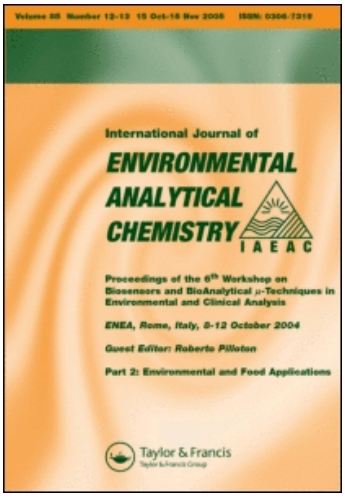

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Fractionation and Characterization of Ozonated and Post Chlorinated Aquatic Fulvic Acid Using Gel Chromatography

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FRACTIONATION AND CHARACTERIZATION OF OZONATED AND POST CHLORINATED AQUATIC FULVIC ACID USING GEL CHROMATOGRAPHY

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Extracted aquatic fulvic acid samples (HO10FA) from a brown lake Hohloh in the Black Forest (Germany) were ozonated at two different ozone doses and then chlorinated. In connection with liquid chromatography and further detection systems (UV and DOC) on gel matrix, a combined system (gel chromatograpy) was used for a detailed characterization of ozonated and post-chlorinated fulvic acid samples. The gel chromatographic characterization showed a slight decrease in DOC (14%) and SAC_{254} (36%) at the end of 20 min ozonation whereas the low ozonation time (5 min) caused increases in DOC (6%) and SAC_{254} (56%).

Keywords: Fulvic acid; ozonation; chlorination; gel chromatography; SAC; DOC

INTRODUCTION

Fulvic acids (FAs) are high molecular weight (about 800 g/mol) organic compounds which constitute the predominant part of the bound organic carbon in aquatic and terrestrial systems[1]. They are characterized as polyfunctional, hydrophilic, and refractory substances which are fairly resistant to biological decomposition. Fulvic acids are soluble under all pH conditions. Therefore, fulvic acids play an important role in several environmental and geochemical reactions[2].

Oxidation reactions are very important in aquatic ecosystems and in water technology. Fulvic acids would comprise the major humic fraction (80%) chlo-

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rinated during water treatment[3,4]. Previous studies on chlorine disinfection of drinking water and model chlorinated humic acid solutions have shown that the dissolved humic material in surface waters serves as the principal precursor of mutagenic by-products namely trihalomethanes in chlorinated drinking water[5,6]. Compared to the amount of literature concerning the chlorination of humic substances (HS), there are only a few studies that have been carried out on the reactions of ozone with these substances[7–10].

The summarizing parameters such as total and dissolved organic carbon (TOC, DOC), color and specific absorption coefficient (UV/VIS, SAC) are used for the quantification and characterization of humic substances. However, due to inherent complexity of HS, summarizing parameters are not sufficient for the detailed characterization. According to the hydrophilic nonvolatile properties of the high molecular compounds, liquid chromatography (LC) turns out to be a promising method for characterization of HS[11]. Liquid chromatography in association with sensitive detection systems (UV/VIS, DOC) can be used for the characterization of dissolved organic matter in aqueous samples. The organic carbon content of a given compound is independent of its physical properties and gives a basic information. Therefore, the continuous OC- determination can be used for the quantification of unidentified compounds and for the assessment of the spectral properties (SAC) of unknown compounds. Even though the chromatographic mechanisms for the fractionation of humic-type organic substances are not fully known, the use of different columns (gels, C-18 phases, etc.) adds significantly to the understanding of the functionality of the organics[12]. Gel filtration mechanism separates the inorganic salts from the organic matter to a large extent. Huber and Frimmel[13,14] showed that gel chromatography in the direct injection mode is a fast and reliable method for the matrix-free characterization of aquatic humic substances.

The aim of the work was to introduce a chromatographic method with the simultaneous determination of DOC and UV detection on gel matrix for the direct characterization of an aquatic fulvic acid treated by ozone and chlorine.

