ANALYSIS OF TOTAL ORGANIC CARBON IN SEVERAL REGIONAL BOTTLED WATERS

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ABSTRACT

We analyzed several different brands of regional-bottled natural spring water for total organic carbon *(TOC)* content using the method of heated persulfate oxidation. Although some distinction can be drawn between the brands considered based on TOC value, all the types of water examined may be considered to be of good quality. We discuss a brief overview of industry and federal standards for bottled water.

Key Words: bottled water analysis, drinking water analysis, TOC analysis

INTRODUCTION

According to the Food and Drug Administration (FDA), bottled water, like all other foods regulated by the FDA, must be processed, packaged, shipped, and stored in a safe and sanitary manner and must be truthfully and accurately labeled. The FDA defines "spring water" as water obtained from an underground formation from which water flows naturally to the surface or would flow if it were not collected underground via a borehole. To be identified as "spring water" on the label, water must be collected at the spring or through a borehole next to the point where it emerges (Federal Register 1993).

Bottled water products also must meet specific FDA quality standards for contaminants (Federal Register 1996). These are set in response to requirements that the U. S. Environmental Protection Agency (EPA) has established for tap water. In addition to the FDA's Quality Standards, bottled water companies must adhere to Standards of Identity (Labeling Regulations) and Good Manufacturing Practices.

The Information Collection Rule - Disinfectant/Disinfection By-Products Rule (ICR-D/DBPR) was promulgated in 1996 by the EPA to determine and establish acceptable levels for occurrence in drinking water of: (1) disease-causing microorganisms, and (2) chemical by-products that form when disinfectants used for microbial control react with naturally-occurring organic compounds already present in source water. The organic material is determined as total organic carbon (TOC) in units of ppm C (mg C/L solution).

Today's ICR-D/DBPR approves three methods for TOC analysis: Standard Method 5310 B (high temperature combustion), 5310 C (persulfate ultraviolet or heated persulfate oxidation), and 5310 D (wet oxidation). To satisfy requirements of the ICR-D/DBPR, a TOC analytical method must have a detection limit of at least 0.5 ppm C and a reproducibility in terms of standard deviation of at least ± 0.1 ppm C over a range of 2-5 ppm C. EPA believes that all of these methods can achieve the precision and detection level necessary for compliance determinations required in today's rule when quality-control procedures contained in method

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descriptions and ICR-D/DBPR are followed. Although any of the three methods may be used, EPA advises that the same method be employed for all measurements to reduce the impact of possible instrument bias.

To demonstrate how the EPA Standard Method 5310 C can be applied, we determined concentration of TOC in laboratory tap water, laboratory deionized (DI) water processed by reverse osmosis (RO), and six different bottled waters. The study was not intended to be exhaustive but rather to reveal any regional differences in the TOC of bottled water.

Some of the additional common abbreviations encountered in the EPA Standard Method 5310 C are: TC = Total Carbon, TIC = Total Inorganic Carbon (from naturally occurring carbonates), POC = Purgable Organic Carbon, and NPOC = Nonpurgable Organic Carbon. TOC generally is identical to NPOC, the carbon that can be oxidized to carbon dioxide after the inorganic and volatile organic carbon species have been removed by acidification and purging. Volatile organic species include benzene, carbon tetrachloride, vinyl chloride, and other low-molecular-weight chlorinated hydrocarbons. Although TOC in water samples should ideally include POC, most laboratories report TOC analyses of samples from which volatile organics have been previously removed. In fact, methods involving persulfate oxidation, which are widely accepted and used, each call for acidification and purging to remove inorganic carbon before oxidation of organics. This purging also removes volatile organics before oxidation. However, the results are still generally accepted as TOC. Methods to measure POC have not been standardized and, therefore, POC was not included in this study. Because natural spring waters generally contain insignificant quantities of volatile organic substances, the conditions employed are the same as those for measuring NPOC, whose value, in practice coincides with that of TOC.

