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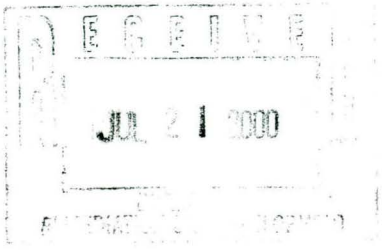
20 July 2000



Mr. Russell D. Hart
Remedial Project Manager (HSRW-6J)
United States Environmental Protection Agency
Region 5
77 West Jackson Boulevard
Chicago, Illinois 60604

RFW Work Order No. 02687.007.003
KMC Work Order No. 40-50-01-AKW-A

Pilot Solid Phase Bio Testing

Re: Revised QAPP Addendum for ~~Groundwater Performance Monitoring~~
SOP for Determination of TOC in Solids and Sludges
Moss-American Site, Milwaukee, Wisconsin

Dear Mr. Hart:

Attached is a complete copy of the above-referenced SOP that was inadvertently left out of our 14 July 2000 submittal.

If you have any questions or require additional information, please do not hesitate to contact me at (847) 918-4142, or Keith Watson at (405) 270-3747.

Very truly yours,

ROY F. WESTON, INC.

Thomas P. Graan

Thomas P. Graan, Ph.D
Principal Project Manager

TPG:cz

Attachments

cc: K. Watson, KMC
G. Edelstein, WDNR

Determination of TOC in Solids and Sludges

Reference:

1. *Chemical Analysis of Water and Wastes*, 415.1, EPA 600/4-79-020, Modified.

2. Method 9060, *Test Methods for Evaluating Solid Waste*, Physical/Chemical Methods SW-846.

3. *Model 700 Total Organic Carbon Analyzer Operating Procedures and Service Manual*, O. I. Corporation, 1986.

4. Method 505C, *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, 1985, pp. 513-515.

5. *Ampule TOC Trapping and Desorption Module Operating Procedures and Service Manual*, O. I. Corporation, 1986.

6. *Purging and Sealing Manual*, O. I. Corporation, 1986.

Scope:

This method is applicable for the determination of total organic carbon (TOC) in soils and other samples not easily analyzed by the TOC waters method. Because of the extremely low sample aliquots used for this analysis, this method is semiquantitative.

The limit of quantitation (LOQ) for this method is 50 mg/kg assuming a 0.1-g sample aliquot. The LOQ may increase to 5000 mg/kg if the minimum aliquot of 0.001 g is analyzed. Semiquantitative TOC results up to 75,000 mg/kg may be obtained by this method.

Carbon is commonly found in nature. Therefore, extra care must be taken to avoid contamination of reagents, glassware, and any other materials which come in contact with the sample.

Modifications:

The referenced method does not include analysis of solids in the scope. This method cites a modified method reference for analyzing solid samples.

Personnel Training and Qualifications:

Analysts are considered proficient when they have successfully completed a quad study for the analysis. A quad study consists of four laboratory control standards that are carried through all steps of the analysis and that meet the acceptance criteria for the LCS. Documentation for these studies are in each individual's training records.

Basic Principles:

A small amount (1 to 100 mg) of a sample is weighed into a 10-cc ampule. Measured amounts of sodium persulfate, phosphoric acid, and deionized water are added to the ampule. The ampule is then purged with UPC grade oxygen to remove carbonates and ambient carbon dioxide and is flame sealed. The ampules are autoclaved to quantitatively oxidize the organic carbon. The CO_2 produced is purged from the ampule into the TOC analyzer and is trapped on a molecular sieve. The sieve is heated so that the trapped CO_2 is desorbed and carried into the nondispersive infrared detector (NDIR). The CO_2 detected is thus used to determine the mass of TOC in the sample. Samples analyzed by this method include solids such as soils or sediments, slurries, sludges, brines, and corrosives.

Sampling Handling, Preservation, and Storage:

Samples should be collected and stored in glass containers. Samples should be stored under refrigeration at 2° to 4°C. The holding time for samples is 28 days. Because very small amounts (1 to 100 mg) of sample are used for the analysis, the sample should be as homogeneous as possible.

