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6.0   QUALITY CONTROL

6.1   Performance Testing

System blanks are performed at the beginning of each week to insure the system is not introducing bias in the carbon results and to insure that the laser signal is not temperature dependent. Contamination is potentially due to:

- Operator practices, such as improper cleaning of tweezers and punch.

- Teflon particles on the push rod getting into the heated zone of the quartz oven.

- The sample boat contamination.

- The carrier gases contamination.

A temperature-dependent laser signal is potentially due to:

- Physical coupling of the push rod to the boat during the run.

- A quartz rod (laser light pipe) ready for replacement. Microscopic cracks in the quartz rod will increase internal reflectance of the laser light; as the number of these cracks multiply, the effect of temperature on these cracks, and thus on the reflectance, becomes an interference in the laser signal.

As described in Section 5.1, the calibration peak at the end of each analysis run serves as a regular standard; the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration gases further serve as standards. Primary standards in the form of NIST-traceable spiked filter punches do not exist.

6.2   Reproducibility Testing

Replicates of analyzed samples are performed at the rate of one per group of ten samples. The replicate is selected randomly and run immediately after a group of ten is completed. The $\mu g/cm^2$ values for OC, EC, and TC are compared with the original run. The values should fall into the following criteria:

Range	Criteria
< 10 $\mu g/cm^2$	< ±1.0 $\mu g/cm^2$
> 10 $\mu g/cm^2$	< 10 % of average of the 2 values

Notice that the criteria converge at 10 $\mu g/cm^2$. Replicates which do not fall within the above criteria must be investigated for analyzer or sample anomalies. Analyzer anomalies include poor response (as reflected in the calibration peak areas) or poor laser signals affecting the splits between

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OC and EC. Typical sample anomalies include inhomogeneous deposits or contamination during analysis. Inconsistent replicates for which a reason cannot be found must be rerun again.

6.3   Analysis Flags

During Level I validation (see Section 6.4), unusual conditions of the deposit or analysis problems are noted on the analysis printouts. Errors in pre-analysis data entry (e.g., in filter ID, punch area, deposit area) are corrected.

Flags are applied to the dBase file created from the analysis results ASCII file (see Section 6.4). The analysis flags commonly used are presented in Table 6-1. Note that all results flagged with "v" must include a description of the reason for invalidating the sample in the remarks field.

6.4   Data Validation and Feedback

6.4.1   Daily Validation

Level I validation is performed by manually checking the tabular and thermogram printouts the day after the analysis is performed.   The laboratory supervisor or a designated technician is responsible for checking the data. The following items are checked on the tabular data (Figure 6-1):

•   The filter ID is correct.

•   For calibration injection runs, the carrier gas type is He/O$_2$ in the morning and He only in the afternoon, and the injection gas type is reversed between morning and afternoon injections.

•   The analysis date is correct.

•   The punch area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.

•   The deposit area is correct; errors in entry require that the calculated carbon concentrations be recalculated by hand.

•   The calibration peak area is in the correct range (Section 4.1).

•   The initial and final FID baseline are within 3 counts of each other; excessive FID baseline drift is cause for reanalyses. NOTE: Some very heavily loaded filters will have an FID baseline drift greater than 3 counts no matter which carbon analyzer the sample is run on, but typically a FID baseline drift greater than 3 counts signals either a problem with the run or with the carbon analyzer.

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```
                        CARBON ANALYSIS RESULTS
    Analyzer #4                                        Technician: KGG
    ------------------------------------------------------------------------

    Analysis ID     :  EL051Q-1.OEC
    Sample ID       :  NEL051Q
    Punch area      :  0.536 cm2
    Deposit area    :  17.30 cm2

    Analysis        :  12/11/95  10:23      Calculation    :  01/03/96  15:11
    ------------------------------------------------------------------------
    Anal program ver:  P4.1  (11/21/95)     Parm file ver  :  D4.04  (11/21/95)
    Calib. slope    :  22.25 ug C/peak ratio Baseline time  :    90 sec
    Calib. intercept:   0.00 ug C           Baseline window :    1 counts
    Reflectance unc.:    10 counts          Transmission unc.:  10 counts
    Sample transit  :    28 sec             Calib. transit  :    45 sec
    ------------------------------------------------------------------------
    Calibration peak area:  23577 counts
    Initial FID baseline :    205 counts
    Final FID baseline   :    206 counts
    ------------------------------------------------------------------------
                     Reflect Split Time      Laser       FID Split Time
        Lower split  :     1348 sec      1661 counts     1376 sec
        Regular split:     1350 sec      1678 counts     1378 sec
        Upper split  :     1352 sec      1694 counts     1380 sec
    ------------------------------------------------------------------------
                      Peak Area                    Carbon
    OC Peak #1        :    356 counts   0.63 ug C/cm2     10.84 ug C/filter
    OC Peak #2        :   1848 counts   3.25 ug C/cm2     56.29 ug C/filter
    OC Peak #3        :   3681 counts   6.48 ug C/cm2    112.12 ug C/filter
    OC Peak #4        :   2390 counts   4.21 ug C/cm2     72.80 ug C/filter