METHODS

The instrument design of the OI Model 700 TOC Analyzer allows for automated preacidification and purging of the sample aliquot inside the reaction vessel. In this investigation, the water sample was introduced into the digestion vessel of the instrument by means of a 5.00-mL sample loop. The sample loop injection affords greater consistency of volume than would the other option of syringe injection. The sample was then pre-acidified with 200-mL of 5 percent (v/v) phosphoric acid (Baker, Reagent-Grade). After acidification, a gas stream of ultra-pure nitrogen purged out any CO_2 formed from inorganic and volatile organic carbon species. This CO_2 was vented from the instrument. When purging TIC and POC was complete, purge gas to the reaction vessel was shut off, the reaction vessel was heated to 100 ∞C, and 1000-mL of sodium persulfate (Baker, Reagent-Grade, 100 g/L) reagent was added to the sample. Persulfate quickly reacts with organic carbon in the sample to form CO_2, which accumulates in the reaction vessel. After a pre-set reaction time (nominally 3 min), the reaction vessel was placed in-line with the molecular sieve trap and a gas stream purged out any CO_2 produced by the persulfate oxidation. This CO_2 was carried to the trap held at 25 °C where it was retained and concentrated. The trap was then placed in-line with the detector and heated to 200 °C to release the CO_2. The CO_2 was carried into the detector, which is a linearized, non-dispersive, single-beam analyzer sensitized to detect 0-50 mg carbon as CO_2. The resulting concentration of TOC in the sample was displayed/ printed.

Sample (bottle) size was 500 mL and the instrument was pre-flushed with the sample to remove any residual traces of the previous sample. The minimum detection limit (MDL) of the instrument was calculated as three times the standard deviation of detector response (in mV) to 20 external blanks consisting of ultra-pure reagent water (EM Science OmniSolv®).

We determined concentrations of TOC in the analytical samples using a two-concentration calibration curve generated with primary-standard grade potassium hydrogen phthalate (Baker) in ultra-pure reagent water and spanning a concentration range from zero to 1.0 ppm C. Ten samples each of the blanks and of the standards were analyzed in duplicate, and the responses from all 40 analyses were used to generate the curve, which was then programmed into the instrument. The calibration was routinely verified prior to the determination of each different analytical sample.

We analyzed 10 samples of each brand of natural spring water in triplicate/bottle. The samples were obtained in batches from several different retail outlets in the region. All brands selected were supplied in PET (polyethylene terephthalate) bottles. HDPE and LDPE bottles, which tend to impart the distinct taste of plastic, were avoided.

No specific preliminary preparation of the samples was carried out, but because of the sensitivity of the method, we carefully washed and rinsed all glassware with ultra-pure water.

RESULTS AND DISCUSSION

The MDL of the instrument was determined to be 0.0155 ppm C as TOC and this compares very favorably with the TOC range of 0.004 to 10,000 ppm C specified by the manufacturer. Results from the analysis of TOC in six bottled drinking waters appear in Table 1. Concentrations in the bottled waters ranged from 0.162 to 0.573 ppm C. All results were well above the MDL for this instrument. The largest differences in TOC within one brand of water appeared in the Giant Springs brand. The data for Giant Springs had a surprisingly large standard deviation over the range 0.183-0.461 ppm. Application of

