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Modified dissolved organic matter fractionation technique for natural water

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Abstract

A technique to fractionate dissolved organic materials (DOMs) from low DOM water (<5 mg/l) was developed by using triple columns of DAX-8 adsorption resin, one column of AG-MP-50 cationic resin, and another column of WA 10 weak anionic resin in sequence. The procedure was then applied to fractionate water samples obtained at various sampling locations throughout two surface water treatment plants (WTPs) in central New Jersey to study its effectiveness, DOM occurrence, and variation along treatment units. The treatment plants utilize different treatment methods, hence producing variability in DOM fractions suitable for examining the procedure's effectiveness. This procedure was compared with current fractionation protocols and proved to be accurate in fractionation of low DOM water.
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1. Introduction

Resin fractionation of dissolved organic materials (DOM) in water is a technique to concentrate and categorize the water organic complex into structurally more specific, physicochemically more analogous subgroups by retaining DOMs onto a series of types of resin followed by eluting with eluants. By applying this technique, DOMs of natural water can be characterized into hydrophobics, which mainly consist of fulvic and humic acids, and hydrophilics, which comprise of carbohydrates with low molecular weight, proteins and amino acids. Hydrophobics are more structurally aromatic than hydrophilics and more prone to conventional treatment. This technique has been widely applied to investigate various

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properties of DOM. It has been shown that it greatly facilitates subsequent studies associated with DOM, such as the formation of disinfection by-products (DBPs) [1].

There have been some resin procedures proposed and applied to fractionate DOM [2–9,21]. All these procedures can broadly fall into two categories dependent on the types of resin. In the first, a system of non-ionic DAX-8 and ionic resins [2–4,9] is applied to fractionate DOM in water. In the second, only non-ionic resins (DAX-8 and XAD-4) are utilized [6,7]. Procedures of both categories unanimously accept the DAX-8 resin for the partition between hydrophobics and hydrophilics since its property and performance have been well studied [5,7,10,11]. It is also recognized that each fraction is more defined in operation than in structure. Furthermore, no universal fractionation procedure exists for all applications in accordance with the variety of research objective and sample matrix [9,12].

The procedure developed by Leenheer [4], which was more or less based on the Leenheer and Huffman [3], is the most widely adopted. The initial procedure is designed to determine the fraction distribution of DOM in water, therefore analytical. The latter is aimed to prepare organic-concentrated fractions for subsequent tests without further coping with tremendous volumes of sample, thus preparative. This procedure is also comprehensive for it fractionates all DOMs of samples rather than humic substances, in which researchers are typically interested. Another advantage of this procedure is that the associated operations (resin adsorption, ion exchange, and solvent extraction) more or less imitate natural conditions, such as some properties of soil and sediment surfaces [13]. In water treatment, these operations may provide clues to remove the most troublesome candidates (i.e. precursors) to DBPs formation.

While both procedures have been applied to natural water systems with success, they are not recommended for samples with DOM less than 5 mg C/l [2], such as within water treatment plants (WTPs). It is likely due to the relatively significant error in DOM tests, which are on eluted hydrophobic fractions. The Duolite A7 resin used in the preparative method [4] for hydrophilic acid (HPIA) fraction has a severe resin bleeding. Although the resulted contamination could be remedied to some degree by re-adsorption of pollutants on additional cationic resin, a possible loss of collected fractions may occur as well as it would be laborious. It is then less preferable than preventing such contamination from occurrence. Therefore, based on the procedures of Leenheer [3] and Leenheer and Huffman [3,4], this paper introduces a new procedure intended for low DOM samples. The proposed procedure was experimented with samples from two surface WTPs to assess its feasibility in terms of analytical and preparative fractionations. The two plants having different unit processes but sharing a common intake were unique in demonstrating the changes of DOM fractions. The procedure has potential applications, especially for development of rapid spatial and temporal fluorescent characterization techniques [14] and determination of precursory character of DBPs [15,22].

