RAPID DETERMINATION OF DISSOLVED ORGANIC CARBON BY PERSULFATE OXIDATION VIAL AND UV/VIS SPECTROPHOTOMETER

By

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Abstract: Dissolved organic carbon (DOC) has long been studied to determine and characterize natural organic matter (NOM). The goal of this thesis is to test a simplified ultraviolet-visible (UV/VIS) spectrophotometric procedure for determination and characterization of dissolved organic carbon (DOC) in water using the TOC direct method (HACH Company).

Laboratory tests of known samples were analyzed by this technique to ascertain the performance (precision and accuracy) and its applicability as an alternative to traditional measurements. The detection limitation of the method has been determined through a laboratory method detection limits guide from an EPA certification program, and the method detection limit was calculated to be 1.00 mg/L. The value of this concentration is slightly larger than the given lower limits of 0.3 mg/L expected.

For most of the organic matter, the resulting data indicated that the TOC direct method is easy to use, accurate and effective for determining the carbon content. However, for large, complex organic particles, such as humic acid, their DOC may be underestimated due to incomplete persulfate oxidation. Careful handling and practice is very necessary to achieve the optimal of the method performance. The method is easily prepared and portable compared with the traditional DOC analyzer, while the reagent solution and equipment is minimal.

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CHAPTER I

INTRODUCTION

1.1 Background information

Natural organic matter, or NOM, refers to a group of carbon-based compounds that are found in surface water and some groundwater supplies [1]. Dissolved organic carbon (DOC) is defined as the concentration of carbon remaining in water after the sample has been passed through a filter (filters with nominal pose pore size that generally range in size between 0.7 and 0.22 μm). Conversely, the rest of the organic carbon that is too large and is filtered out of a sample is particulate organic carbon (POC) [2]. Most commonly, DOC is the fraction of total organic carbon (TOC) passing through a 0.45 μm filter [3]. The fractions of total carbon are defined as: inorganic carbon (IC) - the carbonate, bicarbonate, and dissolved CO_2; total organic carbon (TOC) - all carbon atoms covalently bonded in organic molecules; dissolved organic carbon (DOC) - the fraction of TOC that passes through a 0.45 μm pore-diameter filter; particulate organic carbon (POC) - the fraction of TOC retained by a 0.45 μm filter; volatile organic carbon (VOC) - also referred to as purgeable organic carbon, the fraction of TOC removed from an aqueous solution by gas stripping under specified conditions; and nonpurgeable organic carbon (NPOC) - the fraction of TOC not removed by gas stripping, NPOC correlates to the type of organic compounds that form hazardous disinfection byproducts in water treatment [3, 4]. While the purgeable organic carbon is always dissolved, the non-purgeable may be either dissolved or

particulate, and in most nature water samples, the purgeable organic carbon fraction is insignificant when compared to the NPOC [5].

Organic carbon is ubiquitous in natural waters, which can be allochthonous, or sourced from outside the water system (e.g. degradation of terrestrial vegetation and atmospheric deposition or transported long distance via stream flow) or can be autochtonous, or sourced from the immediate surroundings of the system (e.g. excretion and decay of plant and microbial matter and sediments/ soils within the catchment) [6]. Based on molecular weight, DOC is composed of relatively high apparent molecular weight humic and fulvic acids, as well as low apparent molecular weight proteins, organic acids, carbohydrates and other compounds [7].

1.2 Why study DOC?

NOM is the product of various decomposition and metabolic reactions in the water supply and is impacted by the soil and vegetation surrounding catchments, and is also affected by seasonal variations. NOM in surface water which can be the cause of various problems in drinking water, are part of what water treatment facilities target for removal before water is sent flowing into the drinking water supply [8, 9]. They can lead to a number of challenges to water treatment facilities. First, NOM can be responsible for water taste, odor and color. Another important consideration is that NOM may lead to the formation of byproducts (DBPs). Coincident with the passage of the Safe Drinking Water Act of 1974, it was discovered that chloroform (one of a class of compounds called trihalomethanes) was a disinfection by-product (DBP) resulting from the interaction of chlorine and natural organic matter in water [10]. As the increasing concern over the presence of DBPs in drinking water and their potential to adversely affect human health, EPA enforces regulatory limits (see Table 1) aimed at reducing the level of two primary groups of

DBPs with potential health risks, total trihalomethanes (TTHM) and haloacetic acids (HAA5) [11].

Table 1. MCLGs and MCLs for Stage 2 disinfectants and disinfection byproducts rule [12].

	Disinfection Byproduct	**MCLG, mg/L**	**MCL, mg/L**
Total Trihalomethanes (TTHM) [1]	Bromodichloromethane	0	0.080** as an annual average
	Bromoform	0	
	Dibromochloromethane	0.06 (60ppb)	
	Chloroform	0.07 (70ppb)	
Haloacetic acids (HAA5) [2]	Dichloroacetic acid	0	0.060** as an annual average
	Trichloroacetic acid	0.02 (20 ppb)	
	Monochloroacetic acid	0.07 (70 ppb)	
	Bromoacetic acid	N/A*	
	Dibromoacetic acid	N/A*	
	Bromate	0	0.010 as an annual
	Chlorite	0.80 (800 ppb)	1.0 (ppm)

1. TTHM is the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform.
2. HAA5 is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.
* This byproduct is regulated with this group but has no MCLG.
** Sum of the concentrations of all byproduct in the category.

In the regulation, EPA established maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for total trihalomethanes, haloacetic acids, chlorite and bromate [12]. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies [13]. TOC is also required in the rule, to represent a specified percentage of organic materials, for these water systems that use surface water and use conventional filtration treatment because organic matters may react with disinfectants to form DBPs [14]. The quantitative measure of

TOC or DOC is the most commonly used parameter to quantify NOM. The widely-employed detection measurements, TOC and DOC, provide an indication of the total organic matter concentration for surface and drinking water [8]. And water treatment plants have to comply with these stringent DBPs and HAA5 regulations on water quality.

1.3 Advantage and disadvantage of organic carbon in nature water

A lot of studies have primarily focused on the fate of carbon in NOM. Studies of Amazon River provided a conclusions that 70% or more of the DOC in rivers is contained in high molecular weight (HMW) compounds [15, 16]. And this part of HMW carbon that a considerable portion of HMW DOC in rivers is readily used by bacteria as demonstrated in some studies [15, 17]. Therefore, high TOC values are viewed as evidence of frequent algal blooms in the overlying waters [18]. It was also found that there is a positive correlation between total phosphorus and TOC measurements. The carbon productivity rate is well correlated with total phosphorus (r^2 = 0.94) [19]. Meanwhile, many previous papers have identified significant empirical relationships between phosphorus concentration and various indicators of algal growth in lakes and reservoirs. This correlation indicates that the measurement and removal of TOC is significant [20]. Much attention has been paid to dissolved organic matter like TOC and DOC, basically as a source of organic pollution, but further as an energy source for microbial- based aquatic food webs for phytoplankton and bacteria [21].

