Standard Operating Procedures for Temperature Calibration of the Sample Thermocouple in a Sunset Laboratory or a DRI Model 2001 Carbon Aerosol Analyzer

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1.0 Scope and Application

This is a step-by-step procedure for calibrating the sample oven thermocouple of a carbon aerosol analyzer to achieve a desired sample temperature profile for thermal-optical analysis. This procedure applies to both Sunset Laboratory carbon aerosol analyzers and the Desert Research Institute DRI Model 2001 carbon aerosol analyzer. The procedure is non-destructive to any component of the analysis system and therefore may be used to calibrate the thermocouple in the same system that will be used for analysis of filter samples.

2.0 Summary of Method

This procedure uses a second thermocouple positioned to just touch a punch from a quartz filter in the center of the spot illuminated by the red light laser used to determine the OC/EC split time. The sample boat and filter punch are in the same position both would be in during analysis of filter samples. Actual sample temperature readings from the second thermocouple are paired up with sample oven thermocouple readings taken at the same time are then used to develop a calibration curve, which in turn is used to calculate sample oven thermocouple temperatures required to achieve the target sample temperatures for analysis.[1,2]

3.0 Interferences

None

4.0 Required Equipment

4.1 Omega HH306 Thermocouple Data Logger, or equivalent

4.2 Omega Type K Thermocouple

4.2.1 P/N TJC36-CAIN-032U-9-CC-SB-SMPW-M, 0.75 mm (0.032 in) diameter, or equivalent, for 1-mm ID quartz tube

4.2.2 P/N TJC36-CAIN-032U-9-CC-SB-SMPW-M, 1.0 mm (0.040 in) diameter, or equivalent, for 2-mm ID quartz tube.

NOTE: Data Logger and Thermocouple must be calibrated as a unit to NIST-traceable standards by Omega Engineering Inc., or an equivalent metrology laboratory.

4.3 Equipment specific to Desert Research Institute DRI Model 2001 OC/EC Analyzer

4.3.1 Quartz tube, 1-mm or 2-mm ID (to fit OD of external thermocouple) of same OD (3 mm) and length as upper light pipe, available from URG, Inc., or equivalent provider

4.3.2 Swagelok union with 1/8-in fittings

4.3.3 Teflon front and back ferrules (1/8-in, to seal quartz tube inside Swagelok union)

4.3.4 1/8-in OD septum cut to about 2-mm thick (to seal thermocouple inside Swagelok union). With a needle probe, make a small hole through the center of the septum.

4.3.5 Quartz cross oven upper arm high temperature seal (P/N 2001-006) and quartz light pipe to arm high temperature seal (P/N 2001-007).

4.4 Equipment specific to Sunset Laboratory OC/EC Analyzer

4.4.1 Quartz boat with extended hollow handle (for thermocouple), available from Sunset Laboratory, Inc., or an equivalent device.

4.4.2 Swagelok union T with 1/8-in fittings on base and one side arm and 1/4-in fitting on remaining side arm.

4.4.3 1/8-in OD septum cut to about 2-mm thick (to seal the external thermocouple and the end of the quartz tube boat handle inside the Swagelok union T).

5.0 Equipment Setup and Handling

The same thermocouple and data logger could be used for both analyzers; however, the tip of the thermocouple must be bent slightly for the Sunset Laboratory temperature calibration setup. Ideally, separate thermocouples, each separately calibrated as a unit with the Data Logger, should be used for the two different analyzers.

6.0 DRI Model 2001 Temperature Measurement

6.1 Position the quartz boat in the Load position,

6.2 Place a clean quartz filter punch in the quartz boat of the analyzer and insert the boat into the quartz sample oven to the Analyze position. The filter punch will be centered under the end of the quartz tube and the external thermocouple.

6.3 Turn the analyzer power switch to the off position, and disconnect the power cord from the electrical outlet.

NOTE: To prevent unwanted movement of the quartz boat, leave the DRICarb analyzer control software running on the computer throughout the following temperature calibration setup and procedures.

