Analysis of Total Organic Carbon

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As performed at the University of Massachusetts, Environmental Engineering Research Laboratory

Prepared by:
David A. Reckhow 413-545-5392
18 Marston Hall reckhow@ecs.umass.edu
University of Massachusetts
Amherst, MA 01003

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Standard Operating Procedures

Analysis of Total Organic Carbon

This guidance document was prepared to assist research assistants, post-docs and lab technicians in conducting analysis of TOC and DOC in the UMass Environmental Engineering research laboratories. It aspires to outline our standard operating procedures, as they exist at the present time. It also emphasizes elements of quality control that are necessary to assure high quality data. Please help me keep this document current by alerting me to any errors or long-term changes in methodology or equipment. Special thanks to Ken Mercer for help with preparation of version 2.

Dave Reckhow
Faculty QC officer for TOC analysis

Scope

This method has been used in the UMass Environmental Engineering Laboratory for analysis of TOC and DOC in clean water samples (i.e., drinking water, surface waters and uncontaminated groundwaters). It has been found to meet data quality criteria with all waters of these types for which it has been tested. This method should not be used for other media without further validation.

Recoveries using the high temperature oxidation method are generally considered to be complete (i.e., ~100%)[1]. Most tests with purified standards have shown complete recovery within the range of error. The compounds that have been reported to be incompletely recovered are summarized in the table below.

Compounds Reported to be Incompletely Recovered by HT Combustion TOC Analysis

Compound	Average Recovery	Source
Dodecylbenzene sulfonic acid	80%	Aiken et al., 2002
Caffeine[2]	90%	Aiken et al., 2002
Guanine	50%	Kim, 2005
m-Xylene	65%	Wei et al., 1998
Antipyrine[3]	85%	Alvarez-Slagado et al. 1998

[1] Recoveries are, of course, all based on an assumed 100% recovery of Potassium Acid Phthalate
[2] This compound has been shown to be completely recovered by the UMass Shimadzu 4000 (Kim, 2005)
[3] Based on N-recovery

Compounds tested at UMass, and known to be Completely Recovered by the Shimadzu 400

Anthranilic acid	4-pyridinealdoxime	Caffeine
3 Aminobenzoic acid	Nicotinic acid	Thymine
4 Aminobenzoic acid	2-hydroxynicotinic acid	Cytosine
2-aminophenol	6-hydroxynicotinic acid	Uracil
Acetanilide	Nicotinamide	3,4,5-Trimethoxybenzamide
1,4-phenylenediamine	Adenine	3,4,5-Trimethoxy phenylacetonitrile
4-hydroxypyridine		Urea

Additional compounds tested by others showing complete recovery[4]

Isonicotinic Acid	Glutaric Acid	Sodium Hexane-1-sulfonate
Glutaric acid	Citric Acid	Lignosulfonic Acid
Tryptophan	1,4-Benzoquinone	Lauric Acid
Oxalic Acid	Phenylalanine	Cysteine
Glycine		

Other compounds exhibiting complete recovery of N in a Shimadzu 5000 combustion system[5]

Arginine	Caffeine	EDTA
Histidine	Nicotinic Acid	Sulphathiazole
Thiourea	Thymidine	Urea

Some have analyzed complex environmental carbon source and compared these to results from classical elemental analysis. Notably, Aiken and co-workers (2002) found that the carbon in aquatic humic and fulvic acids was about 92% recovered on average. Wallace and co-workers (2002) recovered 100% of the carbon in a terrestrial humic acid.

[4] From: Wallace et al., 2002
[5] From Alvarez-Salgado e tal., 1998

Method Overview

Reproduced below is a simple, step-by-step outline of our TOC method for quick reference.

Table 1: Summary of Procedure for TOC Analysis

1. Filter samples if necessary
2. Turn on Analyzer and start log book record
3. Install Autosampler tray
4. Check Gas flow and pressures
5. Check liquid levels
6. Activate furnace from Computer
7. Prepare **calibration standards** (Table 2) and **QC samples** (Table 3)
8. Load samples and standards on tray
9. Record sample identities in log book
10. Start run on computer
11. Verify initial autosampler operation
12. Inspect data and report on QC

Table 2. Typical Preparation of Calibration Standard

1. Prepare primary standard containing 1000 mg/L of TOC in the form of Potassium Hydrogen Phthalate, if needed
2. Prepare intermediate standard (100 mg/L) from the primary standard
3. Prepare working standards (typically 0-10 mg/L) from intermediate standard.

Table 3. Typical Preparation of QC Samples

1. Prepare Spiked samples for determination of matrix recovery (laboratory fortified sample matrix). Select 10% of analytical samples and set aside an additional 30 mL aliquot of each.
2. Prepare a continuing calibration check standard at mid-range concentration.
3. Prepare any other QC samples as needed (see Table 6, page 26).

Detailed Procedures

Basis for Method

We use a protocol that is closely aligned with Standard Method 5310B, "Total Organic Carbon: High Temperature Combustion Method". Please refer to the latest version of this method (currently from the 20th edition, dated 1999; attached as Appendix 1) for all details. However, the analyst should keep in mind that we have occasionally made some specific modifications. Such modifications are itemized below in Table 4.