Measuring organic carbon in a natural water body is a basic component of studying the global carbon cycle because DOC is an important component of the carbon cycle and the energy balance in nature water. Carbon in the system, which consists of the "carbon dioxide – organic carbon – carbonate" cycle, is the building block of life and serves as a primary food sources for aquatic food webs. DOC can alter aquatic ecosystem chemistries by contributing to acidification in a low-

alkalinity, weakly buffered water body [22]. In addition, trace metals in the natural environment can complex with DOC, creating water-soluble complexes which can be transported and taken up by organisms. Furthermore, organic carbon can affect light penetration in aquatic ecosystems, which is significant for the ecosystem's phototrophs that need light to survive [6].

1.4 Measurement of DOC

This section provides an over view of the various methods used to estimate or determine TOC. These methods are well-established, fully-developed, and widely-accepted because of the long history that they have long been applied for measurement of TOC. Since DOC is a portion of TOC, the TOC method can be directly adopted to measure DOC with a suitable sample filter or when all the solution analyte is absolutely soluble (DOC= TOC).

1.41 UV Absorption Method

A number of organic compounds are found in natural water and industry wastewater, including humic substances, lignin, tannin, and various aromatic compounds which contain structures that are likely to form DBPs. These compounds containing aromatic rings can strongly absorb ultraviolet (UV) radiation in a range from 200 to 400nm with the value of 245 nm being used for measurement most commonly [23]. The basic assumption in this approach is that the DOC concentration is proportional to the UV absorbance [24, 25]. This hypothesis may not always be true because of the presence of interfering substances, like iron, nitrate, nitrite, and bromide [26, 27]. But with properly pretreatment samples, the UV absorbance at 254 nm (A254) is strongly

correlated (R^2 =0.911; P< 0.0001) with the DOC concentration measured by high-temperature catalytic oxidation (HTCO) [24].

The specific ultraviolet adsorption (SUVA) is defined as the UV absorbance of a water sample at a given wavelength normalized for dissolved organic carbon (DOC) concentration, that is, the ratio of UV254 to DOC [28]. Despite the UV measurement is correlated to the DOC, SUVA is in fact a measure of the nature of the carbon in the sample being analyzed, more specifically the extent to which the carbon is aromatic. The SUVA test has been used to assess the potential for the formation of trihalomethanes [29, 30].

Although UV absorption can be used to detect certain individual organic contaminants after separation (e.g., by HPLC), it is not suitable for detection of trace concentrations of individual chemicals. The correlation between UV254 and DOC for raw water and treated water samples in a river in Australia was shown in Figure 1. Good correlation can only be obtained with similar water quality. UV absorption was intended to be used to provide an indication of the aggregate concentration of UV-absorbing organic constituents [31]. The ultraviolet method tends to include only the more complex NOM character [15]. However, UV254 is useful in the on-line analysis of high purity water because this technique only requires very simple instrumentation and can be performed by the operators in the treatment plant [32, 33].

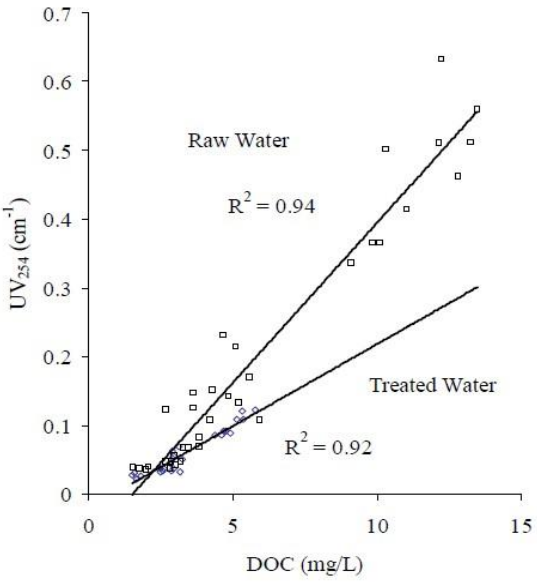

Figure 1. The correlation between UV254 and DOC for raw water and treated water samples [31].

1.42 Standard TOC methods

As a fraction of TOC that can pass a filter paper with 0.45 μm pore size, DOC is also named the dissolved total organic carbon, DTOC. Hence, TOC methods can be directly adapted to determine DOC. The principle of most TOC methods is to determine the quantity of organically bound carbon. The organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively [4]. The test methods for TOC or DOC utilize heat and oxygen, UV radiation, chemical oxidations, or some combination of these methods to convert organic carbon to carbon dioxide, which is usually measured with an infrared analyzer or by other means [4]. The persulfate oxidation method, which now is widely used to measure DOC in natural water and industry wastewater, are first being developed for soil extract DON [34] and for fresh water DOC [35].

EPA documents released three approved techniques to measure DOC, including Combustion-Infrared and UV/persulfate oxidation, and wet-oxidation. Table 2 lists the technique information for each method to select suitable method to measure DOC at different concentration range.

Table 2. General introduction of combustion- infrared method, UV/persulfate method and wet-oxidation method [4, 31, 33].

Methods Features	Combustion-Infrared	UV/persulfate oxidation	wet-oxidation
Oxidation	Catalytic combustion	Heat with persulfate; UV irradiation with persulfate	Heat in an autoclave with persulfate
CO_2 Measurement	CO_2 is measured by non-dispersive infrared analyzer (NDIR) or converted to CH_4 measured by a flame ionization detector		
Interference	The loss of VOC purging with gas; large carbon particles failed to inject; DOC loss or gain depending to compounds physical properties and filter		
Scope, conc. of organic carbon	Minimum 1mg/L	Below 1 mg/L, minimum 0.05 mg/L*	Minimum 0.1 mg/L*
Application	Domestic and industry wastewater analysis	Trace analysis	Analysis of water, water-suspended sediment, brines. Not suitable for VOC

*Minimum can be detectable when sample contamination and method background are negligible

1.5 The TOC direct method

The TOC direct method was applied in this study to determine TOC concentration. This method uses persulfate to oxidize dissolved organic carbon to carbon dioxide, and heat to drive the persulfate oxidation. Each TOC tube consists of two vials, an outside one containing digesting reagent, and an inside tube containing color indicator. In the outside vial, organic carbon in the sample is digested by persulfate and acid and is converted to carbon dioxide (CO_2). During 2-hour digestion process, the carbon dioxide diffuses into the indicator forms carbonic acid. Carbonic acid changes the pH of the indicator solution which, in turn, changes the color. Hence, the amount of color change is related to the original amount of carbon present in the sample. The

amount of carbon present in the sample tube is proportional to the concentration of carbonaceous material in the samples [36].

1.6 Study objectives

The goal of this study is to test the method performance of the TOC direct method vial set, evaluating the quality of the method by calculating accuracy, precision and detection limits. Different kind of organic compounds has been made into solution, measured by TOC direct method. Based on the oxidation efficiency of each chemical, the study would give a conclusion on which kind of organic carbon is most suitable for the TOC direct method.

1.61 Accuracy

Accuracy is the difference between "true" value and a particular measurement under the condition. Precision is defined as the degree of agreement between replicate measurements of the same quantity. There is a distinction between precision and accuracy that is to say even if the measurement's precision is excellent, it may be inaccurate if a determinate error is present [37].