EXPERIMENTAL

Samples

The experiments were performed by aquatic fulvic acid (HO10FA) isolated from a bog lake Hohloh (Black Forest, 1000m above sea level) with DOC of 1.4 g/L.

The isolation of FA was done with an XAD-8 extraction technique that has been described by Abbt-Braun and *et al.*[15].

The FA samples were diluted (as 20 mg/L DOC) with double-distilled water (DDW) for ozonation. Ozonated and post-chlorinated samples prefiltered through 0.45 μm cellulosenitrate membrane for the DOC measurements.

Ozonation

The applied ozone dose (7 mg/L) was generated by Anseros (Type Com/R) ozone generator. Generator was fed with oxygen gas. Ozonation was carried out in 1000 mL glass cylindrical vessel which had a glass cover containing inlets for feeding the gas, temperature and pH measurement, sampling and venting. A stirrer kept the liquid phase mixed. The data for ozone concentrations, temperature and pH continuously evaluated with a PC connected with ozone generator. The details of experimental setup was presented elsewhere[16]. The sample contact times with ozone were 5 min and 20 min. pH values of FA solutions were 4.3 – 4.5.

Chlorination

The solutions of FA (c_{DOC}: 3 mg/L) were reacted with hypochlorite solution (c_{Cl}: 10 mg/L) in 0.1 M phosphate buffer at pH = 7.0. The reactions were completed by adding of $Na_2S_2O_3$ after 48 h. Detailed description of the chlorination is given by Schmiedel[17]. The adsorbable organically bound halogen (AOX) was performed according to German standard methods[18]. Quantitative analysis of THM (as $CHCl_3$) was done on a GC/ECD- System (Chrompack CP 900). Error of the method was ± 8% (range >100 μg/L $CHCl_3$).

Dissolved Organic Carbon (DOC)

DOC measurements of ozonated and post-chlorinated samples were made by the persulfate-ultraviolet oxidation method[19]. The DOC Analyzer (Dohrman Model DC 80) was calibrated with a 10 mg/L (as carbon) potassium hydrogen phthalate (KHP) standard before each run of samples. Measurements were conducted in triplicate. Error of the method was ± 1%.

Gel chromatographic characterization

Ozonated and ozonated/post-chlorinated reaction products were characterized by a liquid chromatographic system on gel matrix with simultaneous determination

of UV, DOC and inorganic carbon (IC) in the mg/L to μg/L concentration range improved by Huber and Frimmel[12]. In Figure 1 the outline of the gel chromatography system is shown.

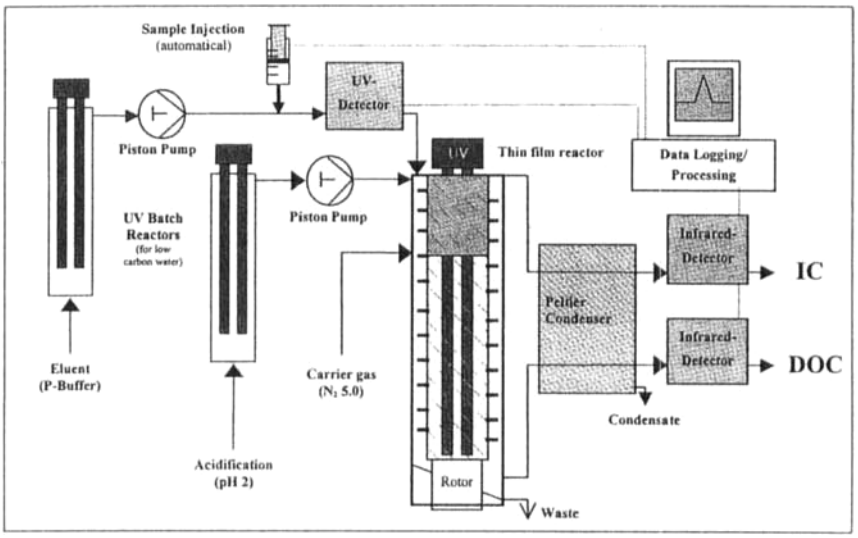

FIGURE 1 General outline of fully automated gel chromatographic system with simultaneous detection of UV and DOC for the characterization of aquatic humic substances

