
- Allow 15 minutes after the trace plateaus.
- Record the values using the ten count.

Figure 5.1: Calibration Data Form
Ecology Calibration Check For Continuous Ozone Analyzers

Site Name _____ AIRS # _____ Date _____ Disabled at: _____ PST
 Operator _____ Enabled at: _____ PST

Ozone Tr Standard SN _____ Correction Factor _____ Ozone Analyzer SN _____
 Sample Flow: _____ LPM Bar. Pres. _____ Atm. Sample Flow: _____ LPM Bar. Pres. _____ Atm.
 Generator Flow: _____ LPM Inst Temp. _____ C Inst Temp. _____ C
 Sample Freq: _____ KHz Cntrl Freq: _____ KHz Sample Freq: _____ KHz Cntrl Freq: _____ KHz

Thumbwheel settings			Analyzer Response			
000	090	400	Reading #	Point 1	Point 2	Point 3
			1			
			2			
			3			
			4			
			5			
			6			
			7			
			8			
			9			
			10			
			Average			
			← True ozone			
			Difference →			

$True\ Ozone = (Average\ Display) \times Factor - Average\ zero$

$Difference = \frac{Analyzer\ average - True\ ozone}{True\ ozone} \times 100$

The difference must be within $\pm 10\%$



The Span Check

- Set the thumb wheels to 400.
- Allow for the trace to plateau.
- Record the values using the ten count.
- Multiply
- Match output of analyzer to data logger and chart recorder



Determining the Precision of the Instrument

- The precision of the instrument is the difference between the “actual” or true ozone value (measured by the Ozone Transfer Standard) and the “indicated value” (measured by the analyzer).

Percent Difference

$$\frac{\text{Indicated} - \text{Actual}}{\text{Actual}} \times 100 = \text{Percent Difference}$$

Percent Difference

$$\frac{\text{Analyzer} - \text{Standard}}{\text{Standard}} \times 100 = \text{Percent Difference}$$

Figure 6.1: Completed Monthly Precision Check Summary Form
Monthly Precision Check Summary

AIRS NUMBER: 530010001

PARAMETER: Ozone YEAR: 2004 MONTH: July

STATE TAG OR ID #: E120444

LOCATION: Mt. Washington OPERATOR: Dave Davies

DATE			ACTUAL CONC.	INDICATED CONC.	UNITS	*PASSED?	COMMENTS
Month	Day	Year				Y or N	
7	4	2004	.090	.091	ppm	Y	Manual Check
7	12	2004	.089	.090	ppm	Y	Automated Check
7	18	2004	.091	.091	ppm	Y	Manual Check
7	25	2004	.088	.090	ppm	Y	Automated Check

*Shaded area to be completed by QA Personnel

PRECISION CHECK EQUIPMENT:

Gas Cylinder Serial #: _____

Calibrator Model: Dasibi 1008PC

Calibrator Serial #: 5310

Permeation Tube #: _____

Decimal Placement:	
CO	2
SO2	3
NO2	3
O3	3
NEPH	3

COMMENTS:

After the Calibration Check

- Record the sample chamber temperature.
- Record the unadjusted sample frequency.
- Record the sample chamber pressure.
- Record the control frequency 50.000.

Performance Checks

- Sample Flow Check
- Span Check
- Control Frequency Check
- Sample Frequency Check

