# Total Organic Carbon and Soot in Soil, Sediment

**References:** USEPA, "Method 9060 Total Organic Carbon," in Test Methods for Evaluating Solid Waste, SW846, Third Edition, Final Update, December 1996.

Perkin Elmer, "PE 2400 Series II CHNS/O Analyzer User's Manual," The Perkin-Elmer Corporation, April 1998.

USEPA, Region II, Lloyd Kahn, "Determination of Total Organic Carbon in Sediment", July 27, 1988.

"Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability" published in Environmental Science and Technology, Vol. 31, No. 1, 1997 by Gustafsson, Haghseta, Chan, McFarlane and Gschwend.

*"Reinterpreting Literature Sorption Data Considering Both Absorption into Organic Carbon and Adsorption onto Black Carbon"* published in Environmental Science and Technology, Vol. 37, No. 1, 2003 by Accadi-Dey and Gschwend

## 1. Scope and Application

**Matrices:** This method is applicable for solid samples (soils, sediments, sludges).

**Definitions:** Refer to Alpha Analytical Quality Manual.

The organic carbon in a sample consists of a variety of organic compounds in various oxidation states. Some of these compounds may be oxidized by biological or chemical processes and can be measured by the Biochemical Oxygen Demand or Chemical Oxygen Demand tests. To measure the amount of organically bound carbon, the organic carbon molecules are broken down into single carbon units, and converted into a form that can be measured quantitatively.

The PE 2400 Series II CHNS/O Analyzer can simultaneously determine carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) in organic material. In the CHN mode, the PE 2400 Series II CHNS/O Analyzer uses a combustion method to convert the sample elements to simple gases ($CO_2$, $H_2O$, and $N_2$). The resulting gases are homogenized and controlled to exact conditions of pressure, temperature, and volume. The homogenized gases are allowed to de-pressurize through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivity and reported as a percentage for solid samples. Treated with phosphoric acid prior to analysis, the Total Organic Carbon (TOC) content is determined by the amount of $CO_2$ in the sample. If the sample is analyzed without pretreatment, the Total Carbon (TC) content is determined. Total Inorganic Carbon can be determined by subtraction of the TOC from the TC values.

This method is applicable to the measurement of TOC and Soot in solid samples $\geq$ 100mg/Kg or $\geq$ 0.01%, dry weight. According to the instrument manufacturer, a sample of up to 70% carbon can be analyzed without dilution.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one or more of the following laboratory personnel before performing the modification: Area Supervisor, Department Supervisor, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the TOC Analyzer and in the interpretation of the data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the Quality Assurance Officer and/or Laboratory Director on a case-by-case basis.

# 2. Summary of Method

An aliquot of solid sample is homogenized, dried at 103 - 105°C, re-homogenized, and the particle size is reduced by mortar and pestle. The sample is pre-treated with phosphoric acid to convert the inorganic carbon (*i.e.,* carbonate and bicarbonate in the form of $CO_2$) prior to analysis. The sample is re-dried at 103 - 105°C and another aliquot is removed for analysis, by weighing on the Microbalance, which is linked to the TOC analyzer.

Organic carbon is measured using combustion and a carbonaceous analyzer. The sample is oxidized in a pure oxygen environment, introduced into a furnace by a 60-slot Autosampler, then combusted. The carrier gas ($O_2$) is combined with the carbon content of the combusted sample to form $CO_2$. Elements, such as halogens and sulfur, are removed by scrubbing reagents in the combustion zone. A thermoconductivity detector then measures the $CO_2$. The amount of $CO_2$ derived from a sample is directly proportional to the concentration of organic carbonaceous material in the sample.

For Soot, the dried sample will be reduced to a powder by grinding it with a mortar and pestle. An aliquot of sample, approximately 2-5 gm, will be transferred into an aluminum tin. The tins will be placed in an oven or muffle furnace for 24 hours at 375°C. After sample is in the muffle furnace for 24hrs sample is treated with phosphoric acid then re-dried and reduced to a powder with a mortar and pestle. At the end of this time they will be cooled to room temperature, and are ready for analysis on the TOC Analyzer.

## 2.1 Method Modifications from Reference

None.

# 3. Reporting Limits

The Practical Quantitation Limit (PQL) or Reporting Limit (RL) is 0.01% (or 100mg/Kg) for solid samples.

# 4. Interferences

**4.1** To determine the TOC/Soot content, the inorganic fractions (carbonate and bicarbonate) must be removed prior to analysis by lowering the pH of the sample to $\leq$ 2. When removing the inorganic carbon, care must be taken in sample pretreatment to minimize the potential of loss of volatile organic carbon present in the sample.