Table 4. UMass Protocol Specifics and Departures from Standard Method 5310B

§ from 5310B	Step or Apparatus	5310B protocol	UMass protocol

UMass Detailed Procedures

Sample Preservation and Pretreatment

1. **Filter if Dissolved Organic Carbon (DOC) is to be measured.**
   a) Assemble and clean the filtration apparatus
      - May be either glass Millipore-type or in-line syringe filter
   b) Pre-wash a Whatman GF/C glass fiber filter
      i. Place filter in housing
      ii. Rinse with 50 mL deionized water; repeat 5 times
      iii. If practical, final rinse with 10 mL of sample

2. **Drop pH to 2 with one of the following preservatives.**[6]
   - Sufficient H_3PO_4 to bring pH $\leq$2.0
     - General preservative of choice, unless precipitate forms
   - 100 µL of 6 N HCl for every 100 mL of sample.
     - Use this only with pyrolytic system (e.g., Shimadzu 5000)[7]
     - Requires that halide scrubber be frequently changed
     - This should be sufficient to lower pH below 2

3. **Place aqueous samples in a refrigerator until analysis.**
   - Samples should be analyzed as soon after collection as possible, but under no circumstances should more than 7 days be allowed to elapse.

Selection of TOC Analyzer

In the environmental engineering laboratory (room 308, Elab II), we have two batch TOC analyzers with autosamplers: the Shimadzu TOC-5000A, and the Shimadzu TOC-V. Both use high-temperature combustion with the same proprietary catalyst and NDIR detection. If analysis of total nitrogen is also desired, you should select the TOC-V as it is coupled with the TN module. Otherwise, the selection of an analyzer is largely a matter of convenience and availability

[6] Nitric acid may be used with UV-persulfate systems, but should be avoided in pyrolytic ones (corrosive N_2O_4 is formed and incompletely removed by scrubber, sulfuric acid should be avoided due to formation of SO_3 in both types of systems (this gas will interfere with CO_2 detection); see Tekmar-Dohrmann application note or Wallace, 2001 [WQTC proceedings]
[7] chloride will scavenge radical oxidants in UV/persulfate systems.

Startup of TOC Analyzer

Shimadzu TOC-5000A Analyzer[8]

1. **Begin Entry in Log Book**
   - Record you name, date, number of samples, types of samples
   - Also record any problems or unusual performance noted

2. **Turn on the TOC-5000A Analyzer**
   - Activate switch on lower left side of analyzer
   - Wait for indicator to change from "initializing" to "initialized"

3. **Install autosampler tray.**
   c) Place tray in autosampler, making sure that the positioning slot in the tray is lined up with the positioning pin on the autosampler
   d) Place turntable cover on top; being sure that the arrow on the cover lines up with the arrow on the autosampler
   e) Presss ASI Initial (F5)
   f) Wait until autosampler is recognized. The Initial Start screen will reappear when instrument is ready

4. **Check gas flow and pressure**
   g) Open the knob on the top of the carrier gas cylinder (must be "Ultra Zero" grade air)
   h) Note first stage pressure on the regulator
      - Cylinder must be replaced when it falls below 500 psi
   i) Second stage pressure gage on regulator must read 70-85 psi
      - Re-adjust if it doesn't fall in this range
   j) Open front door of analyzer to reveal gas settings
   k) Check that the instrument carrier gas pressure gage[9] reads 4-5 kgf/cm^2
   l) Check that the instrument carrier gas flowmeter reads 150 mL/min
   m) Verify that the IC reaction vessel is bubbling

5. **Check Liquid levels**
   n) Verify that the rinse water bottle (located behind autosampler) is full and end of tubing is at the bottom of the bottle
      - If not full, fill with super-Q water and re-adjust tubing
   o) Verify that the humidifier water level (inside front door of analyzer) is near top white line (the bottle should be at least half full).
      - If not, unscrew black cap and fill with Super-Q water from a squeeze bottle
   p) Verify that dehumidifier drain container (also inside front door of analyzer) is full

[8] This must be done at least 1 hour before starting sample analysis
[9] As long as the pressure from the tank is OK, this setting should be correct. If it is not correct, and the pressure at the tank is within range, there may be some blockages in the gas lines

6. **Activate furnace from computer**
   q) Choose "Next" from the "Initial Start" screen
      - This accesses the main menu.
   r) Select "3", "general conditions"
   s) In the "general conditions" screen, scroll down with the arrows keys to "Furnace On/Off" and type "1" followed by the 'Enter" key.
      - This turns the oven on
      - Do not change any other settings on this page
   t) Select "Main menu" and from the "main menu" screen, select "6" (Monitor).
      - This shows the status of the analyzer
   u) Allow analyzer at least 1 hour to warm up

Shimadzu TOC-V/TN Analyzer[10]

1. **Begin Entry in Log Book**
   - Record you name, date, number of samples, types of samples
   - Also record any problems or unusual performance noted

2. **Turn on the TOC-V/TN Analyzer**
   - Make sure gas is flowing to the instrument (as observed by bubbling in the IC Reagent Vessel)
   - Activate switch on lower left side of analyzer
   - Turn on ozone generator if measuring TN
   - Wait for indicator to change from "initializing" to "initialized"

3. **Install autosampler tray.**
   a) Place tray in autosampler, making sure that the positioning slot in the tray is lined up with the positioning pin on the autosampler
   b) Place turntable cover on top; being sure that the arrow on the cover lines up with the arrow on the autosampler
   c) Press ASI Initial (F5)
   d) Wait until autosampler is recognized. The Initial Start screen will reappear when instrument is ready