    Lower pyro'd OC :     533 counts   0.94 ug C/cm2     16.23 ug C/filter
    Reg.  pyro'd OC :     602 counts   1.06 ug C/cm2     18.34 ug C/filter
    Upper pyro'd OC :     673 counts   1.18 ug C/cm2     20.50 ug C/filter

    EC Peak #1        :   3310 counts   5.83 ug C/cm2    100.82 ug C/filter
    EC Peak #2        :    265 counts   0.47 ug C/cm2      8.07 ug C/filter
    EC Peak #3        :     58 counts   0.10 ug C/cm2      1.77 ug C/filter

    ***********************************************************************
                     Regular   High Temp   Regular   High Temp
            VOC        OC         OC         EC         EC        TC
          ---------  ---------  ---------  ---------  ---------  ---------
  Lower split :  0.6     15.5       14.9        5.5        0.6       21.0    ug C/cm2
                10.8    268.3      257.4       94.4        9.8      362.7    ug C/filter

  Regular split:  0.6    15.6       15.0        5.3        0.6       21.0    ug C/cm2
                10.8    270.4      259.5       92.3        9.8      362.7    ug C/filter

  Upper split :  0.6     15.8       15.1        5.2        0.6       21.0    ug C/cm2
                10.8    272.6      261.7       90.2        9.8      362.7    ug C/filter
    ***********************************************************************