1.62 Detection limits

Another purpose of this study is to determine the detection limits. Detection levels are somewhat controversial, principally because of inadequate definition and confusion of terms [25]. Despite the various terms used, it is basically agreed that the ability to quantify a trace element or molecule using specific analytical methods is the limit of detection [38]. To be more precise, the

detection level is the smallest amount that can be detected above the noise in a procedure and within a stated confidence level is the detection level [39]. In this study, the method detection limits (MDLs) was selected and calculated through EPA MDL procedure (CFR 136) [40] and made comparison with the method detection limits given by the manufacturer.

CHAPTER II

REVIEW OF LITERATURE

2.1 General discussion

The pollution of the water is frequently described using aggregate parameters such as the chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC) or the spectral absorption coefficients (SAC). The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized further by biological or chemical processes, and the BOD and COD may be used to characterize these fractions [4]. However, the BOD method is frequently replaced by the COD method due to problems of repeatability and inhibition by commonly occurring ions and compounds [41, 42]; also COD method results in the production of hazardous wastes including mercury and hexavalent chromium, sulphuric acid, silver and other hazardous materials, depending on the method used [43].

Unlike BOD or COD, TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements, such as nitrogen and hydrogen, and inorganics that can contribute to the oxygen demand measured by BOD and COD. If a repeatable empirical relationship is established between TOC and BOD or COD, then TOC can be used to estimate the accompanying BOD or COD [4]. To insure the practical capability, this relationship must be established independently for each set of matrix conditions, such as various points in a treatment

process. According to a HACH company document which dealing with wastewater in airport, experience shows that the parameters behave similarly such that correlations between the individual summing parameter can be used for specific water sample [44].

A valid relationship has been established by Dubber, D et al. [37] via examining the replacement of COD with TOC for general monitoring by comparing the relationship between the results of TOC, BOD and COD tests performed on influent and effluent samples of 11 wastewater treatment plants. The study showed significant linear relationships between TOC, COD and BOD_5 in influent domestic and municipal wastewaters, but only between COD and TOC in treated effluents [37].

TOC is a convenient and direct method that can be used as a measure of NOM characteristics in drinking water and wastewater, while BOD and COD are more informative about oxygen consuming matter. While all these linear relationship been computed, it is not saying that TOC measurement can replace BOD and COD testing. In some cases TOC, however, can be possibly used as a replacement of BOD and COD values [45].

Another measurement is UV absorption, usually at 254 nm. Roy, S. et al. [46] reported a good correlations between DOC and TOC and between DOC and UV254 (Figure 2) over the entire range of concentrations in the Central Valley, comprising the Sacramento and San Joaquin River

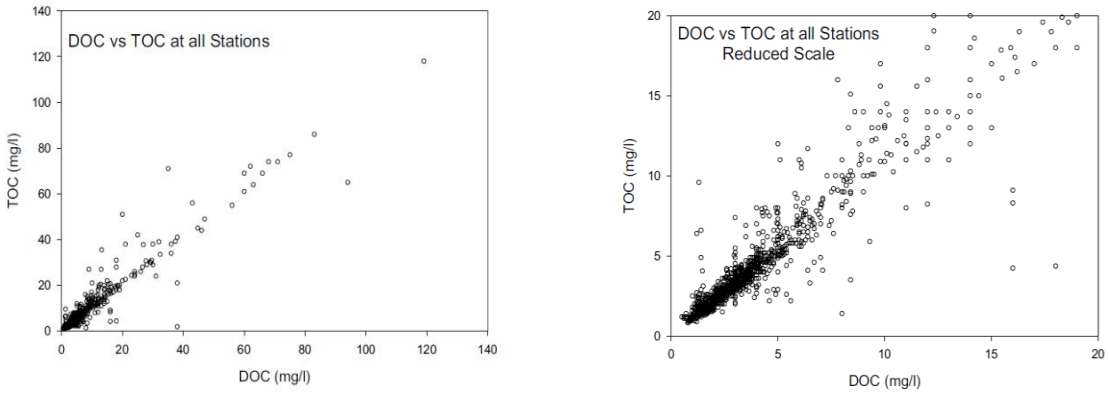

Figure 2. Contemporaneous DOC and TOC at all stations in the Center Valley, CA [46].

watersheds. However, over the range of concentrations of most interest in surface waters, i.e., less than 20 mg/l, the correlations appear weaker, particularly between DOC and UV254 [47, 48]. Similar research has been done, and the correlation between TOC and DOC was generated in the surface water layer at Lake Isąg, Poland. Variability of TOC observed on was affected by the changes in DOC while in the shallower water layers [49]. Hence, it is possible to build a DOC-TOC relationship model for measurements of TOC and DOC parameters, and that suggest organic carbon from multiple sources is likely to have a clear DOC-TOC relationship for a specific river. But for wastewater, such kind of relationship is usually mentioned to DOC-TOC ratio with 0.8 value [45].

2.2 Characterization, fractionation and isolation

Characterizing the NOM using a range of techniques, such as measuring the very hydrophobic (VHA) fraction, allows an understanding and prediction of a water susceptibility to coagulant dose to optimize DOC removal [31]. The available tools are displayed in Table 3 for NOM characterization. True and apparent colors are used as rough estimates of NOM content. Because some NOM compounds with light absorbing chemical structures can absorb UV radiation in a range from 200 to 400nm, UV absorption has been used as a surrogate measure for NOM.

Total organic carbon is the most comprehensive measurement used to quantify the presence of NOM in aquatic systems [50]. TOC is often synonymous with NOM because organic contaminants in nature systems generally represent an insignificant fraction of the TOC. Some NOM occurs as particulate matter or is adsorbed to particulate, requiring a TOC test, and for others, especially drinking water supplies, the majority of NOM exists as dissolved compounds and is often measured as DOC. The defined fraction like DOC or POC based on the subdivision of TOC is the most fundamental part of characterization of NOM. In the real, the rules

promulgated by U.S. EPA for DBPs contain monitoring NOM during and in the finished part of treatment by measuring both TOC and DOC [7, 23, 29].

Table 3. A range of analytical techniques offer more information on NOM character [31].

Parameters	**Analytical Tools**
Color	Visible Spectrophotometry
	Visual Comparators
Aromaticity (UV absorbance)	UV Spectrophotometry
Total Organic Carbon	DOC Analyzer
Dissolved Organic Carbon	
Biodegradable Organic Carbon	
Assimilable Organic Carbon	Bacterial Regrowth Potential
Bacterial Regrowth	
Molecular Weight Distribution	High Performance Size Exclusion Chromatography
Hydrophobicity/ Hydrophilicity	Rapid Fraction
Functional Groups (Aliphatic, Aromatic, Nitrogen Containing)	Gas Chromatography
	Gas Chromatography-Mass Spectroscopy
	Nuclear Magnetic Resonance

In spite of monitoring NOM concentration, the nature and properties of NOM in water are topics of significant environment interests. And characterizing NOM can act in turn to improve the measurement of NOM concentration. Lots of sophisticated test methods as discussed in Table 2 are aiming to determine the characterization of NOM, including the composition and structure of the NOM, the presence of specific polymers or chemical functions, and the apparent molecular weight [51]. Among all these properties, attention has been paid to molecular weight distribution; HPLC chromatography method was established to fractionate NOM in water into molecular weight groups. Date revealed that DOC in fresh water contains at least three distinct component fractions (MW less than 200, MW in 500-1000, and MW larger than 20,000) [52, 53]. Leenheer

used a series of resin adsorbents to isolate mixtures of NOM from water through a multistep separation scheme, also calculating the composition of DOC in each fraction [54].