Table 1. TOC values of brands of bottled spring water analyzed

Brand of Water (Source, if available)	TOC (ppm) of 10 Samples per Brand with 3 Replicate Measurements per Sample Bottle*					Mean TOC (ppm) with Std Dev from Mean of 10 Samples
Cascade Clear	**0.168**	**0.196**	**0.148**	**0.154**	**0.158**	0.162 ± 0.018
	(0.004)	(0.065)	(0.004)	(0.014)	(0.005)	
	0.149	0.149	0.151	0.151	0.194	
	(0.003)	(0.003)	(0.005)	(0.001)	(0.069)	
EarthH2O (Opal Springs)	**0.164**	**0.176**	**0.212**	**0.207**	**0.180**	0.194 ± 0.022
	(0.003)	(0.001)	(0.052)	(0.054)	(0.001)	
	0.186	0.181	0.186	0.226	0.225	
	(0.002)	(0.008)	(0.004)	(0.047)	(0.018)	
Giant Springs	**0.444**	**0.431**	**0.275**	**0.324**	**0.291**	0.320 ± 0.095
	(0.062)	(0.055)	(0.023)	(0.002)	(0.014)	
	0.461	**0.183**	**0.300**	**0.258**	**0.236**	
	(0.070)	(0.069)	(0.010)	(0.031)	(0.042)	
Montana Silver Spray	**0.456**	**0.494**	**0.519**	**0.487**	**0.573**	0.528 ± 0.054
	(0.010)	(0.059)	(0.110)	(0.071)	(0.108)	
	0.546	**0.515**	**0.628**	**0.585**	**0.476**	
	(0.086)	(0.083)	(0.038)	(0.058)	(0.051)	
Mountain Mist (artesian water)	**0.546**	**0.568**	**0.613**	**0.550**	**0.589**	0.573 ± 0.035
	(0.087)	(0.072)	(0.052)	(0.081)	(0.079)	
	0.600	**0.587**	**0.501**	**0.612**	**0.564**	
	(0.043)	(0.065)	(0.004)	(0.082)	(0.075)	
Red Lodge (Crystal Springs)	**0.250**	**0.246**	**0.247**	**0.235**	**0.230**	0.237 ± 0.013
	(0.014)	(0.018)	(0.013)	(0.008)	(0.012)	
	0.218	**0.226**	**0.227**	**0.233**	**0.259**	
	(0.019)	(0.004)	(0.007)	(0.005)	(0.016)	

(*Numbers in parentheses are respective standard deviations of three replicates.)

the Student's *t*-statistic indicated that this noticeably large difference in TOC is probably real at the 95 percent confidence level. Within other brands, however, there is no apparent difference in the TOC measured. Table 2 lists the typical TOC in laboratory tap water, in laboratory DI water prepared by reverse osmosis, in ultra-pure reagent water, and in a 1.000 ppm carbon commercial standard (Ultra Scientific). The laboratory tap water, which is unfiltered municipal water, may have a slightly higher than normal TOC, presumably because of drought conditions that existed in the region at the time of this study. Although these data have a large standard deviation, significance testing indicated that an apparent discrepancy was no greater than what might be found by chance simply because of natural variability. The level of TOC in laboratory DI water, 0.119 ppm C, is typical of this large-throughput water purification system. The accuracy (1.009 ppm) and the small standard deviation (± 0.033 ppm) in the TOC value for the commercial (1.000 ppm C) standard indicated high precision for this method.

According to the International Bottled Water Association (IBWA) the deteriorating taste and quality of tap water and fear of unknown contaminants have lead many Americans to believe that bottled water is of higher purity than tap water. According to a recent study performed by the IBWA, (International Bottled Water Association 2000), 63 percent of Americans are not aware that the FDA regulates bottled water as a food product. Among those with the knowledge that the FDA regulates bottled water, most people (53%) feel more confident about bottled water's purity and safety. Seventy-one percent of Americans feel that the quality of bottled water is high, 30 percent feel that it is extremely or very high, while another 41 percent feel it is somewhat high.

However, the Natural Resources Defense Council (1999) issued a report concluding that bottled water is insufficiently regulated by federal and state agencies and by the bottled water industry. Further, based on an analytical product survey conducted by NRDC, bottled water may not be as pure as we are led to believe.

The solution recommended by NRDC (1999) was to overhaul the FDA's regulatory regime for bottled water or give the program to EPA and impose additional

Table 2. Typical TOC values of laboratory tap water, laboratory DI water, ultrapure water, and 1.000 ppm external standard

Sample	TOC (ppm) of 1 Replicate per Sample					Overall MeanTOC (ppm)with Std Dev
Laboratory tap water (municipal)	1.401	1.407	1.395	1.425	1.419	1.441 ± 0.089
	1.728	1.528	1.426	1.362	1.477	
	1.390	1.386	1.558	1.466	1.515	
	1.389	1.388	1.433	1.389	1.326	
Laboratory DI water (by RO)	0.036	0.088	0.131	0.131	0.141	0.119 ± 0.023
	0.131	0.120	0.148	0.128	0.122	
	0.114	0.114	0.122	0.123	0.122	
	0.114	0.118	0.129	0.118	0.120	
Ultra-pure (OmniSolv“)	0.036	0.016	0.025	0.026	0.028	0.032 ± 0.007
	0.026	0.026	0.026	0.028	0.031	
	0.030	0.035	0.033	0.040	0.038	
	0.032	0.037	0.037	0.040	0.039	
1.000 ppm Standard (Ultragrade‘)	1.066	1.041	1.049	1.005	0.989	1.009 ± 0.033
	0.962	0.969	0.981	0.986	1.005	
	1.024	0.978	1.031	1.053	1.058	
	1.003	0.982	1.022	0.961	1.022	

disclosure requirements on the bottled water industry.