2. Materials and methods

2.1. Sample collection and preservation

Samples of two surface water treatment plants (Elizabethtown Water Company, Westfield, NJ) with a common intake were studied. The Raritan/Millstone (RM) treatment plant

uses conventional treatment (coagulation, sedimentation, and filtration) with intermediate free chlorination and post chlorination while the Canal Road (CR) plant uses conventional treatment with pre and intermediate ozonation, and multimedia filtration unit operation. Samples from both WTPs both were collected in June 2002 and stored in a cooler room with a temperature controlled at 4 °C prior to filtration. The water samples were filtered through MFS Nylon 0.45 μm membranes (Advantec MFS Inc., Pleasanton, CA) usually within 24 h after sample collection to remove particles. Original source samples and fraction samples were refrigerated and stored in the dark to prevent any interference.

2.2. Organic carbon analysis

DOM in samples is represented as mg/l of dissolved organic carbon (DOC) and were measured with a Phoenix 8000 TOC Analyzer (Tekmar Dohrmann, Cincinnati, OH) using the UV/Persulfate oxidation method (Standard Methods 5310-D, 1995). The running mode was selected as simultaneous DOC 0.1–20 mg/l. 0, 1, 2.5, 5 and 10 mg/l standards prepared with a 1000 mg/l DOC stock solution (LabChem, Pittsburgh, PA) were run to calibrate the TOC instrument. The instrument error was controlled within 4% with runs of 5 mg/l standards after every five samples and sample precision of three repeats was controlled within 5%. All fraction samples were appropriately pH adjusted and diluted to reduce the contribution of eluant chemicals to DOC if necessary Milli-Q (Millipore Corp., Bedford, MA) was used for all dilutions, sample preparation, and final glassware washing. All sample glassware was oven dried at a temperature of 500 °C.

2.3. Fractionation procedure

The fractionation procedure reported in this paper was consistent with [4] regarding the separation theory. However, some changes have been made and are discussed in the results section.

The amount of DAX-8 (Superlite^{TM} DAX-8, SUPELCO, Supelco Park, Bellefonte, PA) resin was determined according to Leenheer [4] with a capacity factor of 50 ($K' = 50$) and a porosity of 0.60. DAX-8 resin was intensively refined with 0.1N NaOH for 24 h and sequentially extracted with acetone and hexane for another 24 h in a set of Soxhlet extraction apparatus. The refined DAX-8 resin was transferred into columns (2.5 cm × 120 cm, Kontes, Vineland, NJ) in slurry of methanol. The packed resin was rinsed with two times 2.5 bed volumes of 0.1N each NaOH first, then HCl, and finished with Milli-Q water until the conductivity and DOC of the effluents were below 10 μs/cm and 0.2 mg/l, respectively. This resin cleanup was necessary to eliminate any impurities brought during the resin manufacturing process.

Hydrophobic neutral (HPON) was the first fraction to be fractionated. The water sample pH was adjusted around 7 ± 0.2 and then filtered by gravity through the DAX-8 resin bed with a flow rate less than 12 bed volumes/h. Sample solution constrained inside resin bed was displaced with 1 bed volume of Milli-Q water and discarded. The column was then turned up side down and the resin was air-retrieved, stored, and dried in a desiccator. The HPON was extracted with methanol, which is rotary vacuum evaporated.

The operation for hydrophobic base (HPOB) and hydrophobic acid (HPOA) was similar to that of HPON. The sample effluent after HPON was de-protonated to arbitrated pH 10 with 10N NaOH, loaded through the second DAX-8 resin column. The fraction was collected with 0.25 bed volume of 0.1N HCl, followed by 1.5 bed volumes of 0.01N HCl at a flow rate less than 2 bed volumes/h, forming a total of 1.75 bed volumes of this fraction, HPOB. The effluent of the second DAX-8 resin column was acidified to pH 2 with concentrated H_2SO_4, loaded on the third DAX-8 resin column. Elution of HPOA was conducted using 0.25 bed volumes of 0.1N NaOH followed by 1.25 bed volumes of 0.01N NaOH at no great than 2 bed volumes/h. H_2SO_4 instead of HCl was used for pH adjustment due to the chloride interference with the UV/Persulfate oxidation of carbon.