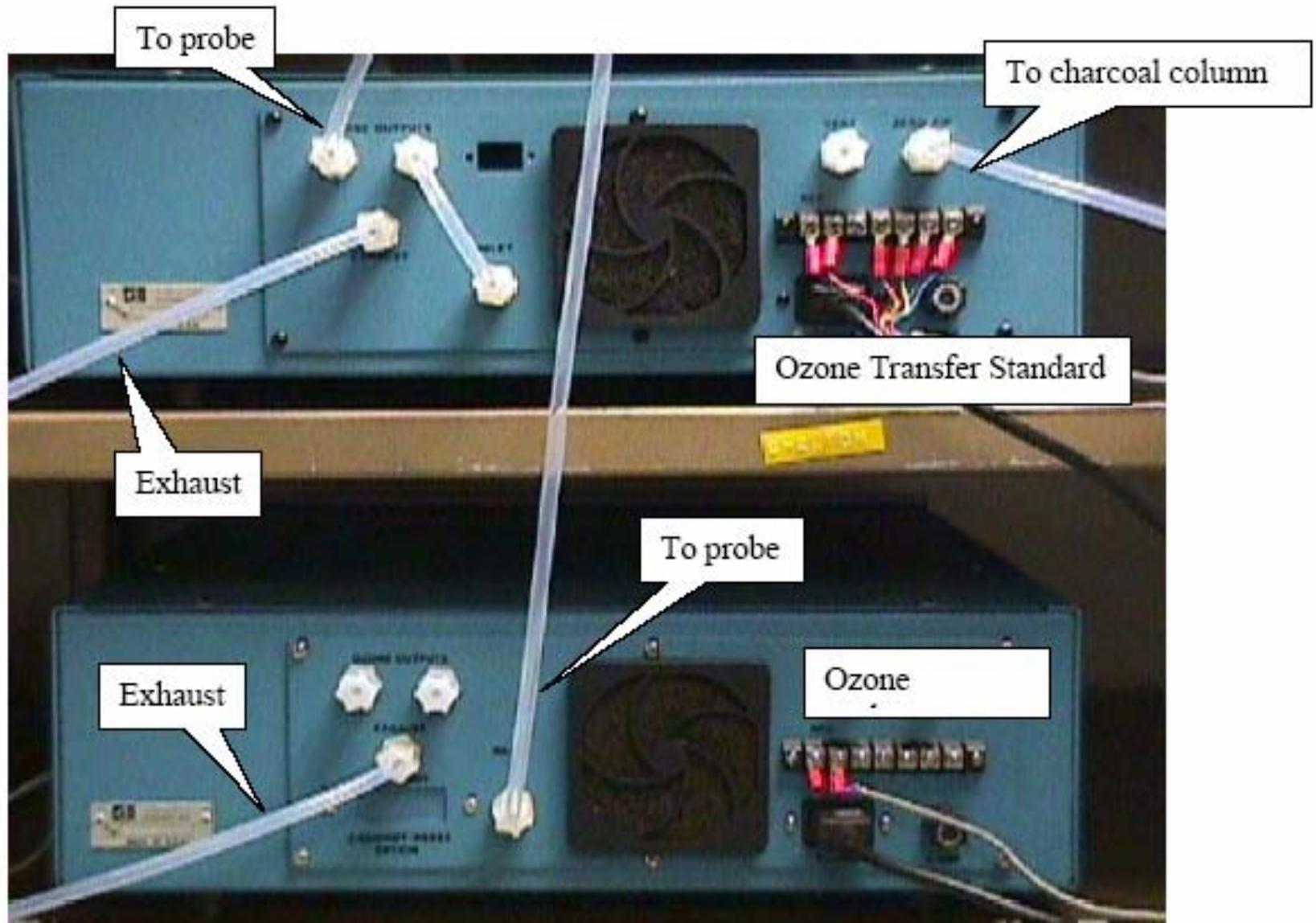
Sample Flow Check



- Tap the flow meter to make sure the float is not stuck.
- Should read @ 2.0 L/min.
- Adjust if less than 1.8 L/min or greater than 2.2 L/min.
- Never lower than 1.5 or higher than 3.5 L/min

Span Check

- Turn mode switch to SPAN.
- Should read 30.8xx
- Set in lab. Do not adjust.
- If it does not read 30.8xx, contact David at the lab.



Control Frequency Check

- Should always be 50.000 on the display
- If not, contact David.

Sample Frequency Check

- Should not be below 410 KHz.
- Track the degradation.
- Large drops indicate dirty optics.
- Adjust frequency between 460 KHz and 410 KHz.