The NRDC (1999) contended that federal bottled water regulation is weaker than the tap water regulations facing public water systems because, in part, the FDA regulatory structure for setting allowable contaminant levels and associated monitoring and treatment requirements is not as stringent as that of the EPA for tap water.

Closer examination of the water quality standards for chemical contaminants revealed that the FDA bottled water quality standards are the same as EPA's tap water standards for 62 out of 71 chemical substances highlighted in the NRDC Report (1999: Chapter 4, Table 6). FDA standards for lead, copper, and fluoride are stricter than EPA's. For three of the remaining contaminants—asbestos, acrylamide, and epichlorohydrin—FDA has determined, as the law allows it to do, that establishing specific standards for bottled water is unnecessary.

States are under no legal obligation to adopt the FDA bottled water standards, and state regulations for bottled water, if any, vary widely. Although some states, such has California, Texas, and Washington, have bottled water programs that are relatively well developed, other states, such as Alaska, Utah, and North Dakota, have no or virtually no program. Of interest in this study is the fact that Montana's state bottled water program, which is stricter than that set by the FDA, requires that all in-state bottlers become Public Water Systems and meet EPA drinking water standards prior to start-up. In the final analysis, individual consumer's taste and perception of cleanliness apparently will determine the quality of bottled water.

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CORRIGENDUM

Benjamin, Lyn. 2000. Groundwater hydrology of the Henry's Fork springs. Int. J. Sci. 6:119-142.

… Recharge Area

The size of the recharge area of each spring system was estimated using established values for spring discharge, local precipitation, and evapotranspiration in the following equation for a water budget in a watershed

$$P = ET + R + G + \Delta S \qquad (7)$$

where P is precipitation, ET is evapotranspiration, R is surface runoff, G is groundwater recharge, and ΔS is the change in storage (Manga 1997). Change in storage for the short time period under consideration here would make a relatively small contribution to the total water budget and this term was therefore omitted. I assumed that each spring system was fed by groundwater; thus, G was estimated by the measured discharge in the springs. Surface runoff in the study area is negligible with no evidence of perennial streams or developed stream channels other than those supplied with water from springs. Precipitation values for the proposed recharge areas were derived using regression analysis from mean precipitation values at Snotel sites in the region obtained from the NRCS and Dirks and Martner (1982) (Table 3, Fig. 5). Potential evapotranspiration values were obtained from Martner (1986) and Wyoming Water Development Commission and University of Wyoming (1990). Given mean annual precipitation and evapotranspiration rates, an estimate of the area needed to supply enough water for each spring system's discharge was calculated from equation (7). I used a 1:100,000 scale topographic map of the region and a 50-cm by 35-cm transparent grid with 1-cm squares to estimate recharge areas for each of the spring systems based on the areas calculated above and regional surface topography.

Table 3. Mean annual precipitation rates for Snotel sites in the Henry's Fork region (1961 to 1991).

Site	Elevation (m)	Precipitation (mm)
Black Bear, MT	2423	1567
Madison Plateau, MT	2362	1084
Whiskey Creek, MT	2072	929
Big Springs, ID	1981	779
Ashton, ID	1584	523
Island Park, ID	1917	767
White Elephant, ID	2350	1219
Lewis Lake Divide, WY	2392	1447
Grassy Lake, WY	2214	1422

Heat Flux

The total heat, H, discharged by each of the Henry's Fork springs was calculated using the equation

$$H = \rho C q \Delta\theta \qquad (8)$$

in which ρ and C are the density and heat capacity of water, q is the discharge from the spring, and $\Delta\theta$ is the change in temperature of the groundwater between recharge and discharge (Manga 1998, in press). It is assumed that groundwater movement in the aquifer advects all the heat horizontally. The mean heat flux entering the base of the aquifer is equal to the total heat flux divided by the surface area of the aquifer. …

RESULTS

Stable Isotopes

Trends evident in $\delta\ ^{18}O$ and $\delta\ D$ values of spring water, snow cores, and summer precipitation in the Henry's Fork region (Table 2)* included: 1) little year-to-year or seasonal variability in the stable isotope values for the spring waters; 2) Snow Creek

*See original article Vol. 6 (3).