The removal of hydrophobic substances was concluded after runs of the triple DAX-8 resin columns. The hydrophilic base (HPIB) fractionation followed the procedure of Leenheer [4] with two modifications. The use of 1.0N $NH_3{\cdot}H_2O$ was substituted with 1.0N NaOH as the eluant for releasing the HPIB from the AG-MP-50 cationic resin (BIO-RAD, Hercules, CA). The service flow rate and the resin regeneration were at no greater than 5 and 2 bed volumes/h, respectively. These two procedural changes allowed enough contact of samples and eluants with resin due to the low recovery of HPIB.

Diaion WA 10 (SUPELCO), a weak anion exchange resin, was the final resin applied to isolate HPIA. Effluents after HPIB fractionation were put through the WA 10 resin for the HPIA. The service flow and elution rates were 8 and 4 bed volumes/h, respectively.

3. Results and discussion

3.1. Modification of fractionation procedure

The proposed procedure herein uses a combination of resins in a sequence of DAX-8, AG-MP-50, and WA 10. The distinct difference of it from the one of [4] is the setup of three columns of DAX-8 independently for HPON, HPOB, and HPOA. It also differs in the use of WA 10 resin in place of Duolite A7 for the HPIA. Furthermore, the HPON is advanced as the first to be fractionated instead of the last of hydrophobics [2–4] considering natural water pH approximation to 7. All these modifications allow analytical fractionation of all six fractions through directly sampling influents and effluent of each run while still potentially fulfilling the goal of preparative fractionation [4].

In their analytical procedure, Leenheer and Huffman [3] reported HPOA and HPOB by measuring the collected fractions. However, they reported each hydrophilic fraction as a change of DOM between influents and effluents after every run of respective adsorption. It is noted that DAX-8 resin does not discriminate the adsorption between HPON and HPOB in their procedure [2,8,13]. Qualls and Haines [13] raised a concern that the HPON analysis, based on difference of DOM, could include some HPOB. Gasparvoic et al. [8] also indicated the adsorbates on DAX-8 under natural pH contain both fractions. Consequently, the analytical fractionation of either of them, if measured as DOM difference after each adsorption run, is not appropriate since the mass decrement is the summation of them. Therefore, Leenheer and Huffman [3] suggested DOM tests directly on both HPOA and HPOB fractions to quantify all hydrophobic fractions. Direct measurement on HPOA or HPOB fractions is

