OCTOBER 2007

AIR RESOURCES BOARD

STANDARD OPERATING PROCEDURE FOR THE CERTIFICATION AND VERIFICATION OF OZONE PRIMARY AND TRANSFER STANDARDS USING THE STANDARD REFERENCE PHOTOMETER

MLD METHOD 5720

QUALITY MANAGEMENT BRANCH
MONITORING AND LABORATORY DIVISION
STATE OF CALIFORNIA
1927 13th STREET
SACRAMENTO, CA 95814

TABLE OF CONTENTS

	Page
1. INTRODUCTION	1
2. SUMMARY OF METHOD	1
2.1 Method Nomenclature	1
2.2 Analysis Method	1
3. INTERFERENCES AND LIMITATIONS	3
4. INSTRUMENTATION AND EQUIPMENT	4
5. PROCEDURES	4
6. INSTRUMENT SOP	16
6.1 General	16
6.2 Dasibi 1008-PC	16
6.3 Dasibi 5009-CP	17
6.4 Dasibi 1003-PC/AH	17
6.5 API 400/401	18
6.12 Environics 6103	18
6.12.5 Tanabyte 300	18
7. QUALITY CONTROL PRACTICES	19
7.1 Quarterly Practices	19
7.2 Annual Practices	19
8. REFERENCE	20

1. INTRODUCTION

1.1 This standard operating procedure describes the certification of ozone transfer standards and verification of ozone primary standards. Ozone standards are required for the calibration and auditing of ambient ozone monitors.

1.2 This procedure uses Standard Reference Photometer (SRP) #4 to measure ozone levels. The SRP #4 was manufactured by the National Institute of Standards and Technology (NIST). The SRP is owned by U.S. EPA; however, it is operated by the Standards Laboratory.

1.3 This procedure will determine the client's primary or transfer standard's ability to accurately measure levels of ozone. The client's instrument response is compared to the SRP's response to levels of ozone.

2. SUMMARY OF METHOD

2.1 METHOD NOMENCLATURE

2.2 Calibration - establishes a correction factor to adjust or correct the output of an instrument. This is determined through a comparison between an instrument and SRP at varying levels of ozone.

2.3 Certification - establishes traceability of a transfer standard to the SRP. The certification of an instrument requires the results of six calibrations to meet requirements established by U.S. EPA.

2.4 Verification - establishes comparability of a primary standard to the SRP. The verification of an instrument requires the results of one calibration to meet requirements established by U.S. EPA; however, the output of the instrument is not to be corrected based upon the results of the calibration.

2.5 Transfer standards – a transportable device or apparatus that is capable of accurately producing or assaying ozone concentrations. These types of instruments undergo a certification process.

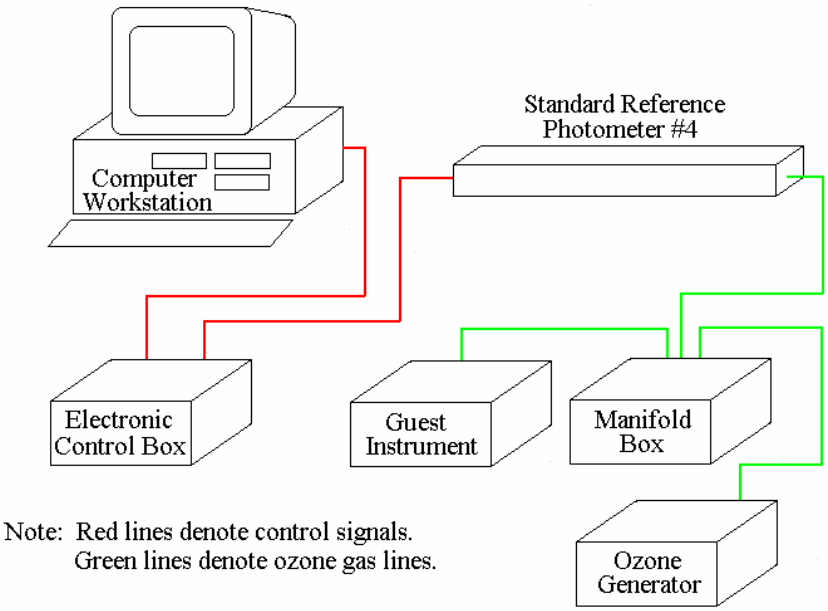
2.6 Primary standards – a device capable of assaying ozone concentrations by UV photometry in accordance with the Code of Federal Regulations, part 50, Appendix D (40CFR50). Essentially, these types of instruments are ozone photometers that require a source of reference gas separate from sample gas (including purified sample gas). Agencies are encouraged to compare primary standards to SRPs as part of their routine quality assurance programs. These types of instruments undergo a verification process.