The NOM generally includes humic substance (humic and fulvic acids), and non-humic materials including hydrophilic acids, amino-acids, proteins, carbohydrates, carboxylic acids and other trace compounds [54, 55, 56]. Because of the interest in the chemical constituents that make up the DOC, advanced methods of analysis have been developed to quantify the constituent group as illustrated on Table 4 [50]. Indeed, operationally defined humic substances typically compose about 50% of DOC of an average river [47]. However, DOC concentration, composition, and chemistry are highly variable and depend on the sources of organic matter, temperature, ionic strength, pH, and the presence of photolytic and microbiological degradation processes [7].

Table 4. Fractions and procedure for the characterization of the dissolved organic carbon [7, 54, 57].

Conc.	Polarity	Acid-base character	DOC*, %	Compound classes	Molecular weight range
Dissolved organic carbon	Hydrophobic organic carbon Total DOC* 49%	Acids	19	Anionic detergents, Humic and fulvic acid	450 to 1000
		Neutrals	17	Chlorinated hydrocarbon insecticides	100 to 70000
		Bases	13	Polynuclear amines	250 to 850
	Hydrophilic organic carbon Total DOC* 51%	Acids	29	Polyuronic acids	250 to 850
		Neutrals	10	Polysaccharides	120 to 900
		Bases	12	Amino sugars	100 to 1000

* Analytical DOC of Omega-9 Retort water with a total DOC of 977 mg/L.

Rapid Fractionation (RF) describes the NOM as a mixture of four organic fractions, very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged (CHA) and hydrophilic neutral (NEU), by using adsorption on various resins [31]. RF of supplies from around Australia indicated that waters with higher DOC tended to have a higher proportion (percentage) of hydrophobic fractions (VHA/SHA) whereas water supplies with lower DOC tended to have higher proportions of the hydrophilic neutral (NEU) fractions. Most waters surveyed in Australia tended to have very low concentration of CHA and NEU fractions with the greatest concentration of the DOC present as hydrophobic fractions (VHA/SHA) [31].

2.3 The underestimation of persulfate oxidation

The TOC direct method from HACH Company uses persulfate as oxidant for TOC measurement. This new method detects the amount of color changing in the vial which distinguishes itself from previous traditional infrared TOC analyzer. Test results are measured at 598 and 430 nm [36]. Instead of purchasing a TOC analyzer or outsourcing TOC determination to a professional detection laboratory, HACH's TOC direct method can test TOC or DOC result anywhere, anytime without any hazardous waste. For DOC determination, procedure requires that the sample be passed through a 0.45 um filter prior to analysis to remove particulate organic carbon from the sample. But a historical perspective on DOC measurement is that DOC concentration could be significantly underestimated by the commonly used persulfate digestion approaches comparing with high temperature combustion method especially when seawater DOC is determined [58,59].

Persulfate oxidation depends on peroxydisulfate ($K_2S_2O_8$) decomposition into the persulfate radical (HSO4•), which is the active oxidizing agent. The process is shown in the Figure 2 with a three step stoichiometry [5].

$$S_2O_8^{-2} \xrightarrow{h\nu} 2SO_4^{\bullet -} + e^-$$

$$H_2O \xrightarrow{h\nu} H^{\bullet} + {}^{\bullet}OH$$

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{-2} + H^+ + {}^{\bullet}OH$$

This decomposition of persulfate oxidation follows an Arrhenius relationship between 50 and 130 ^{o}C [60]; persulfate has a half-life of about 30 s at 130 ^{o}C and 4 h at 75 ^{o}C. The decomposition is the rate-limiting step, and further oxidation steps are rapid relative to free radical initiation [61]. Under some conditions, higher temperature may decrease carbon recovery [62]. Thus, high temperature may increase reaction rate but not necessarily completeness.

It was reported that precipitation of hydrophobic DOC, presumably humic acids, when freshwater samples are acidified to pH 2-3 and sparged externally to an analyzer to remove inorganic carbon can lead to the underestimation of DOC concentrations [63]. Large organic particles or very large or complex organic molecules such as tannins, lignins, and humic acid may be oxidized slowly because persulfate oxidation is rate-limited [4]. Because the efficiency of conversion of organic carbon to CO_2 may be affected by many factors, it must check efficiency of oxidation with selected model compounds representative of the sample matrix. Persulfate oxidation of organic molecules is also slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride; at a concentration of 0.1% chloride, oxidation of organic matter may be inhibited completely. Chloride is reported to interface the progress of persulfate oxidation, and possibly other ions, produce significant interference in the oxidation reaction of organic matter by persulfate. A strong hyperbolic relationship was found between measured DOC concentration and volume of persulfate added for oxidation in chlorinated (NaCl) freshwater samples, whereas freshwater samples showed no such relationship. Analysis of DOC

in seawater, or water with high chloride content, by persulfate oxidation may yield erroneously low, yet precise, results [64].

It is also mentioned by several research that sample handling is the key in DOC persulfate oxidation. Contamination during sample handling and treatment is a likely source of interference leading to the underestimation of DOC. This is especially true of trace analysis. Take extreme care in sampling, handling, and analysis of samples below 1 mg DOC/ L [65].

CHAPTER III

ANALYTICAL METHOD

3.1 Summary of HACH direct method

In both TOC and DOC determination, organic carbon in the water sample is oxidized to produce carbon dioxide, which is then measured by a TOC detection system. The first step is to sparge the sample under slightly acidic conditions to remove the inorganic carbon. Samples are then pipetted into the outside vials, sealed tightly, to react with oxidant persulfate. When the reaction is done, all the organic carbon contained in the sample is released from the covalent bond, goes into the inside vial and changes the color of the liquid in the inside vial. The color of indicator turned from blue to yellow. The resulting color for reagent blank is dark blue. The more carbonic acid that goes into the indicator solution, the more yellow the inside tube will be. The amount of carbon present in the sample tube is proportional to the concentration of carbonaceous material in the sample [36]. For DOC analysis, as stated in Chapter One, samples would be passed through a 0.45 μm filter to remove particulate organic carbon from the sample.

Both TOC and DOC procedures require that all inorganic carbon be removed from the sample before the sample is analyzed for organic carbon content. If the inorganic carbon has not been completely removed, significant error will occur, which is seen by the results of the laboratory test described below.

3.2 Instrumentation and apparatus

The instrumentation set-up for DOC analysis includes DR5000 spectrophotometer (Hach Company, Loveland, CO) with a stored program for low range organic carbon; total organic carbon direct method low range test 'N Tube ™ reagent set (Hach Company, Loveland, CO); reactor with adjusted temperature at 105 °C and magnetic stirrer. Also used were graduated cylinder (10 mL), Erlenmeyer flask (50 mL), pipet (1mL, 5mL, and 10mL), magnetic stir bar, test tube rack and disposable wipes.

3.3 Sampling and reagents

Reagent water was generated using a water deionization process with filter reverse osmosis system, and stored in a plastic container (using plastic container is not recommended by the Hach method direction, but data obtained has proved reagent water in plastic container wouldn't add the carbon content for samples). Organic carbon free water is recommended, and their calibration water was purchased from Hach company (organic free, 500 mL).