It consist of UV detector, two infrared detectors, two pumps, a UV-thin film reactor with an actively rotating inner cylinder and UV-batch reactor. To guarantee the high sensitivity of the system, purified nitrogen was used as a carrier stream for the OC reactor. Chromatographic characterizations were performed under the following conditions:

Reactors

The UV thin-film reactor and UV batch reactors are of the design by Gräntzel, Karlsruhe (Germany) for the production of water with low organic carbon. The reactors are made of silica glass. The UV lamp of thin-film reactor was set at 300 mA. An apparent OC background concentration of 4 μg/L was found.

Column

A polyacrylate gel (particle size, 40 μm; pores, 40–80 nm range) packed column (TSK-HW-40S) (distributed by Merck) had a dimension of 21-cm length, 1.6-cm

diameter with nominal upper separation limit of 4000 g/mol. Calibration of the column was performed with polyethylene oxides (PEOs).

Eluent

Isocratic (1 mL/min) with 0.028 M phosphate-buffered (pH = 6.58) mobile phase.

Sample

Injection volume of 2 mL (loop injection with reduced pressure). Samples were diluted with 1:10 elution solution to 5.0 mg/L of DOC and chromatographed, after 0.45 μm polycarbonate filtration. Organic free water (zero water) was used for sample preparation and prewashing of filter. Zero water was prepared from DDW by UV-irradiation in batch reactors for at least 30 h.

Detection

Simultaneous quantification of UV-Detection (Gamma Analysen Technik GmbH, GAT-PHD601) and DOC-Detection (Gräntzel, Thinfilm-UV-TOC with IR-Detectors Siemens, Ultramat 5E for OC and Siemens, Ultramat 3 for IC). UV setting was 254 nm and 10 mAUFS (milliamper units full scale) for 100 μg/L OC solutions. The nominal sensitivities of infrared detectors were set at 10 IAUFS (infrared absorption units full scale) for the organic flow. Measurable DOC range was 0.01–10 mg/L.

Data logging, data processing and data presentation were by Rhrothron, Homburg-Saar (Germany), on ATARI-compatible computers. The data was analyzed using a program of numeric analysis (Simplex Numerica 5). Details of the analytical system were described elsewhere[20].

RESULTS AND DISCUSSION

The gel chromatograms are well suited to give information on polarity and molecular weight distribution of HS. The separation principle is a filtration process with the high molecular fractions eluting first and the low molecular fractions eluting later. Figure 2 shows the gel chromatograms of HO10FA gained by gel permeation. The chromatograms were run with simultaneous detection of the DOC and the UV absorbance at 254 nm. UV activity is caused by delocalizable electron systems as they are present in aromatic structures and functional groups like ketones, aldehydes and double bands in humic material. The areas under