4. **Check gas flow and pressure**
   a) Open the knob on the top of the carrier gas cylinder (must be "Ultra Zero" grade air)
   b) Note first stage pressure on the regulator
      - Cylinder must be replaced when it falls below 500 psi
   c) Second stage pressure gage on regulator must read 70-85 psi
      - Re-adjust if it doesn't fall in this range

[10] This must be done at least 1 hour before starting sample analysis

d) Open front door of analyzer to reveal gas settings
e) Check that the instrument carrier gas pressure gage[11] reads 4-5 kgf/cm^2
f) Check that the instrument carrier gas flowmeter reads 150 mL/min
g) Verify that the IC reaction vessel is bubbling

5. <u>Check Liquid levels</u>

a) Verify that the rinse water bottle (located behind autosampler) is full and end of tubing is at the bottom of the bottle
   - If not full, fill with super-Q water and re-adjust tubing

b) Verify that the humidifier water level (inside front door of analyzer) is near top white line.
   - If not, unscrew black cap and fill with Super-Q water from a squeeze bottle

c) Verify that dehumidifier drain container (also inside front door of analyzer) is full

6. <u>Refer to Analysis Section to Turn on the Furnace</u>

[11] As long as the pressure from the tank is OK, this setting should be correct. If it is not correct, and the pressure at the tank is within range, there may be some blockages in the gas lines

Analysis of samples/standards[12]

Shimadzu TOC-5000A Analyzer

1. **Prepare standards and QC samples**
2. **Load samples and standard on to autosampler tray**
3. **Verify that TOC analyzer has warmed up**
   - all status indicators on the "monitor" screen should read "OK"
   - the baseline, shown on the graph, should be flat (although it need not read exactly zero)
4. **Place the tray and turntable cover onto the autosampler**
   - make sure the positioning pins and arrows line up
   - See Table 7 (page 27) for typical sample sequence with QC samples
5. **Write down in the log book, sample number and sample identity**
6. **Run samples through commands on the computer**
   a) Return to the main menu and select "9" (autosampler)
   b) Enter information on samples, standards and analysis conditions on the "Sample Measurement (ASI)/Conditions" screen:

#	Sample group number. If all samples are to be analyzed under the same conditions, all information is entered under sample group number 1. For multiple sample groups, enter information in more than one group number.
Type	Type of analysis. Choices are NPOC (non-purgeable organic carbon), TC (total carbon) and IC (inorganic carbon). Most work will use *#4, NPOC* to analyze for TOC and DOC. Note that for TOC analysis, use #4, NPOC (not #3, TOC).
IS	Initial Sample. The vial number of the first sample.
FS	Final Sample. The vial number of the final sample.
C1-C3 and F1-F3	C1-C3 specify the generation of calibration curve from standards in the autosampler. F1-F3 specify using a calibration curve that was previously generated and stored in a file. In general, when the analyzer has been shut off and turned back on, a new calibration curve must be created. However, if more than 16 samples (capacity of tray) are to be analyzed, a curve can be initially generated, stored in a file, and used for all samples. To specify use of a calibration curve from file, enter the number of the calibration curve under F1. To create a new calibration curve, enter the number under which the new curve will be stored under C1 (from 2 to 18). The **Calibration (ASI)/Conditions** screen will appear. Enter the following information and select "Return" when completed:

TYPE	1 (1=TC for NPOC; 2=IC for IC)
1st STD CONC, VIAL # etc.	Enter the conc. in ppm and vial # for each standard. Standards must be in conc. order with the highest conc. standard first
RANGE	Automatically set based on standard conc's
INJ VOL	Automatically set based on standard conc's
NO OF INJECTS	3 (The # of injections for repetitive measurement of each standard)

[12] typically requires 10 hours of analyzer time for a run of 30 samples

MAX NO OF INJ	5 (The maximum # of injections for each standard)
SD	200 (default value for allowable standard deviation between repetitive measures)
CV	2.0% (default value for coefficient of variation between repetitive measures)
SPARGE TIME	3 min (for NPOC analysis)
SHIFT TO ORIGIN	2 (Off)
ACID ADDITION	2 (Off: standards/samples are pre-acidified)

RG Range. Set automatically based on the standard concentrations.
VOL Injection Volume: This is set automatically based on the standard concentrations.
W Injection Syringe Washes. This was previously set in the General Conditions screen and should be 4.
NO Number of injections for repetitive measurement of each sample. Set to 3.
MAX Maximum number of injections for each sample. Set to 5.
SD Allowable standard deviation between measurements. Set to 200.
CV Allowable coefficient of variation between measurements. Set to 2.0%.
SP Sparge Time. Set to 3 min. for NPOC analysis
DIL Dilution Factor if sample was diluted prior to analysis

c) Choose "Next". At this point the "ASI Conditions" screen appears. Here you can set conditions which control the autosampler. Enter information as follows:

Option	Typical Value	Comments
RINSE	1	Always choose 1=Rinse (prevents cross-contamination)
NO OF NEEDLE WASHES	1 or 2	Prevents build up of salt. Higher number for samples w/ more particulates & salts
FLOW LINE WASHES	3	Prevents clogging. Choose 3 if samples are pre-acidified
CALIBRATION BEFORE	2	Analyzes each sample group separately
PRINT INFORMATION	2	Prints data report for samples
AUTO ADDITION OF ACID	2	2=Off (samples are pre-acidified)
ACID VOLUME	0	Not used
RINSE AFTER ADDITION	2	Not used
KEY LOCK	2	2=Unlock (retain keypad control during analysis)
FINISH OR RUNNING	1	Choose 1=Finish to shut off analyzer after analysis or 3=No Change to leave oven on after analysis

d) Choose "Next", and press the "START" button per instructions on the screen.