Apparatus:

1. O.I. Corporation Model 700 TOC analyzer with printer
2. O.I. Corporation Model 524 PS purging and sealing unit
3. IBM PC compatible computer with "Solid TOC Calculations" program
4. 2-stage gas regulators (2 required)
5. 10-cc ampules
6. Purge tubes
7. One canister propane
8. Analytical balance, capable of accurately weighing to 0.0001 g
9. Automatic pipettes
10. Glassware - General laboratory glassware is needed for preparing reagents and standards
11. Striker or acceptable flame source

Reagents and Standards:

NOTE: All chemicals used must be ACS reagent grade unless otherwise noted.

Different volumes or weights may be used provided the ratios remain equivalent.

See SOP-QA-110, "Reagents," for the appropriate labeling and documentation of reagent and standard preparation.

1. Ultra pure nitrogen gas (30 psi)

2. Ultra pure oxygen gas (10 psi)

3. Sodium persulfate ($Na_2S_2O_8$) solution (100 g/L)

   Dissolve 100 ± 1 g $Na_2S_2O_8$ in about 500 mL deionized water in a 1000-mL volumetric flask. Dilute to volume with deionized water. This solution is stable for 6 months and may be stored at room temperature.

4. Phosphoric acid (20% v/v)

   Phosphoric acid, 85% (H_3PO_4) 118 mL

   Fill a 500-mL volumetric flask to about 250 mL with deionized water. Slowly add 118 mL of 85% phosphoric acid. Mix thoroughly and dilute to volume with deionized water. Store at room temperature. Prepare fresh solution every 6 months.

5. TOC stock QC standard (500 mg C/L)

   Same preparation as described in Lancaster Laboratories Analysis #0273, "Determination of Total Organic Carbon in Water and Wastewater."

6. Working standards for calibration linearity check

Pipette a volume of the TOC stock QC standard into the appropriate volumetric flask and dilute to the final volume with deionized water that has been acidified with 1 to 2 drops of concentrated sulfuric acid (H_2SO_4). Prepare new standards each day the ampules are to be prepared.

Working Std. (mg/L)	Vol. Stock TOC Std. A (mL)	Final Vol. (mL)
5	1.0	100
10	2.0	100
25	10.0	200
50	10.0	100
75	15.0	100

7. TOC stock calibration standard (500 mg C/L)

Same preparation as described in Lancaster Laboratories Analysis #0273, "Determination of Total Organic Carbon in Water and Wastewater."

8. Working standard for calibration (25 mg/L)

Pipette 5.0 mL of the TOC stock calibration standard into a 100-mL volumetric flask containing about 50 mL deionized water which has been acidified with 1 to 2 drops of concentrated sulfuric acid (H_2SO_4). Dilute to volume with deionized water. Prepare each day the ampules are to be prepared.

9. Ampule preparation - standards

NOTE: Each standard or blank ampule that is prepared for this analysis shall be labeled with the concentration and the date of preparation. Using ampules from more than one date is acceptable. However, an ampule shall be considered expired and not suitable for use 29 days after the date of preparation. The date of preparation must be documented in the analysis notebook.

Prepare a 25-µg carbon calibration standard and a series of linearity check standards (5, 10, 25, 50, and 75 µg carbon). Add the appropriate amount of the reagents to the 10-cc ampule in the order listed below:

1 mL persulfate solution

1 mL appropriate working standard

1 mL 20% H_3PO_4

2 mL deionized water

Prepare 6 ampules each of the 5-, 10-, 50-, and 75-µg linearity check standards. Prepare 12 ampules of the 25-µg linearity check standard and 6 ampules of the 25-µg calibration standard. Label each standard ampule with date of preparation.

NOTE: The numbers of ampules to be prepared as listed above are suggestions. The number required may vary from one run to the next.

10. Ampule preparation - blanks

Prepare 18 ampules to be used for calibration blanks, method blanks, and continuing calibration blank verification. Add the appropriate amounts of reagents to the 10-cc ampule in the order listed:

1 mL persulfate solution

1 mL 20% H_3PO_4

3 mL deionized water

Label each blank ampule with date of preparation.

NOTE: The number of ampules to be prepared as listed above is a suggestion. The number required may vary from one run to the next.

11. Ampule preparation - preparation blank (PBS)

Each day samples are prepared, a preparation blank must be prepared for every 20 samples. Four ampules should be prepared and labeled with the date of preparation on the ampule and *PBS*. Prepare as described in step 10 above.