**4.2** Maintaining the samples at 4±2°C, and analyzing within the specified holding time minimizes bacterial decomposition and volatilization of the organic material.

**4.3** Elements, such as halogens and sulfur, are removed by scrubbing reagents in the combustion zone. Large and/or complex organic molecules such as tannins, lignins, or humic acids may be

oxidized slowly. If these compounds are suspected to be present, it is advisable to check the efficiency of the oxidation procedure with a selected representative sample, and adjust the analysis (sample size) as needed.

**4.4** Chlorides at a concentration of greater than 0.1% may completely inhibit the oxidation of organic matter. The sample size may need to be adjusted to compensate for this interference.

**4.5** Oils from skin, or contact with any organic material, such as plastic containers and rubber tubing, can contaminate samples. Handle the weighing tins with tweezers.

**4.6** Sample heterogeneity can be a major source of imprecision in TOC/Soot results. Recommend to clients to perform a client-specific duplicate, to evaluate precision and representativeness of the TOC/Soot results to the site.

# 5. Health and Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

The use of laboratory equipment and chemicals exposes the analyst to several potential hazards. Good laboratory techniques and safety practices shall be followed at all times. All relevant Material Safety Data Sheets (MSDSs) are kept on file.

Approved PPE, which includes Safety Glasses, Gloves and Lab Coats, must be worn at ***all*** times when handling samples, reagents, chemicals, or when in the vicinity of others handling these items, so that dermal contact is avoided. All standards, reagents and solvents shall be handled under a hood using the proper PPE. All flammable solvents must be kept in the flammable storage cabinet, and returned to the cabinet immediately after use. When transporting chemicals, use a secure transporting device and/or secondary outer container. Chemical storage is properly segregated and adequately ventilated to reduce the possibility of hazardous reactions. Chemical storage in work areas shall be kept to a minimum. Storage on bench tops or other work surfaces, except temporary, is not permitted.

All standards and reagents shall be prepared in a hood while using the proper PPE.

Analytical instrumentation poses the unique possibility of exposure to high voltages. Other than the *routine* instrument maintenance, as listed in the front of every Instrument Maintenance Logbook, at no time shall an instrument operator attempt to maintenance an instrument alone, or without the proper training, supervision or instruction. Caution must always be used in the presence of moving parts (autosamplers) and hot surfaces (injection ports).

All additional company safety practices shall be followed at all times as written in the *Chemical Hygiene Plan*.

All TOC standard solutions must be handled with caution. See pages 5-3 through 5-5 of the PE 2400 Series II CHNS/O Analyzer User's Manual for additional and specific Warnings and Precautions.

# 6. Sample Collection, Preservation, Shipping and Handling

## 6.1 Sample Collection

A minimum of 5 grams of sample must be collected in a glass jar.

## 6.2 Sample Preservation

Soil samples must be refrigerated and maintained at 4°±2°C until drying and analysis.

Sediment samples are either processed within 28 days (or 14 days for Lloyd Kahn) or can be frozen at -15C to -20C until processing.

## 6.3 Sample Shipping

The *Sample Receipt & Login SOP* (01-01) describes how samples are normally shipped or obtained by the laboratory, precautions to be used in opening sample shipments, and sample storage conditions.

## 6.4 Sample Handling

Soil samples must be refrigerated and maintained at 4°±2°C until drying and analysis.

Sediment samples are either processed within 28 days (or 14 days for Lloyd Kahn) or can be frozen at -15C to -20C until processing.

All solid samples (NOT requiring the *Lloyd Kahn* Calibration method) must be analyzed within 28 days from the date of collection. **Note:** If samples require the *Lloyd Kahn* Calibration method, the hold time is 14 days.

The *Sample Receipt & Login SOP* (01-01) describes the responsibilities of sample custody including all proper documentation, verification, and tracking procedures, following Chain of Custody (COC) protocols and sample receipt procedures using the *Sample Receipt Checklist*, which includes the check for proper sample preservation and cooler temperature verification.

Internal COC procedures for sample tracking include the use of sample tracking logbooks. These procedures are also described in the *Sample Receipt & Login SOP* (01-01).

# 7. Equipment and Supplies

**7.1 Instrument:** Perkin Elmer 2400 Series II CHNS/O Analyzer with computer and PE software

**7.2 Detector:** Thermal Conductivity

**7.3 Mortar and pestle**

**7.4 Oven:** 103° - 105°C

**7.5 Dessicator**

**7.6 Volumetric Flasks:** Class-A, various volumes

**7.7 Microbalance:** Perkin-Elmer, Model AD-6, linked to the instrument. See the Manufacturer User's Manual, Section 1.2, pages 3-4, for Microbalance and weighing instructions. The

Microbalance calibration is verified every day using 2.0mg - 200mg weights, in the range of daily use, and be accurate within +/1%. If the balance needs to be re-calibrated, see the Manufacturer User's Manual SOP, Section 1.1, page 3, for details.