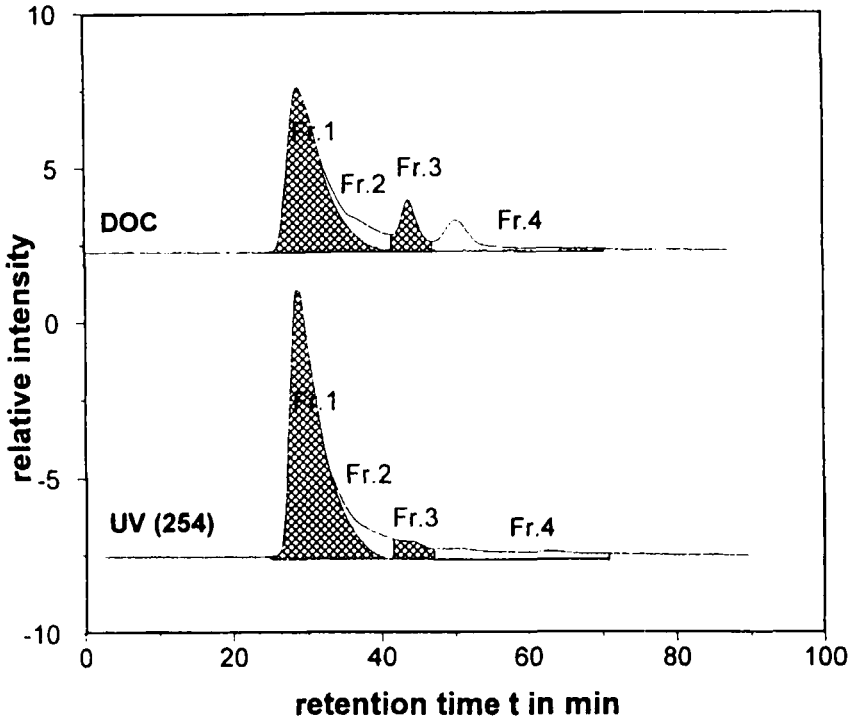

FIGURE 2 Gel chromatograms of aquatic fulvic acid (HO10FA) with UV (254 nm) and DOC detections

both chromatograms were integrated to give the apparent molecular weight distribution. These are shown below the chromatograms in Figure 2.

The first fraction (Fr.1) included hydrophilic constituent of FA and represented about 55.5% of DOC (2.80 mg/L) and 84% of SAC (22.47 m^{-1}) of the whole sample (DOC: 5.05 mg/L, SAC: 26.7 m^{-1}). It has high SAC/DOC ratio (8.01 L/mg.m) reflects aromatic character of this fraction. Material of the fulvic acid is present mainly in this peak. The second fraction (Fr.2) is building blocks for humic material absolute units such as high substituted aromatic acids. Third fraction (Fr.3) is likely caused by negative charged low molecular substances such as carboxylic acids, aldehydes and ketones having UV activity. Low SAC/DOC ratio (2.76 L/mg.m) corresponds to higher aliphatic character of Fraction 3. Fraction 4 included the hydrophobic or amphiphilic constituents. This fraction components can be characterized as nitrogen having structures such as protein, amino acids and amino sugars. Because of the electrolytic neutrality of components, this fraction eluted the last.

Apparent molecular weights of fractions were estimated from the calibration function calculated from calibration line of PEOs. In gel chromatograms, the fractions of FA with high molecular weight (HMW) (t_R= 28.7 min with MW = 880 g/mol) show a relatively sharp peak, whereas the low molecular weight fractions (LMW) (MW<800) were broadly distributed. As the retention time increased, the distribution of DOC shifted from HMW fractions toward intermediate and smaller ones (Figure 2). A similar chromatogram was seen for the UV-detection (Figure 2). The fastest fraction is among the area HMWs (t_R = 23 min to about 38 min, MW>800). After 5 min of ozonation, there is no significant difference between unozonated and ozonated samples in LC/UV chromatogram (Figure 3), but a significant increase in LC/DOC chromatogram was observed (Figure 4). DOC of ozonated sample was much higher (17%) than untreated sample. Mallevialle[21] attributed this behavior to the transformation of HMW fulvic acid into LMW molecules. This may be evidence of oxidative polymerization and improved recovery of higher molecular weight organics during DOC analysis[8].