6.4 Remove the left and right top covers from the analyzer.

6.5 Remove the front sample oven heater plate, and then remove the optical cable from the top quartz light pipe.

6.6 Carefully remove the top quartz light pipe from the upper arm of the quartz sample oven.

6.7 Slide the Swagelok nut then the Teflon ferrules onto the upper end of the 3-mm OD quartz tube.

6.8 Insert the quartz tube into the upper arm of the quartz sample oven.

6.9 Attach the septum to one end of the Swagelok union with a Swagelok nut.

6.10 Insert several inches of the thermocouple through the septum, and then carefully slide the thermocouple into the quartz tube until the Swagelok nut on the quartz tube can be attached to the Swagelok union.

NOTE: At this point, the Swagelok union will extend vertically above the quartz tube with the thermocouple passing through the union. The Teflon ferrules in the lower nut of the union will form a seal between the quartz tube and the union, and the septum in the upper nut of the union will form a seal between the thermocouple and the union.

6.11 Carefully slide the thermocouple downward through the quartz tube until the tip just touches the quartz filter on the quartz boat.

6.12 Reinstall the front sample oven heater plate.

6.13 Route the portion of the thermocouple above the light pipe such that both analyzer covers can be reinstalled.

CAUTION: Make sure that the portion of the thermocouple extending outside the sample oven remains a safe distance from the heater power wires.

6.14 Connect the external thermocouple lead to the Data Logger.

6.15 Reinstall both the left and right analyzer top covers.

6.16 Load the heating profile named cmdExtTherm_IMP_A_yyyymmdd, where yyyymmdd is the date of the previous temperature calibration.

NOTE: This heating profile is exactly the same as the IMPROVE_A_yyyymmdd profile of the same date, but all sample boat movements have been removed from this profile. The boat must not move while the thermocouple tip is touching the quartz filter punch on the boat.

6.17 Type in a name (TCTempCal_n, where n = run number) for the temperature calibration run as the Sample ID. Fill in the other required fields on the display screen, but do not start the run yet.

6.18 Power on the Data Logger; and start recording data to the Data Logger.

6.19 Start the temperature calibration run on the DRI software.

6.20 Allow the Data Logger to collect data until the DRI software ends the temperature calibration run.

6.21 Run at least three temperature calibration runs (Sections 6.17 through 6.20) using the Data Logger to record the external thermocouple readings.

6.22 When sufficient data for the temperature calibration have been obtained and an acceptable temperature calibration curve has been calculated, turn the analyzer power switch to the off position, and disconnect the power cord from the electrical outlet.

6.23 Remove the external thermocouple, Swagelok union, and quartz tube.

6.24 Replace the quartz cross oven upper arm high temperature seal (P/N 2001-006) and quartz light pipe to arm high temperature seal (P/N 2001-007).

6.25 Reinstall the top quartz light pipe and optical cable, and put the covers back on the analyzer.

6.26 Re-connect the power cord and turn the analyzer power switch to the on position.

6.27 Verify that there are no leaks in the system before proceeding with any analyses.

7.0 Sunset Laboratory Carbon Aerosol Analyzer Temperature Measurement

7.1 Power off the analyzer and unplug it from the electrical outlet.

7.2 Remove the cover from the analyzer.

7.3 Remove the reflectance photometer from the top vertical tube of the quartz sample oven by loosening the two set screws on the photometer and lifting the photometer straight up.

7.4 Remove the front oven quartz cap with its Swagelok union.

7.5 Replace the Swagelok reducing union (1/4-in to 1/8-in) with a Swagelok T (1/8-in fittings on base and one side arm and 1/4-in fitting on remaining side arm).

7.6 Place a small septum in the 1/8-in end of the crossbar and seal it in place with a Swagelok 1/8-in nut. If the septum does not already have a small hole in it, pierce the center of the septum with a needle probe.

7.7 Insert the thermocouple through the septum, through 1/8-in Teflon ferrules, through the crossbar on the Swagelok union T, through a ¼-in Swagelok nut with Teflon ferrules on the other end of the crossbar, through the oven cap, and finally through the handle of the Sunset Laboratory special quartz oven boat.

7.8 Make sure that:

- the thermocouple is sealed in the hole through the septum;
- the quartz tube handle of the quartz boat is sealed in place by the 1/8-in Teflon ferrules around it and by the septum at its end; and
- the quartz oven cap is sealed to the union T by the ¼-in Teflon ferrules.

7.9 Place a quartz filter punch of the appropriate size in the special quartz boat, and bend the tip of the thermocouple until the tip just touches the center of the surface of the quartz filter punch on the boat.