**7.8 Tweezers:** Anti-Magnetic

**7.9 Tin Boats:** Small and Large; Baked at 180°C for 30 minutes prior to use

**7.10 Glass Beads:** Filter Aid 400, High-density; from Perkin Elmer or 3M. Used as the CCB/Method Blank media.

**7.11 Gas-tight syringes:** Various measuring sizes, including 10µL for direct sample spiking

**7.12 Printer :** OKIDATA Microline 320 Turbo-9 Pin

**Note:** All maintenance records including routine upkeep and outside service visits are maintained in the instrument maintenance logbooks. See the Manufacturers User's Manual for detailed troubleshooting instructions and routine maintenance, as needed.

## 8. Reagents and Standards

Use reagent grade chemicals for all reagents. All reagents and standards must be stored at 4±2°C and expire 6 months from preparation, unless otherwise indicated below.

**8.1 Deionized (DI) water:** All references to DI water refer to ASTM Type II reagent grade water which has been boiled, cooled and capped to eliminate $CO_2$.

**8.2 Phosphoric Acid solution:** Add 20mL of $H_3PO_4$ to 400mL of DI water. Mix thoroughly and cool to room temperature before use. Store in a glass bottle and keep at room temperature. This solution is stable for 6 months.

**8.3 Potassium Hydrogen Phthalate (KHP), Calibration Solution/CCV or K-Factor for TOC:** 10,000mg/L equivalent to 10,000mg/Kg Carbon, or 1.0 % TOC. NIST SRM 185h

Dissolve 2.128g of potassium hydrogen phthalate (primary standard grade) in ASTM DI water, and dilute to 100mL in a volumetric flask. This standard is good for 6 months, stored at room temperature. Discard solution if discoloration or any signs of bacterial growth are observed.

**Note:** When preparing this solution for the *Lloyd Kahn* Calibration method, double the weight (4.256g) to 100mL in a volumetric flask for a 2% TOC solution. This will be the stock for the highest point of the calibration curve. Appropriate dilutions can then be made from this stock for the rest of the calibration curve outlined in Section 10.2.4.

**8.4 Potassium Hydrogen Phthalate (KHP) Spiking Solution/MS:** 10,000mg/L equivalent to 10,000mg/Kg Carbon, or 1.0 % TOC. From a separate source than the solution in Section 8.3, Sigma Aldrich or equivalent.

Dissolve 2.128g of potassium hydrogen phthalate (primary standard grade) in ASTM DI water, and dilute to 100mL in a volumetric flask. *Use a separate source or different lot of KHP from that used to prepare the calibration standard.*

This stock may be stored up to six months at room temperature. Discard solution if discoloration or any signs of bacterial growth are observed. Use at 1.0 % TOC concentration for solid samples, and at 10,000mg/L for aqueous samples.

**8.5 Reporting Limit Standard:** An appropriate dilution is made from the stock standard (Section 8.3), which is prepared and analyzed to confirm the reporting limit for the given matrix (Section 3).

**8.6 Acetanilide – LCS/SRM for Total Carbon**: NIST SRM 141d with certified concentration of Carbon = 71.089%.

**8.7 Cystine – CCV for Total Carbon**: From Perkin Elmer with value of carbon = 29.99%

**8.8 Solid Laboratory Control Sample / Independent Calibration Verification (LCS/ICV):** Standard Reference Material (SRM) NIST 1944, a separate source from the calibration standard that is certified at the concentration of 4.4% TOC for solid samples. SRM 1649 for Total Carbon or Soot certified at the concentration of 17.68% Total Carbon.

# 9. Quality Control

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

## 9.1 Blank(s)

**9.1.1 Method Blank:** A method blank must be analyzed once per every 20 samples or per TOC/Soot batch, whichever is more frequent. The Blank consists of 30mg of Filter Aid (Section 7.10).

TOC must not be detectable in the method blank at a concentration greater than the reporting limit for the given matrix (Section 3).

Corrective Action: Analysis of the method blank and all associated samples must be performed until the blank is in control. Samples cannot be analyzed until an acceptable method blank analysis is obtained. Exceptions may be made with approval of the Department Manager, if the samples associated with the out of control method blank are non-detect for TOC/Soot, or if sample TOC/Soot concentrations are greater than 5X the blank levels. In such cases, the sample results are accepted without corrective action for the high method blank and the client is notified in a project narrative associated with the sample results.