2.7 ANALYSIS METHOD

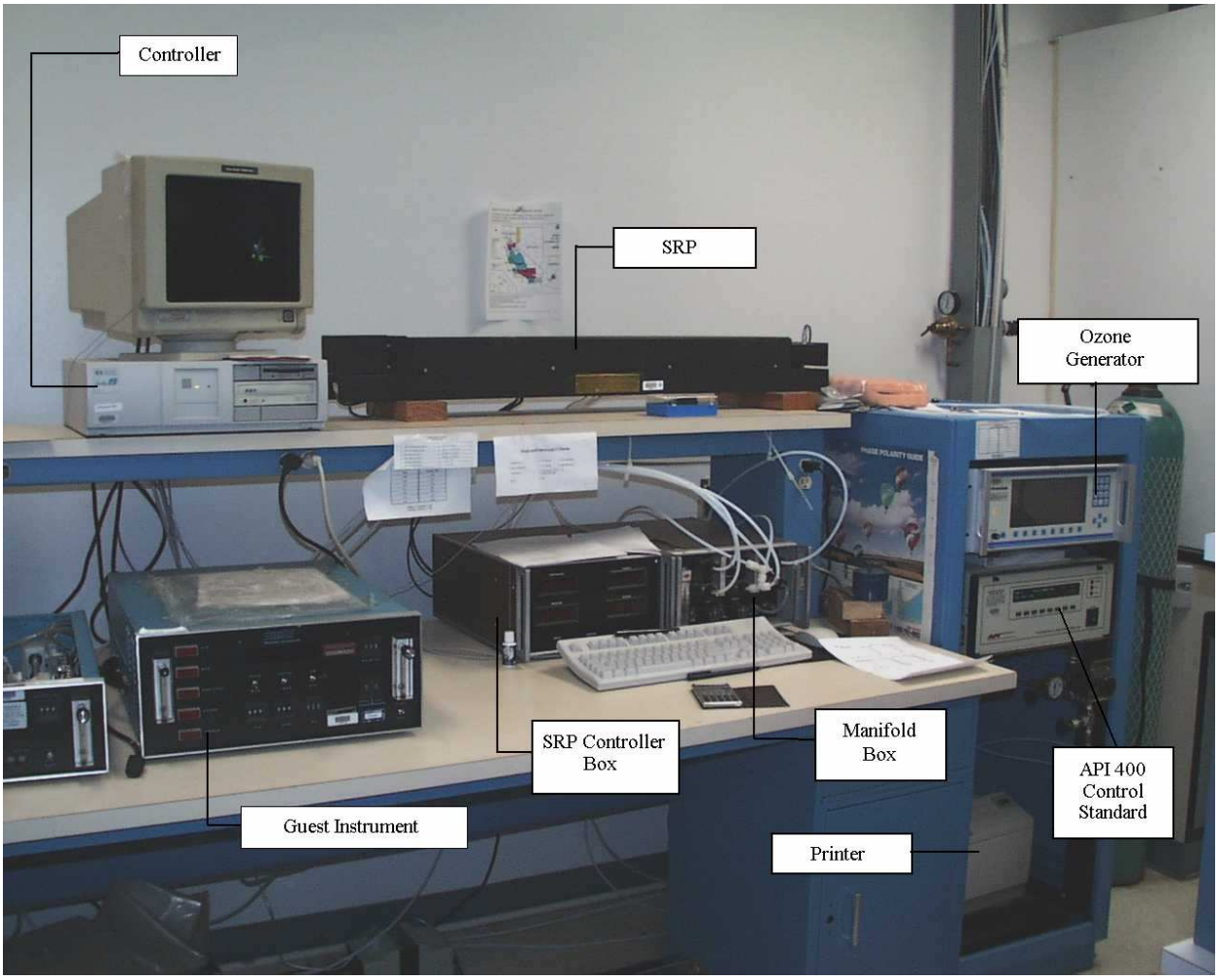
2.8 This method of assaying ozone is based upon the tendency for it to absorb light at a specific wavelength (254 nanometers). The amount of light absorbed is directly proportional to the amount of ozone present.

2.9 The SRP introduces a clean gas (reference gas) into the photometer and measures the amount of light (254 nanometers) through it. Then, a sample gas is introduced and the amount of light passed is measured. Based upon the previously mentioned variables, an ozone concentration can be calculated.

2.10 Schematic diagram of SRP Station.



2.10.1 View of SRP Station.



3. INTERFERENCES AND LIMITATIONS

3.1 Avoid contamination of the SRP and guest instruments. Only clean, filtered gas should pass through the sample or reference manifolds.

3.2 Avoid over pressurization of guest instruments. Ensure that the sample and reference manifolds are vented to atmosphere. The guest instruments should be connected directly to the manifolds.

3.3 The sample lines should be initially conditioned with ozone. New sample lines may initially absorb ozone until properly conditioned and may bias the guest instrument's response.

3.4 Allow guest instrument to warm-up for a minimum of 2 hours.

3.5 Allow guest instrument and SRP to stabilize at each ozone concentration level for a minimum of 20 minutes.

3.6 Ensure the flow from the Environics 9100 is greater than the sample flow rate of the guest instruments and SRP (5 lpm).

4. INSTRUMENTATION AND EQUIPMENT

4.1 SRP and support equipment.

4.2 Environics 9100 calibrator, ozone source.

4.3 Computer and monitor, with associated software.

4.4 Ultra pure grade air.

4.5 Teflon gas lines.

4.6 High accuracy barometer, for ambient pressure reading.

4.7 High accuracy thermometer, for ambient temperature reading.

5. PROCEDURES

5.1 Turn on guest instrument. Allow it to warm up for a minimum of 2 hours.

5.2 Connect sample line “O3A” or “O3B” to sample inlet port on back of instrument.

5.3 If instrument is a primary standard photometer, connect reference gas line “ZEROA” or “ZEROB” to reference leg of sample solenoid inside instrument. Some instruments require pressurized reference gas, use Teflon line labeled “PRESS AIR”.

5.4 Obtain ambient pressure using the Barometer SOP.

5.5 Perform Instrument SOP; see section 6 for specific instrument model.

5.6 Turn power switch on Environics 9100 to “ON” position.

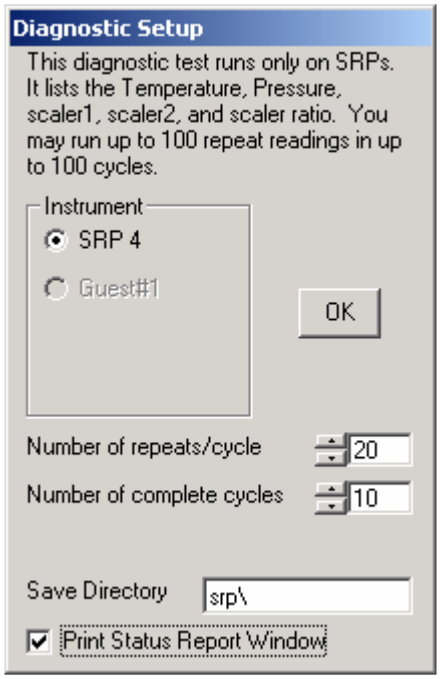
5.7 Turn on the black zero air toggle valve at back of the Environics 9100. (Up is the “OPEN” position).

5.8 Set the house air regulator supplying air to the Environics 9100 to 35 psi.

5.9 On the Environics 9100, select the “Flow Mode” from the menu screen. Enter “0.0” for the flow rate of mass flow controller (MFC) #1, “13.0” for MFC #2, and “0.0” for ozone concentration. Then, select “Update” on menu screen.