To adjust the sample frequency

- Set mode selector switch to SAMP/TEMP with T/P off.
- Loosen the dual screws on the Light Source Block.
- Push lamp in to increase, pull out to decrease the lamp intensity, or rotated. Small movements needed.
- Tighten screws when done.

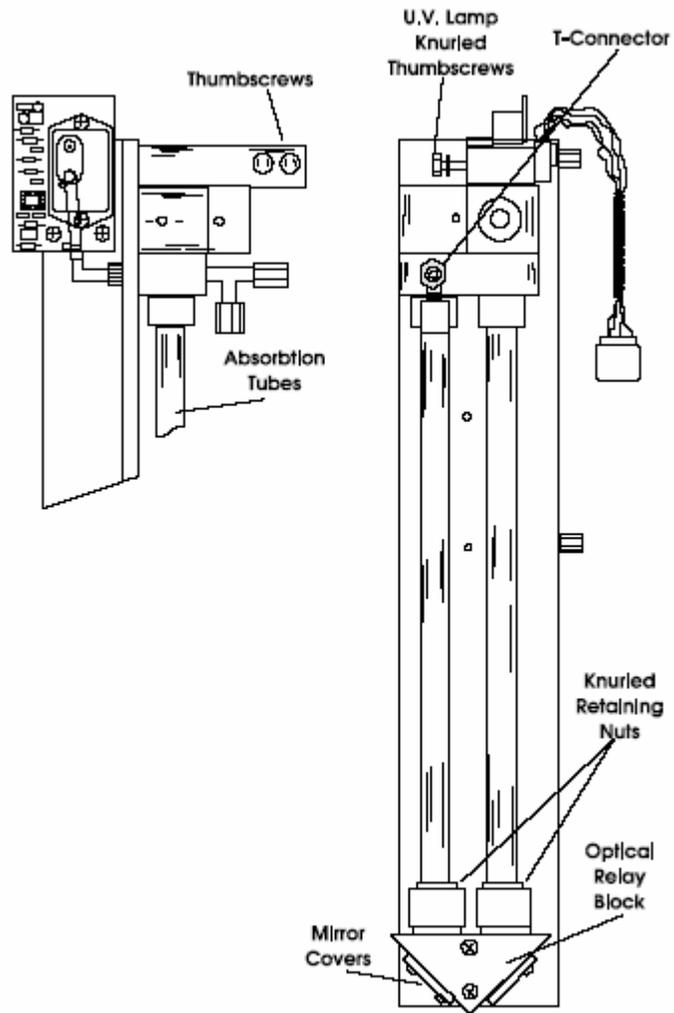


Figure A-6: Thumbscrew Location

Pressure Check

- Check the analyzer pressure against a certified barometer.