12. Ampule preparation - laboratory control standard (LCSS) and laboratory control standard duplicate (LCSSD)

Each day samples are prepared, a laboratory control standard must be prepared for every 20 samples. An LCSD may also be prepared if requested by the client. Four ampules should be prepared and labeled with the date of preparation and *LCSS*. To prepare, add the appropriate amounts of reagents to the 10-cc ampule in the order listed below:

1 mL persulfate solution

1 mL 25-mg/L working check standard

1 mL 20% H_3PO_4

2 mL deionized water

Sample Preparation:

As stated previously, samples should be as homogeneous as possible before analyzing for TOC. Before a sample is prepared, determine what type of sample it is and what matrix classification it is according to the chart below:

Classification	Matrix Types	Est. TOC Levels
Type A - low	clean sand reagents blanks	<50 to 750
Type B - high	oils tars contaminated soils/sludges	>5000 to 75000
Type C - other	most ordinary soils soil/sand mixtures clay most ashes miscellaneous solids most other sludges	>500 to 7500

When samples are prepared, if the classification is uncertain, the analyst should select a classification in accordance with the matrix types listed above. Then the prep analyst should prepare four ampules of the sample within that weight range. Also, more than one classification can be chosen for a sample. If this occurs, four ampules in each chosen classification should be prepared.

Classification	Sample Aliquot Weight for Analysis (g)
Type A	~0.100
Type B	~0.001
Type C	~0.010

To prepare the ampules, weigh the appropriate amount of sample and reagents to the 10-cc ampule in the order listed below:

x mg of sample

1 mL persulfate solution

1 mL 20% H_3PO_4

3 mL deionized water

Record the sample number, matrix type, replicate number, weight, balance ID, prep time, and batch number in the preparation logbook.

To prepare a spike, weigh the appropriate amount of sample and reagents to the 10-cc ampule in the order listed:

x mg sample

1 mL persulfate solution

1 mL 25 mg/L working check standard

1 mL 20% H_3PO_4

2 mL deionized water

Safety Precautions:

1. Normal laboratory practices for safety should be followed.

2. The ampules should not be bumped after they have been autoclaved since they can explode when stressed.

3. Extreme caution should be used when the propane O_2 flame is in use.

   CAUTION: DO NOT LEAVE FLAME UNATTENDED. DO NOT TOUCH ANYTHING THAT HAS BEEN NEAR THE FLAME.

4. Handle ampules with care especially when removing from the breaking assembly.

Procedure:

A. Ampule preparation, purging, and sealing

1. Prepare ampules of standards, samples, and blanks as described in previous sections of this method.

2. Turn on the oxygen flow to the purging and sealing unit (about 10 psi).

3. Make sure the switch for "Catalyst Temperature" is off and the temperature reads 0°F.

4. Light the flame used for sealing the ampules. Take care to turn on the propane flow first, light the propane, adjust the height of the flame to approximately 1" to 2" and then adjust the intensity with the oxygen flow.

5. Insert purge tube into ampule so that it is under the surface of the liquid and purge with O_2 for 5 to 6 minutes.

6. Seat ampule into clamping assembly and raise the purge tube so that it is even with the underside of the clamping assembly.

7. Center the flame around the ampule neck. Pull the ampule down about 3/8" when the glass begins to soften. Turn gently so that the top and bottom separate.

8. Remove ampule from clamping assembly, change purge tube, and begin purging a new ampule. Repeat steps 5 and 6 for the next ampule in line.

9. Turn off purging and sealing unit by turning off the O_2 first and then the propane.

10. Turn off oxygen flow at the tank and close the valve on the propane tank.

11. Autoclave ampules for 45 ± 5 minutes at 120° ± 5°C (set autoclave timer for 65 minutes).

B. Ampule analysis

1. Start up the TOC analyzer as described in Lancaster Laboratories Analysis #0273.

2. After running the clean-out blanks, if necessary, disable the auto-run option and enable the ampules option. Enter 25 µg C as the standard mass and 1.0 mL as the sample volume.

3. Hook the ampule-breaking assembly to the instrument on the gas flow line between the syringe injection port and the digestion vessel making sure the N_2 flows into the ampule through the purge tube.

4. Raise the stainless steel purge tube at the top of the ampule-breaking assembly so that the bottom of the tube is inside the cutter plunger.

