

IMPROVE Carbon Analysis

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Objectives

- Report status of IMPROVE carbon analyses
- Enumerate improvements on carbon analyzers

Summary of Carbon Lab Operations

- Maintained 24 hours per day/6-7 days per week operation with 2 full-time and 4 part-time staff
- Recruited Post-Doctoral Fellow Jerome Robles (Chemical Engineer) to perform calibration and maintenance
- Completed IMPROVE backlog (June 2009)
- Analyzed over 23,000 IMPROVE samples (June 2010)

IMPROVE Carbon Analysis following the IMPROVE_A^a Protocol (7/09 – 6/10)

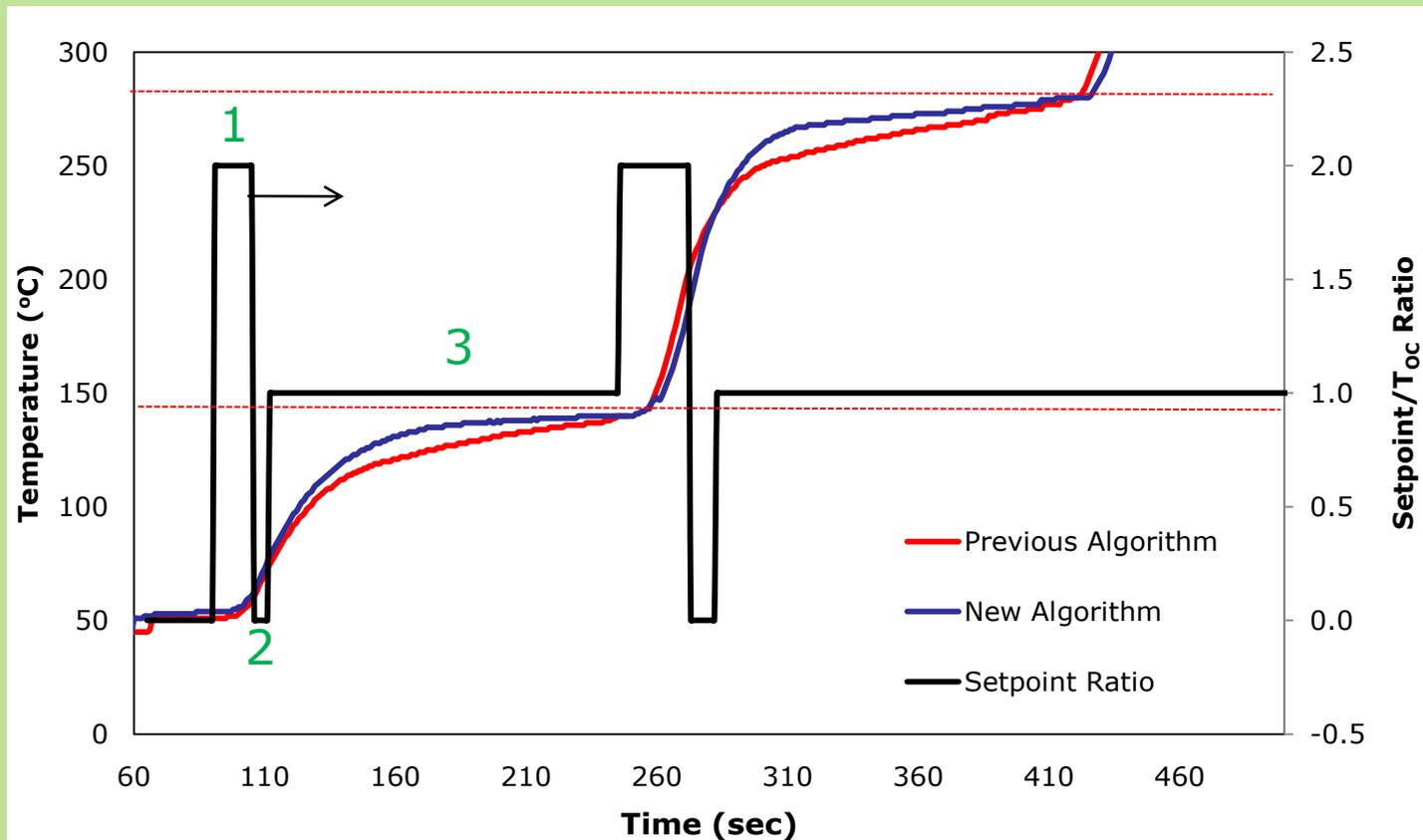
Sampling Period	Samples Received	Analysis Completion Date^b
7/1/09-12/31/09	11,390	2/21/10
1/1/10-6/30/10	10,880	9/9/10