7. **Verify initial autosampler operation**
   a) After pressing the "START" button, watch as the needles move into the first standard or sample. Verify that the needle is in the right position
   b) After sparging, make sure that the sparge gas flowmeter reads approximately 100 mL/min.
      - If it doesn't, open the first door of the analyzer and adjust the flow rate. Note that the sparge gas flow rate may take a while to stabilize, and may need to be re-checked in 20-30 minutes and adjusted again.

8. **Inspect the first few printouts**
   - make your first QC report by email (see "Data Analysis" below).
9. **Finish the IC run and Process peak data when analysis is complete.**

Shimadzu TOC-V/TN Analyzer

1. **Prepare standards and QC samples**
2. **Load samples and standard on to autosampler tray**
3. **Place the tray and turntable cover onto the autosampler**
   - make sure the positioning pins and arrows line up
   - See Table 7 (page 27) for typical sample sequence with QC samples
4. **Write down in the log book, sample number and sample identity**
5. **Initiate Sample Run**
   a) Open TOC-V
   b) Select Table Editor (user name TOC)
   c) Open File Tab
      - Select New
      - Select Sample Run
      - Select UMass TN in System Options
      - Save data file template to appropriate location
   d) Open Insert Tab
      - Select Autogenerate
      - Select appropriate Calibration Curve
      - Next
      - If performing calibration at the beginning of the sample run then select the appropriate option, otherwise Next
      - Choose location of Control Samples
      - Finish
   e) Sparge/Acid Screen
      - Select OK
   f) Click on the Lightning Bolt Icon to Connect to the Instrument
      - Use Settings on PC
      - Let instrument initialize
6. **Verify that TOC analyzer has warmed up**
   - all status indicators on the "monitor" screen should read "OK"
   - the baseline, shown on the graph, should be flat (although it need not read exactly zero)

7. **Initiate Sample Run**
    - Click on the Stoplight Icon to Begin Sample Run
    - Select Standby Option
    - Confirm Samples/Locations
    - Check external acid addition if desired
    - START

8. **Verify initial autosampler operation**

    g) After pressing the "START" button, watch as the needles move into the first standard or sample. Verify that the needle is in the right position
        - The TOC-V sparges internally

9. **Inspect the first few data points**
    - make your first QC report by email (see "Data Analysis" below).
10. **Finish the TOC run and Process peak data when analysis is complete.**

TOC Analyzer Shut-down procedure

Shimadzu TOC-5000A Analyzer

11. If "Finish" was selected in the "ASI Conditions" screen

h) Analyzer will shut off after the last sample was run
i) You will see a countdown on the screen
   - "Wait ____ minutes to turn main switch off"
j) When countdown is complete, the message "You may now turn main switch off" will appear
k) Turn off the analyzer

12. If "No Change" was selected in the "ASI Conditions" screen.

- You can either re-use the analyzer or shut it down manually
- If you choose to shut down right away, do the following:

l) Select "7" (Standby options) from the "Main Menu" screen
m) Choose "1=FINISH" and press "Standby" to initiate.
n) From this point follow procedure in 11i)-k) above.

Shimadzu TOC-V/TN Analyzer

1. If "Finish" was selected in the "ASI Conditions" screen

a) Analyzer will shut off after the last sample was run
b) You will see a countdown on the screen
   - "Wait ____ minutes to turn main switch off"
c) When countdown is complete, the message "You may now turn main switch off" will appear
d) Turn off the analyzer

2. If "No Change" was selected in the "ASI Conditions" screen.

- You can either re-use the analyzer or shut it down manually
- If you don't choose to shut down right away, shut down the instrument manually later

Data Analysis & QC Reporting

1. **Data Analysis begins with the first few injections.**
   a) The analyst must inspect the first few injections to see that:
      - the Super-Q blank is below the threshold for laboratory grade water
      - the first standard exhibits good peak shape
      - reproducibility is acceptable

2. **Assessment of Instrument Calibration and Standard Curve**
   - We use least squares best linear fit of the standard peak areas regressed against their known concentrations.
   - Standard curves must also include the zero standard (sometimes called the laboratory reagent blank)
   - Standard curves must be visually inspected for non-linear behavior and the possible presence of outliers
      - When noted, an outlier may be excluded from the calibration curve, after consultation with the graduate QC officer. Removal of an outlier should:
      - Substantially improve the standard curve linearity or correlation
      - Improve agreement with the calibration check standard
      - Bring the regressed slope closer to the expected values based on recent data from the calibration slope control chart