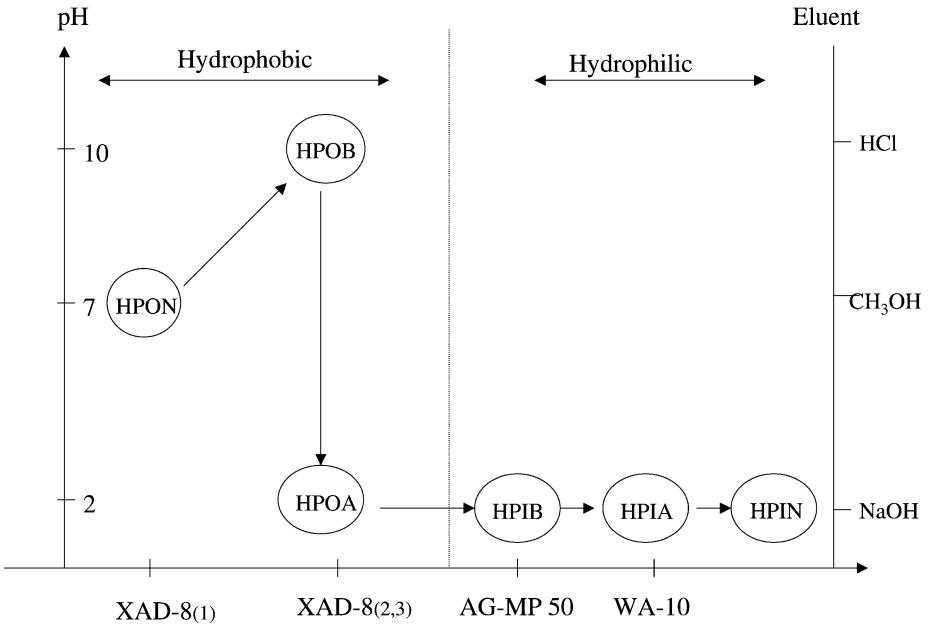

Fig. 1. Resin fractionation procedure.

favorable only if the test signal of organics in fractions can sufficiently overcome the noise from eluants and instrument. This often requires DOM in original samples above 5 mg/l or large volumes of sample have to be fractionated. It is proposed herein, for low DOM samples, that only HPON be first fractionated onto the DAX-8 by protonating HPOB to pH 7. Instead of using those resins already served for HPON, another column packed with refined raw DAX-8 is exclusively set up for HPOB. HPOB is de-protonated by raising sample pH to 10 and eluted through that column. Analytical fractionation of both fractions is thus possible as shown in the Fig. 1. It appears that the HPON herein is defined different from that of Leenheer [4]. The HPON designated in this paper is the organic mixture that is first adsorbed on DAX-8 at neutral pH and then eluted with methanol. Leenheer [4] considered the HPON as the DAX-8 adsorbates unable to be eluted with either HCl or NaOH. However, due to the proposed pH adjustment, both definitions should connote the same type of organics.

In the procedure of Leenheer [4], the DAX-8 resins serve all hydrophobic fractions. Repeating the service of the DAX-8 resins results in that the analytical fractionation by DOM difference may be impossible to carry out for HPOA. Several studies following the protocol of Leenheer's [4] by the authors found that there was a slight wash out of the previous adsorbed organics during the adsorption for HPOA (unpublished data). The reasons of this redistribution remain unclear. It has been reported that some organics in water may be of intermediate polarity [16]. Their relative degree of hydrophobicity or hydrophilicity may change when exposed in varied media, and so may their adsorption to DAX-8. In the study of Malcolm and MacCarthy [7], effluents of DAX-8 were considered to contain not only hydrophilics but also hydrophobics. They suggested that most of the isolates of XAD-4

were hydrophilics but mingled with 5% of fulvic and humic acids lost from DAX-8, and the isolates were therefore named as XAD-4 acids. Aiken and Leenheer [12] acknowledged that such XAD-4 isolates contained a large amount of humic-like, "hydrophilic fulvic acid" compounds. Dickenson and Amy [17] simply named the separated fractions as hydrophobic, transphilic, and hydrophilic fractions, corresponding to the DAX-8/XAD-4 adsorption stages. The "transphilic" is used to describe fractions of an intermediate polarity between hydrophobic and hydrophilic [9,16]. Thorough examination of all above cited studies, it can be demonstrated that these expressions had addressed a same type of fraction. The procedure in Qualls and Haines [13] was the most similar to the Leenheer's [4] with little change. However, the authors by design reserved their hydrophobic base in water beyond the DAX-8 adsorption. It is thus likely that dissolution of adsorbates with intermediate polarity may occur during the fractionation of HPOA in Leenheer's [4] procedure. Dissolution of HPOB remnants on DAX-8 when exposed to acidic samples might contribute to the redistribution. The solution to it is the setting up of the third column of fresh DAX-8 resins solely for HPOA and thus allows analytical fractionation by DOM difference for all hydrophobics.