^a Chow et al. (2007)

^b Currently analyzing August and September 2010 samples

Refine Temperature Ramping for OC1 and OC2

- Create three set points:
 1. Force a 100% controller output (rapid heating)
 2. Turn heater off (stabilization)
 3. Provide fine adjustments



Software Enhancements

- Integrate maintenance database
 - Improved maintenance guide
 - Revised electronic/mechanical trouble shooting guide
- Establish analyzer status program
 - Provides real-time monitoring of instrument operation with direct access to data summary
 - Improved database of maintenance, calibration, and analyses

Integrated Maintenance Database

Temperature Calibration

Date Performed	Tech		
<i>Next Scheduled Temp. Cal.: 1/29/2011</i>			
2010/07/29	JAR		
2010/01/21	CJO		
2009/07/19			
2009/01/26			
<i>Next Scheduled Temp. Cal.: 3/29/2011</i>			
2010/09/29	JAR		
2010/02/17	JAR		
2009/10/08			
2009/07/19			
2009/06/30			
2009/03/09			
2009/02/20			
<i>Next Scheduled Temp. Cal.: 3/29/2011</i>			
2010/09/29	JAR		
2010/03/29	JAR		
2010/01/22			
2009/07/31			
2009/06/01			
2009/01/09			

Scheduled Temperature Calibrations

Analyzer Maintenance Status

Date	Time	Status	Problem Class	Description	Tech
28-10-10	9:40 AM	OFFLINE	Other Accessory in comments	Motor starting when H2O2 valve opens. This occurs in the middle of a test.	JAR
28-10-10	1:37 PM	OFFLINE	Other Accessory in comments	Testing the H2O2 valve. This may have been responsible for the motor starting during the start of the BCT portion of the run.	JAR
29-10-10	6:47 PM	OFFLINE	Analyzer still being used for monitoring	Analyzer still being used for monitoring. Schedule a follow-up test. Results show reducing ferrous.	WTS
2-10-2010	10:08 AM	OFFLINE		Reduced reducing ferrous. Instrument currently used for sulfate testing/modification.	JAR
2-10-2010	1:12 PM	OFFLINE		LT and LR drop during H2O2 portion of test.	JAR
2-10-2010	9:28 AM	OFFLINE		Performing sulfate test. Problem with unknown. LT drop did not surface in H2O2 portion.	JAR
2-10-2010	2:00 PM	OFFLINE		Checked monitor wire connecting to the outside of cell body if service could affect monitoring at the next moment when the problem occurs.	JAR
2-17-2010	9:08 AM	OFFLINE		Checked thermocouple control. Performing blank runs to determine constant motor error. Seems to have been eliminated by restricting wire.	JAR
2-17-2010	8:48 AM	OFFLINE		Beer drift corrected. rechecked LT section and testing in R.	JAR
2-17-2010	10:48 AM	OFFLINE		Performing sulfate test.	JAR
2-17-2010	11:27 AM	OFFLINE		Passed sulfate test. Performing FREQUENCY comparison.	JAR
2-17-2010	1:13 PM	ONLINE		Passed RTI comparison.	JAR
28-10-10	5:14 PM	OFFLINE	Hardware Issue	MOTOR GRINDS	WFL
28-10-10	8:24 AM	OFFLINE		Motor grinding starts after BCT portion. Failed to observe motor BCT portion.	JAR
28-10-10	10:57 AM	OFFLINE		Loose wire where oxygen dissolved that may cause the motor grind. Secured the wiring and performing tests.	JAR
28-10-10	12:10 PM	ONLINE		Motor grinding most likely due to wiring problem. Secured wires and test.	JAR

Maintenance History For CA#10

Carbon Analyzer Maintenance

Summarized Entry (old Log Book)

by Analyzer

by Problem Type

by Date

Add Entry/
Write
Summary

Status Logger Maintenance Entry (new Log Book)