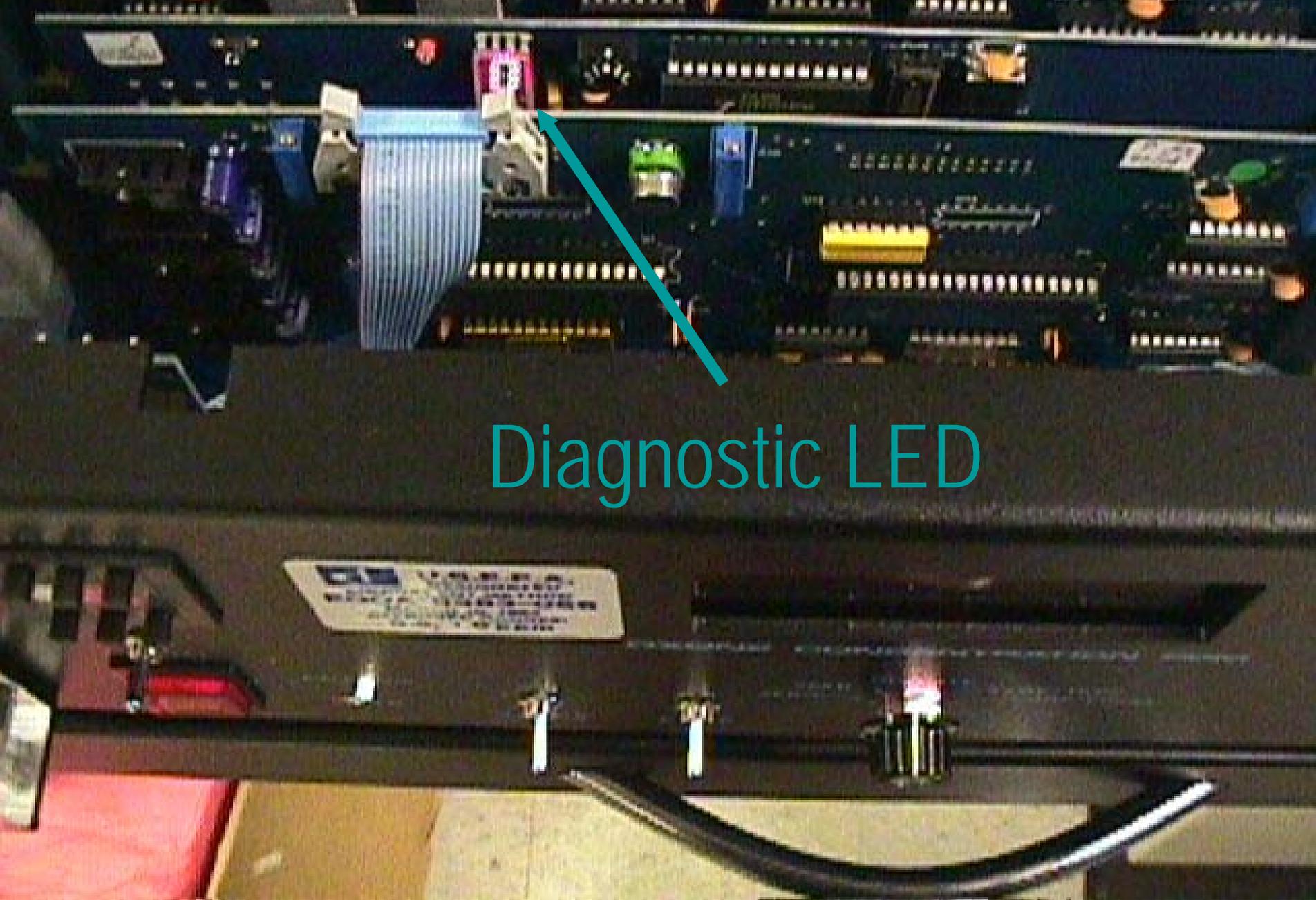
0.5-micron Teflon® Filter

- Installed before entering the analyzer.
- Will not degrade the ozone concentration.
- Change filters regularly.