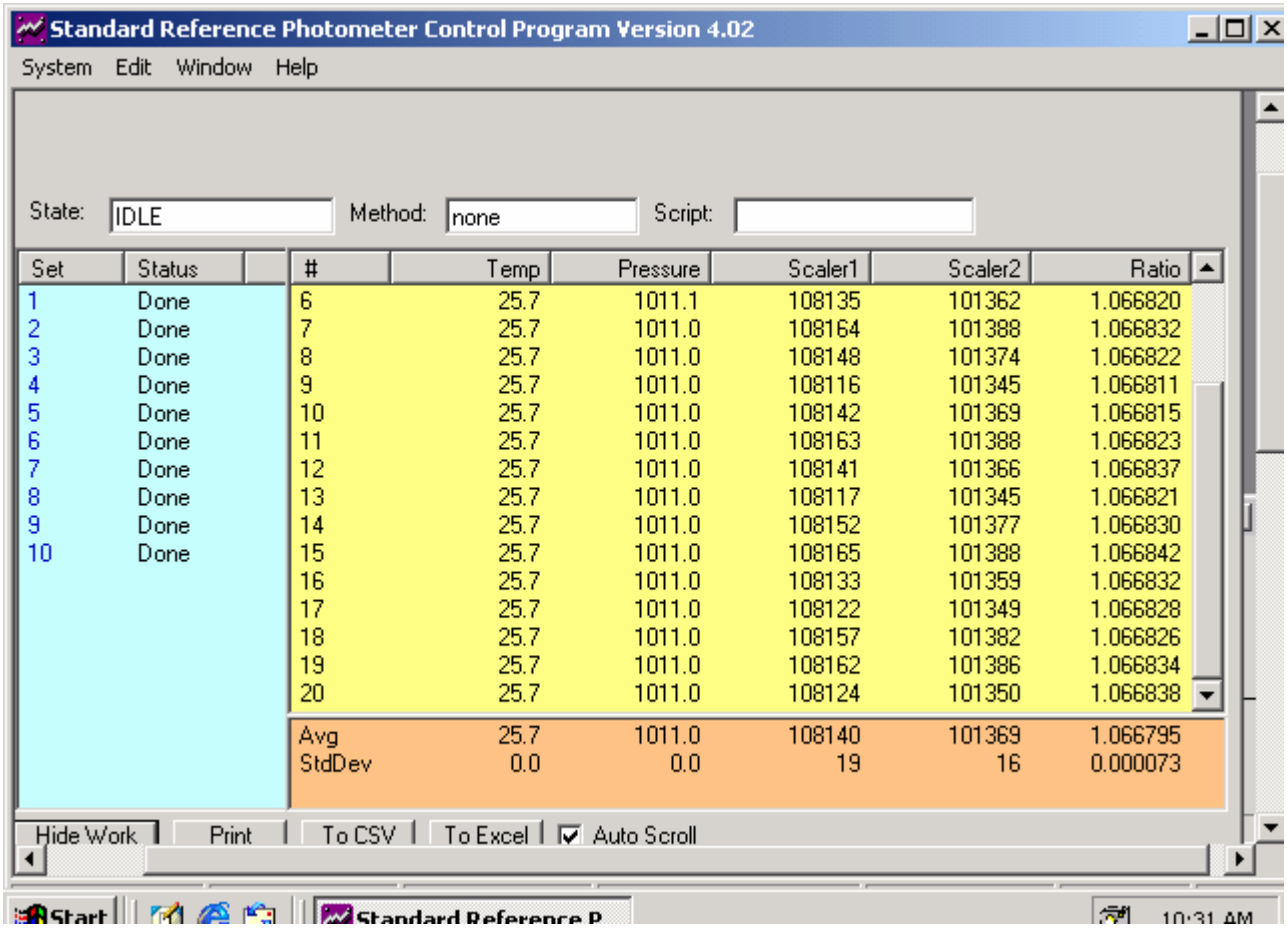
5.10 Set the service air regulator to 20 PSI on the Environics 9100 calibrator rack.

5.10.1 Left click on **SRP Control** on the computer desktop. Click on **System,** then **Diagnostics**, **Stability Monitor.**



5.10.2 To start the Stability monitor, click **SRP 4** and **Print Status Report Window** as illustrated. After 20 complete cycles, the desktop will look like the following illustration. **StdDev** should be less than 25 for Scaler 1 and Scaler 2. Scaler 1 and Scaler 2 should be greater than 90,000.

5.10.3 At the conclusion of the Stability monitor test the printer will output a hard copy of the results as shown below. As well as ensuring that the **StdDev** of both scalers is less than 25, transpose the temperature, pressure and Scaler 1 and 2 onto the SRP section of form ozone 2007, illustrated in section 5.13.



Set	Status
1	Done
2	Done
3	Done
4	Done
5	Done
6	Done
7	Done
8	Done
9	Done
10	Done

#	Temp	Pressure	Scaler1	Scaler2	Ratio
6	25.7	1011.1	108135	101362	1.066820
7	25.7	1011.0	108164	101388	1.066832
8	25.7	1011.0	108148	101374	1.066822
9	25.7	1011.0	108116	101345	1.066811
10	25.7	1011.0	108142	101369	1.066815
11	25.7	1011.0	108163	101388	1.066823
12	25.7	1011.0	108141	101366	1.066837
13	25.7	1011.0	108117	101345	1.066821
14	25.7	1011.0	108152	101377	1.066830
15	25.7	1011.0	108165	101388	1.066842
16	25.7	1011.0	108133	101359	1.066832
17	25.7	1011.0	108122	101349	1.066828
18	25.7	1011.0	108157	101382	1.066826
19	25.7	1011.0	108162	101386	1.066834
20	25.7	1011.0	108124	101350	1.066838
Avg	25.7	1011.0	108140	101369	1.066795
StdDev	0.0	0.0	19	16	0.000073