3. **Evaluation of calibration check standard and other QC data by the analyst**
   a) This must be done as soon as possible, but no later than 24 hours from the end of the TOC run. Compare with quantitative criteria in Table 9.
   b) Send an email report on the success or failure of these first few injections to the graduate QC officer or his/her designee if he/she is not available. It should include information on:
      i. Sample types (e.g., field samples from Stamford), field collection date, laboratory treatment date (if any), and analysis date
      ii. Calibration check performance
      iii. Blank water (e.g., Super-Q) response
      iv. Statistics on sample and standard relative standard deviation and number of injections
      - The message must also include the address of the Faculty QC officer in the "cc:" line (reckhow@ecs.umass.edu).
      - The subject line of this email message must simply read "TOC QC report"

4. **Validation of QC data**
   a) The graduate QC officer or his/her designee then must compile the analyst's data into the running QC data files, and examine the updated control charts.
   b) The graduate QC officer or his/her designee then must send an email message to the faculty QC officer stating whether the QC data are within control limits, and if they are not, what actions will be taken.
      - Again, the subject line of this email message must simply read "TOC QC report".
      - This must be done as soon as possible, but no later than 24 hours from the time of receipt of the detailed QC report (per #3).

Clean Up

- All glassware used for TOC analysis must be "organic-free"
  - All the vials and any glassware should be rinsed with tap water, let them soak in soapy water overnight and then rinse with RO water and leave them in the acid bath overnight. Then take them out, rinse them with distilled water (3 times) and once with super Q water. Dry them in the oven (The graduated glassware should be placed in the cooler oven)
- Pipette tips may be rinsed with water and super Q water, and let them dry
- Acid baths must be cleaned and refreshed on a weekly basis

Standard Solutions, Solvents and Supplies

Preparation of Calibration Standards[13]

5. **Prepare Stock Primary Standard.**
   a) Dry about 0.75 gm of Potassium Hydrogen Phthalate in oven at 103-110°C for 30 min. Cool in desiccator for 20-30 min.
   b) Weigh exactly 0.5314 gm using analytical balance. Add to a 250 mL volumetric flask and fill to mark with Super-Q water.
   c) Result is stock primary standard (1000 mg/L).
   d) Store in an brown glass bottle. Label with your name, the date and "1000 mg/L KHP standard." Note: 1 mL = 1 mg TOC.
   e) Store in refrigerator. Discard after 2-3 weeks.

6. **Prepare intermediate standard.**
   a) Prepare on the day TOC/DOC samples will be analyzed.
   b) Make a volumetric dilution of the Stock Primary Standard. Pour about 15 mL of the Stock Primary Standard into a beaker. Transfer 10 mL of the stock primary standard with a volumetric pipette to a 100 mL volumetric flask half filled with Super-Q water. Fill to mark with Super-Q water.
   c) Intermediate stock concentration is 100 mg/L TOC. Store in refrigerator. Discard after 2 days.

7. **Prepare Working standards.**
   a) Prepare 3 working standards that bracket the sample concentrations. For example, for low level TOC and DOC analysis, a typical calibration curve consists of a 5, 2 and 0 ppm standard.
   b) Use three 100 mL volumetric flasks. Fill each half way with Super-Q water. Add 100 μL of 6 N HCl to each flask (acid addition for NPOC analysis).
   c) Add the appropriate volume of intermediate stock to each flask (number of mL of intermediate stock = concentration in mg/L of working stock). Fill to mark with Super-Q water. An example for low level TOC and DOC analysis as shown below.

Working Standard (mg/L)	Volume of intermediate stock added (mL)
10	10
5	5
2	2
0	0

[13] typically requires 20 minutes

Preparation of Challenge Standards

These are compounds that are relatively resistant to oxidation, especially in low temperature systems.

1. **Prepare Stock chondroitin sulfate.**

Preparation of QC Samples

a) Prepare Spiked samples for determination of matrix recovery (laboratory fortified sample matrix). Select 10% of analytical samples and set aside an additional 30 mL aliquot of each. Add requisite volumes of the intermediate stock so that the TOC will approximately double.
b) Prepare a continuing calibration check standard at a mid-range concentration.
c) Prepare any other QC samples as needed (see Table 6, page 26)
    i. Dilute chondroitin sulfate stock to a theoretical TOC level of 5 mg/L.

Supplies

Table 5. Summary of Supplies for Organic Carbon Analysis

Item	Catalog #	Approx. Price	Approx # used/run[14]
Pasteur Pipettes	Fisher: 13-678-20A	720/ $46.10	10
Integrator Paper			
Ink Cartridges	Fisher: 07-684-61	$15.20 each	
DIUF Water	Fisher: W2-20	$32.29	Not normally used
H_2SO_4	UMass Stockroom		34 mL
Autoampler vials			
Autosampler needles			
Potassium Acid Phthalate			
Chondroitin Sulfate			

[14] Assuming about 30 samples analyzed

Maintenance and Troubleshooting

Regular Maintenance Activities

- When measurement sensitivity, repeatability or accuracy has dropped, the TC catalyst or IC solution may need to be regenerated. This is conducted from the Maintenance screen.
- When regeneration of the TC catalyst does not correct repeatability and sensitivity problems, the catalyst must be washed or replaced.
- Replace the Ultra Zero air when tank pressure falls below 500 psi.
- Replace the CO_2 absorber annually.
- Replace the halogen adsorber before the colored area reaches the front end.
- Replace the rinse water pump head after 300 hours of use.