**9.1.2 Continuing Calibration Blank:** A CCB must be analyzed immediately after every CCV. The CCB is 30mg of Filter Aid (Section 7.10).

The CCB concentration must not be greater than the reporting limit for the given matrix (Section 3).

Corrective Action: Repeat analysis once to see if an analytical error occurred. If the CCB still exceeds the control limits, re-calibrate and/or re-analyze a fresh blank. All samples associated with the out of control CCB must be re-analyzed (since the last acceptable CCB). Exceptions may be made with approval of the Department Manager if the samples associated with the out of control method

blank are non-detect for TOC/Soot or if sample TOC/Soot concentrations are greater than 5X the blank levels. In such cases, the sample results are accepted without corrective action for the high CCB and the client is notified in a project narrative associated with the sample results.

**9.1.3** **Instrument Blank:** An Instrument Blank must be analyzed during Calibration.run2. The Instrument Blank consists of 30mg of Filter Aid (Section 7.10).

## 9.2 Laboratory Control Sample (LCS)

Laboratory control sample (LCS or ICV) must be from a second source or lot number to verify the accuracy of the standard curve. The LCS/ICV is analyzed along with the samples. A LCS/ICV must be analyzed once per every 20 burns or per TOC batch, whichever is more frequent. For *solid* samples, the LCS is the NIST SRM at 4.4% TOC.

**ICV/LCS** consists of approximately 3.0-5.0mg of SRM 1944 with a true value of 4.4% TOC (Section 8.6). This SRM is NOT evaluated for Soot since no certified concentration for Soot is published.

The acceptable recovery QC range is 75%-125% for the LCS/ICV.

Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the LCS/ICV recovery is still out of control, re-calibrate and re-analyze the LCS/ICV and all associated samples. Samples cannot be analyzed until an acceptable LCS/ICV is obtained. Exceptions may be made with approval of the Department Manager if the samples associated with the out of control LCS/ICV are also associated with a matrix spike that is in control. This is an acceptable measure of accuracy of the analytical procedures. An explanation of this out of control LCS/ICV recovery must be included in the project narrative to the client and the sample data reported with the acceptable MS results as batch QC.

## 9.3 Initial Calibration Verification (ICV)

Refer to Section 9.2 above.

## 9.4 Continuing Calibration Verification (CCV)

A CCV must be analyzed at a minimum of every 10 burns and at the close of an analytical sequence. This standard monitors instrument performance throughout the duration of the analytical run.

The **CCV** is approximately 10.0mg of Filter Aid tared to zero and spiked with 10µL of *Calibration Solution* (Section 8.3), with a 1% TOC true value. The weight recorded is the Calibration Solution only. (10µL of solution should weigh approximately 10mg).

The acceptable recovery QC range for the CCV is 80-120%.

Corrective Action: Repeat analysis once to see if an analytical error occurred. If the CCV still exceeds the control limits, re-calibrate and re-analyze all samples since last acceptable CCV.

## 9.5 Matrix Spike

A matrix spike must be performed once per 20 samples (5% frequency). When project specifications dictate, a Matrix Spike Duplicate (MSD) may also need to be performed at the same frequency as the MS. Prepare the MS according to Section 8.4 for the given matrix.

A **Matrix Spike** sample is spiked with 10µL of *Spiking Solution* (Section 8.4), at a 1.0 % TOC true value. The weight recorded is the sample weight prior to spiking.

The acceptable recovery QC range is 75%-125% for the MS/MSD. Calculate the %RPD as in Section 9.6 when analyzing a MS/MSD pair. The acceptable %RPD is ≤ 25% for solid samples.

Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the % recovery or %RPD still exceeds the criteria and the LCS is compliant; include a project narrative with the results to the client noting that there may be potential matrix effects on the accuracy or precision of the TOC/Soot results as evidenced by matrix spike recovery or %RPD outside of QC limits.

## 9.6 Laboratory Duplicate

Duplicate analyses (matrix duplicate) must be performed once per 20 burns (5% frequency).

A **Matrix Duplicate** sample is weighed to represent the sample in consistency, and weight.

Acceptable relative percent difference (RPD) of duplicates is ≤ 25% for solid duplicates and ≤ 20% for aqueous duplicates. Acceptance criterion is not applicable to sample concentrations less than 5X the reporting limit. Calculate RPD as follows:

$$\%RPD = \frac{R1 - R2}{\frac{[R1 + R2]}{2}} \times 100$$

where:

R1 = highest result
R2 = lower result

Corrective Action: Repeat analysis once to see if an analytical error has occurred. If the % RPD still exceeds the control limits; include a project narrative with the results to the client noting that there may be potential matrix effects on the precision of the TOC/Soot results as evidenced by the matrix duplicate RPD exceedance.