5.10.4 Diagnostic Test Report, printed at the conclusion of the diagnostic test run.

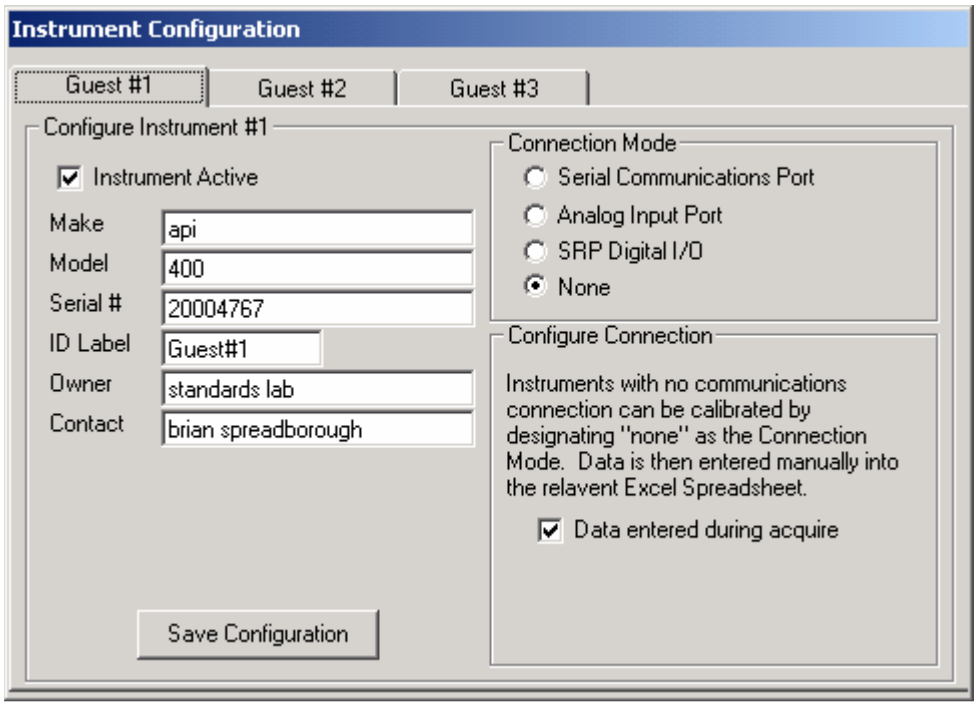
Diagnostic Test Report
Stability Monitor

Calibrating Institute: CARB
Operator: Brian Spreadborough
Instruments: SRP 4
Comment: Reps = 20; Cycles = 10

Date: 7/12/2007
File Name: dstab020.xls

		Temp	Pressure	Scaler1	Scaler2	Ratio
1	Average:	25.80	1015.7	105970	99681	1.063096
	Std Dev:	0.00	0.0	22	20	0.000011
2	Average:	25.87	1015.7	105928	99643	1.063081
	Std Dev:	0.05	0.0	19	17	0.000010
3	Average:	25.90	1015.7	105907	99624	1.063068
	Std Dev:	0.00	0.0	17	16	0.000010
4	Average:	25.96	1015.7	105905	99623	1.063053
	Std Dev:	0.05	0.0	19	17	0.000008
5	Average:	26.00	1015.7	105903	99622	1.063041
	Std Dev:	0.00	0.0	18	17	0.000012
6	Average:	26.00	1015.7	105911	99632	1.063020
	Std Dev:	0.00	0.0	16	15	0.000009
7	Average:	26.00	1015.8	105905	99627	1.063017
	Std Dev:	0.00	0.0	19	17	0.000010
8	Average:	25.95	1015.8	105903	99625	1.063016
	Std Dev:	0.05	0.1	24	22	0.000009
9	Average:	25.90	1015.8	105967	99685	1.063019
	Std Dev:	0.00	0.0	22	21	0.000008
10	Average:	25.85	1015.8	105993	99708	1.063035
	Std Dev:	0.05	0.0	18	16	0.000011

5.10.5 To configure the instrument under test, click on **Edit** then **Configurations** to reveal the following screen.



5.10.6 Type in the test instrument **make**.

5.10.7 Type in the instrument **model**.

5.10.8 Type in the CARB **instrument serial #.**

5.10.9 Type in the instrument **owner**.

5.10.10 Type in the instrument **contact**.

5.11 Left click the **Instrument Active** box.

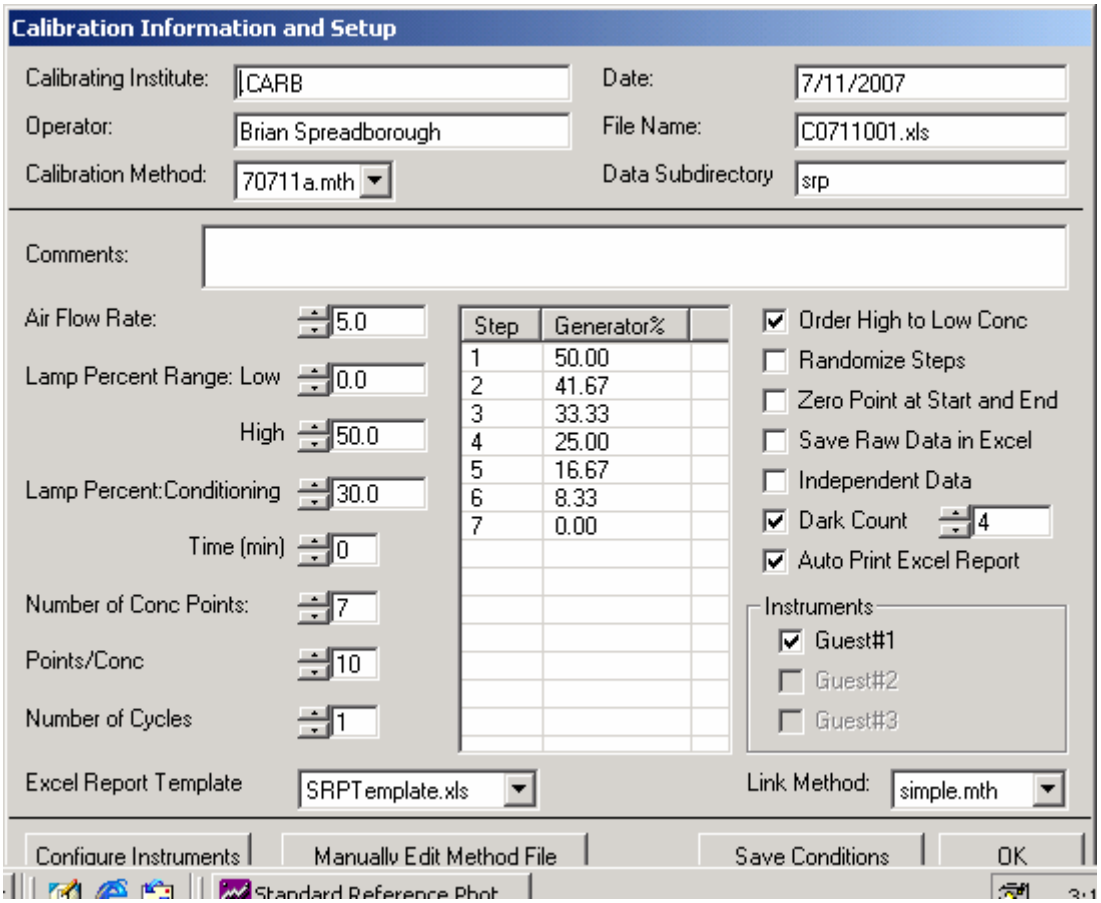
5.11.1 Click **None** for **Connection Mode.**