The procedure of Leenheer [4] is generally modified regarding the bleeding of Duolite A7. Qualls and Haines [13] added one column of cationic resin after the Duolite A7 to remedy the bleeding contamination. Day et al. [18] replaced the Duolite A7 with anionic resin, AG-MP-1. In fact, it was from their concerns about Duolite A7 bleeding, recovery of HPIA, and increase of salinity in collected fractions that Malcolm and MacCarthy [7] developed what now is one of the two most adopted fractionation protocols (DAX-8/XAD-4 protocol), besides the one of Leenheer [4]. However, this DAX-8/XAD-4 procedure usually fractionates all DOMs into only hydrophobic, transphilic, and hydrophilic fractions, not as specific as Leenheer [4]. The XAD-4 is more hydrophobic than the DAX-8. However, the sorption of HPIA to XAD-4 was attributed to its large surface area, four times greater than of DAX-8 (725 and 160 m^2/g for XAD-4 and DAX-8, respectively) [7]. Size exclusion of XAD-4 was first reported by Aiken et al. [11] and considered to possibly include some humic-like hydrophilics to XAD-4 resin. It can be seen that such XAD-4 isolation differs from the one of Leenheer [4], in which the HPIA is exchanged/adsorbed by hydrophilic, anionic resin, Duolite A7.

To maintain the concept "hydrophilic to hydrophilic" as that of Leenheer [4], WA 10, another type of weak anionic resin but less hydrophilic than the Duolite A7, was studied. The reason of WA 10 selection was due to its known strong physical and chemical stability.

The capacity (meq./g wet) of WA 10 to adsorb H_2SO_4 was determined with a procedure [19]: pH 1, 3.5; pH 1.5, 1.9; pH 2, 1.5; and pH 3, 1.4. The amount of WA 10 was calculated with the same formula as in Leenheer [4] and further multiplied with a safety factor of 1.5. Fig. 2 shows the adsorption of H_2SO_4 solution (pH 1.9, conductivity 6.6 ms/cm, with or without 1 mg/l DOC added as glycolic acid) by 70 g of wet WA 10 (supposed for 1000 ml of H_2SO_4). It can be seen that the breakthrough of pH and conductivity occurred after 1300 ml of H_2SO_4. The addition of glycolic acid as 1 mg/l DOC did not affect the location of breakthrough point. It was thus concluded that the determined capacity, formula [4], and a safety factor of 1.5 were appropriate to calculate the amount of WA 10 needed. Results of a complete test including the adsorption of 1000 ml of H_2SO_4 solution (pH 1.86, conductivity 6.6 ms/cm, and DOC 1.06 mg/l added as glycolic acid), MQ water replacement, and the desorption with 0.1N NaOH followed with 0.01N NaOH are shown in Fig. 3. It was