Show Complete Log

Show Log by Analyzer

Show Log by Date

Show Log by Specific Problem

Calibrations/Maintenance Guide

View Temperature Calibrations

Carbon Calibration

Print Temperature Calib. Checklist

Maintenance Manual

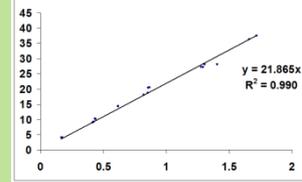
Print Troubleshoot Guide

Punch Calibration Calculator

Punch Calibration Calculator

Cal. Mtd	Run ID	Volume (g/L)	Inject Peak Counts	Cable Peak Counts	Tech	C in % H2O	Inject Peak/C	Calc. Peak/C	Slope	Dev. Slope average
SIC	SL_3	5	11020	20685	JAR	1.374	0.4323	22.19	-0.60	
SIC	SL_20	20	22675	20289	JAR	1.106	0.5564	21.56	-0.63	
SIC	SL_15	15	37478	29721	JAR	1.326	1.403	20.02	-2.53	
SIC	SL_10	10	32478	29721	JAR	1.188	1.302	21.63	-0.57	
SIC	SL_20	20	44659	26731	JAR	1.106	0.719	21.88	-0.33	
KMP	KMP_20	20	44243	26699	JAR	1.224	1.657	21.98	-0.43	
COL	CL_200	200	44697	24889	JAR	1.086	0.187	24.75	-1.14	
COL	CL_500	500	11337	26648	JAR	1.118	0.4323	23.85	-2.56	
COL	CL_700	700	14288	24994	JAR	1.128	0.615	23.48	-0.86	
COL	CL_1000	1000	23255	24872	JAR	1.128	0.386	23.83	-1.231	
OW	MC_500	500	4859	24673	JAR	1.128	0.175	23.43	-0.848	
OW	MC_500	500	11683	24748	JAR	1.141	0.437	23.43	-0.839	
OW	MC_700	700	18335	28939	JAR	1.134	0.614	23.34	-0.743	
OW	MC_1000	1000	23897	17633	JAR	1.128	0.584	23.86	-1.365	
KMP	KMP_15	15	34187	26553	JAR	1.201	1.298	21.18	-1.41	
KMP	KMP_10	10	33923	28627	JAR	1.182	1.274	21.45	-1.15	
KMP	KMP_20	20	22780	24642	JAR	1.121	0.819	22.34	-0.30	
KMP	KMP_3	3	10798	26331	JAR	1.186	0.413	22.06	-0.34	

Calibration Summary and Slope



Carbon Calibration Data Entry and Plot

Calculate Punch Area

Calibration of Punchers

Filter Size (mm)

No. of Punches

Put Info

Mass of Filter

Before Punch (g)

After Punches (g)

CALCULATE

Troubleshooting Guide

(accessible through Maintenance Database)