5.11.2 Click **Data entered during acquire** box.

5.11.3 Left click on **save configuration**.

5.11.4 Click on **System**, **Calibration,Standard.**

5.11.5 Calibration Information and Setup screen.



5.11.6 Type in operators name in **Operator** box.

5.11.7 Ensure **Air flow rate** is 5.0, **Lamp percent Range: Low** is 0.0, **High** is 50.0, **Lamp percent conditioning is 30.0**, **time(min)** is 0**, Number of Conc. Points is** 7, **Points/Conc**. 10**, number of Cycles** is 1.

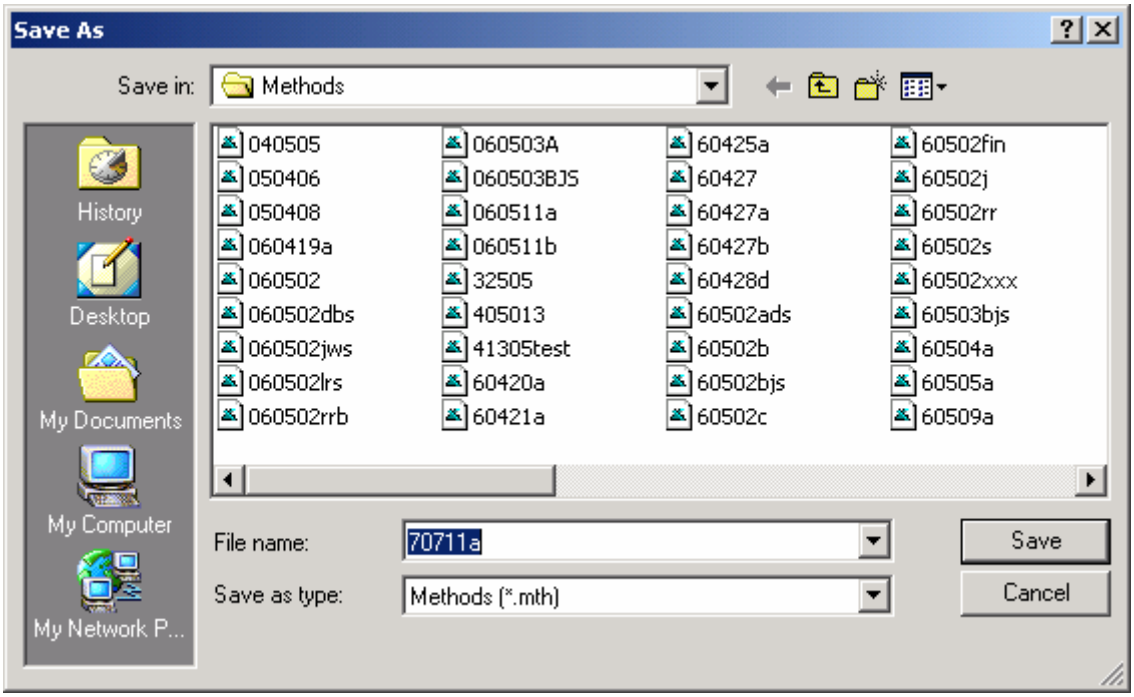
5.11.8 Ensure steps 1 through 7 are selected, **Generator %** is arbitrary as Environics 9100 is used for ozone generation rather than the SRP internal ozone generator.

5.11.9 **Order High to Low Conc**. **Dark Count** 4, **Auto Print Excel Report**, **Guest #1** boxes are active. If a second instrument is being assayed **Guest #2** should also be active.