5. Place an ampule support collar over the neck of the ampule to be analyzed. Slide a gum rubber O-ring over the tip of the ampule until the ring seals against the top of the collar.

6. Raise cutter plunger to avoid contact with the tip of the ampule. Insert ampule neck up into the breaking assembly. Tighten the bottom screw to clamp the ampule in place. Continue tightening until the O-ring slips inside the glass cutter plunger barrel and seals. Press RUN.

7. After 24 seconds, the instrument will give a cue to break the ampule and insert the purge tube. Do so by pressing firmly down on the cutter plunger handle breaking the ampule. Insert the purge tube into the ampule and press RUN.

8. Run reagent blanks (minimum of three) until a reproducible millivolt response (generally <10 millivolt variation) is observed. Average the mV values and enter this as the OC blank.

9. Run 25-µg carbon calibration standards (minimum of three) until a reproducible millivolt response (generally ≤20 millivolt variation) is observed. Average the mV values and enter this as the standard average in the microprocessor.

10. Press PRINT. The instrument will automatically calculate the response factor and list the calibration data.

11. Run a linearity check as follows: method blank, 5 µg, 10 µg, 25 µg, 50 µg, 75 µg, and ICB/RB.

12. Samples may now be analyzed along with the appropriate laboratory control standard and preparation blank. A check standard (CCV) of 25 µg carbon and a continuing calibration blank (CCB) must be run after every ten samples.

Sample Analysis and Calculations:

Samples should be reported as the average of two replicates. The replicates must meet the following criteria:

1. The raw results must fall within the linear range of the instrument calibration for the run.

2. Both of the results should have a difference of less than or equal to the limit of quantitation. If not, the relative percent difference between the replicates must be ≤35%.

If the above criteria cannot be met, a third replicate must be prepared and analyzed. If the third replicate is within 35% RPD of one of the other replicates, the Dixon Test should be performed on the other replicate to determine if it may be discarded as a statistical outlier. If it can be discarded, the average of the two remaining replicates may be reported. If it cannot be discarded, the average and all three replicate results shall be reported.

1. Data manipulation

   To determine mg/kg TOC

$$mg / kg\ TOC = \frac{\mu g\ carbon}{g\ sample\ weight}$$

   To determine mg/kg TOC spike added

$$mg / kg = \frac{25\ \mu g}{g\ sample\ weight}$$

   To test for rejection of data (Dixon Test)

   See SOP-LA-022, "Use of the Dixon Test for Rejecting Outlying Observations."

   To determine relative percent different

$$RPD(\%) = \left[\frac{|(mg / kg\ Replicate\ 1) - (mg / kg\ Replicate\ 2)|}{\frac{(mg / kg\ Replicate\ 1 + mg / kg\ Replicate\ 2)}{2}} \right]$$

To determine the LOQ

$$LOQ = \frac{5}{average\ weight\ of\ samples(g)}$$

To determine sample dilution factors

$$DF = \frac{Maximum\ sample\ aliquot\ weight\ (0.1g)}{average\ weight\ of\ samples\ (g)}$$

NOTE: The above calculations can be performed automatically using the "solid TOC calculations" program on an IBM PC. The analyst needs only to input the µg carbon raw result and the sample weight for each sample.

2. Data entry and reporting

   All replicate results should be entered into the data entry system. The average of the appropriate replicates (see above) shall be reported. If more than two trials have been analyzed, the individual replicate results shall be listed in the analysis comments for the sample (Comment #882).

   QC spikes shall be entered against the average replicate value that was reported.

   Batch blanks shall be calculated assuming the maximum sample aliquot weight (0.100 g).

Statistical Information:

1. Precision

The precision of this method based upon a pooled standard deviation from five different matrices is 31.7% RSD. Fourteen replicates of five different matrices (oil, sand, soil, clay, and sandy soil mixture) were prepared and analyzed for this study. The data for this study may be found in Laboratory Data Notebook #7956, pages 1 to 9.

2. Accuracy

The accuracy of this method as determined by fortification of samples with a known standard addition is 106.2% recovery. The background concentrations of 19 samples were determined. Each sample was then spiked with a known addition. The recovery of the spike was determined after correcting for the background concentration. The results of this study indicate that the sample matrix does not contribute unacceptable bias to the analytical result. The data for this study may be found in Laboratory Data Notebook #7956, pages 9 and 71.