    OC/TC:   0.75
    EC/TC:   0.25
    OC/EC:   2.93
```

Figure 6-1. Example Level I Validated Tabular Printout.

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Table 6-1

Common DRI Analysis Flags

Flag	Description
b1	Field blank
b2	Lab blank
b6	Transport blank
f1	Filter damaged outside of analysis area
f2	Filter damaged inside analysis area
i2	Inhomogeneous filter deposit - random areas of darker or lighter deposit
g4	Deposit falling off (usually occurs on heavily loaded samples)
i4	Abnormal deposit area, possible air leakage during sampling
m2	Non-white sample punch after analysis
r1	Replicate on same analyzer
r5	Replicate on different analyzer
v	Sample void

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- The lower laser split time and the upper laser split time are within 10 seconds of each other. If the times differ by more than 10 seconds, check that the lower split OC and upper split OC differ by no more than 5%. OC values which differ by more than 5%, unless due to a small change in laser signal resulting from an extremely clean or very dark sample, requires reanalysis.

- Calculated carbon values for calibration injection runs are within 10% of the current mean value for the injected gas type on that analyzer.

- Acceptance runs for prefired quartz filters result in < 1.5 $\mu g/cm^2$ OC, < 0.5 $\mu g/cm^2$ EC, and < 2.0 $\mu g/cm^2$ TC. Filters which exceed these levels must be refired.

Items which are found to be okay are underlined in red. Items which have problems are circled in red.

The thermograms are checked for the following (Figure 6-2):

- The initial FID baseline is flat, indicating that the analyzer has been thoroughly purged before analysis began.

- The final FID baseline prior to the calibration peak is within 3 counts of the calculated FID baseline; excessive drift is cause for reanalysis.

- The laser signal during the first 90 seconds appears near the bottom of the graph (no reflectance); an excessively high initial laser is an indication that the internal reflectance of the quartz rod is too high, either due to too many internal cracks or a complete fracture of the rod. High initial laser signals should result in a physical inspection of the analyzer.

- The initial laser line drawn on the thermogram matches the laser signal immediately after the rod is pushed in. A laser line which is too low is an indication that the sample was not pushed into the oven in time; a laser signal which exceeds the calculated initial laser signal is a symptom of physical coupling between the sample boat and the push rod, although some automobile emission samples also show this characteristic; a spike or a number of jumps in the laser signal indicates that the operator had difficulty in decoupling the boat from the push rod. All of these problems are grounds for reanalysis if severe.

- The laser signal should dip below the initial laser line until oxygen is introduced at 550°C, at which the signal should rise steeply.

- The laser signal at the end of the analysis is flat; if the laser signal dips as the oven begins to cool, the boat is physically coupled to the push rod and the laser signal during the rest of the analysis is suspect.
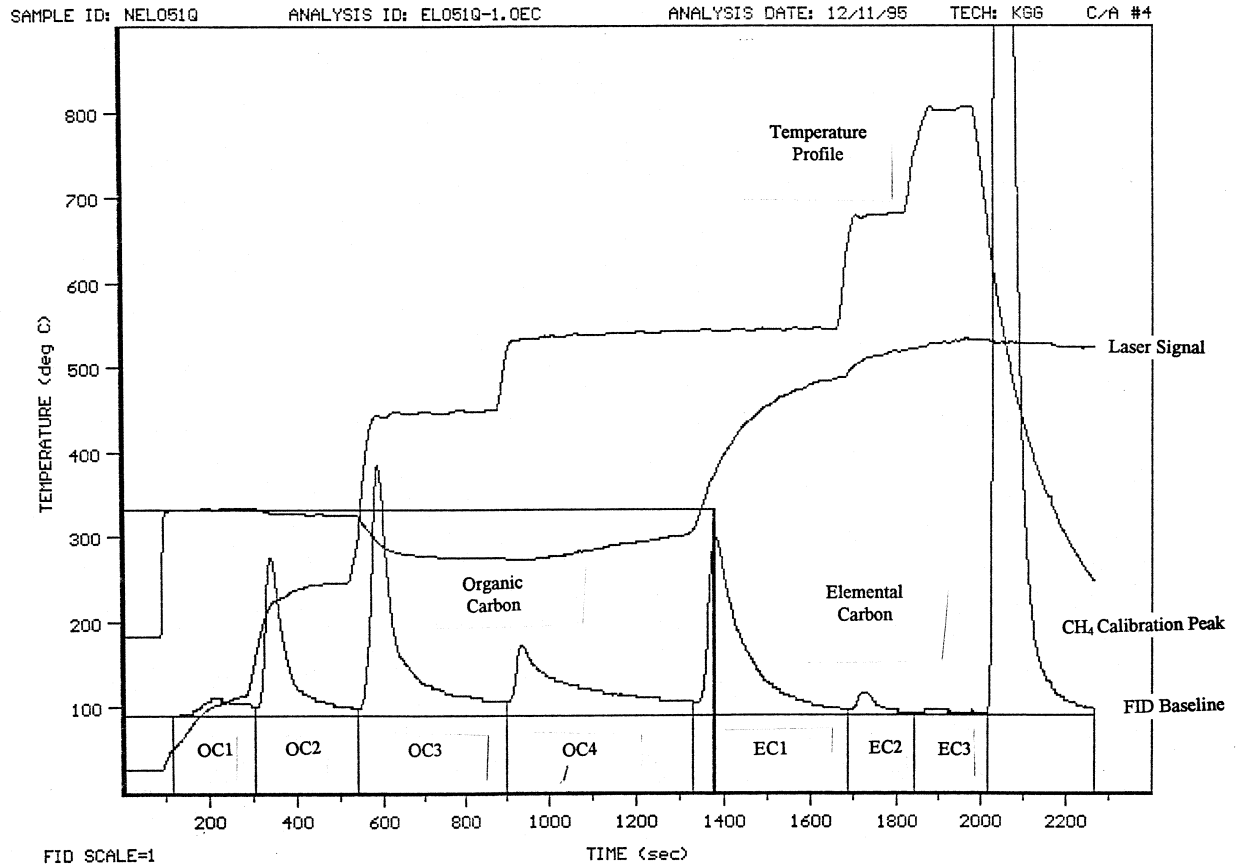
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Figure 6-2. Example Level I Validated Thermogram Printout.

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- The temperature readings reflect stable and smooth temperatures at each level and quick transitions between levels.

Problems or deviations from normal should be circled in red. If the sample punch taped to the thermogram is not white, it is also circled.

If examination of the tabular and thermogram printouts result in a decision that a sample should be reanalyzed, write "Rerun" in red on the printouts and prepare a reanalysis list. This list should be posted immediately after the validation is complete, and those samples should be rerun as soon as they can be conveniently fit into the current day's analyses.

Evidence of persistent analyzer problems must be resolved, either by physically examining the analyzer or reviewing the problems with the analyzer operator.

6.4.2   Validation of Final Data File

The following steps are followed to create a dBase file containing carbon data and to perform Level "I" validation on it:

- Obtain copies of the latest version of the summary file from the directory corresponding to the desired project. These files are called **CPEAKS.n**, where n is the carbon analyzer number. These files may be either copied from the backup files or copied directly from the carbon analyzer computers. The latter method is recommended, as it guarantees that the summary files retrieved are the latest versions. These files are updated at the end of each analytical run, so the latest version is necessary to insure that all of the analyses are included.

- Copy the files to the working directory:

  The ASCII **CPEAKS.n** file is reformatted, sorted, and placed into a dBase III file by the following:

  INPCARBN <Return>

  The **INPCARBN** program will prompt the user for an output file name. The dBASE file naming convention calls for a name in the following format:

  xxOETnnt.DBF

  where:

  xx   is the 2 character project identifier

  OET   stands for organic/elemental carbon