The .5 micron Teflon[®] filter
holder



Remember to change filter
when dirty

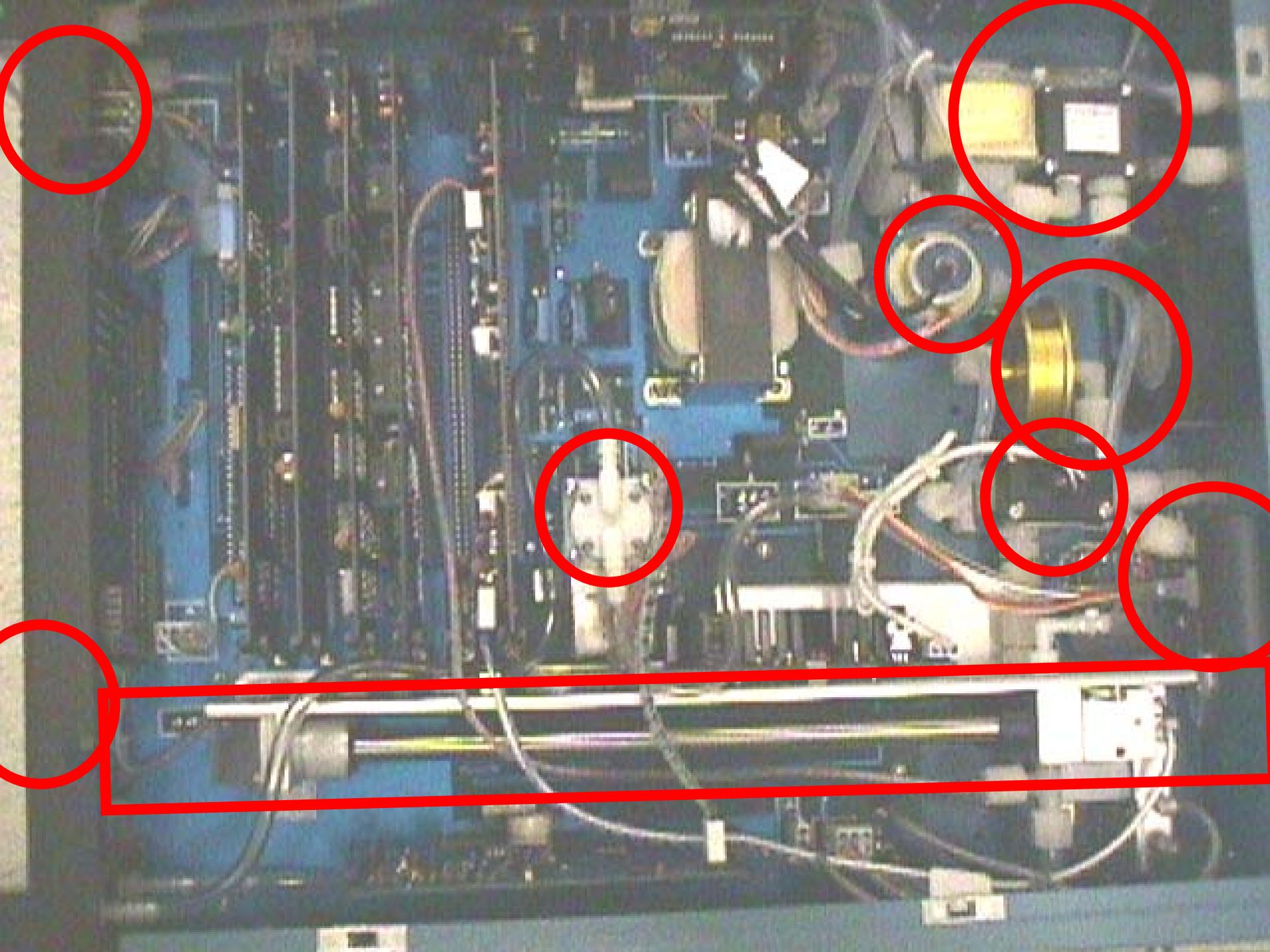


Diagnostic LED

Diagnostic LED

- 0 = No faults
- 1 = Not used yet
- 2 = Sample Frequency is not above 300 KHz, or is not below 480 KHz.
- 3 = Control Frequency is not at 500 KHz.
- 4 = Lamp heater voltage is incorrect.
- 7 = CPU reset occurrence.
- 8 = Displayed whenever any front panel switch not in the correct position for proper operation.