NOTE: Current statistics may be obtained through the Quality Assurance Department.

Quality Assurance:

1. A series of linear range standards (5, 10, 25, 50, and 75 µg carbon) prepared from the TOC QC standard shall be run after every calibration. The acceptable range is ±10% of the true value for the 10- through 75-µg standards and ±50% of the true value for the 5-µg standard (2.50 to 7.50 mg). If these criteria are not met, the standard must be repeated twice to confirm the analysis is in control. The instrument must be recalibrated if either of the replicates are not within the acceptable range.

2. A method blank shall be run at the beginning of every linearity check and an initial calibration blank (ICB) shall be run at the end of every linearity check. The acceptable result for both is less than the limit of quantitation. If the method blank and/or ICB does not meet the acceptance criterion, it should be rerun twice. If either of the replicates do not fall below the limit of quantitation, the instrument must be recalibrated.

3. A batch shall contain no more than 20 field samples.

4. A batch blank (PBS) shall be prepared and analyzed every batch or each day samples are prepared (not to exceed 20 samples). An acceptable result is less than the limit of quantitation. If the batch blank does not meet this criterion, it should be rerun twice. If either of the two additional trials do not meet the acceptance criterion, all samples in the batch must be reprepared.

5. A laboratory standard (LCSS) shall be prepared and analyzed every batch or each day samples are prepared (not to exceed 20 field samples). The acceptable recovery range is statistical and can be found in the Wang.
   NOTE: If the LCSS does not meet the acceptance criterion, it should be repeated twice. If either of the two additional trials do not meet the acceptance criterion, all samples in the batch must be repeated.

6. A laboratory control standard duplicate (LCSD) may also be prepared when requested, under the same conditions as the LCS. The acceptable range and corrective action for this standard is the same as the LCS. The RPD between the LCS and LCSD is statistical and can be found in the Wang. If the RPD is outside of this criteria, consult your coordinator or group leader to determine if reanalysis is necessary.

7. Since the minimum requirements for this method demand that all samples be run in duplicate, a QC duplicate need not be entered for this analysis.

8. A spike shall be prepared and analyzed for every batch. The spike shall be compared to the mean value of the background that was reported. The acceptance range is statistical and can be found in the Wang. If a spike recovery does not meet the acceptance criteria, see SOP-IC-004, "Quality Control for Analyses Performed on Alpkem Flow Analyzer," for the corrective action which must be taken.

9. Based upon client requirements, a matrix spike duplicate may also be prepared and analyzed under identical conditions as the matrix spike. If a spike recovery does not meet the acceptance criterion, see SOP-IC-004 for the corrective action which must be taken. The RPD between the MS and MSD is statistical and can be found in the Wang. If the RPD is outside the control limit, see your coordinator or group leader to determine if reanalysis is needed.

10. A check standard (CCV) and blank (CCB) must be run after every ten samples (including blanks and standards). The acceptable range for the CCV is ±10% of the true valve. An acceptable CCB result is less than the limit of quantitation. If either or both of these injections do not meet the acceptance criterion, the unacceptable original should be repeated twice. If either of the two additional trials do not meet the acceptance criterion, all samples since the last compliant CCV/CCB must be reanalyzed.

11. The instrument calibration shall be performed at the beginning of each run. At any time when the instrument has been idle for a period of 4 hours or more, a CCB and CCV must be analyzed. If either of these parameters cannot meet specifications, the instrument must be recalibrated.

Revision Log:

Initiated Date: 05/23/88

Ver. #	Effective Date	Change
00	09/11/95	Previous Issue
01	11/21/97	Major changes are as follows: • Quality Control - Addition of laboratory control standard duplicate and spike duplicate • Delete Figures 1 and 2
02	09/23/98	Major changes are as follows: • Incorporated Procedural Amendment #1 • Changed acceptance criteria for all spikes, duplicates, and LCS's to the Wang statistical program
03	MAY 25 1999	Major changes are as follows: • Analysis #6370 added to method number • Delete LCSD and MSD

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Prepared by: Tonya M. Beck Date: 5/7/99

Approved by: [signature] Date: 5/7/99

Approved by: [signature] Date: 5·11·99