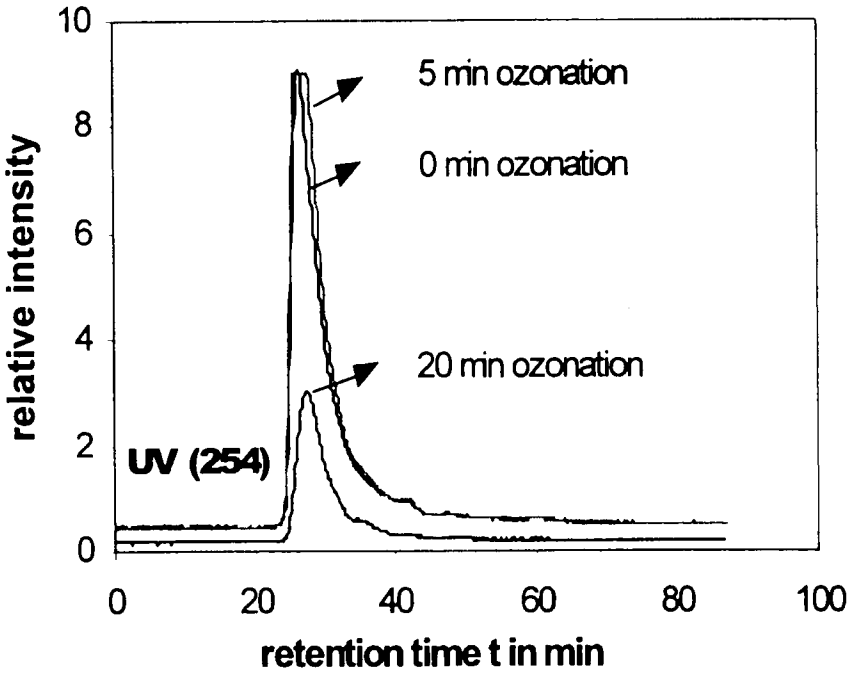

FIGURE 3 Gel chromatograms of ozone treated (5 min and 20 min) aquatic fulvic acid with UV (254 nm) detections

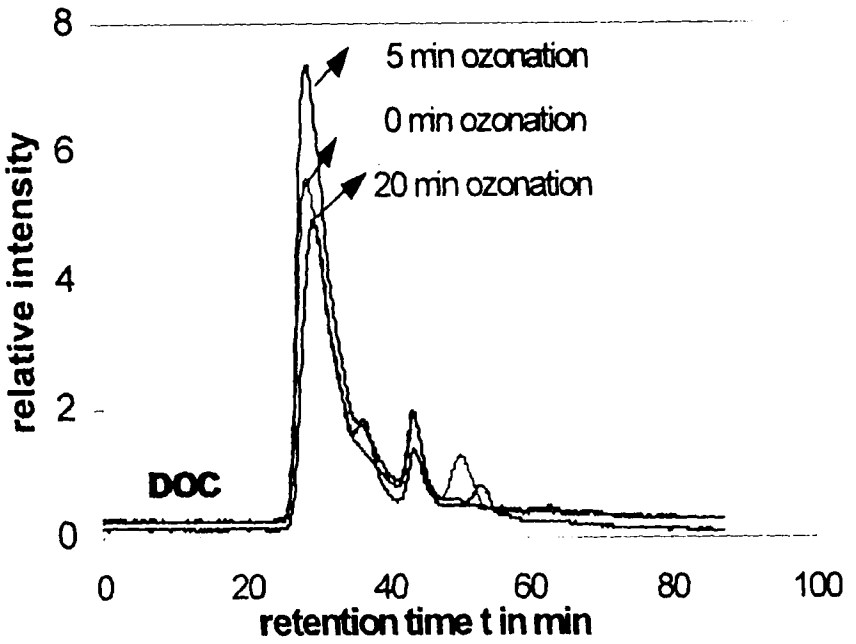

FIGURE 4 Gel chromatograms of ozone treated (5 min and 20 min) aquatic fulvic acid with DOC detections

After 20 min of ozonation, a significant part of the high molecular substances is broken down into smaller molecules, which appear at higher retention times (smaller apparent molecular weight, MW: 710 g/mol) in the LC/DOC chromatogram (Figure 4). There is loss of organic carbon from all molecular size fractions which can be attributed to organic carbon oxidation to produce either volatile organics or carbondioxide. The decrease in the spectral absorbance at 254 nm (Figure 3) can be interpreted as being due to the degradation of the double bond system and the oxidation of chromophoric group components such as –OH and $-NH_2$[7].