PROBLEM	POSSIBLE CAUSE	CORRECTIVE ACTION
Analyzer is on but lamp is not lit.	Lamp bulb is blown	Replace the lamp bulb.
Analyzer is not operating	Blown fuse	Replace the blown fuse.
	Power cord is loose or disconnected	Reinsert power cord.
Analyzer operating without digital display	200 VDC Power Supply inoperative	Contact the Air Monitoring Unit. The problem may be in the voltage or in the plug in display.
Zero ozone output when monitoring ambient air.	Pump stopped	Check the power to the pump or change the pump if necessary.
Low sample flow	Flowmeter may be adjusted wrong	Adjust the flowmeter to the correct setting.
	Dirty sample line filter	Replace the filter.
	Leak in the system	Refer to Section 6.5.9 of Manual.
Recorder trace erratic when analyzer is sampling	Loose absorption tubes	Tighten the absorption tube checking the O-rings for proper seal. Refer to Section 6.7
Recorder trace periodically goes to zero and remains there for a period of time, and then returns to ambient ozone reading.	Solenoid not switching	Contact the Air Monitoring Unit. The problem may be in the solenoid driver card or the solenoid may be defective.
Excessive temperature drift	Temperature sensor may be out of adjustment.	Adjust the trimpot on the Temperature Circuit Board. Refer to Section 6.5.7.
Low sample control frequency readings.	U.V. lamp out of adjustment	Adjust the U.V. lamp. Refer to Section 3.4.2.2.1
	Dirty optics	Clean the optics. Refer to Section 6.7.
Loss of the sample control frequency.	Faulty detector	Replace the electrometer assemble. Contact the Air Monitoring Unit.
Unstable sample control frequency.	Loose lamp or detector	Tighten the set screws holding the lamp and detectors.



Patience is a Virtue

- Allow yourself enough time.
- How fast you can do it means nothing.
- If you rush you are bound to make mistakes.
- Mistakes usually cost lost data, time and money.
- The best operators take their time, are methodical and thorough.

Before Leaving the Station.....

- Record the results of the calibration check and any changes that were made to the instruments.
- Make sure that the analyzer is running and that all the switches are in their correct positions.
- Enable the data logger.
- Make sure that the station is secured.

Before you leave.....

- Check to see if the power is on.
- Is the sample flow set to 2.0 LPM?
- Is the selector switch in the “operate mode”?
- Can you hear the solenoid valve cycling?
- Has channel 03 on the data logger been disabled?

Strip Charts

- Before performing any calibration checks, annotate the strip chart.
- Make your entry into the logbook.
- Sean Lundblad (360) 407-6843

Quarterly Quality Assurance Audits

- A Quality Assurance representative visits the site quarterly.
- Challenges the station analyzer with concentrations generated by the QA transfer standard.
- Checks for the accuracy of the analyzer.
- Discusses issues that arise during the audit.

The Critical Criteria Table

OZONE CRITICAL CRITERIA TABLE			
Criteria	Acceptable Range	Frequency	40 CFR Reference
Standard Reporting Units	ppm	All data	40 CFR, Pt 50.9
Completeness (seasonal) Maximum 1-hour concentration	75% values from 9:01 AM to 9:00 PM (LST)	Daily	40 CFR, Pt 50, App H, S 3
Precision Single analyzer Reporting organization	None (See note A below) 1/3 months	1/2 weeks for seasonal sites or sites where manual QC checks are performed. 1/4 weeks at year round automated sites. (See note B below) 95% CI < +/-15%	40 CFR, Pt 58, App A EPA-600/4-83-023 Vol II, App 15, S 6
Accuracy Single analyzer Annual accuracy	None (See note C below) 95% CI < +/-20%	25 % of sites quarterly (all sites yearly)	40 CFR, Pt 58, App A EPA-600/4-83-023 Vol II, App 15, S 6
Quality Control Check Zero/span check -level 1 If Cal updated at each zero/span Zero/span check -level 1 If fixed Cal used to calculate data	Zero Drift < +/- 20 to 30 ppb Span Drift < +/- 20 to 25% Zero Drift < +/- 10 to 15 ppb Span Drift < +/- 15%	1/ 2 weeks	Vol II, S 12.6 Vol II, S 12.6

Data Validation Tables

- Critical precision and accuracy
- Operational shelter temperature
- Systematic certified ozone standard or SRP comparison



Bad data...

is worse than no data at all.

Maintaining Your Monitoring Equipment

- ◆ Break to the Technical Assistance Lab.
- ◆ Calibration Lab (360) 407-6030