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- Lock the carbon analysis room.

5.0   QUANTIFICATION

5.1   Calibration procedures

The calibration procedures for the carbon analyzers are of three types: the end-of-run calibration peak, the manual calibration injections of CH_4/He and CO_2/He, and instrument calibration using KHP, sucrose, and the two calibration gases.

The end-of-run calibration consists of a set quantity of CH_4/He calibration gas which is automatically injected by the Carbon program. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. The end-of-run calibration occurs automatically at the end of each analysis run and requires no operator intervention. The integrated calibration peak counts should be checked by the operator immediately after each run to insure that the analyzer is operating satisfactorily.

The manual calibration injections are performed at the beginning and ending of each analysis day, and serve to verify proper analyzer performance. The procedure for manual injections are described in Section 4.1 and 4.3.

Instrument calibration, performed twice a year or when a new calibration gas cylinder is started, establishes the calibration slope used in converting counts to μg of carbon, as explained in the next section. Instrument calibration involves spiking prefired quartz punches with various amounts of the 1800 ppm KHP and sucrose solutions (Section 3.1) and injecting various volumes of the CO_2 and CH_4 gases.

A clean blank quartz punch is baked in the analyzer oven at 800°C for 10 minutes using option 4 from the main menu of the carbon program. After the punch has cooled to less than 50°C, the KHP or sucrose solution (prepared as described in Section 3.1) is injected onto the punch using a 20 ml syringe. The following volumes are used:

- 5 ml KHP or sucrose solution
- 10 ml KHP or sucrose solution
- 15 ml KHP or sucrose solution (do twice)
- 20 ml KHP or sucrose solution
- no injection (as a system blank; see Section 4.2.2)
- 20 ml acidified DDW only (check of background level of DDW)

The sample port is sealed and the spiked filter punch is pushed to 1 cm from the sample oven. In this position the punch will experience a temperature of 35 to 40°C due to the heat from the oxidation oven. Allow the punch to dry thoroughly; the punch will turn from translucent to opaque as it dries. The punch must be dry to avoid water vapor effects on the FID. The OC/EC analysis

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option from the main menu is selected and started. The integrated peak counts for all seven temperature fractions for the sample peak and the calibration peak are recorded.

The CO_2 and CH_4 calibrations are run using the calibration options from the main menu. The following volumes are injected:

- 100 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 250 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 500 ml CO_2 or CH_4 gas (use 1000 ml syringe)
- 1000 ml CO_2 or CH_4 gas   (do once with 1000 ml syringe and once with 2500 ml syringe)
- 2000 ml CO_2 or CH_4 gas (do with 2500 ml syringe)

Again, the integrated peak counts are extracted manually from the tabular printouts.

Calibration values are plotted as actual μg carbon vs. the ratio of the integrated sample peak counts to the calibration peak counts (Figure 3-1). Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH_4/He, and CO_2/He). The calibration slope derived from the CO_2 injections typically has a slightly different slope and does not fit as well. The slope (m) is calculated from:

$$\left(m = \frac{\sum (y_i x_i)}{\sum (x_i)} \right)$$

and the standard deviation (s) is calculated by:

$$\sigma = \sqrt{\frac{1}{n-1} \frac{\sum (y_i - mx_i)^2}{\sum x_i^2}}$$

where:

$$x_i = \frac{(\text{injected carbon peak area})}{(\text{calibration peak area})}$$

and:

$$y_i = \text{calculated carbon in spiked filter or manual injection} (\mu g)$$

Note that this is a special form of the regression formula, which insures that the curve passes through the origin.

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The resulting slope is compared to previous calibration results. New values should be no more than ±10% different than previous calibrations if no major analyzer changes have been made.

The new slope for each analyzer (derived from combined CH$_4$, KHP, and sucrose data) is placed into the CARBON.DAT file for each analyzer; this file contains analyzer parameters which are read into the Carbon program when it is first started. The date and version number in the CARBON.DAT file is also updated.

Calibration data and plots are retained in file folders in the file cabinet with raw analysis data.

5.2   Calculations

The conversion of integrated peak counts to µg of carbon for each peak in the thermogram is performed by the computer at the end of the analysis program. For reference purposes, the calculation is:

$$\text{peak µg C/punch} = \frac{(\text{Integrated peak counts above baseline})(\text{calibration slope})}{(\text{Internal calibration counts})}$$

The peaks reported are: four organic peaks (OC1, OC2, OC3, and OC4) corresponding to 120, 250, 450, and 550°C, respectively; three elemental carbon peaks (EC1, EC2, and EC3) corresponding to 550°C after the introduction of O$_2$, 700, and 800°C, respectively; and three pyrolyzed organic carbon peaks (Lower, Regular, and Upper Splits) corresponding to the peaks after the introduction of O$_2$ and before the Lower Split Time, Regular Split Time, and the Upper Split Time, respectively (see Section 1.7 and Figures 4-9 and 4-10).

Carbon values per punch are converted to µg C/cm^2 by:

$$\mu g \ \ C/cm^2 = \frac{(\mu g \ C/punch)}{(\text{punch area})}$$

Finally, carbon values are converted to µg C/filter by:

$$\mu g \ \ C/filter = (\mu g \ C/cm^2)(\text{filter deposit area})$$