Troubleshooting

Past difficulties have resulted from:

- Improper positioning of the ASI unit with respect to the analyzer.
    - If the ASI is pushed too far back, it cannot properly collect samples, nor is it obvious that this is the source of the problem

For further assisance:

- Consult Shimadzu manuals
- Call Shimadzu technicians (800-)

Quality Assurance/Quality Control

General Approach

Quality assurance is an essential and integral part of a research study. The purpose of any QA plan is to insure that valid and reliable procedures are used in collecting and processing research data. The procedures outlined are designed to eliminate or reduce errors in experiments, sample preparation and handling, and analytical methods. Emphasis must be given throughout one's lab work to incorporate the plan into the research project by all research personnel.

Any equipment and experimental procedures that are used to provide numerical data must be calibrated to the accuracy requirements for its use. Records are to be kept of all calibrations. Calibration schedules are generally established for all aspects of physical and chemical measurements and these must be strictly followed. Physical standards and measuring devices must have currently valid calibrations, traceable to national standards. Most chemical standards are acquired from commercial suppliers, and they should be of the highest purity available. When necessary, unavailable standards should be synthesized using the best methodology available.

As a general rule, experiments should be replicated to assure reproducibility. All data reported should include a statement of its uncertainty, and the means for the determination and assignment of such limits. Standard reference materials are used for this purpose where possible. Statistically established confidence limits and an analysis of sources of systematic error are to be used in the absence of experimental demonstration of limits of inaccuracy.

All data will be subject to review by the faculty QC officer before release. The analysts involved will certify reports as well as all who review them. All analysts and QC officers must attest that the data and associated information contained in the report are believed to be correct and that all quality assurance requirements have been fulfilled, unless exceptions are approved and noted. Careful and detailed laboratory records will be maintained by each analyst, including source of reagents, meticulously detailed procedures (referring to an SOP, and any departures or clarifications), instrument and conditions of analysis, failed experiments, etc. Data output will be archived.

Regular meetings will be held to review the results and project progress, and to plan further experiments. The results will be analyzed promptly and summarized by means of internal reports or formal reports for external review. The experimental and analytical procedures will be reviewed for their performances and changes will be made as necessary. The quality assurance program as described in this document must be strictly observed.

Quality Assurance Objectives

The precision, accuracy and method detection limits will be evaluated, and where there are existing methods, held within the control limits set forth in the accepted references (e.g., APHA et al., 1999; USEPA-EMSL, 1990; ASTM, 1994). In addition to the analysis of sample replicates, a minimum of 10 percent of the time is typically involved in analytical determinations that are devoted to quality control. The precision of each test is determined through analysis of sample replicates. These are commonly presented in the form of control charts (e.g. Section 1020B of APHA et al., 1999).

The accuracy of each analysis will be determined by measuring spike recoveries in the matrix of interest. The relative errors will be calculated and will be considered acceptable if they fall within the control limits determined for the particular test. For new methods developed at UMass or for modifications of existing methods, we will have to establish criteria on acceptable control limits. In general, a test will not be deemed useful if its precision or accuracy is found to be equal to or greater than 20% of the highest values observed. Where possible, external performance standards will also be run. This serves as a measure of accuracy both for the analysis and for standard preparation.

Data generated by the QA program will be incorporated into a Quality Control (QC) archive that is used to monitor the fluctuations in precision and accuracy so that chance or assignable causes of error can be determined. Control charts such as X-charts for simple successive samples or cumulative sum techniques may be employed to record both precision and accuracy data (Taylor, 1987).

General Procedures

General sample collection and handling will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All previously established analytical methods used in laboratory research will follow approved methods in the standard compilations (e.g., ,APHA et al., 1999; USEPA-EMSL, 1990, or ASTM, 1994).

Reagent grade chemicals or higher quality when needed will be used throughout the research. Super-Q water (purified by reverse osmosis, deionization, and carbon adsorption) will be used for preparation of reagents, sample blanks, and dilution water. Where necessary, this water will be further purified using batch UV irradiation. All glassware used in the experiments and in analytical analyses will be thoroughly cleaned with a chromium-free sequence of detergent, oxidant and acid to prevent interferences from trace contaminants.

Data Quality Indicators

A wide range of data quality indicators are normally calculated for the purpose of assessing method performance. Some of these are defined below.

Precision

Precision may be expressed as the relative percent difference (RPD) from duplicate measurements (C_1 and C_2) of the same sample:

$$RPD = \frac{|C_1 - C_2| x100\%}{(C_1 + C_2)/2}$$

When three or more replicates are available, the relative standard deviation (RSD) should be used:

$$RSD = \left(\frac{s}{\bar{y}}\right) x100\%$$

where the standard deviation (s) is determined from:

$$s = \sqrt{\sum_{i-1}^{n} \frac{(y_i - \bar{y})^2}{n-1}}$$

Accuracy

Accuracy is best assessed by analysis of a standard reference material (SRM) prepared in the matrix of interest. It is quite rare that such materials are available, so two possible compromises may be used instead. These are the laboratory-prepared matrix spikes, and the independent SRM prepared in a standard matrix. One or both may be analyzed and the percent recovery (%R) calculated as a measure of accuracy.

$$\%R = \left(\frac{S - U}{C_{sa}}\right) x100\%$$

where:

S = measured concentration in spiked aliquot

U = measured concentration in unspiked aliquot

C_{sa} = actual concentration of spike added

$$\%R = \left(\frac{C_m}{C_{srm}}\right) x100\%$$

and:

C_m = measured concentration of SRM

C_{srm} = actual concentration of SRM

Method Detection Limit (MDL)

The method detection limit (MDL) will be defined as:

$$MDL = s_7 \bullet t_{(n-1,1-\alpha=0.99)}$$

where:

s_7 = standard deviation of 7 replicate analyses where the mean is no more than 10 times the MDL

$t_{(n-1,1-\alpha=0.99)}$ = Students' t-value for a one-sided 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.