The chromatograms in Figure 5 show that chlorination did not lead to a complete rearrangement of the humic structure, but rather reduced non-specifically a certain percentage of high molecular weight fraction. Humic fraction was not completely eliminated but broken down into fractions of LMW (MW: 638 g/mol) which are UV active and show a sharp peak at t_R = 45 min (Figure 5). Although no nominal molecular weight determination (which depends on substances and conditions used for calibration) was done this peak can be interpreted as chlorination byproducts of fulvic acid. A number of researchers have shown

excellent correlations between THMFP and UV absorbance[7,22,23]. Oliver and Thurman concluded that molecular size also gives a good correlation with THMFP[24].

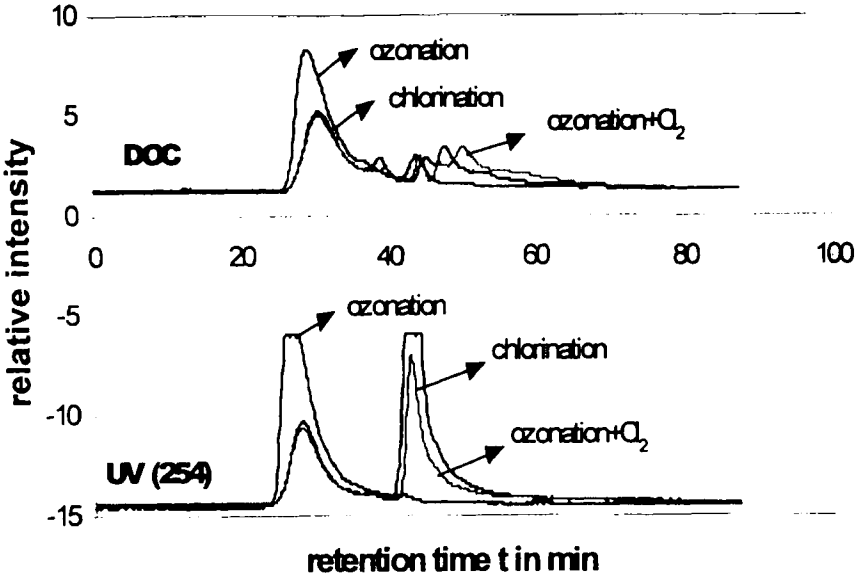

FIGURE 5 Gel chromatograms of ozonated (5 min) and post-chlorinated aquatic fulvic acid with UV (254 nm) and DOC detections

Results given in Table I show that the removal level of DOC concerning AOXFP and THMFP is proportional to the amount of applied ozone dose. The AOXFP and THMFP can be decreased about 58% and 39% respectively, by 20 min ozone reaction. Consequently, the ozone treatment could effectively remove organic precursors (DOC) which can be seen in gel chromatograms (Figure 5) and result in decreasing THMFP and AOXFP in the ozone treated fulvic acid solution (Table I).

TABLE I Effect of ozonation on various parameters

Parameter	*before ozonation*	*5 min ozonation*	*20 min ozonation*
DOC (mg/L)	5.05	5.36	4.34
SAC_{254} (l/m)	26.8	41.9	17.05
AOXFP (μg AOX/mg DOC)	1162	916.3	493
THMFP (μg THM/mg DOC)	111	93.5	67.4

CONCLUSION

Determination of the real molecular weights of FA fractions is restricted by the model substances because of the chemical differences in the FA and the calibration standards. Only apparent molecular weights of FA can be estimated. The key advantage of the gel chromatography system is that FA need not to be preconcentrated, since samples can be directly analyzed. This reduces analysis time drastically and minimizes the risk of inorganic matrix and the loss of FA. A detection limit of <10µ/L can be achieved. Also, the low amounts of sample (a few milliliters) enables the rapid analyses of fresh water samples taken from any part of the world.

Acknowledgements

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