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nn   is the 2 digit batch number (generally used to distinguish between different projects for the same client or between sampling quarters for an extended project)

t   stands for the sample type based on sampler technology:
        A   Agricultural burn emissions dilution sampler
        C   Combination particle/gaseous sampler
        D   Dichot (both $PM_{2.5}$ and PM_{10})
        G   Gaseous
        H   High-volume sampler
        I   IMPROVE/NPS sampler
        P   Portable Survey Sampler
        Q   Audit samples
        R   Resuspension chamber
        S   Sequential filter sampler (SFS)
        W   Wet Deposition
        X   Unknown
        Y   Y-sampler (DRI source sampler)

The final dBase file name is specified in the analysis list posted in the carbon room.

After the **INPCARBN** program produces the dBase output file, the program will alert the operator that it is ready to print the contents of that file. Although the **INPCARBN** program is capable of printing the carbon data file, it is recommended that *Microsoft Excel* be used to print the file. If the file is opened in *Excel*, the uncertainty columns deleted, and the page setup set to landscape mode and fit to one page wide by many pages long, a good printout will be produced on a laserjet printer. If you must use the INPCARBN program to print the carbon data file, a wide carriage dot matrix printer is recommended.

After the printout is produced, immediately label the top of the printout with the file name and printout date. This can also be accomplished by using a labeling header in *Excel*.

Begin validation by matching the filters listed on the analysis list with the filters listed on the dBase printout. There must be at least one entry on the printout for every filter listed on the analysis list.

Flag field and lab blanks as the list is reviewed by placing "b1", "b2", or "b6" in the second column of the printout. Because the dBase printout is sorted by ID number, replicates and reruns will be grouped together.

Indicate missing data by writing the missing filter ID in the margin with an arrow drawn to the appropriate place of insertion. Scan the printout for unusual IDs which may have been mistyped during analysis. Generally these will appear at the beginning or end of the printout due to the sorting process. Make sure that all samples listed on a rerun list appear on the printout.

Resolve all missing data. If a large amount of data is missing because of analysis in the incorrect subdirectory, it is generally easier to retrieve the summary file from that incorrect

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subdirectory, trim the unnecessary data from that file using a word processor, combine the remaining data with the **CPEAKS.n** file, and rerun the **INPCARBN** program. If only a few data points are missing, it is generally not too much trouble to simply write the correct values from the daily folders on the printout and add those values manually to the dBase files at the same time the flags and other corrections are made.

Scan the deposit area column for incorrect entries. Circle the incorrect entries to insure that corrected values replace those currently in the database.

Scan the filter IDs for multiple entries of ID numbers. Under normal conditions, the only times multiple entries should occur are reruns and replicates. All multiple entries must be flagged to indicate the reason for their existence.

Scan for missing runs. The most common example is the first run being aborted or lost for some reason, and the only entry in the dBase file is the second run. An entry for the first run must be inserted, flagged as invalid, and labeled as to the reason it was invalid. All punches taken from the filters MUST be accounted for.

Scan the OC and EC columns looking for unusually high or low values. At this time make sure that the field blanks and/or lab blanks are all close to one another. Circle any possible outliers for further investigation.

Finally, pull the analysis folders and go through the analysis summaries and thermograms one by one. At this time, resolve all circled items and all missing flags. Determine if analyses flagged by the operator are legitimate. These flags are determined by the operator at the end of the analysis run (Section 4.2 and Figure 4-11); these flags are defined in Table 6-2. If the temporary flag is not warranted, draw a line through the flag to indicate it should be removed. If the sample should be rerun, add it to a rerun list. If the analysis has some anomaly but still appears to be legitimate, either flag or add notes to the comments field as appropriate. Analysis flags are defined in Section 6.3. All samples flagged as invalid must have an entry in the comments field to describe the reason that the sample is invalid. Common notes and comments are presented in Table 6-3.

All operator-generated flags must be either converted to standard analysis flags or removed. The flags in Table 6-2 are temporary flags only and are not recognized as legitimate analysis flags at DRI.

After all thermograms have been reviewed and all possible reruns have been identified, post the rerun list in the carbon room and have the reruns done as soon as possible.