Linearity

The calibration curve linearity (L) is defined as the ratio of the slope using the highest standards (S_U) divided by the slope determined from the lowest standards (S_L) as follows:

$$L = \frac{S_U}{S_L}$$

The highest standards shall be all those that fall within the top 50% of the calibration range including the 50% standard if it is used. If only one standard falls within that range, the S_U shall be calculated based on the top two standards. The lowest standards are all those that fall within the bottom 50% of the calibration range including the 50% standard if it is used. Least squares linear regression is used to determine slopes.

Sampling Custody

In most cases analyses will be performed immediately upon return from the field or after preparation of samples in the laboratory. Problems with sample custody are minimized, because the same people who receive (or sometimes, collect) the samples also analyze them. In general sample collection, handling, and preservation will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All samples must be fully labeled with the sample identity, date, and name of researcher.

Sample Collection and Storage

Samples are collected and stored in clean borosilicate (e.g., Pyrex, Kimax) glass containers. Containers must be capped with either Teflon-lined septa or ground glass stoppers. Exceptions are made for large volume samples which may be stored and shipped in clean polyethylene carboys. Glass containers are cleaned with detergent, followed by 5% sulfuric acid soak, and final rinsing with reagent-grade water. These containers are dried in a 150ºC oven.

Samples for TOC analysis must be acidified and kept in a refrigerator from the time of collection to the start of analysis. Some organics are biodegradable, so care must be taken to minimize this type of loss.

Data Reduction, Validation and Reporting

To ensure the accuracy and permanency of collected data, all research data are recorded with permanent ink in bound notebooks and all QC data (precision, accuracy) are recorded in instrument log notebooks. Summary QC graphs and tables are reviewed at least quarterly by the Faculty QC officer to observe noteworthy trends or inconsistencies. These are maintained in loose leaf notebooks for subsequent use in preparing progress reports, final reports, and theses. Major concerns and conclusions are reported to the external Project Officer via the progress reports.

Pages from the laboratory data books are regularly duplicated so that a file copy of raw data can be placed in safe storage in the event that the book is lost or destroyed. At the end of the project, all bound data books and any loose leaf data will be stored by the project team for at least ten years. Summary data files will be put on magnetic media so that statistical analysis of the data can be done. Our laboratory has several personal computers that can be used for this purpose.

Procedures specific to TOC Analysis

General Analytical QC

Many types of QC procedures are required as indicated under standard method 5310B. The guidelines below are prepared assuming that samples are run in groups, whereby a "daily" frequency refers to once every day that the analytical method is being used.

Table 6. Summary of QC Elements as Applied to TOC Analysis

Types of Samples or Standards	§ in Std. Meth.	Purpose	Frequency	Timing	QC data
Laboratory Performance Check Standard (LPC)		To establish basic analyzer performance	1 standard per day	Beginning of each day	Noise, response
Initial Demonstration of Capability (IDC)		To show that an analyst's technique and equipment are adequate for OC analysis	4-7 standards when first learning method, otherwise not done		Mean % recovery and standard deviation
Method Detection Limit (MDL)		To determine the lowest concentration level that the analyst can report	7 standards run		MDL and EDL
Laboratory Reagent Blank (LRB)		Test lab conditions and quench for interferents	1 per day	Beginning of day	Response
Field Reagent Blank (FRB)		Test all field conditions for interferents	1 per day, if sampling occurred outside of the lab	mid day	Response
Spiked sample, or Laboratory Fortified Sample Matrix (LFM)		To test recovery in the sample matrix	1 for every 10 samples[15]	Mixed throughout day	% recovery, mean and standard deviation
Calibration Standards		To provide a basis for determining the concentrations in unknowns	3 levels including zero		Calibration curves including slopes and intercepts
Continuing Calibration Check		To verify the accuracy of the calibration	Usually one per day	mid-day	

[15] These are generally done using the calibration compound (e.g., KHP). Spike recovery studies may also be done with a "challenge" compound.

Standards (CCC)[16]		standards			
Challenge standard[17]		To test the method with a "difficult" compound	Irregular: e.g., when catalyst is changed		% recovery
Unknowns or "samples"		This is what you really want to measure	As many as desired	Mixed throughout day	Relative standard deviations

Table 7 shows a recommended sequence for a typical run of about 16 samples. The first two samples require immediate attention, as they are simple indicators of unacceptable QC. When these NDIR response traces show abnormally elevated noise levels or drifting baseline, the operator must intervene before proceeding. The problem must be diagnosed, solved and the sequence restarted at vial #1.