7.10 Insert the special quartz boat-thermocouple assembly into the sample oven of the Sunset Laboratory analyzer and attach the oven cap to the oven with the usual clamp.

7.11 Looking down through the top vertical arm and upper quartz window of the sample oven while shining a light in from the front of the sample oven, position...

- the boat in the oven so that the punch is in a horizontal position and centered under the top quartz window; and
- the thermocouple tip is

  = bent slightly downward,

  = just touching the center of the punch, and

  = centered under the top quartz window.

NOTE: The hollow-handled quartz boat used for temperature calibration can be moved in or out of the oven by a few mm by altering the distance the quartz oven cap is inserted through the Teflon ferrules into the Swagelok T.

7.12 Reinstall the reflectance photometer on top of the upper vertical tube of the quartz oven.

7.13 Disconnect the helium supply line from the operational front oven quartz cap Swagelok union and connect the helium supply line to the Swagelok tee on the test quartz cap.

7.14 Put the top cover back on the analyzer.

7.15 Plug the analyzer back into the electrical outlet, and power up the analyzer.

7.16 Start the Sunset Laboratory instrument control software.

7.17 Let the analyzer warm up until the temperature of the back (oxidation) oven is within its acceptable operating range.

7.18 Type in a name for the temperature calibration run as the Sample ID. Fill in the other required fields on the display screen, but do not start the run yet.

7.19 Connect the test thermocouple to the Data Logger.

7.20 Power on the Data Logger, and start recording data to the Data Logger.

7.21 Start the temperature calibration run on the Sunset Laboratory software.

7.22 Allow the Data Logger to collect data until the Sunset Laboratory instrument control software ends the temperature calibration run.

7.23 Run at least three temperature calibration runs using the Data Logger to record the external thermocouple readings.

7.24 When sufficient data for the calibration have been obtained and calculations have verified a successful temperature calibration:

7.24.1 Disconnect the gas supply line from the Swagelok T,

7.24.2 Remove the horseshoe clamp, and

7.24.3 Carefully remove the oven cap, Swagelok T, quartz boat with extended hollow handle, and thermocouple either as a unit (if calibrating another analyzer) or as separate pieces (for storage).

7.24.4 Reassemble the original oven cap, Swagelok union, and gas supply line.

8.0 Calculations

8.1 Create an Excel workbook for the temperature calibration.

8.1.1 Create a Raw Data spreadsheet, and paste the raw data for the run from the analyzer raw data file into the spreadsheet.

DRI Model 2001 Raw Data: The DRI Model 2001 analyzer software generates one row of data per second in the Raw Table. The row number in the Raw Table is the number of elapsed seconds for the analysis.

Sunset Laboratory Analyzer Raw Data: The Sunset Laboratory software generates one row of data per 60/57 seconds. To get an accurate measure of elapsed time for a temperature calibration:

1- Paste the raw data for the temperature calibration run into a spreadsheet.

2- Insert two columns to the left of the raw data in the spreadsheet. Type Row No. and Elapsed Time as the headers to the two columns.

3- Type a 1 in the first cell under Row No. Select all cells in the Row No. column from the 1 to the bottom of the data set. Use the Edit, Fill, Series, and Linear commands to place a row number beside each row of data.

4- Type an equation in the first cell under Elapsed Time that will multiply the Row Number by 60 divided by 57. Select all cells in the Elapsed time column from the equation just typed in to the bottom of the data set. Use the Edit, Fill, and Down commands to copy the formula to the bottom of the data set. Use the Elapsed Time column as the x-axis in all plots.

8.1.2 Paste the raw data for the run from the Data Logger into the same Excel spreadsheet beside the raw data from the analyzer. The Data Logger records a temperature reading every second.

8.1.3 Create a Temperature Profiles chart showing elapsed time (in seconds) for the analyzer data on the x-axis and temperatures from both the analyzer and the Data Logger thermocouples on the y-axis.

8.1.4 Move (by copying and pasting or by changing the ranges) the block of Data Logger data up or down in the spreadsheet until the sharp temperature increases associated with oven temperature ramps occur at about the same elapsed analysis time (on the x-axis).

