

Effects of Sampling, Shipping, and Storage on Total Organic Carbon Levels in Water Samples

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An estimation of the organic content of water has been used for some time as an indicator of water quality (E.P.A. 1975). The carbon adsorption method (CAM) was developed in 1951-52 for this purpose but is no longer recommended (CAPELLI et al. 1977, OTSON et al. 1979). With recent improvements in analytical instrumentation, total organic carbon (TOC) determinations are being used to assess water quality, particularly for relatively pure water (MAIER & SWAIN 1978). Although TOC determinations will not indicate the presence of potentially harmful chemicals, they are of value in estimating the concentration of organics in water. TOC analysis may be used to monitor industrial and municipal waste effluents as well as water sources containing man-made pollutants and naturally occurring organics of plant and animal origin. The efficiency of waste water treatment plants and potable water purification plants can be assessed, and the effectiveness of adsorbents for removal of organics from water (CAPELLI et al. 1978) can be determined, by means of TOC measurements. Also, a correlation between trihalomethane levels in finished water and the organic carbon content of the raw water supply has been found (H.W.C. 1977, SYMONS 1975).

Common TOC analysis methods have been compared (ARIN 1974, GOULDEN & BROOKSBANK 1975, KEHOE 1976), and their limitations, including problems of discriminating between inorganic and organic carbon content and the detection and quantitation of organic compounds in water, have been discussed (REIJNDERS et al. 1977, KEHOE 1977). Recent advances in TOC instrumentation (GOULDEN & BROOKSBANK 1975, TAKAHASHI 1976) have improved the reliability of organic carbon measurements and good precision has been claimed for TOC determinations at levels below 100 µg/L in water.

The use of TOC measurements for estimating the effectiveness of water treatment and for studies correlating TOC with other water quality parameters often requires sampling at a distance from the analytical laboratory. The reliability of TOC measurements obtained for water samples after collection, shipping, and storage has not been fully investigated. Due to

our extensive involvement in drinking water monitoring studies, we have investigated the effect of sampling, shipping, and storage on TOC levels of water samples ranging from 400 $\mu\text{g/L}$ to 7500 $\mu\text{g/L}$ in organic carbon content.

EXPERIMENTAL

Equipment. All analyses were performed by means of a Model DC-54 Ultra Low Level Total Organic Carbon Analyzer (Dohrmann Div., Envirotech Corp.) operated as prescribed in the instrument manuals.

All glassware was soaked in chromic acid for 24 hr, rinsed well with low TOC water (approx. 200 $\mu\text{g/L}$), air dried, and heated at 400°C overnight just prior to use. Water samples were collected and stored in 50 ml, amber, glass bottles, containing 1 drop of conc. H_2SO_4 , and were sealed immediately with screwcaps and Teflon liners (cleaned in chromic acid).

Reagents. Low TOC water (approx. 200 $\mu\text{g/L}$), prepared by deionization, passage through activated carbon, and subsequent distillation (all glass still) was used to prepare carbon free water (CFW, TOC < 80 $\mu\text{g/L}$) by exposure to ultra-violet irradiation in the Model DC-54 irradiation chamber for at least 4 hr.

Standard solutions were prepared by diluting freshly prepared stock solutions containing 200 mg/L TOC in the form of potassium hydrogen phthalate (Baker, primary standard) in carbon-free water (CFW). The measured TOC value of the diluent CFW was considered in calculation of standard solution concentrations. Solutions of known TOC concentrations near 2000 $\mu\text{g/L}$ were prepared daily for instrument calibration. A stock standard solution of similar concentration (2150 $\mu\text{g/L}$ TOC) was stored in a 3 L, clear, glass bottle equipped with an all glass, 50 mL dispenser (Repipet, Lab Industries Ltd.) and was used for comparison throughout the study.

Linearity. Standard (potassium hydrogen phthalate) solutions with calculated concentrations of 426, 2042, 3192, and 8062 $\mu\text{g/L}$ TOC were analyzed. The precision of TOC measurements was determined and the experimental mean values and the calculated concentrations were used for regression analysis.

Raw water, obtained by passing river water through a fritted glass disc (ASTM, 10-15M), was diluted with CFW to obtain mixtures containing 100%, 50%, 15%, and 5% v/v raw water, which were then analyzed for TOC content. The precision of these measurements was determined and the experimental mean TOC values and the percent raw water in the mixtures were used for regression analysis.