Table 7: Typical Vial Sequence for TOC Analysis

Vial #	Sample type	QC objectives
1	Water Blank	To check on IC condition
2	Zero Standard	To check for gross contamination of water or lab environment
3-5	Remaining calibration standards	Calibration
6-13	Analytical Samples	
14	Spiked sample	Spike recovery
15	Calibration check standard	Check on accuracy of calibration samples
16	Calibration standard (one intermediate)	Final check to verify that calibration hasn't changed during run

Special QC Tests

The following are "special" tests that are not part of the normal QC protocol. They are used when first learning this analytical method (e.g., IDC), and they may be used when there are suspected problems or there is a need for method performance evaluation.

[16] Prepared from the calibration solution (eg., KHP stock)
[17] these are compound that are not as easily oxidized, such as caffeine, dodecylbenzene sulfonic acid, and chondroitin sulfate. Sometimes standard solutions of humic substances can be used.

Initial Demonstration of Capability (IDC)

This is normally performed by each analyst when he/she is first learning to measure TOC or DOC.

Procedure

a) Prepare a full standard curve
b) Perform an MDL test for TOC and DOC (DOC can be skipped if it is not an analyte of interest)
c) Prepare 3 sets of samples with matrix spikes, and evaluate spike recovery in 3 different matrices

Performance

IDC results are expected to meet the LFM and MDL QC criteria from Table 8.

Recovery of Volatile Organic Carbon

Analysis of water samples spiked with VOCs to determine VOC loss during sample purging.

Method Detection Limit (MDL)

Procedure

a) Secure a 1000 mL sample with a low level of TOC (preferably below 1 mg/L). This may be a bulk sample of tap water diluted 50/50 with Super-Q water.
b) Separate this into 7 aliquots of 30 mL each.
c) Analyze each for TOC on the same day.
d) Determine MDL based on the standard deviation of these 7 sets of measurements (refer to section on: MDL calculations on page 28 of this document)
e) Repeat, but analyze all 7 for DOC (not necessary if you do not plan to measure DOC in your work)

Performance

We expect that MDLs for TOC and DOC will be below 0.1 mg/L. It is expected that MDLs for DOC would be slightly higher than the MDLs for TOC due to possible sample contamination during filtration.

QC Criteria

Quality control data must be analyzed as soon as possible. The best practice is to have the QC data tabulated and evaluated as the run is underway. However, it is recognized that there will be times when this is impossible. QC and calibration data must always be analyzed and reported within 24 hours of completion of a run (see section on

Data Analysis & QC Reporting, page 16). Quantitative criteria (Table 8) must be applied, and violations must be immediately reported to the faculty QC officer. The graduate and faculty QC officer along with the analyst will then work out a plan for returning the analysis to acceptable levels of QC. Table 8 lists some typical corrective action, however the actions taken may differ depending on the particular circumstances. Excursions from QC criteria can be quite complex, and many analytical characteristics and conditions must be considered before a decision can be made on the most effective steps to be taken.

In several cases, quantitative criteria are based on long term trends, and these must be monitored by means of appropriate control charts. Calibration check standards, spike recovery and blank water values are documented over time in this way. All summarized QC data (tabular and graphical) must be kept in a notebook in the Marcus Hall TOC room (Rm 5). A duplicate set must be deposited with the faculty QC officer (D. Reckhow).

Table 8: Quantitative Criteria for Judging Data Acceptability

Types of Samples or Standards	Frequency	Timing	QC data Acceptance Criteria	Typical Corrective Action
Spiked sample, or Laboratory Fortified Sample Matrix (LFM)	1 for every 10 samples	Mixed throughout day	Mean % recovery = 80%-120%	❖ Re-run matrix spikes ❖ Re-examine entire run for errors ❖ Possibly change SOP
Calibration Standards[18]	4 levels including zero		Calibration slopes = ±30% of long-term average	❖ Run new set of standards ❖ Prepare new anion stock ❖ Examine TOC analyzer for problems, needed maintenance
			Calibration linearity must not fall below 0.5	❖
Continuing Calibration Check Standards (CCC)[19]			Calculated Conc. = ±20% of expected value	❖ 1. Prepare new calibration check standard ❖ 2. Prepare new standard curve based on new stock
Method Detection Limit (MDL)	At IDC and once per year		Below 0.1 mg/L	❖ Examine sample handling ❖ Check instrument of baseline noise level
			MDL for DOC should be no more than 0.02 mg/L above MDL for TOC	❖ Re-evaluate filtration procedures
Lab Reagent Blank	Daily		≤0.02 mg/L	❖ Seek alternative reagent water

[18] Prepared from the currently-used calibration stock (less than 1 month old)
[19] Prepared from the previously-used calibration stock II

				❖ Change cartridges
Unknowns or "samples"	As many as desired	Mixed throughout day	RSD or RFD for replicate analyses ≤20%	❖ Re-run samples and/or discard outliers[20] until precision can be brought under control
			Estimated concentration in unknowns must not exceed highest standard	❖ Re-run samples with higher level standards ❖ Dilute and re-run samples ❖ If within 150% of max standard, concentrations may be flagged as tentative

Literature Cited

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Spyres, Georgina, Malcolm Nimmo, Paul J. Worsfold, Eric P. Achterberg and Axl E. J. Miller (2000) Trends in Analytical Chemistry 19(8)498
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[20] using Dixon's Q Test, or some logic test (e.g., monotonic increase with timed data series; unlikely sudden changes in natural system).

Appendix

Standard Method 5310B:

(20th edition, 1999)