8.1.5 Create a Temperature Calibration chart showing the External Thermocouple Temperature (from the Data Logger) on the x-axis and the Analyzer Thermocouple Temperature on the y-axis. Add a Trendline (see NOTEs below) to the chart, and turn on the “Display equation on chart” and “Display R-squared value on chart” options in the Format Trendline window.

NOTE: The sample oven and external thermocouples have different diameters, and the smaller diameter thermocouple generally responds more quickly to changes in oven heater output. This difference will be obvious on the Temperature Calibration chart.

NOTE: A linear Trendline works well for a DRI Model 2001 analyzer.

NOTE: A 4^{th} order polynomial Trendline works best for a Sunset Laboratory analyzer. (The Sunset Laboratory analyzer software allows individual control settings for temperature, power constant, time constant, and blower mode for each stage of the analysis. As a result, the temperature can be controlled more precisely but the mathematical relationship between the temperatures measured by the analyzer and external thermocouples is more complex.)

8.2 Display the Temperature Calibration curve.

8.2.1 Insert a column in the Raw Data spreadsheet between the analyzer raw data and the Data Logger raw data. Type in "Use?" as the header for the inserted column.

NOTE: If necessary, split the view of the spreadsheet until both temperatures (analyzer thermocouple and Data Logger thermocouple) can be easily compared.

8.2.2 Look at the Heating Profiles chart to determine the time ranges when both thermocouples were giving stable, constant or nearly constant readings (i.e., the plateaus in the heating profiles). In the spreadsheet, place an x in rows of data where both thermocouples were at their respective plateaus in the heating profiles during a particular time period.

8.2.4 In the Raw Data spreadsheet, select all of the data including the header row. Turn on the Excel Auto Filter feature by clicking Data, Filter, AutoFilter. Click the arrow in the down box in the "Use?" column and select "x".

8.2.5 The Raw Data spreadsheet, the Heating Profiles chart, and the Temperature Calibration chart should now display only the points marked with an "x," which corresponds to the temperature plateaus of the two profiles. The Trendline equation in the Temperature Calibration chart is now calculated based on only the displayed data points, which will be clustered in small areas corresponding to the temperature plateaus in the heating profile.

8.3 Prepare a Raw Data spreadsheet, Heating Profiles chart, and Temperature Calibration chart for each temperature calibration run.

NOTE: The one spreadsheet and two charts required for each of the three runs can be created in the same Excel workbook or in separate workbooks. Creating them in the same workbook allows the possibility of using within-workbook links to prepare a summary table across all three runs.

8.4 Use the equations from the Excel Trendlines of the three (or more) Temperature Calibration charts to calculate the specific target analyzer thermocouple temperatures needed to obtain the Target Temperatures required for the particular OC/EC analysis method. The table below illustrates the results obtained from a temperature calibration for IMPROVE_A on a Sunset Laboratory Dual-Mode Analyzer using 4th order polynomial trend lines.

IMPROVE_A Temperature	Target SSL F Analyzer Thermocouple Reading			
	From TempCal1	From TempCal2	From TempCal3	Average
140°C	212°C	212°C	214°C	213°C
280°C	364°C	366°C	366°C	365°C
480°C	545°C	547°C	547°C	546°C
580°C	646°C	648°C	647°C	647°C
740°C	826°C	828°C	826°C	827°C
840°C	936°C	938°C	934°C	936°C

9.0 Implementation of Calibrated Heating Profiles

9.1 DRI Model 2001

9.1.1 Start the CarbonNet Access database application and load the most recent temperature-calibrated analysis parameter file.

9.1.2 Adjust the temperature ramps in the parameter file to give the desired temperature-calibrated target temperatures during a regular analysis.

9.1.3 The final parameter file should look something like the table below.

Typical Parameter File for Temperature-Calibrated IMPROVE_A Analysis on a DRI Model 2001