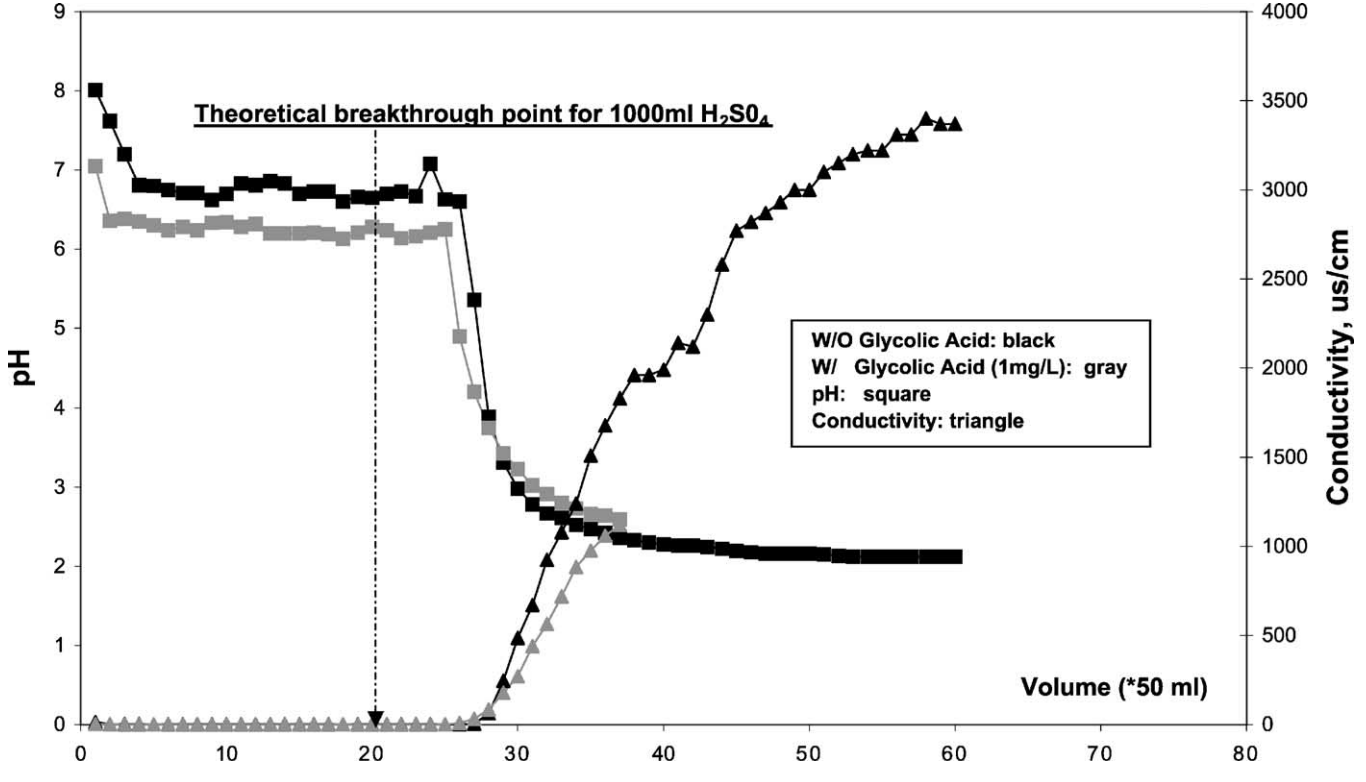

Fig. 2. Adsorption of H_2SO_4 with or without 1 mg/l DOC.

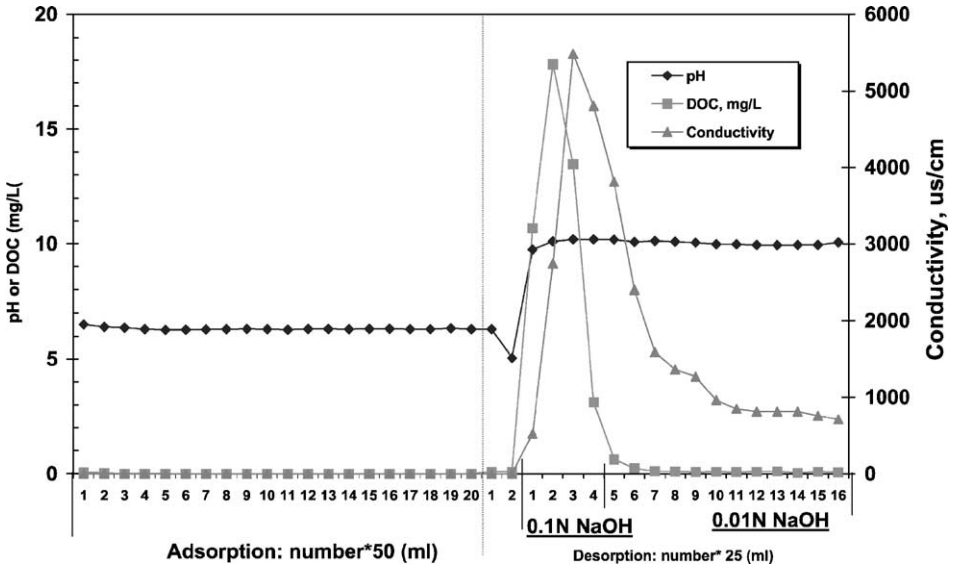

Fig. 3. Adsorption and desorption of glycolic acid.