Dissolved organic carbon data were collected using laboratory samples in reagent (blank) water, preparing a laboratory standard (analyte in reagent water) at a concentration which was equal in dissolved organic carbon for all the testing components. Eight chemicals which could be categorized into small molecular weight (MW) and large MW were chosen to represent the most commonly existed organic matter in nature water system, meanwhile they were easily to find in any chemistry laboratory. Potassium hydrogen phthalate (KHP), as the wide accepted standard chemical used in the calibrate solution was also included in the selected compound list in Table 5.

All samples used in this study were made within the laboratory. For preparation of the analyte, dry solid was placed in a drying oven for 1 hour at temperature 105 °C to remove excessive

water. Chemicals were then removed from the oven and placed in a desiccator for 1 hour to cool. Because it is a low range method, the given maximum concentration is no more than 20 mg/L; the dissolved organic carbon values were set to be 5 mg/L, 10 mg/L, and 20 mg/L of DOC. Reagent blank was made by both distilled water and organic free water, for comparison and to control the reagent water carbon content to an acceptable range.

Table 5. Sample grade and manufacture information, molecular weight, carbon percent and weight of sample reagent for 250 mL stock solution with 1000 mg/L.

Sample	**Grade & manufacture**	**MW, g/mol**	**Carbon percent, %**	**Weight for 250mL stock, g**
KHP	Fisher Scientific, ACS reagent	204.22	47.08	0.5318
K_2CO_3*	Fisher Scientific, 85% min	138.21	8.68	2.8793
Humic acid I (sodium salt)	Sigma-Aldrich Chemical Company	226.14	47.76	0.5235
Humic acid II**	American Colloid Co. from N.D. Leonardite, IHS std	Around 250	40%- 50%	0.5000
D-Glucose	AR	180.16	39.96	0.6256
Sucrose	Fisher Scientific, Reagent Grade	342.3	42.00	0.5943
Urea	Fisher Scientific, 99%	60.06	19.98	1.2504
L-Glutamic Acid	Assay, 99%	147.13	40.78	0.613

* K_2CO_3 is put in the analysis to test how the new method reacts with inorganic carbon; both the carbon content and weight are mean to inorganic carbon.

**This humic acid II is slightly soluble in water, most of its compound floating on the surface of solution in flask, and weight is calculated based on average organic carbon percentage.

The weight of analyte was calculated to make stock solution with carbon concentration equal 1000 mg/L (1.00 mL= 1.0 mg C). When analyte was weighed, they were quantitatively transferred to volumetric flask. Use distilled water to dissolve reagents, then brought to volume. Each stock solution should be mixed thoroughly. Working solutions were generated by dilutions

of stock solution. Compounds' molecular weight (MW), weight, grade and manufacture are listed in Table 5, too.

All reagents are retained in clean glass containers and stored at room temperature for maximum of 30 days. For most DOC measurement for fresh water or industry wastewater, ideally, sample must be filtered prior to analysis to remove POC. But, in our study, no POC exist because solutions are made by dissolving soluble analyte.

3.4 Interferences

In most nature water samples, the inorganic carbon (IC) fraction is many times greater than the TOC fraction [4]. IC interference can be eliminated by acidifying samples to pH 2 or less to convert IC species to CO_2, and then remove it. Usually, the next step is to purge samples with purified gas to remove VOC and carbon dioxide after acidification. But here, a magnetic stirrer is applied instead of purging. Inorganic carbon can be removed by stirring the acidified sample [36]. Thus, at the low pH and 10 minutes stir, all inorganic carbon species are expected to be converted and removed [36]. Moreover, in many surface and ground waters the VOC contribution to TOC is negligible.

Other interference comes from water samples containing large concentrations of chloride ion. The chloride ion can lead to persulfate oxidant decomposition. The interference becomes significant when chloride concentration is equal to or greater than 0.1 % of 1000 mg/L [66].

3.5 Standard materials

The standard solution in this study is KHP (Potassium hydrogen phthalate) stock solution. KHP stock solution is made by dissolving dry KHP compound into reagent water with concentration 1000 mg/L. The stock solution is valid for a period of 30 days and was stored in glass volumetric flask. The working solution was diluted from the stock. Based on the method detection range, three theoretical concentrations are selected to be 5 mg/L DOC, 10 mg/L DOC and 20 mg/L DOC to evaluate method performance. MDL is also calculated from KHP samples at low concentrations.

3.6 Analytical procedure

Samples were diluted to expected concentrations from stock solutions. Label each sample and then follow the total organic carbon direct method instruction [36]. Tubes were inserted into the heat reactor for 2 hours at 103- 105 ^{o}C. Then remove the vial from reactor, put in a test tube rack, and cool down for at least one hour. Organic free water is used to calibrate UV/vis spectrophotometer and for quality control of reagent blank sample. The liquid in the reagent blank vial should be dark. Before place tube into UV/vis spectrophotometer, samples need to be wiped with a damp towel, then with dry wipes. After verifying proper operation of the TOC tubes and UV/vis spectrophotometer, samples were placed in the machine to determine DOC concentration. The time consumed in the whole procedure was approximately to be 4 hours based on the eight samples and each sample done once test.

3.7 Percent difference

Distill water spike samples were prepared by dissolving a known amount of eight chemicals in an exact volume of distilled water. Three sample groups were tested to analyze the method percent difference as in the below formula.

$$D\ \% = \frac{theoretical\ concentration - detected\ concentration}{theoretical\ concentration} * 100\%$$

Accuracy in this study is expressed in the difference percent (D %) [41]. Each group is done three replicates with expected concentration at 5 mg/L DOC, 10 mg/L DOC and 20 mg/L DOC separately.

3.8 Linear regression analysis and precision

Eight replicates of KHP with concentration at 10.0 mg/L DOC were tested to find precision. Precision was evaluated between the tested value and expected value by average absolute deviation and statistical precision, the standard deviation. The average absolute deviation will usually be slightly smaller than the half range, but it is another reasonable estimate of uncertainty [37].

$$average\ absolute\ deviation:\ <|\Delta w|> = \frac{1}{N-1}\sum_i |w_i|\,, \qquad \Delta w_i = w - \Delta w$$

$$standard\ deviation:\ <\delta w^2> = \frac{1}{N-1}\sum_i (w_i - < w >)^2$$

Where w is the values' mean; N-1 is the degree of freedom.

Standard deviations of the same concentration samples were also used to judge the method performance. Another three groups of KHP with low concentration DOC were run on this

method. Linear regression analysis was used to calculate bias and correlation. The group concentrations ranged from 0.2, 0.4, 0.5, 1.0, 2.0, 4.0, and 5.0 mg/L DOC.