5.11.10 Excel Report Template should be selected as SRPTemplate.xl

5.12 Simple.mth should be selected in Link Method box.

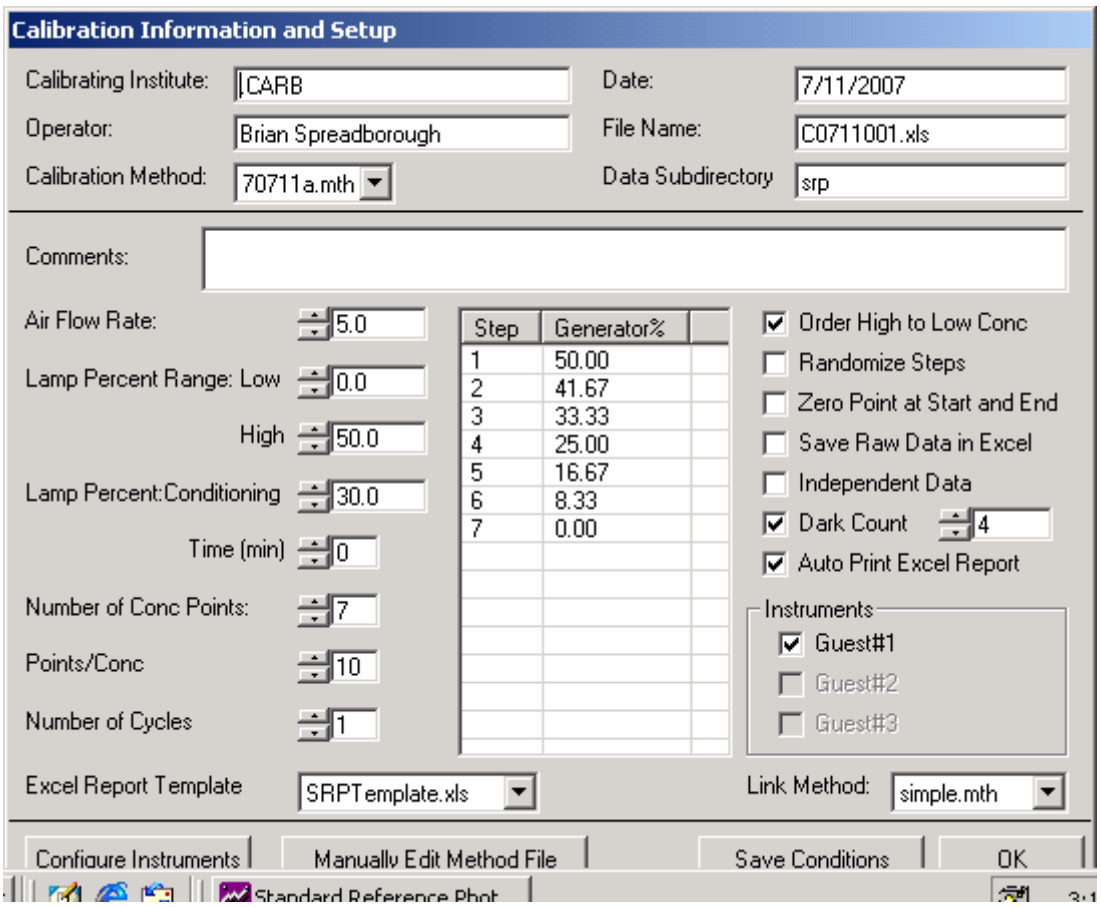
5.12.1 Click on **Save conditions**.



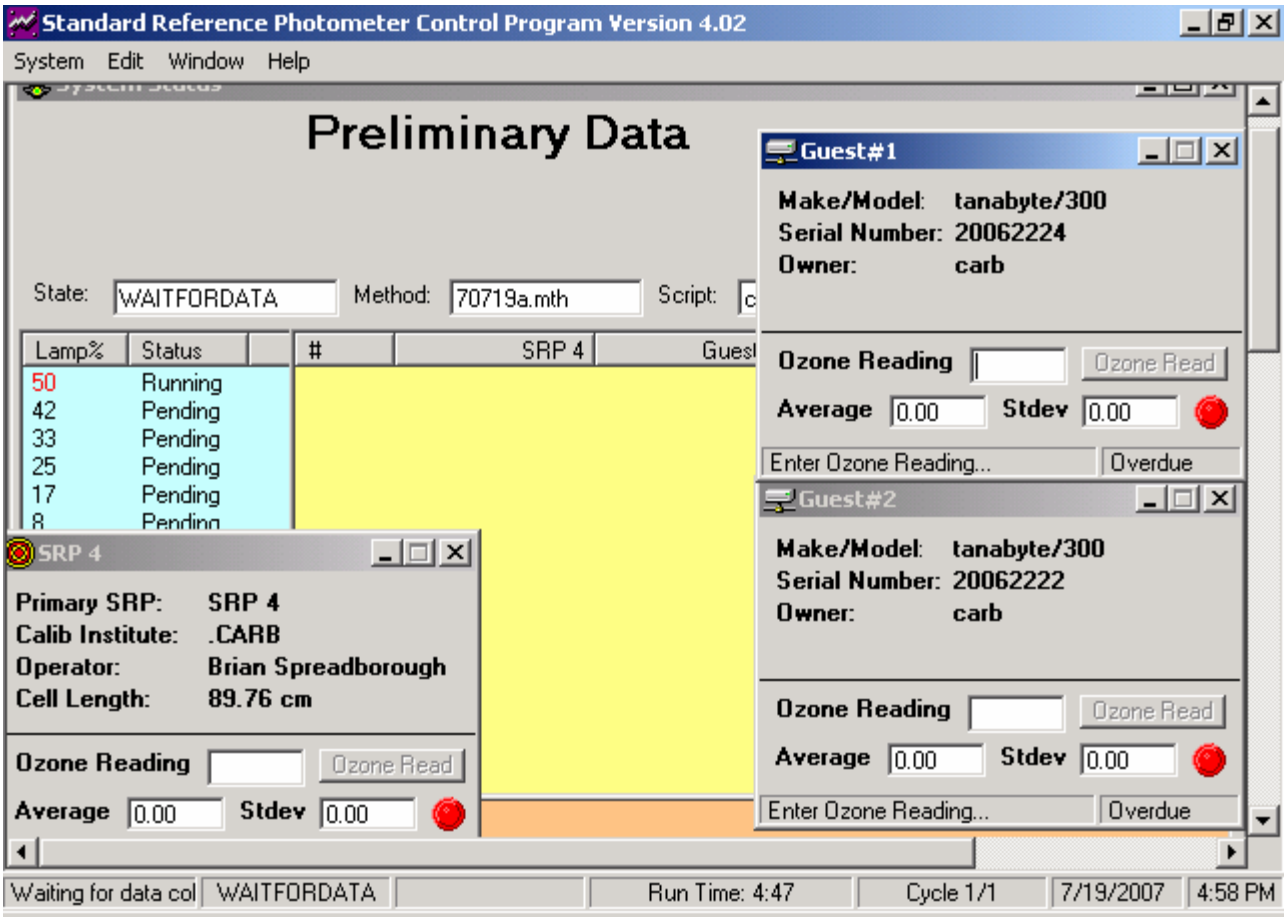
5.12.2 In the File name area, type the date, i.e. 70711a would indicate the year 2007 (7), the month (07) and the day (11). a indicates the first assay of the day, b would indicate the second, c the third etc.

5.12.3 Click **Save**.

5.12.4 Calibration Information and Setup screen will be displayed again. Click on **OK** to start the assay.



5.12.5 Standard Reference Photometer Control Program Version 4.02



5.12.6 Switch the pump on the Standard Reference Photometer pneumatics.

5.12.7 The SRP program is now ready to accept data from the ozone instrument(s) being assayed. The ozone generator of the Environics 9100 will be set at the following points throughout the assay.
Range 1000ppb. 0, 900, 90,740, 260, 420 and 50.
Range 500ppb. 0, 450, 45,370, 130, 210 and 25.