## 9.7 Method-specific Quality Control Samples

None.

## 9.8 Method Sequence

- Calibration Curve generation
- Method Blank
- LCS/ICV
- Laboratory Duplicate
- Matrix Spike
- Samples 1 – 8
- CCV

- CCB
- Samples 9 – 18
- CCV
- CCB

# 10. Procedure

## 10.1 Equipment Set-up

Samples are prioritized by the Department Manager for analysis based on hold time and client due date. Section 15.5 outlines the steps for final TOC reporting that will contain the sample analysis final results.

The analyst initials, date, sample ID #'s, sample weights (solids), or volumes (aqueous), of all Standards, QC samples and field samples, are entered into the TOC logbook. Include the standard, LCS and MS IDs and concentrations.

### 10.1.1 Pretreatment for Total Organic Carbon:

This procedure is used to remove the inorganic compounds in the sample prior to the determination of Total Organic Carbon. If Total Carbon is to be determined, addition of the phosphoric acid solution is omitted.

**10.1.1.1** Aliquot 2-5g of pre-dried (103°-105°C) solid sample into an aluminum weigh dish. (This aliquot may be taken from the Percent Solids Determination aliquot, assuming Percent Solids have already been performed). Note: Any sample to be analyzed for Total Organic Carbon must be dried and acidified and dried again before analysis on the TOC instrument.

**10.1.1.1.1** If samples are received that do not require percent solids, the samples must be dried and then acidified and dried again.

**10.1.1.1.2** Sample aliquots that have already been dried for percent solids analysis may be acidified and redried for TOC.

**10.1.1.1.3** If Soot analysis is required, take a portion of the dried sample aliquot, approximately 2-5 gm, and place into a muffle furnace at 375°C for 24 hours. Once the sample aliquot is cooled to room temperature, proceed to the acid addition step, Section 10.1.1.2. Samples for Soot are read analytically in the same way as Routine TOC.

**10.1.1.2** Add Phosphoric Acid Solution (Section 8.2) drop wise to the solid sample in the tin dish and check for effervescence. If effervescence is observed, continue adding drop wise until the effervescence stops to ensure removal of inorganic carbon compounds (carbonate and bicarbonate). Report any excessive effervescence or change in sample consistency to the client in the project narrative.

**10.1.1.3** Place the tin dish containing the treated sample into the drying oven at 103°-105°C until dry. Remove the tin and place in a dessicator to cool. The sample is

considered dry when the weight change is less than 4%, or 50mg of a previous weight, whichever is less. Samples may need to dry overnight in the oven.

## 10.2 Initial Calibration

On the accompanying computer, or "PC", Perkin Elmer software has been loaded to collect and save sample and standard analysis data. Create a file to store the data from each day's analytical sequence by clicking on the PE 2400 icon, go to "new" and "save" the file "as" the name of the date of the analysis (*i.e.,* 060503.chn). Data from each standard or sample analysis will be automatically stored in this file for future reference

**10.2.1** Follow the instrument Manufacturers User's Manual for instrument set up and see Sections below for an outline of the initial, daily calibration procedure.

See the Manufacturers User's Manual, page 5-69, for the default instrument conditions when in the CHN operating mode.

**10.2.2** *Routine* TOC/Soot Calibration Method:

TOC analyses use K-Factors (3 repeat analyses of a 1.0% TOC standard, Section 8.3) and Blanks, calculated and averaged by the instrument when the calibration is being performed. Follow the instrument Manufacturer's User's Manual, page 4-67. Calibration of the instrument using K-Factors and Blanks is performed once per day of analysis.

Load the Autosampler (Section 10.3.2) for combustion to analyze Blanks and Standards in the order listed below. All "Blanks" and "K-Factors" are prepared in the same way. Analyze the standards following the procedure in Section 10.3.

- **Instrument "Primer"** (~20.0mg of SRM 1944, with true value of 4.4% TOC) only if new column.
- **Blank 1** (30.0mg of Filter Aid) only if new column
- **K-Factor 1** (10µl of *Calibration Solution*, Section 10.3,)
  The weight recorded is the Calibration Solution, only.
- **Blank 2** (30.0mg of Filter Aid)
- **K-Factor 2** (10µl of *Calibration Solution*, Section 10.3,)
  The weight recorded is the Calibration Solution, only.
- **K-Factor 3** (10µl of *Calibration Solution*, Section 10.3,)
  The weight recorded is the Calibration Solution, only.