Storage and Shipping. Bulk samples of low TOC (approx. 200 $\mu\text{g/L}$), tap (approx. 3000 $\mu\text{g/L}$ TOC), and river (approx. 7500

µg/L TOC) water were dispensed from all-glass 2 L separatory funnels. Six TOC determinations at each concentration were done immediately and the remaining bulk samples were distributed directly from the funnels into labelled, 50 mL, amber glass bottles. The contents of 4 bottles for each concentration were analyzed in duplicate on the same day (day 0). For each concentration, 10 bottles were stored at 4°C (refrigerator), 10 bottles were stored at 25°C (incubator), and 7 bottles for shipping were wrapped in newspaper and placed in an insulated plastic cooler containing styrofoam chips. The cooler was stored in the trunk of a passenger car for 3 days as it travelled approximately 300 km and as the outside temperature ranged -10°C to +8°C. The cooler was then stored in a boiler room at 88°C for 3 days. When the cooler was opened it was found that the contents of three bottles had been lost. Two intact bottles for each concentration were left at room temperature (approx. 25°C) for analysis on the following day. The remaining bottles were stored at 4°C (refrigerator) until the day before scheduled analysis at which time they were left at room temperature.

TOC analyses. The model DC-54 sample reservoirs and purgeable organic carbon sparger were always rinsed with a portion of the sample prior to analysis. An aliquot (1.0 mL) of the oxidizing reagents was added to the sample in a reservoir 0.5 hr prior to analysis to permit thorough mixing. Triplicate determinations were done for both daily and stored standard solutions at the 2000 µg/L TOC level after calibration with the daily standard solution.

One day prior to scheduled analysis (14, 28, 42, 56, and 70 days) 2 bottles for each water type and at each storage temperature (4°C and 25°C) were selected at random and stored at room temperature (approx. 25°C). Thus, for each water type the contents of 4 bottles were analyzed in duplicate on each analysis day. Similarly, for the shipping experiment, 2 bottles for each water type were randomly selected and the contents were analyzed.

Statistical tests. Two-way analysis of variance tests were used to determine if time and temperature had significant effects. In addition Student t-tests were used to compare mean values where appropriate and Duncan's Multiple Range Test was used to locate differences among TOC values for different days.

RESULTS AND DISCUSSION

The precision of replicate measurements for the linearity study (TABLE I) was below 2% relative standard deviation (RSD) except in the case of the 426 µg/L TOC standard solution. Linear regression lines with correlation coefficients better than 0.999 were obtained for both the raw water and the standard solutions. Since the standard solutions gave a straight line plot with a slope of 0.987, calibration of the instrument at a

single concentration, i.e. 2000 µg/L is valid for the 400-8000 µg/L TOC range. These raw water results and reports (GOULDEN & BROOKBANK 1975) of nearly 100% conversion of some organics by wet oxidation methods suggest that the calibration is valid for the water samples under study.

TABLE I
Linearity and Precision for Standard Solutions and
Raw Water TOC Measurements

Water Type	Organic Carbon Content			
	Calculated		Measured ^a	
	TOC µg/L	Raw Water ^b %	Mean TOC µg/L	RSD %
Standard	426	-	482	6.6
	2042	-	2105	1.0
	3192	-	3119	0.7
	8062	-	8020	0.8
Raw	-	5	396	1.0
	-	15	839	1.4
	-	50	3610	1.7
	-	100	7044	0.5

^a Each value is based on six determinations.

^b Percent of raw water in raw water - carbon free water mixtures.

TABLE II summarizes mean TOC values and associated RSD values for both the daily prepared calibration solutions and the stored (2150 µg/L TOC) solution. All RSD values of these standards were less than 3% throughout the study and, with the exception of day 0 analyses of the stored solution, no significant ($p > 0.05$) variation in results was observed over the 70 day period. Thus a single standard solution prepared and stored as described can be used for instrument calibration for at least 10 weeks and frequent standard solution preparation can be avoided.

Results of the storage and shipping studies are summarized in TABLE III and can be categorized as follows.

TABLE II
Precision of Total Organic Carbon (TOC)
Calibration Measurements

Analysis Day	Standard Solution, TOC ^a , & RSD ^b			
	Daily		Stored	
	TOC μg/L	RSD %	TOC μg/L	RSD %
0	2122	2.0	2226	0.2
7	2133	2.3	2110	1.7
14	2081	0.2	2112	1.4
28	2052	1.0	2114	0.4
42	2091	1.2	2134	2.9
56	2088	0.9	2130	2.9
70	2059	1.5	2073	1.3
0 - 70	2090	1.7	2128	2.6

^a Each value is based on three determinations.

^b Relative Standard Deviation.

Values and precision. All mean values were calculated from uncorrected individual readings (method blanks generally less than 50 μg/L). Except in the case of low TOC water samples, the precision of replicate determinations was better than 5% (RSD). Similar precision was obtained for standard and raw water solutions (TABLES I and II) and was judged adequate for detecting the effects of bottling, storage, and shipping. The range in TOC values, their overall mean, and precision for the 3 water types under all conditions were: low TOC, 132-358 μg/L, 212 μg/L, 31%; tap, 2908-3533 μg/L, 3138 μg/L, 3.7%; and river, 6867-8219 μg/L, 7575 μg/L, 4.2%.