3.9 Calculation of the MDL

Current practice identifies several detection levels, including instrument detection level (IDL), the lower level of detection level (LLD), the method detection level (MDL), and the level of quantitation (LOQ). The relationship among these levels is approximately IDL:LLD:MDL:LOQ= 1:2:4:10 [29]. With all these limitations, MDL is selected in this thesis because MDL provides a useful mechanism for comparing different analytical methods within the same laboratory, or the same analytical techniques in each individual laboratory. When choosing an appropriate analytical method, it's essential to consider the relationship between MDL and expected detection range. Also, standardization of reporting MDL with low level data significantly enhances data analysis and interpretation because it is comparable. The EPA procedure (40 CFR 136, EPA MDL procedure) is used in calculation with confidence level set to be at 99% for MDL procedure, according the U.S. EPA, as the inequalities listed below.

$$\text{Calculated MDL} < \text{Spike Level} < 10 \times \text{Calculated MDL}$$

MDL is calculated using the following equation: $MDL = T_{(N-1,\ 1-\alpha=0.99)} \times SD$

Where T part is the student's t value appropriate for 99% confidence level and a standard deviation estimate with N-1 degrees of freedom. Where N is the number of replicates collected for MDL study. The values for student's t value at 99% confidence interval can be extracted from EXCEL. Seven replicates of concentration 0.4 mg/L DOC were analyzed to calculate MDL through the algorithm.

Due to the nature of MDL, that is, 50% of spike sample could fall above the limits and the other 50% fall below, no perfect procedure has been established to evaluate MDL. Even the widely used EPA procedure has been criticized as having “faulty statistical assumptions”, the method is relatively straightforward and practical based on experiment operations; on the other hand, similarly complex flaws are found with any alternative [39].

CHAPTER IV

RESULTS

4.1 General description

The result discussion consists of three sections. In the first section, the method accuracy is discussed primarily through calculation of percent difference. Also, a well-established COD vial method and the TOC direct method measurement is used to compare the validation and reliability of the TOC direct vial method. Second part includes regression analysis and precision. Linear regression was used to evaluate any bias between test result and theoretical value, and to determine the degree of correlation for each individual experiment data set. In the section three, MDL was selected to representative the detection limits and was generated through EPA MDL procedure. The validation of EPA MDL procedure is also involved in this chapter.

4.2 Method accuracy

The expected or theoretical values of the spike solution was 5 mg/L, 10 mg/L, and 20 mg/L DOC. Table 6 compares the expected value with the detected concentrations. The detected concentrations given are means of three replicates samples. It can be seen from the table that five out of eight analytes (KHP, D-glucose, sucrose, urea and L-glutamic acid) that tested concentration are close to the expected value. Most of them got standard deviation less than 1.0

which means the method is practical and has good repeatability. The five samples fluctuate around the expected concentrations 10 mg/L DOC, but run little lower for both 5 mg/L and 20 mg/L groups. This was caused by a 10 mg/L group data measured higher than theoretical concentration, which may be resulted from sample handling progress like pipetting or different stock solution (the stock solution was re-prepared every 30 days).

Table 6. The standard deviation for same analyte and comparison between tested concentrations and theoretical values ***.

Sample	**Theoretical 5 mg/L**		**Theoretical 10 mg/L**		**Theoretical 20 mg/L**	
	measured	**Std. Dev**	**measured**	**Std. Dev**	**measured**	**Std. Dev**
KHP	4.40	0.46	11.07	0.92	19.75	0.06
K_2CO_3*	N/A**	-	0.90	0.28	0.90	0.35
Humic acid Ⅰ	3.10	0.44	7.43	0.55	16.80	2.12
Humic acid Ⅱ	N/A	-	1.50	0.28	N/A	-
D-Glucose	4.50	0.10	10.23	0.56	19.40	0.40
Sucrose	4.20	0.26	10.27	0.60	19.60	0.12
Urea	4.50	0.15	10.83	1.06	19.50	0.31
L-Glutamic Acid	4.70	0.21	10.83	0.87	19.60	0.20

*All concentration values are supposed to be organic carbon concentration as DOC except K_2CO_3.

**N/A refers to that samples are not analyzed due to abnormal previous data.

*** Standard deviation is in the right row of each concentration group.

Accuracy or relative deviation between the detectable value and expected value was evaluated by taking the absolute difference between each pair divided, and expressing the results as a difference percentage of the “true” concentration, demonstrated in Table 7. The tendency from 5mg/L theoretical DOC concentration to 20 mg/l is clear, the higher the expected value, the better the accuracy. And the tendency can be used as an indicator when calculating the MDL as show below.

But when looking at the remaining three samples, humic acid I, humic acid II, and K_2CO_3, the results are as expected. The two organic humic acid compounds, humic acid I is a sodium salt (soluble), and humic acid II (sparingly soluble), get D% to be 38% and 90% separately. For humic acid II, the low detected concentrations demonstrate that only very little of the compounds would be dissolved in water or none dissolved. Notably, this TOC direct method is designed to determine TOC and for samples which were not filtered to remove all the particles, the result derived from the method should be TOC concentration. In fact, in the situation of slight soluble humic acid II, its stock solution is well mixed before pipetting into the volumetric flask for dilution, and some insoluble particles would exist in the dilution solution. It is very likely that these sample turbidity is dissolved during the digestion stage, and carbon content was released into vial and detected by the UV/vis spectrophotometer, causing an increase in the detected concentration. But the actual result of humic acid II was not satisfying comparing with the expectation.

Table 7. Accuracy of TOC direct method for nine organic and inorganic samples.

Sample	**Difference percentage***		
	Theoretical 5 mg/L	**Theoretical 10mg/L**	**Theoretical 20 mg/L**
KHP	12.00	10.67	1.25
K_2CO_3**	-	-	-
Humic acid I	38.00	25.67	16.00
Humic acid II	-	90.00	-
D-Glucose	10.00	2.33	3.00
Sucrose	16.00	2.67	2.00
Urea	10.00	8.33	2.50
L-Glutamic Acid	6.00	8.33	2.00

* Percent is either plus or minus, only keep positive number here.

** Expected TOC is 0.0 for K_2CO_3, there exists no percent of difference.

Another compound also generated unexpected data. Compared with KHP or sucrose, humic acid I drew our attention for the obvious detected concentration value much less than expected value but more that humic acid II. As an important constituent of NOM, hydrophobic humic acid is often used as a key compound for recovery studies [65]. Some of the questions of recovery in the past have existed because of the highly complex polymeric properties of humic acids that can vary in form and structure depending on environmental conditions [67]. For instance, humic acids may fold in structure at high ionic strengths and open at low ionic strengths [65]. Also, the incomplete oxidation of chemically recalcitrant molecules with the persulfate technique may account for these minor differences [4]. As the humic acid I, the D % is not satisfied but still acceptable.

Second question is the concentration of carbon content coming from inorganic compound K_2CO_3. Since all sample were acidified to reduce pH <= 2 to convert all carbonate. After adding 0.4 mL of buffer solution, bicarbonate forms of inorganic carbon became carbonic acid, and should be removed from solution by constantly stirring, as seen in figure 3.

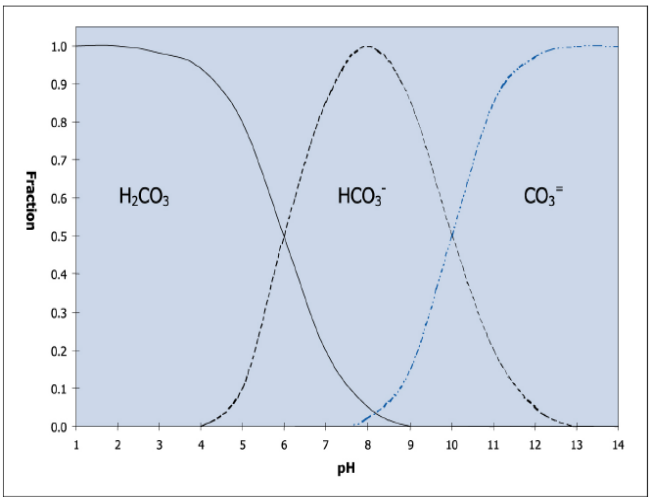

Figure 3. CO_2 fraction distribution in water versus pH [65].