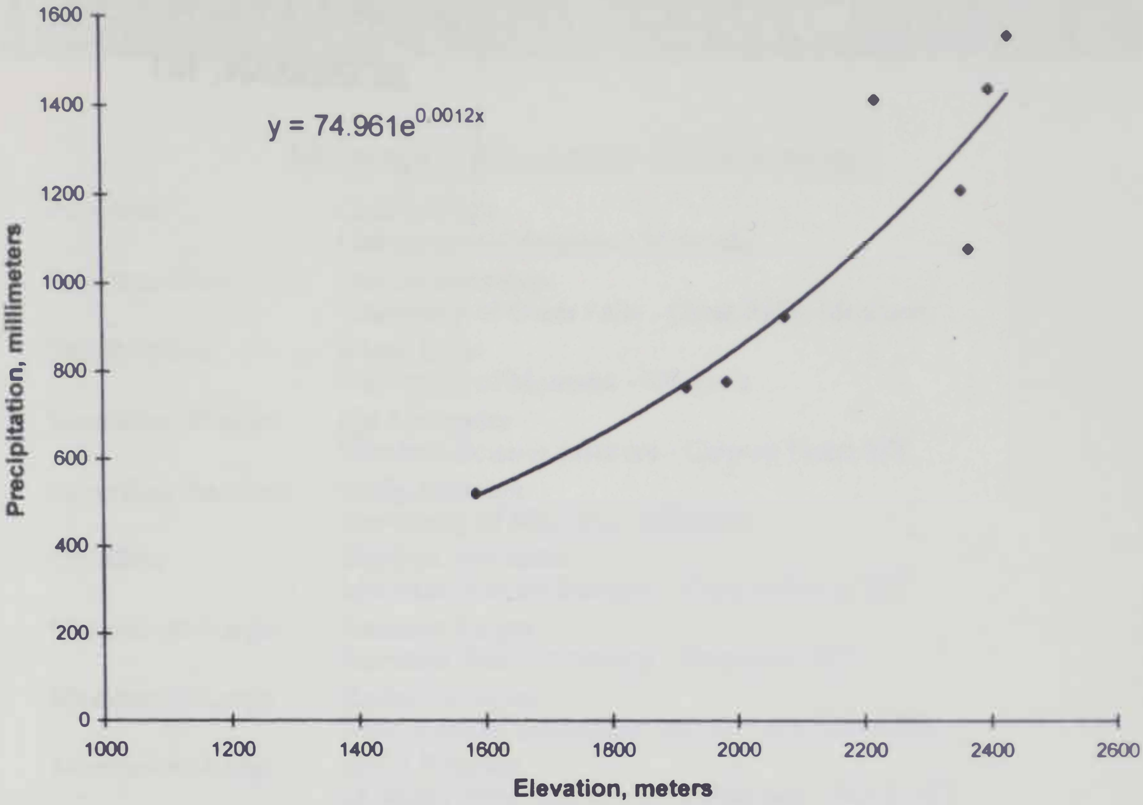

Figure 5. Mean annual precipitation as a function of altitude in western Yellowstone National Park and eastern Island Park, Idaho.

and Warm River water had the heaviest stable isotope ratios; 3) stable isotope ratios of snow cores were lighter than spring water at Big Springs and Lucky Dog, heavier than spring water at Warm River springs and the same as spring water at Snow Creek; 4) stable isotope values of all spring waters and snow cores were significantly lighter than of summer precipitation; 5) stable isotope values of summer precipitation were heaviest at Warm River and became progressively lighter to the north; and 6) the lightest stable isotope values of snow cores were those on the eastern side of the Continental Divide. …