found that the HPIA desorption was completed after elution with 100 ml of 0.1N NaOH and 50 ml of 0.01N NaOH, given 70 g of WA 10 or 85 ml of bed volume.

3.2. Efficiency of the proposed fractionation procedure

The proposed procedure was experimented with samples from CR and RM WTPs for its efficiency in analytical fractionation of low DOM waters. The two plants having different unit processes exhibited variable changes to DOM fractions. Table 1 summarizes the analytical fractionation results based on DOM decrement after obtaining each fraction fractionation and the respective fraction results based on DOC tests on unpurified fractions acquired according to the procedure of Leenheer [4].

Original samples in this study contained less than 5 mg/l of DOC. Therefore, the analytical procedure of Leenheer and Huffman [3] may not be applicable to determine the content of fractions due to relatively significant test errors from eluants and/or instrument. For example, eluted according to the protocol [4], 210 ml of HPOB fraction fractionated from 6 l of original samples in this study contained no greater than 4.9 mg/l and no less than 800 mg/l for DOC and Cl^-, respectively. Chloride ion can interfere in DOC tests by reacting with $K_2S_2O_8$ [13] (technique note, Tekmar Dohrmann). Therefore, instead of being performed on collected fractions, DOC of HPOB fraction was based on analyses on water samples, which contained only original background level of Cl^-.

The results of HPON based on DOC decrement are similar to those tested on HPON fractions. An average of 90% of recovery was obtained for this fraction. It is not surprising to see this high quantitative recovery from DAX-8 resins. The DAX-8 is concluded as quantitative since the HPOA and HPON can be quantitatively concentrated onto and eluted from this resin [7]. Another reason for this high recovery of HPON is little interference of

Table 1
Fractionation results based on (DOC difference/tests on fractions), mg/l in original water

Location	Original	HPON	HPOB	HPOA	HPIB	HPIA	HPIN
CR and RM raw	4.92	1.91/1.89	0.14/0.11	0.63/0.70	0.28/0.35	1.68/1.50	0.37
CR preozonated	4.38	1.57/1.43	0.03/0.05	0.52/0.68	0.40/0.42	1.45/1.52	0.30
CR settled	2.29	0.66/0.60	0.00/0.08	0.25/0.32	0.27/0.20	0.87/0.65	0.42
CR filter influent	1.97	0.60/0.65	0.00/0.06	0.13/0.20	0.20/0.29	0.80/0.76	0.33
CR no. 6 effluent	1.61	0.20/0.13	0.12/0.05	0.06/0.10	0.24/0.18	0.75/0.70	0.26
CR no. 8 effluent	1.65	0.28/0.20	0.09/0.08	0.00/0.09	0.38/0.45	0.59/0.64	0.28
CR finished	1.68	0.28/0.26	0.00/0.07	0.01/0.10	0.35/0.32	0.71/0.75	0.29
CR high pump	1.68	0.35/0.32	0.00/0.09	0.10/0.12	0.35/0.45	0.57/0.50	0.30
RM settled	2.46	0.76/0.70	0.01/0.08	0.29/0.35	0.43/0.42	0.54/0.50	0.33
RM influent	3.02	1.07/0.99	0.17/0.08	0.28/0.29	0.30/0.40	0.46/0.51	0.66
RM effluent	2.59	0.84/0.76	0.00/0.06	0.30/0.40	0.41/0.39	0.70/0.75	0.27
RM finished	2.40	0.50/0.55	0.05/0.08	0.27/0.35	0.36/0.46	0.86/0.90	0.37

eluants on the HPON tests since methanol was used for HPON extraction but then evaporated off by a vacuum rotary device.