Stoichiometrically, the inorganic carbon containing within K_2CO_3 should react with hydrogen-ion to produce carbon dioxide, then carbon dioxide should be released through stir process. But with 0.9 mg/L DOC for K_2CO_3 being detected by the UV/vis spectrophotometer, it appears that there is

some inorganic carbon left, and that the stirring do not remove all CO_2. From Table 5, K_2CO_3 exhibited two standard deviations of 0.28 and 0.35, indicating there was almost no change between the three replicates, which lead us to think maybe it was a fixed tested value. In our case, 0.9 mg/L took a 10 % of the theoretical value, but if it was determining the hard water, for example, groundwater, the 0.9 mg/L was ignorable.

COD is widely used for wastewater monitoring. The method is mature and unaffected by the presence of toxic substances; meanwhile it can achieve better precision and reliability [43]. A small group of three chemicals were tested through COD method (low range 0-150 mg/L), as shown in Table 8, as well as the percent of difference. When we looked KHP, sucrose and L-glutamic acid at the two tables, Table 7 and 8, the difference in percent from HACH TOC vial method was very close to, even better than COD method. For KHP, 10.67 in TOC vial set, 10.26 in COD method, the two matched perfectly. When concentration was around 10 mg/L, sucrose and L-glutamic acid samples behaved better than the difference percent of COD method. In both two concentration range, the TOC vial set was more accurate than COD method for L-glutamic acid. The TOC vial direct method is a reliable and practical means for natural water measurement.

Table 8. Comparison between theoretical COD with measurement for KHP, sucrose and glutamic acid [Fiddler, unpublished data].

Sample	**Theoretical conc. mg/L**	**Detected conc. mg/L**	**D* %, conc.**	**Theoretical conc. mg/L**	**Detected conc. mg/L**	**D %, conc.**
KHP	11.7	10.5	10.26	23.5	24.1	2.55
Sucrose	11.2	10.4	7.14	22.4	21.8	2.68
L-Glutamic acid	9.8	8.3	15.31	19.6	18.2	7.14

* D % is short for difference in percent.

Oxidation efficiency data was derived from the HACH document [64] was listed in Table 9. On the average the result produced by the method can be expected to agree within about ± 5% percent when analyzing spike distilled water sample. These chemicals were tested in this method in pure water-soluble organic standards. Their relative recoveries were compared to KHP.

In real cases, such as drinking water and wastewater monitoring, it is recommended to run interference studies under applied condition. Although it is reported that typical substances in field case were tested using this method and did not show significant interference [69]. Extreme ionic strength, turbidity, temperature, pH value, alkalinity may lead to a potential interference. For high alkalinity (>1000 mg/L) could be overcome by adjusting sample pH < 7 with acid; most sample turbidity is either dissolved during the digestion stage or settled during the cooling period.

Table 9. Oxidation efficiency substances from HACH Company document [68].

Compound	Percent relative recovery, %
Caprolactum	99.5
Citric acid	98.0
Sodium EDTA	101.0
Sodium Hexane-Sulfonate	98.4
Hexamethylenetetraamine	98.6
Leucinol	99.9
Sodium Acetate	101.8
Sucrose	94.6
Tryptophan	101.4
Urea	101.0
Valine	98.2

4.3 Regression analysis and precision

A linearity regression analysis was exhibited in Figure 4 to evaluate any bias between the experiment results from our method. Simple regression analysis begins with the assumption that each datum consists of the real value plus some random noise [37].

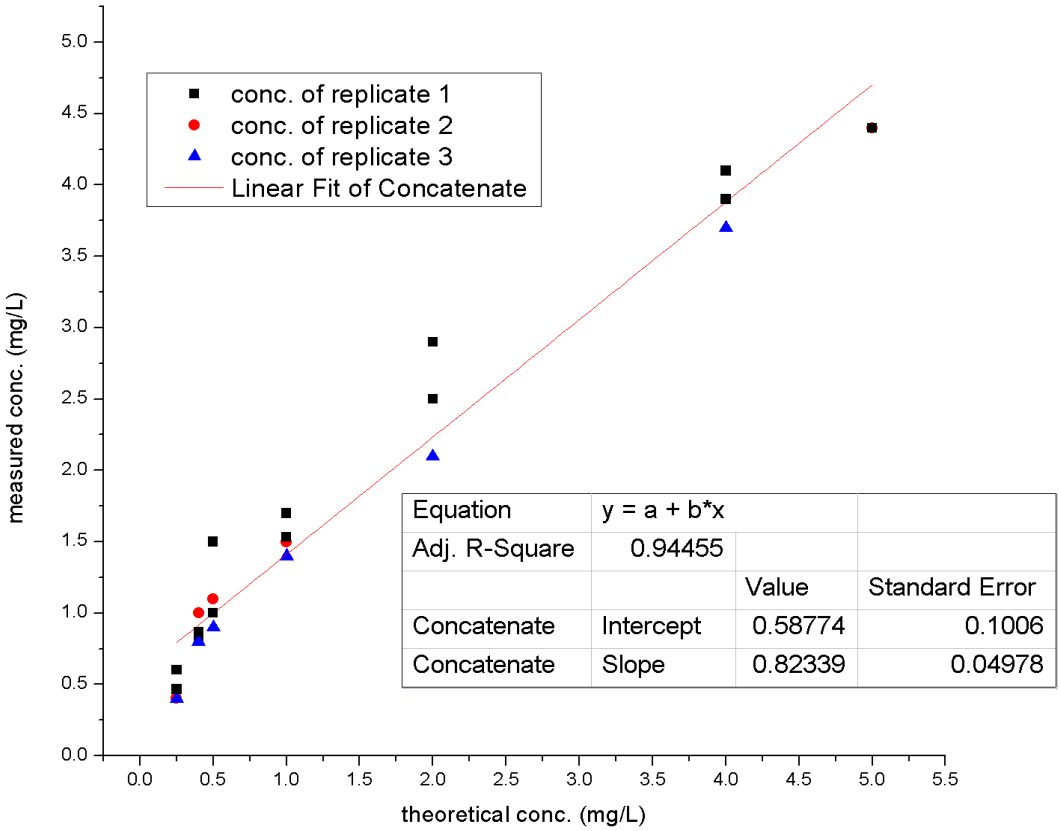

Figure 4. Regression analysis of three replicates at lower concentration ranging from 0.25 to 5.0 mg/L DOC, linear fit of concatenate.

For linear regression the deviations that are perpendicular to the x axis is what we need to consider, and the uncertainty is expressed as the correlation factor, r, or its square. If every point falls exactly on the theoretical line then we got a perfect fit with $r^2 = 1$. The correlation coefficient was 0.94455 in this fit, and formula for the regression line listed in the figure, suggesting a slight bias exists. And for the same data, another linear regression is done between the average and the expected concentration, in Figure 5 to compare the difference. The linear fit of average produced a higher r square 0.97747 than fit of concatenate, which was predictable because the action of average reduced error as well as increased the precision. The precision was evaluated by taking the absolute difference between detected value and theoretical concentration divided by 2, and expressing as the percentage of the mean between the two values [70].