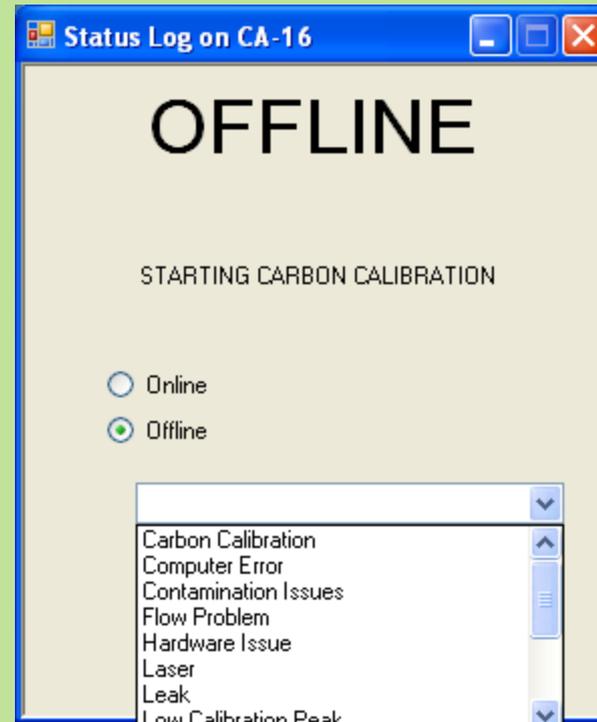
Troubleshooting Guide

Problem	Possible Cause	Explanation/Solution
Contamination in the EC3 region	Contaminant in the breech and in the "cooler" regions of the pushrod thermocouple	Wipe the entire length of the pushrod with Kimwipes and quartz filter. Bake oven. Perform blank runs until system is contaminant-free. There should be notable decrease in EC3 values for succeeding blank runs; otherwise this is not a contaminant-related issue.
	Electronic noise due to the sample oven temperature controller	This shows up as multiple "noise-like" peaks in the EC3 region. Confirm the temperature controller parameters (PidA, PidB, etc) and make appropriate adjustments.
	Electronic noise/drift due to damage in electrometer or improper grounding	This can show as a drift in the baseline that starts in any temperature region. The drift may also occur at random occasions for unknown reasons. If available, replace the electrometer circuit board and check if the old electrometer is indeed defective. If spare parts are not available, try grounding the electrometer and shield the entire FID assembly.
Low or Sudden Drop in Calibration Peak Area	Insufficient methane injected in the system due to system leaks	Test for system leaks. If detected, fix the leak and perform auto calibration to confirm that calibration peak is restored. The most common source of leak is the orange O-ring in the breech area. Replace this O-ring if signs of damage are observed.
	Fluctuations in gas flow	Check the rotameters. Confirm that the flows are equal to the specified values. Make all the necessary adjustments and confirm results with auto calibration run.
	Misaligned pushrod causing leaks and affects calibration peak area	This problem can sometimes cause leak when the boat is in one position but not in other positions. One of the major reasons for the misalignment is a wobbly breech because the support is not securely fastened. Try tightening the support by rotating until it penetrates more securely into the breech.
	Contamination in the calibration line due to the installation of new methane gas cylinder.	During calibration gas replacement, the calibration gas line may have allowed air into the system. Purge the gas line by connecting a syringe into the methane gas injection port and remove the syringe's plunger to allow faster purging of the calibration gas. Perform autocalibration to test calibration gas response. Check other carbon analyzers since this affects more than one instrument.
	No calibration gas flowing	Make sure that calibration gas is flowing into the system. Check the rotameter to determine if there is enough gas flowing. Sometimes, adjusting the calibration gas rotameter has a very long lag time that, in some cases, operators mistakenly close the valve

Analyzer Status Programs

- **Status Logger** program allows operator to record abnormal findings and provides analysis updates every two minutes
- **Status Viewer** program stores and provides real-time monitoring on any network PC

Status Logger Program



- Technician changes status on analyzer computer
- Instrument status is updated to server database every 2 minutes

Status Viewer Program

Carbon Analyzer Status



Carbon Analyzer Status

17



cmdBakeOven - JAR
labblk\lb\09242010
bake-1

19



ImproveA - TLB
IMPROVE\B10\F27
S26002-1

18



ImproveA - CDW
YALE\19NQ
Q6588500-1

11



ImproveA - TLB
IMPROVE\B10\F27
S26005-1

13



ImproveA - TLB
IMPROVE\B10\F27
S26006-1

8



cmdAutoCalibCheck - KMS
CALIB\102010\07
C0820101007-1

6



ImproveA - TLB
IMPROVE\B10\F27
S26004-1

12



ImproveA - TLB
YALE\19NQ
Q6588213-1

9



ImproveA - TLB
IMPROVE\B10\F27
S26009-1

7



ImproveA - TLB
IMPROVE\B10\F27
S26003-1

10



ImproveA - TLB
IMPROVE\B10\F27
S26007-1

16



ONLINE
10/11/2010 3:38:09 AM
IMPROVE\B10\F27
S26008-1

Maintenance Details of CA#16

08/27/2010	16:31:28	JAR	OFF	-REPLACED METHANATOR AND OXYGE NATOR OVENS; THERMOCOUPLE
08/30/2010	14:35:33		OFF	-
09/01/2010	13:17:15	JAR	OFF	-New calibration slope program med
	13:47:46	JAR	OFF	-testing temperature profile
	17:03:15	JAR	OFF	-Temperature testing showed ac curate profile
09/03/2010	14:01:44	JAR	ON	-Comparisons are comparing;
09/10/2010	4:01:30		ON	-
09/22/2010	6:34:01	EES	OFF	STOPPED PRINTING OUT-
	13:51:10	JAR	ON	-Passed sucrose test
10/06/2010				

- Hovering mouse over analyzer box gives current status
- Single clicking on the instrument brings up scrollable maintenance history
- Double clicking on any instrument brings up list of PDF thermograms

EAF is Going Green!