The results of HPOB based on DOC measurements were generally different from their correspondents by DOC decrement calculation. There is always a dilemma to deal with the HPOB fraction test. Dilution can bring down the error due to retarded carbon oxidation of Cl^-. Meantime, it also makes the HPOB test more erratic due to very low DOC in diluted HPOB samples. The constant concentration of HPOB for direct measurement shown in Table 1 may indicate an over-dilution of the tested samples; however, the dilution is definitely needed to eliminate the chloride impact. The results of HPOA, HPIA, and HPIB by measuring fractions were generally close to those based on mass decrement. It is likely that the DOC in these fractions sufficiently overcame the matrix background. However, the matrix background effect on DOC test cannot be eliminated for samples with a concentration of DOC below 0.20 mg/l. The direct measurements for these samples are slightly higher than the respective analytical fractionation. This matrix background is also observed by carefully examining the flat part of desorption curve in Fig. 2. Experiences by the authors found that the residual DOC in desorption samples after the desorption peak remained at an average 0.08 and 0.22 mg/l for 0.01 and 0.1N NaOH, respectively. Therefore, it was very important to conduct preliminary titration, adsorption, and desorption tests with characterized chemicals such as glycolic acid for HPIA in this study to determine the type, concentration, volume of eluants for application to field samples. It is also concluded that for lower DOC water samples, analytical fractionation based on DOC difference is preferable to fraction tests.

Accurate DOC determination on fractions still presents a challenge to this proposed procedure. This is a result of low DOC but high matrix in collected fractions. Preparative fractionation can be achieved further through a very complicated post fraction purification procedure [4,9]. It is moderate to be postulated that loss or transformation of certain organics during the purification is unavoidable. However, since the proposed procedure can provide an accurate distribution of DOM in each fraction, the loss of collected organics during purification becomes a less concern in the context of understanding DOM distribution. As a matter of fact, the current tendency of preparative fractionation is that “recovery of representative portions . . . that is suitable for various spectral characterization and reactivity

studies" rather than "necessarily defined as 100% recovery of the DOM" [9]. With these points of view, the proposed fractionation procedure herein should be considered more accurate in low DOM water than the analytical procedure of Leenheer and Huffman [3], however with a sacrifice of two more separate runs, as well as potentially same successful to generate representative fractions as the preparative procedure of Leenheer [4].

3.3. Application of the proposed procedure

The proposed fractionation procedure could provide a basis to accurately predict and evaluate water treatment plant performance on the removal of DBP precursors. As an example, surface water plants with source water of non-humic type or low DOC, should monitor, in the view of authors, not only SUVA but also the hydrophilic materials by this technique. The reasoning is that hydrophilic material seems to produce a large part of DBPs in finished water and SUVA is not effective to determine non-aromatics. Further, association of this technique with fluorescence spectrum may present a refined, rapid method to detect the distribution and variation of DOM along treatment train of water utilities [20] and even water sources. Therefore, the proposed procedure can be used for spatial and temporal characterization of DOM fractions that have special interests (e.g. DBP precursors, coagulant types, etc.). Such information could be a key to understanding the formation and removal of potentially carcinogenic DBPs following disinfection or oxidation [15].

Results shown in Table 1 may be analyzed with other temporal data to examine the variation of DOM and its relation to DBP formation. This will be a subject of a future paper and will not be discussed herein.

4. Conclusion

The proposed procedure, herein:

- is intended to fractionate low DOM water (<5 mg C/l);
- is reasonable and applicable to low DOM water fractionation;
- can be used to characterize DOM in terms of DBP precursors; and
- can be used in the development of rapid analytical techniques (e.g. fluorescence) for spatial and temporal characterization of natural water.

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