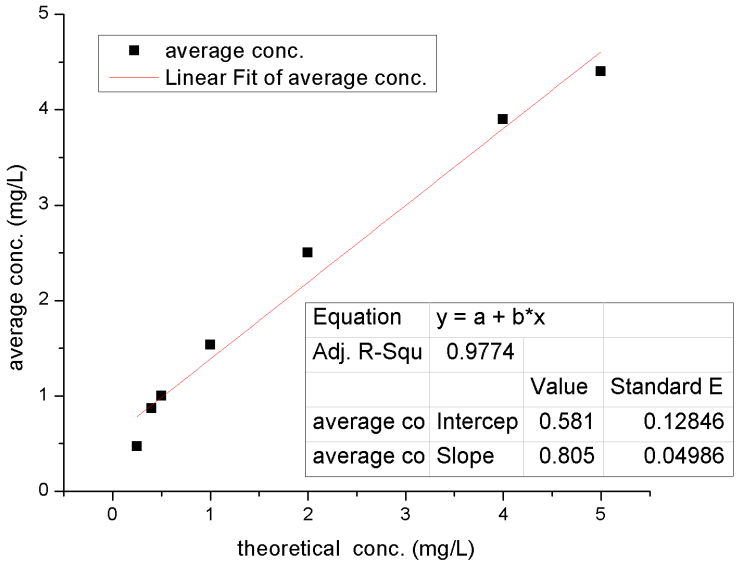

Figure 5. Regression analysis of three replicates at lower concentration ranging from 0.25 to 5.0 mg/L DOC, linear fit of average concentration.

When the two linear fit lines were extended to cross Y axis, neither of them would go through the origin of coordinate. The intercepts of two linear fit functions were quite close but not equal to zero, which means the extension was invalid, and the function could only exist within the experiment detection limits range.

Precision looks good with their mean precision 5.87% and ranged from 3.34 to 9.34%. However, the mean accuracy for the data lower than 1.0 mg/L DOC was 29.74% and ranged from 21.22 to 34.50%, indicating that additional attention need to be paid for the method performance of concentration less than 1.0 mg/L DOC. Another precision evaluation was conducted on a group containing six KHP samples; the variance was 0.8525, and standard deviation was 0.9233.

4.4 Method detection limits

MDL is evaluated by the below spreadsheet which is adapted from a version presented by NET laboratory at 1995 WELA meeting- analytical detection limit guidance. The table consists of three parts. First part contains row number 1-6, providing the basic information about the calculation. Second part is the laboratory data, the 9 replicates of KHP samples with concentration 0.4 mg/L DOC. This 0.4 value was derived from section 4.3 Figure 4, only worked as an approximate reference concentration. The last part is about calculation, equation listing in the value row. Based on the data showed in Table 10, the MDL was calculated to be 1.0 mg/L DOC, presumably.

Although for the low spike check the result is "NOT OK", the spike concentration wasn't larger than the MDL. But when thinking about the MDL we should include several other outlier check, previous MDL data, or calibration information. And, also noted that this spreadsheet is only a model, nor is the only way to calculate MDLs.

Table 10. Sample MDL calculation spreadsheet adapted from U.S. EPA.

	Row number	**content**	**Value**
Basic information, input parameters	1	Analyte	KHP
	2	Method	HACH TOC vial set
	3	Date	May, 2013
	4	Instrument	dr 5000 UV (HACH)
	5	Spike Conc.	0.4
	6	Units	mg/L DOC
Laboratory measurements, mg/L DOC	7	Replicate 1	0.80
	8	Replicate 2	0.80
	9	Replicate 3	1.60
	10	Replicate 4	0.80
	11	Replicate 5	0.90
	12	Replicate 6	1.20
	13	Replicate 7	1.10
	14	Replicate 8	0.90
	15	Replicate 9	1.70
Calculation based on laboratory data	16	Mean	Average = 1.09
	17	Std. Dev.	0.35
	18	MDL	(T value*)× Std. Dev =1.17
	19	LOQ	10× Std. Dev =3.48
	20	High spike Check	If Spike conc.< 10× MDL, OK
	21	Low spike Check	If Spike conc.> MDL, OK
	22	S/N	Mean/ Std. Dev =3.13

* Student's T value for a 99% confidence level and 8 degrees of freedom is 3.355 (two-tailed).

4.5 Organic free water and reagent water

Laboratory made distilled water is used as reagent water to dissolve analyte. In order to eliminate the environmental noise, the carbon content in reagent water must be measured. Two reagent blank samples were prepared to test the quality of distilled water; one tube was injected with organic free water, the other with distilled water. Reagent water was proved to be qualified because the UV/vis spectrophotometer was reading zero when using organic free water to calibrate, to zero the instrument.

CHAPTER V

CONCLUSIONS AND IMPLICATIONS

5.1 Conclusions

The TOC direct method can be used to improve the measurement of surface water pollution by convenient monitoring of wastewater whether in laboratory or in field test. It also allows DOC monitoring that is cost low and readily portable. This method accuracy was proved via the calculation of difference in percentage. The comparison between TOC direct method and COD method demonstrated the TOC method was at least as accurate as COD method, or even better for solutions with low DOC concentration. Reliability and precision were approved through a linear regression analysis. With r^2 very close to 1.0, there was a slightly bias for the TOC method, especially in the range of DOC concentration less 1.0 mg/L. The linear regression of KHP samples analysis confirmed that the quality results with DOC concentrations ranging from 0.4 mg/L to the method upside limitation (20 mg/L). Although the calculated MDLs 1.17 mg/L was higher than the given MDLs 0.3 mg/L, considering this MDL was conducted by an unprofessional laboratory technician with limit time of practice, the MDL could reach its theoretical limits when everything (sample handling, removal of inorganic carbon, and operation time for each step in procedure) was operated perfectly. Besides, it is very possible that the instrumental MDL was derived under the best scenario.

5.2 Implications

This paper examined the properties of Hach TOC direct method in distilled water and comes to a positive conclusion that the method measures carbon content precisely and quickly without any hazardous to dispose, more consistent blanks and a lower amount of instrument maintenance. A prediction can be seen from the results that persulfate oxidation techniques for DOC analysis could be used for drinking water samples with much lower detection limits from accuracy analysis and the comparison with COD data. Although for samples with concentration less than 1 mg/L, the method accuracy is not as good as expectation. The situation can be improved with proper sample handling and more practice. Actually, the need for a more rapid, sensitive and specific test is essential in the water industry. We discussed about these routine and widely accepted techniques like UV, COD and HTO, as are methods have emerged from recent research development. However, accurate measurements of analyte at low to very low concentrations require accurate corrections for chemical blanks and always require expensive equipment. Moreover, the storage and transportation of DOC samples can cause error if sample is not immediately measured.

The use of Hach TOC direct method for DOC determination is an attractive alternative comparing with these classical methods. This method is applicable to measurement of organic carbon above 1 mg/L DOC in natural fresh water and drinking waters, or water with small amount of organic matter such as the final wastewater effluent with the average 4 hours operation time.

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