Effect of bottling. An increase in TOC (46 μg/L) and RSD (7%) was observed for low TOC samples after bottling on day 0. The increase, significant at $p < 0.05$, can be due to contamination from the bottles and the atmosphere during the

TABLE III

Storage and Shipping Study Results

Sample Type, Mean^a Total Organic Carbon (µg/L),
& Relative Standard Deviation (%)

Sample Conditions	Analysis Day	Low TOC		Tap		River	
		µg/L	%	µg/L	%	µg/L	%
NB ^b	0	139 ^c	6.5	3131 ^c	1.3	7774 ^c	1.3
B ^d	0	185 ^e	13.5	3119 ^e	2.0	7821 ^e	1.0
4°C ^f	14	232	30.2	3054	1.2	7274	3.7
	28	262	25.5	3084	1.6	7494	2.6
	42	253	15.6	3180	2.6	7952	0.5
	56	228	19.6	3149	2.2	7858	1.6
	70	244	35.9	3111	2.3	7152	1.0
	14-70	244	5.8	3116	1.6	7546	4.7
25°C ^g	14	165	6.7	3161	1.9	7317	0.9
	28	175	19.7	3034	1.9	7646	1.4
	42	166	13.2	3230	2.4	7792	2.1
	56	154	10.9	3131	2.7	7920	3.7
	70	178	9.0	3248	4.3	7021	1.3
	14-70	168	5.6	3161	2.7	7539	4.9
Shipped ^h	7	228	15.5	2976	2.3	7487	1.1
	28	325	2.5	3238	8.5	7443	2.0
	70	314	16.0	3247	2.8	7196 ⁱ	0.6
	7-70	289	18.4	3154	4.9	7375	2.1

^a Mean of all individual determinations. ^b Not Bottled. ^c Six determinations. ^d Bottled. ^e Contents of four bottles analyzed (eight determinations). All other values are based on four determinations (two bottles) each, except in the case of ⁱ, where only one bottle was available due to breakage. ^f Stored in bottles at 4°C. ^g Stored in bottles at 25°C. ^h Bottled, shipped, and then stored at 4°C.

bottling process. This effect can cause difficulties in the preparation and maintenance of "pure" water but would not be, and was not ($p > 0.05$), noticed for tap and river water samples.

Effect of storage temperature and time. Comparison of mean TOC values showed that neither storage time nor storage temperature had any significant effect ($p > 0.05$) on the TOC values of tap water samples. For river water there was no significant difference ($p < 0.05$) between the overall mean TOC values for samples stored at 4°C ($754 \mu\text{g/L}$) and 25°C ($7539 \mu\text{g/L}$). At each storage temperature the mean TOC values of river water samples for different days of analyses differed significantly ($p < 0.05$) but no trend could be established. However, the precision of instrument calibration ($\text{RSD} = 2.6\%$, TABLE II) and the mean RSD values of 4.7% and 4.9% for river water (TABLE III) indicate that the effects of storage temperature and time are not important for most practical purposes.

A significant difference ($p < 0.05$) was observed in overall mean TOC values for low TOC water samples stored at 25°C ($168 \mu\text{g/L}$) and at 4°C ($244 \mu\text{g/L}$). A significant difference ($p < 0.05$) was also noted between the mean TOC value ($185 \mu\text{g/L}$) of bottled samples analyzed on day 0 and the overall mean TOC value ($244 \mu\text{g/L}$) for those samples stored at 4°C . These results indicate that storage of samples at 4°C causes a slight increase (ca. $50 \mu\text{g/L}$) in TOC levels which can be detected in low TOC water samples but which is not noticeable in tap and river water samples.

Effect of shipping and storage. Simulated shipping and subsequent storage of tap and river water samples showed no significant effect ($p > 0.05$) on TOC values. No significant ($p > 0.05$) change in TOC values for low TOC samples occurred over the seven day shipping period, but a significant ($p < 0.05$) increase (228 to $325 \mu\text{g/L}$ TOC) was observed between the shipping period and the subsequent storage period values. This effect, which would not be noticeable for tap and river water samples, probably is largely due to the previously noted effect of storage at 4°C . During shipping two bottles were broken, probably due to freezing of the contents.

CONCLUSIONS

The sampling, storage, and shipping conditions used in this study were found to have little effect on the TOC levels in tap and river water samples. Therefore, samples from distant water supplies can readily be shipped to a central laboratory for reliable TOC determination ($\text{RSD} < 5\%$), if care is taken in bottle preparation and in sampling, and if the described procedures are followed. However, the procedures for sampling, storage and/or shipping of water samples with low TOC content cannot be recommended, due to contamination of the samples.

ACKNOWLEDGEMENTS

Review of the manuscript by Murugan Malaiyandi and Vic Armstrong is gratefully acknowledged.

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