- Condensed data summary and thermogram from three pages to one double-sided page.

- Store data files in PDF format for easy retrieval.

- Highlight key fields for enhanced validation.

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Carbon Analysis
Analysis ID: S14497-1.0BC      Analyzer #: 9      Technician: RMS
Sample ID: S14497             Project: IMPROVE      Batch: A10, SubBatch: B25
Punch area: 0.530           Punch area: 0.530   Deposit area: 3.530 cm²
Anal Start: 04/16/10 05:09   Stop: 04/16/10 05:41   Calc: 04/16/10 05:41
Program ver: P6.0 (03/29/10)  Parm file ver: V0302
Cal slip: 20.30 ug C/peak ratio  Calib. intercept: 00.00 ug C
LR unc: 010                  LT unc: 010 counts
Cal peak area: 24901 mv-sec,  Init FID baseline: 109
-----
LR minimum, initial, final baseline: 1049 mv at 742 secs, 1302, 1049 mv
LT minimum, initial, final baseline: 267 mv at 739 secs, 641, 267 mv
Laser Reflectance Time Strength FID Split Time
Lower split : 800 sec 1299 millivolts
Regular split: 802 sec 1305 millivolts
Upper split : 805 sec 1316 millivolts
Laser Transmittance Time Strength FID Split Time
Lower split : 860 sec 1416 millivolts
Regular split: 866 sec 1422 millivolts
Upper split : 874 sec 1430 millivolts
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Peak Area Carbon
OC1 OC 94 mv-sec 0.14 ug C/cm2 .51 ug C/filter
OC2 OC 1087 mv-sec 1.67 ug C/cm2 5.90 ug C/filter
OC3 OC 802 mv-sec 1.23 ug C/cm2 4.35 ug C/filter
OC4 OC 449 mv-sec 0.69 ug C/cm2 2.44 ug C/filter
EC1 EC 1380 mv-sec 2.12 ug C/cm2 7.49 ug C/filter
EC2 EC 258 mv-sec 0.40 ug C/cm2 1.40 ug C/filter
EC3 EC 0 mv-sec 0.00 ug C/cm2 .00 ug C/filter
LRPyMin Py 958 mv-sec 1.47 ug C/cm2 5.20 ug C/filter
LRPyMid Py 981 mv-sec 1.51 ug C/cm2 5.32 ug C/filter
LRPyMax Py 1011 mv-sec 1.55 ug C/cm2 5.49 ug C/filter
LTPyMin Py 1306 mv-sec 2.01 ug C/cm2 7.09 ug C/filter
LTPyMid Py 1324 mv-sec 2.04 ug C/cm2 7.19 ug C/filter
LTPyMax Py 1345 mv-sec 2.07 ug C/cm2 7.30 ug C/filter
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Computed carbon - ImproveA Protocol - Negative Pyrolysis Areas Allowed
Reflectance Regular HighTemp Regular HighTemp
Lower Split : .14 5.21 5.07 1.05 .40 6.26 ug C/cm2
Regular split: .14 5.25 5.10 1.01 .40 6.26 ug C/cm2
Upper Split : .51 18.53 18.02 3.57 1.40 22.10 ug C/filter
Lower Split : .14 5.21 5.15 .92 .40 6.26 ug C/cm2
Upper Split : .51 18.69 18.18 3.40 1.40 22.10 ug C/filter
Transmittance Regular HighTemp Regular HighTemp
Lower Split : .14 5.75 5.60 1.51 .40 6.26 ug C/cm2
Regular split: .14 5.78 5.63 .48 .40 6.26 ug C/cm2
Upper Split : .51 20.29 19.88 1.71 1.40 22.10 ug C/filter
Lower Split : .14 5.81 5.66 .45 .40 6.26 ug C/cm2
Upper Split : .51 20.51 19.99 1.59 1.40 22.10 ug C/filter
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Regular Reflectance Transmittance
OC/TC: .84 .92
EC/TC: .16 .08
OC/EC: 5.19 11.94
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