The K-Factors must reproduce from the mean value within +/-0.15% for carbon. The calculation involves the comparison among the latest K-Factor run, the prior K-Factor run, and the current running average K-Factor. An "out of tolerance" message will be displayed if this criterion is not met.

The ICV/LCS and Method Blank are prepared to run immediately following the third K-Factor, given the instrument is "in tolerance".

Corrective Action: If, at any time during the 6–step process of calibration, one of the K-Factors or Blanks fail, the calibration must be re-prepared and re-analyzed until the instrument accepts all factors as "in tolerance".

**10.2.3** *Lloyd Kahn* Calibration Method: **Note:** The *Routine* instrument calibration procedure (Section 10.2.2) must be established before the Linear Regression method is used, otherwise, the best results will not be obtained.

Prepare a curve for *Lloyd Kahn* calibration as outlined below. Additionally, see page 5-82 and 5-83 of the Manufacturers User's Manual for proper set-up of this calibration method.

Analyze each point of the calibration curve following Section 10.3. On an Excel spreadsheet, plot *Carbon (mg*) vs. *Instrument Response*, using five standards and a blank covering the analytical range of interest. See Section 8.3 for Calibration Standard preparation.

Blank = 10 ul of DI water from Barnstead

Point 1 = 0.1% (1,000mg/Kg) Standard

Point 2 = 0.5% (5,000mg/Kg) Standard Point 3 = 1.0% (10,000mg/Kg) Standard Point 4 = 2.0% (20,000mg/Kg) Standard

Point 5 = 4.0% (40,000 mg/Kg) Standard added to 30mg Filter Aid

This is the calibration curve for Linear Regression analysis.

The correlation coefficient (r) of the initial calibration curve must be ≥0.995. The slope of the line must be ± 10% of historical curves.

Corrective Action: If the correlation coefficient or slope QC criteria are not met, the standard curve must be re-prepared and re-analyzed until the correlation coefficient and/or slope are acceptable.

## 10.3 Equipment Operation and Sample Processing

Prepare a Calibration Curve per Section 10.2.

An ICV/LCS and Method Blank are analyzed immediately following the third K-Factor of the Routine Calibration, provided the instrument is "in tolerance".

Remove all pretreated samples from the oven, and allow to cool in a dessicator. Confirm that a constant weight has been achieved as in Sections 10.1.1.1 and 10.1.1.2. Record the weights in the TOC logbook.

**10.3.1 Soil Samples:** The solid samples must be ground using a mortar and pestle into a fine powder, without grinding shells, rocks or other large non-representative material. Carefully pick these materials from the sample with tweezers. Transfer the ground, pre-treated solid sample to a 5.0mL glass vial labeled with the sample ID. Fill the vial to approximately 2/3 full and discard the remainder.

Weigh approximately 2-10mg of sample into a tin boat using the Perkin-Elmer Microbalance, Model AD-6, which is linked to the instrument. Samples that are known to

be high in TOC may use a lesser sample aliquot. Each sample must be weighed in duplicate. (**NOTE:** *Check the paperwork carefully as often 3 replicate analyses are specified by the client.)* Record the weights in the TOC/Soot logbook. Matrix Duplicate and Matrix Spike samples are weighed as separate samples, with their own replicates or triplicates.

Analyze a CCV/CCB (Section 9.4 and 9.1.3) after every 10 “burns”, and at the end of the analytical sequence.

If following the *Lloyd Kahn* Calibration method, analyze the first set of batch QC samples, the ICV/LCS and Method Blank, followed by field samples with a CCV/CCB analyzed every 10 “burns”, and at the end of the analytical sequence.

**10.3.2 Multiple Sample Instrument Loading:**

**10.3.2.1** Each tin boat is carefully folded with anti-magnetic tweezers, and placed into its respective holding tray position. (See the Manufacturer User’s Manual SOP, Section 1.2, page 4, for tin boat folding details.) Weights, sample tray position and Autosampler location are recorded in the TOC/Soot logbook. The analyst must be very careful when transferring samples. Documentation of sample consistency is very important. See Figure 1 for an example logbook page.

**10.3.2.2** Adjust the Autosampler tray to begin sampling at auto-slot #1 and carefully transfer the folded tins containing the samples to the correct auto-slot, using tweezers. All Instrument Calibration Standards (Blanks, K-Factors and/or *Lloyd Kahn* Calibration Standards) are loaded first. Immediately following will be the first batch QC samples, the ICV/LCS and Method Blank for the run, followed by field samples. Rotate the Autosampler in a *counter clockwise* manner.

**10.3.2.3** A maximum of 60 tins can be held on the Autosampler at one time. The instrument only allows for 100 total samples (including calibration/blank samples) to be programmed for any given run.