5.12.8 The program is accepting data, for the first point, 0 **Enter** the instrument reading into the ozone reading box. The program allows 30 seconds to enter the data. Once the readings have stabilized,

indicated by a Stdev of less than 1 of both the SRP reading and the instrument being assayed, the red indicators will turn green. At this point the program will indicate actual data. After ten entries the status column will indicate complete and the Enter ozone reading will indicate done. Repeat this process for the other 6 ozone concentrations. After completion of the data the following results will be printed.

5.12.9 Standard Reference Photometer Calibration Report

Standard Reference Photometer
Calibration Report

Calibrating Institute:	.CARB	**Date:**	19-Jul-07
Operator:	Brian Spreadborough	**Start Time:**	8:26
Instrument:	SRP 4 Cell Length=89.76	**End Time:**	11:12
Comment:		**Filename:**	c0719001.xls

Calibrated Instrument:	Guest#1	**Calibration Results**	**Value**	**Standard Uncertainty**
Owner:	monterey	**Slope**	1.00303	0.00079
Contact:	walt mcdonnell	**Intercept**	1.65699	0.36552
Make:	api	**Covariance**		-3.1281E-07
Model:	401	**Res Std Dev**	0.60145	
Serial Number:	107251			

Calibration Parameters: Dark Count On (4)
Air Flow Rate: 5.0 l/min
Lamp Intensity Range: 0.0 to 50.0 %
Number Conc. Points: 7 **Points/Concentration:** 10
Conditioning: none

Calibration	SRP 4		Guest#1		Guest#1	
Data Points	Result	Std. Dev	Result	Std. Dev	Predicted	Residual
Dark Count 1	7					
Dark Count 2	8					
1	0.1	0.2	2.0	0.2	1.74	0.21
2	871.0	0.9	876.2	0.6	875.29	0.93
3	87.0	0.2	88.9	0.4	88.96	-0.08
4	712.5	1.1	715.4	0.2	716.34	-0.96
5	251.2	0.5	254.0	0.5	253.64	0.31
6	405.0	0.5	407.4	0.1	407.90	-0.48
7	47.8	0.2	49.7	0.1	49.58	0.08
	*		*			

Page 1 of 2

5.12.10 Transpose the data from SRP 4 Result and Guest#1 Result onto the ozone Instrument Data sheet. Note the guest data is entered in ppm and the SRP in ppb.

5.13 Ozone Instrument Assay Data

State of California-Air Resources Board
Ozone Instrument Assay Data Sheet

Log Number: 2007 159 Date: 7 / 19 / 2007

Guest Ozone Instrument	SRP#4
Instrument Model: API 401	Temperature(T): 23.5 °C
Property No. : 107251 Serial No.:	Pressure(P): 1013.1 mb
Samp. Freq : 4011 (Ini) 4160 (Fin)	Scaler 1: 104431
Cont. Freq : 4011 (Ini) 4179 (Fin)	Scaler 2: 98423
Air Flow: 0.822 SLPM at 0.380 Flow Setting	Atm. Pres. (P_A): 760.7 mm Hg
Offset: 2.0 Slope: 1.005	Atm. Temp.(T_A): 21 °C
Chamber Temp.: 24 °C Chamber Pres.: 29.5 atm	File No.: 70719A
Analyzer/Transfer Standard [X] Primary Standard [ ]	

Air Flow	13 LPM								
O_3 GENERATION	0	900	90	740	260	420	50		
Guest (ppm)	.002	.876	.089	.715	.254	.407	.050		
SRP (ppb)	0.1	871.0	87.0	712.5	251.2	405.0	47.8		

COMMENTS:

Calibrated by: BJS Checked by: RK.

Ozone 2007

5.13.1 Entry of data into Instrument Management System IMS

5.13.2 On computer, type “IMS” and press the **Enter** key to accept.

5.13.3 Scroll down to “10. Inst. Calibration”, and press the **Enter** key to accept.

5.13.4 Enter the ARB barcode number for the instrument, and press the **Enter** key to accept.

5.13.5 Enter the instrument log number and date of calibration. Press the **Enter** key to accept.

5.13.6 Enter “Y” if performed an instrument calibration, or “N” if other. Press the **Enter** key to accept.

5.13.7 The computer will display several datapoints. If the datapoints are correct, enter “Y”, or enter “N” to edit the datapoints. Press the **Enter** key to accept.

5.13.8 If enter “N”, edit values to match those targeted during the calibration. Enter “Y” after completing edits. Press the **Enter** key to accept.

5.13.9 Enter initial and final sample and control frequency values from test data sheet. Enter instrument temperature and pressure values. Enter SRP Scaler 1, Scaler 2, Pressure, and temperature values. Enter ambient pressure and temperature values from test data sheet. Press the **Enter** key to accept.

5.13.10 Enter “A” if instrument is a transfer standard or “P” if a primary standard photometer. Press the **Enter** key to accept.

5.14 Enter instrument response from on the test data sheet (entered in ppm) and the SRP response (entered in ppb). Press “Y” after all data entered correctly, or “N” to edit data. Press the **Enter** key to accept.

5.14.1 Print calibration data by selecting the first option. Press the **Enter** key to accept. Press shift and continue on printer when pompted to print results.

5.14.2 Print the certification results by selecting the second option. Press the **Enter** key to accept. If instrument results meets the certification criteria, press shift and continue on the printer when prompted to print.

5.14.3 If instrument results does not meet the certification criteria, enter “Y” or “N” to print certification results. Press the **Enter** key to accept, and press the shift and continue on the printer when prompted.

5.14.4 Print the instrument report by selecting the third option. Press the **Enter** key to accept, and press shift and continue on the printer when prompted.

5.14.5 Press the Esc key twice, and quit the Instrument Management System by selecting the last option. Press the **Enter** key to accept.

5.15.6 At the Dos prompt, type “Exit” and press the **Enter** key to accept.

5.15.7 On SRP control box, turn off pump.

5.15.8 If instrument certification or verification is complete, denenergize instrument. Disconnect power cable and sample lines. Cap the ends of the sample lines to prevent contamination.