Review the data from the reruns, looking for inconsistencies. Insure that the reasons for the rerun have been addressed. Mark the printout with the new values for manual insertion into the dBase file. Previous runs must be flagged as invalid or the reruns flagged as replicates.

Finally, all comments, flags, insertions, and other changes made to the printout are entered into the dBase file. After all changes are made, generate a new printout. Label the new

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printout with the file name and printout date. Forward a copy of the printout and the dBase file on disk to the person putting the final report together.

6.4.3   Use of the CARBVAL Program to Assist in Data Validation

A *Microsoft FoxPro* program named CARBVAL exists which will greatly assist in the validation process. When you use the CARBVAL program, you must specify if you are validating a data file which contains IMPROVE data or not. There are several validation steps that the CARBVAL program performs which are specific to IMPROVE.

The CARBVAL program will perform the following validations:

1. Identify records where the deposit area (deparea) is not equal to the deposit area entered by the user.

2. Identify records with duplicate runids.

3. Identify records before/after which contain gaps in runid sequence

4. Identify filters with more than one original run.

5. Identify records where elemental carbon concentration is greater than organic carbon concentration.

6. Identify blank filters where organic carbon concentration is greater than 3.95*deparea

7. Identify blank filters where elemental carbon concentration is greater than deparea

8. Identify records where organic carbon concentration divided by the total carbon conentration is less than specified value (default is 0.75).

9. Identify voided samples that do not have a value in the comments column.

10. Identify replicate records incorrectly classified as 'r1' or 'r5'.

11. Identify samples where a 'm2' flag was not present in both the original and replicate runs.

12. Identify replicate runs where 'octc', 'ectc', or 'tctc' values are not within 10% or the deparea (in µg/filter) of original run.

13. IMPROVE only: Identify records where filter channel value is not equal to 'C'.

14. IMPROVE only: Identify records where filter type is not primary or secondary.

15. IMPROVE only: Identify secondary filters where 'ectc' value > 3.8 or 'octc' > 18.

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16. IMPROVE only: Identify secondary filters where 'ectc' or 'octc' values are > corresponding primary filter values.

17. IMPROVE only: Identify records where 'samdate' or 'week' values are empty.

18. IMPROVE only: Identify records with incorrect values in the 'day' field.

To use the CARBVAL program, first start *Microsoft FoxPro*. Then type 'DO CARBVAL' from the command window. The program will start and ask you for a file name. The program will then ask you a series of questions:

• the name of file used to store validation results,

• the deposit area of filter in square centimeters,

• the expected number of filters,

• and the octc/tctc ratio threshold (default = 0.75).

After the above values are entered, the CARBVAL program will begin validating the selected file. If the preliminary checks are satisfactory, the program will also ask you if you want to remove the carbon technicians validation flags and if you want to replace the 'r' replicate flag with the appropriate 'r1' or 'r5' validation flag. When the program is finished, it will allow you to browse the problem records on screen and will also print them.

It is recommended that you run the CARBVAL program as a first check after you have put the carbon data file together and then run it again as necessary, but certainly run it again when the final database is assembled. This will serve as a final check on the database.

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Table 6-2

DRI Carbon Analysis Temporary Flags

Flag	Description
EI	Error in sample ID
EA	Error in sample deposit area
ST	Suspect temperature profile
SF	Suspect FID signal
SL	Suspect laser signal
Mi	Miscellaneous problem
v	Invalid run
r	replicate
b	blank
i	inhomogeneous filter deposit
f	filter media damaged
g	sample deposit damaged
d	sample dropped
n	foreign substance on filter deposit
w	sample wet

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Table 6-3

DRI Carbon Analysis Validation Comments

Comments	Description
"Anomalous laser"	Despite good initial laser, laser signal drifted above initial laser signal before dropping (typical of auto emissions)
"Operator error"	Used with "v" flag; operator missed pushing boat in, pushed abort key, pushed manual advance key at an inappropriate time, etc.
"Analyzer malfunction"	Used with "v" flag; analyzer malfunction or problem beyond the control of the operator such as plugged FID, broken oven heater, etc.
"Poor replicate"	Replicate is outside the normal criteria, but no reason can be found for the discrepancy.
"Poor initial laser"	Used with "v" flag; severe coupling or boat not pushed in time for calculation of initial laser signal.
"Sample contaminated"	Used with "v" flag; rerun of sample yields lower values or different peaks. Typically used with blanks or reruns of replicates.
"Temperature problem"	Used with "v" flag, one or more of the temperature steps were not properly obtained. The most common example is the over-shooting of the first (120°C) temperature step.