Sec	Event	Action	Params	Temp	CLV	BVs	FVs	SO	SPS
1	InitTemp	Flat		5					
2	InitDigital	DigOut			Inject	Closed	Close	On	
3	Cool_100	Cool	Temp=100						
5	InitSPS	DigOut	Trigger=Calibrate						Calibrat
28	Cool_50	Cool	Temp=50						
30	Move	DigOut	Trigger=Load						Load
57		SoundO	Wav=LoadFltr.wav;Time=Once						
60		Pause	Delay=0;Prompt=Load Sample						
62	Move	DigOut	Trigger=Calibrate						Calibrat
84		SoundO	Wav=Proceed.wav;Time=Once						
88		Pause	Delay=90;Prompt=Continue?						
90		DigOut				Open		On	
90	DataOn	DataOn							
140	FIDBaseline	Null							
148		DigOut						Off	
150	Move	DigOut	Trigger=Analyze						Analyze
180	OC1	Peak	Trigger=Slope;Min=150						
185		Flat		117					
190	LaserBaselin	Null							
285	OC1	Flat		122					
780	OC2	Peak	Trigger=Slope;Min=150						
781		Flat		245					
831		Flat		261					
138	OC3	Peak	Trigger=Slope;Min=150						
138		Flat		450					
143		Flat		459					
198	OC4	Peak	Trigger=Slope;Min=150						
198		Flat		550					
200		Flat		558					
258	EC1	Peak	Trigger=Slope;Min=150;Xsearch=on						
258		DigOut					Open		
258		Flat		558					
318	EC2	Peak	Trigger=Slope;Min=150						
318		Flat		717					
378	EC3	Peak	Trigger=Slope;Min=150						
378		DigOut			Load				
378		Flat		816					
430		Flat		5					
432	Calib	Peak	Trigger=Slope;Min=150						
432		DigOut			Inject				
468		SoundO	Wav=AnaDone.wav;Time=Once						
468	Report	Report	protocol=improve						
468		DigOut						On	
468	Cool_100	Cool	Temp=100						
480	Move	DigOut	Trigger=Calibrate			Closed	Close	Off	Calibrat
481		SoundO	Wav=NextAnalysis.wav;Time=Once						
482	Stop	Stop							

9.2 Sunset Laboratory Carbon Aerosol Analyzer.

9.2.1 Open the most recent temperature-calibrated parameter file in an ASCII text editor.

9.2.2 Adjust the analyzer target temperatures in the parameter file to achieve the actual target thermocouple temperatures based on the averages from the new temperature calibration plots.

9.2.3 The final parameter file should look something like the one shown in the table below. Save the parameter file with a filename that includes the date (yyyymmdd) of the temperature calibration.

Typical Parameter File for Temperature-Calibrated IMPROVE_A Analysis on a Sunset Lab Analyzer

```
' improve-A.par
' Temperature Calibrated on 24 Sep 2008
' mode <comma> time <comma> temperature
'n.b. regimen must end 'Offline' mode.
Helium, 10, 1,.001, 100, 8
' start ramping the temperature
Helium, -1, 228, .0285, 120, 6
Helium, -1, 373, .07, 95, 4
Helium, -1, 550, .165, 65, 0
Helium, -1, 651, .175, 50, 0
Oxygen, -1, 651, .175, 50, 0
Oxygen, -1, 831, .30, 35, 0
Oxygen, -1, 940, .32, 25, 0
CalibrationOx, 110, 1,.001, 100, 16
' All done!
Offline, 1, 0,.001, 100, 16
' end.'format
'Mode; time; temperature; power constant; time constant; blower mode
'power constant - .0001 to 1; think of it as a percentage
'typical .01 to .4  must be positive
'time constant (seconds) - 1 to 200  must be positive
'typical - 10 to 120
'low temperature - long time constant; low power
'high temperature - high power; short time constant
'blower speed - 0 and 3 to 16; 0 = off; 16 = full
'do not run blower at settings of 1 or 2 - too slow
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End Notes

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[1] Steve Taylor, Jr., and Jewell Smiley of EPA/NAREL in Montgomery, Alabama, used an external thermocouple to measure the temperature gradient along a 1.0 cm wide x 1.5 cm long quartz filter punch during STN/TOT analysis in July 2004. They used a similar arrangement to calibrate the analyzer thermocouple in a dual-mode Sunset Laboratory analyzer in December 2007 to perform IMPROVE_A analysis.

[2] Chin H. Phauh and Ann M. Dillner of the University of California Davis have reported using an external thermocouple to calibrate the temperature at the center of a quartz filter punch in a dual-mode Sunset Laboratory analyzer to do IMPROVE_A OC/EC analysis. Their paper, "Volatility of Organic Material from Quartz Filters: Research Methods and Preliminary Results," was presented at the A&WMA's Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA. May 1–3, 2007.