6 INSTRUMENT UNDER TEST SOP

6.1 General

6.2 The following instrument SOPs are the most common models operated by the Standards Laboratory. For instruments not covered by the following SOPs, refer to the instrument’s operation manual to obtain the following data: sample frequency, control frequency, sample temperature, sample pressure, and sample flow setting. Use a Vol-O-Flow meter to obtain actual sample flow rate.

6.3 DASIBI 1008-PC

6.4 Place the **Mode** selector switch to the **Sample/Temp** position. With the **T/P** switch in the **On** position, record the instrument’s chamber temperature on the test data sheet.

6.5 Place the **T/P** switch in the **Off** position, record the instrument’s sample frequency on the test data sheet.

6.6 Place the **Mode** selector switch to the **Control/Press** position. Record the instrument’s control frequency on the test data sheet.

6.7 Place the **T/P** switch in the **On** position, record the instrument’s pressure on the test data sheet.

6.8 Place the **Mode** selector switch to the **Operate** position.

6.9 Remove the instrument’s cover panel, record the three **SPAN** thumbwheel settings on test data sheet.

6.10 Record the instrument’s **ZERO** thumbwheel setting on the test data sheet.

6.10.1 Replace the instrument's cover panel.

6.10.2 Using a Vol-o-Flow flow meter, measure and record the instruments sample flow rate on the test data sheet. Also record the flow rate setting on the instrument's rotameter.

6.10.3 DASIBI 5009-CP

6.10.4 Record the instrument's **Span** and **Offset** settings from thumbwheels on front panel onto the test data sheet.

6.10.5 Using the **DIAG.** thumbwheel, select diagnostics "3". Record the temperature and pressure readings on the test data sheet.

6.10.6 Using the **DIAG.** Thumbwheel, select diagnostics "5". Record the sample and control frequencies onto the test data sheet. The top value is the sample frequency, and the bottom value is the control frequency.

6.10.7 Return the **DIAG.** thumbwheel to "0".

6.10.8 Using a Vol-o-Flow flow meter, measure and record the instrument's sample flow rate on the test data sheet. Also record the flow rate measure on the instrument's rotameter.

6.10.9 DASIBI 1003-PC/AH

6.10.10 Record instrument **Span** and **Offset** settings from dials on front panel onto the test data sheet.

6.11 sing the mode selector switch, select the **Sample** setting. Allow unit to update the display several times and record value on the test data sheet.

6.11.1 Using the mode selector switch, select the **Cont.** setting. Allow unit to update the display several times and record value on the test data sheet.

6.11.2 Return the mode selector switch to **Operate**.

6.11.3 Using a Vol-o-Flow flow meter, measure and record the instrument's sample flow rate on the test data sheet. Also record the flow rate measure on the instrument's rotameter.

6.11.4 API 400/401

6.11.5 Using the **TST>** key, toggle until “Press = XX.X In-Hg-A” is displayed, record value as instrument’s pressure reading on test data sheet.

6.11.6 Press the **TST>** key once, record value as instrument’s flow setting on test data sheet.

6.11.7 Press the **TST>** key once, record value as instrument’s temperature reading on the test data sheet.

6.11.8 Press the **TST>** key until the instrument’s slope value is displayed. Record value as instrument’s span setting on test data sheet.

6.11.9 Press the **TST>** key once, record the displayed value as instrument’s offset setting on test data sheet.

6.11.10 Using a Vol-o-Flow flow meter, measure and record the instruments sample flow rate on the test data sheet.

6.12 ENVIRONICS 6103

6.12.1 Press **F3** under Photo display, press **F2** under detail.

6.12.2 Record photometer frequencies xxxxxx/xxxxxx, pressure P, temperature T and flow F.

6.12.3 To record offset, press **Exit**, Conc, Flow, Photo will be displayed. Press **Menu** twice; press the **F1** key under system.

6.12.4 Use the down key to scroll to calibrate photo. Press **enter** key, record offset and gain values, press accept. Press **exit,** then **menu**, press photo then detail. Instrument is now ready to assay.

6.12.5 TANABYTE 300

6.12.6 Screen displays O3 Prs ,Phot Temp, record these parameters on form ozone 2007.

6.12.7 Press **Esc**, then 2, Control, then 3, Manual control. From the manual control menu, press 2 for flows and then Enter. Press 4 for air flow (LPM), and then Enter. For gas flows, press 0, and then Enter. Are you sure? Will be displayed. Press up arrow, and then Enter to accept. Manual flow will now start.

6.12.8 On manual control menu press 3 for ozone intensity, enter 0 for intensity % Enter. Are you sure? Will be displayed, press up arrow key**, Ent** to accept. Press **Esc** for the main menu.

6.12.9 From main menu press 4: Test, from test menu press 2: view parameters. From view parameters press 5: Photometer. From view photometer press 2: Photo Cal. Record slope and intercept. Press **En**t. To exit. Record Det I and Det I0 as frequencies on form ozone 2007. The instrument is now ready to assay.

7 QUALITY CONTROL PRACTICES

7.1 QUARTERLY PRACTICES

7.2 An Advanced Pollution Instruments, model 400 (ARB barcode #20004767), is used as a control standard. This instrument is compared to the SRP on a quarterly basis. A control chart is derived from historical comparisons. From the control chart, warning and out of control limits are defined.

7.3 For warning limit violations, investigations are initiated into the quality of house air, parameters associated with the SRP.

7.4 For out of control limit violations, no instrument comparisons are allowed until the cause is found. Perform all the checks associated with a warning limit violation. If no cause is revealed, a request for a comparison with another SRP should be made to U.S. EPA; No further instrument comparisons should be made until the results of the SRP comparison is analyzed.

7.5 ANNUAL PRACTICES

7.6 A second SRP (SRP #7) is used to verify the proper operation of the SRP. Originally, U.S. EPA was performing this verification annually. However, the SRP's historical accuracy and stability has allowed it to be verified on a biennial basis. U.S. EPA ships SRP #7 and the Standards Laboratory perform the comparison. The Standards Laboratory strictly follows Section 9.0 of Reference 9.2 during the performance of the verification.

8 REFERENCES

8.1 Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone. Technical Assistance Document, EPA-600/4-79-056 September 1979, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.