**10.3.3 Sample Analysis**

**10.3.3.1** Select the *Auto Run* option on the keypad on the instrument. The following menu appears:

AUTO RUN NO. 1
1B 2K 3S

where: B = Blank
K = K-Factor
S = Sample

Assuming the *Instrument Standardization* occupies auto-slots 1-6, Enter “3” for Sample, then select “Enter”. Enter the weight of the “Primer” Standard (position 1) and select “Enter”.

**10.3.3.2** You will be prompted for AUTO RUN NO. 2 as in Section 10.3.3.1, except now there is a function “4NP” which allows the analyst to stop/erase everything by selecting this feature.

- Enter “1” for the Blank. The weight will not be asked for.
- Enter “2” for the first K-Factor, then select “Enter”. Enter the weight of your K-Factor (the standard weight should be ~ 10mg). Select “Enter”.
- Enter “1” for the second Blank, then “Enter”.
- Enter “2” for the second K-Factor, then “Enter”. Enter the weight, then “Enter”.
- Enter “2” for the third K-Factor, then “Enter”. Enter the weight, then “Enter”.

**10.3.3.3** All remaining sample weights are added by entering “3” for Sample, and then by entering the sample weight. Continue adding all information to the run sequence, using the keypad. When entering sample identification, and letters are necessary, refer to the Manufacturer’s User’s Manual, page 3-4, for instructions for converting numbers to letters.

**10.3.3.4** When all sequence information is entered and complete, select “Start”. The analyses will begin. The computer will continue to display the “AUTO RUN” menu during sample analysis.

**10.3.3.5** The Standard and Sample data prints out as it is collected on the line printer, and is also collected on the linked computer using the PE 2400 software. The data on the computer is saved in a file named as the date of the analysis (*i.e.,* 060503.chn) for future reference, as noted in 10.2.

**10.3.3.6** When all analyses are complete, refer to the Manufacturers User’s Manual SOP, Section 3.1, page 7, for instructions to “Shut Down” the instrument.

**10.3.3.7** Evaluate all batch QC samples first, to confirm or exclude the need for re-analyses. The ICV/LCS, Method Blank, CCB/CCV samples must meet the acceptance criteria in Section 9. Follow the corrective action for any QC failures.

**10.3.3.8** Evaluate the field samples next. If duplicate or triplicate “burns” of the same sample appear inconsistent, or vary by more than 30%, re-weigh a sample aliquot similar to the initial weight used, and re-analyze the sample. If inconsistencies persist, report this observation in the project narrative to the client.

## 10.4 Continuing Calibration

A CCV must be analyzed as outlined in Section 10.3.3 at a minimum of every 10 burns and at the close of an analytical sequence.

## 10.5 Preventive Maintenance

The column is changed after every 100-200 runs. Other maintenance is performed by a service provider.

# 11. Data Evaluation, Calculations and Reporting

**11.1** Procedures for data and record management for TOC/Soot analysis must adhere to the Quality Systems Manual, other subordinate documents covering record keeping, and the *Document Control* SOP, 08-01. All records are stored in such a manner as to be safe and accessible for at least 10 years.

**11.2** The relevant TOC/Soot laboratory notebooks must follow the specifications in the *Laboratory Notebook Usage* Work Instruction 108-01, and all record keeping and document control practices.

**11.3** Sample results for TOC/Soot are directly reported from the instrument printout.

**11.4 Calculations:** The following calculations are applied by the instrument when determining the percentage of Total Organic Carbon or Soot:

***Carbon Blank (CB):*** Used to make all other determinations, namely, K-Factor and weight percent calculations. When run alternately with samples, the instrument averages the blank values.

Carbon Blank (CB) = Carbon Read – Nitrogen Read

***Carbon K-Factor (C KF):*** K-Factor, or detector calibration factor, is determined when a known standard is analyzed to calibrate the analyzer in terms of micrograms of carbon. This calibration factor is then used to determine unknowns.

**C KF = ( (CR – NR) – CB x 100) / (SW x C Theory Wt. %)**

where: CR = Carbon Read
NR = Nitrogen Read
CB = Carbon Blank
SW= Sample Weight (mg)
C Theory Wt % = 1% (based on the concentration of the K-Factor standard)

***Carbon Weight Percent:***

**Carbon Weight Percent = ( ( (CR – NR ) – CB) x 100) / (SW x C KF)**

where: CR = Carbon Read
NR = Nitrogen Read
CB = Carbon Blank
SW = Sample Weight (mg)
C KF = Carbon K-Factor

***Example Calculation of Percent TOC/Soot from the instrument, converted to mg of TOC/Soot:***

If the result from the instrument is 1.083% and the sample weight is 10.76mg:

1.083% = 100 x [**X** / 10.76mg] (to solve for **X,** divide each side by 100)
0.01083 = **X** / 10.76mg (multiply each side by 10.76mg)
0.116mg = **X**

### 11.5 Reporting Results

The following procedures must be followed for reporting of TOC/Soot results:

Go to the next page in the bound TOC/Soot logbook.

Retain all computer printouts for the standard and sample analyses of this sequence.

Print the sequence from the computer and review it to make sure that no weight or sample ID transcription errors were made.

Calculate the recoveries for the QC samples (IVC/LCS, CCV, MS and RPD between the duplicate samples) and ensure the Method Blank and CCB meet the criteria. Remember any "QC Failures" require corrective action. See Section 9.0 or 12.0.

After reviewing the final logbook entries, make a copy of the logbook page for secondary review.

Go to the LIMS and "batch" and "associate" the set of QC samples and field samples that were just analyzed.

Enter the Final Results into the LIMS report sheet and check for transcription errors.

Transfer all associated sample paperwork to the Department Manager for the second level review and approval.

All TOC/Soot results are reportable without qualification if analytical holding times are met, preservation (including pH and cooler temperatures) are met, all QC criteria defined in the table below are met, and matrix interference was not suspected during analysis of the TOC/Soot samples. If any of the below QC parameters are not met, all associated samples must be evaluated for re-analysis.

| QC Parameter | Acceptance Criteria |
|---|---|
| Initial Calibration Curve, *Lloyd Kahn* | r $\geq$ 0.995 and slope ± 10% the historical curves |
| Initial Standardization (K-Factor) | ±0.15% from average of previous K-Factors |
| Method Blank | < reporting limit for matrix |
| Laboratory Control Sample | 75-125% R |
| Matrix Duplicate | 25%RPD for results <5x reporting limit |
| Matrix Spike | 75-125% R |
| Matrix Spike Duplicate if requested | 75-125%R/25%RPD |
| Continuing Calibration Verification | 80-120% of True Value |
| Continuing Calibration Blank | < reporting limit for matrix |

## 12. Contingencies for Handling Out-of-Control Data or Unacceptable Data

Section 9 outlines sample batch QC acceptance criteria. If non-compliant TOC/Soot results are to be reported, the Department Manager and/or the Laboratory Director, and the QA Manager must approve the reporting of these results. The laboratory Project Manager is notified, and may chose to

relay the non-compliance to the client, for approval, or other corrective action, such as re-sampling and re-analysis. The analyst or Department Manager performing the secondary review initiates the project narrative, and the narrative must clearly document the non-compliance and provide a reason for acceptance of these results.

# 13. Method Performance

## 13.1 Method Detection Limit Study (MDL) / Limit of Detection Study (LOD) / Limit of Quantitation (LOQ)

The laboratory follows the procedure to determine the MDL, LOD, and/or LOQ as outlined in Alpha SOP/08-05. These studies performed by the laboratory are maintained on file for review.

## 13.2 Demonstration of Capability Studies

Refer to Alpha SOP/08-12 for further information regarding IDC/DOC Generation.

### 13.2.1 Initial (IDC)

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method, prior to the processing of any samples.

### 13.2.2 Continuing (DOC)

The analyst must make a continuing, annual, demonstration of the ability to generate acceptable accuracy and precision with this method.

# 14. Pollution Prevention and Waste Management

The *Hazardous Waste and Sample Disposal* SOP (G-006) must be referenced for disposal of used standards, solvents, acids, reagents or other chemicals.

Once satisfactory TOC results have been generated, the sample containers must be scanned back into *LIMS* and returned to the appropriate sample refrigerator and held for 30 days.

All waste generated must be transferred to the waste disposal area. Dispose all solid samples in solid waste container. Aqueous samples must be poured into a 55-gallon drum marked acidic/non-chlorinated waste.

Refer to the Chemical Hygiene Plan and the Hazardous Waste & Sample Disposal SOP (G-006) for further pollution prevention and waste management information.

# 15. Referenced Documents

Chemical Hygiene Plan

PE 2400 Series II CHNS/O Analyzer User's Manual

Sample Receipt & Login SOP (01-01)

Perkin-Elmer, Model AD-6 Manufacturer User's Manual

Document Control SOP 08-01

Laboratory Notebook Usage Work Instruction (WI 108-01)

SOP/08-05 MDL Generation

SOP/08-12 IDC Generation

Hazardous Waste & Sample Disposal SOP (G-006)

# 16. Attachments

None.