

Available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/watres

Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography – organic carbon detection – organic nitrogen detection (LC-OCD-OND)

Stefan A. Huber^{a,*}, Andreas Balz^a, Michael Abert^a, Wouter Pronk^b

^aDOC-LABOR Dr. Huber, Eisenbahnstr. 6, 76229 Karlsruhe, Germany

^bEawag, Swiss Federal Institute of Aquatic Science and Technology, P.O. Box 611, 8600 Dübendorf, Switzerland

ARTICLE INFO

Article history:

Received 5 February 2010

Received in revised form

6 September 2010

Accepted 17 September 2010

Available online 29 September 2010

Keywords:

Humic substances

Fulvic acids

Humic acids

HS-diagram

Organic carbon detector

SEC

Nitrogen detector

Biopolymers

EfOM

ABSTRACT

Size-exclusion chromatography in combination with organic carbon detection (SEC-OCD) is an established method to separate the pool of NOM into major fractions of different sizes and chemical functions and to quantify these on the basis of organic carbon. One specific approach, also known as LC-OCD-OND, is based on the Gräntzel thin-film UV-reactor. This approach is described with recent improvements in fraction assignment (humic substances, biopolymers, building blocks, low molecular weight organic acids and neutrals, hydrophobic organic carbon), the coupling of a novel organic nitrogen detector (OND), and an improved diagram for the characterisation of aquatic humic substances (HS-diagram). The diagram replaces the operational distinction between humic and fulvic acids by a continuum ranging from aquagenic fulvic acids to pedogenic humic acids.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The concept of organic carbon detection (OCD) for chromatography is not new. The first OCD was described by Axt (1969), who coupled a SEC with a customised thermal combustion DOC-analyser. Ten years later a similar design was used to study NOM in Swiss lakes (Gloor and Leidner, 1979). In 1985, a SEC-OCD based on the Gräntzel thin-film reactor with vacuum-UV oxidation was described (Fuchs, 1985). This design was improved in the following years and the detection limit was lowered from the low-ppm range to

the low-ppb range for individual fractions of NOM (Huber and Frimmel, 1991). In 2002, an OCD based on a modified commercial DOC-analyser with a detection limit of 100 ppb was described (Her et al., 2002a) and in 2007 an OCD based on UV oxidation in a quartz coil (Allpike et al., 2007). A detection limit was not given but was found to be sufficient for most natural waters.

The SEC-OCD design based on the Gräntzel thin-film reactor was applied to study NOM in drinking waters (Gruenheid et al., 2005; Cornelissen et al., 2008), waste waters (Amy and Her, 2004) and marine waters (Huber and Frimmel, 1994; Dittmar

* Corresponding author.

E-mail address: doc@doc-labor.de (S.A. Huber).

0043-1354/\$ – see front matter © 2010 Elsevier Ltd. All rights reserved.

doi:10.1016/j.watres.2010.09.023

and Kattner, 2003). More recent applications of SEC-OCD focus on membrane fouling issues, probably caused by biopolymers (Huber, 1998; Jacquemet et al., 2005; Lesjean et al., 2005; Rosenberger et al., 2005; Laabs et al., 2006; Haberkamp et al., 2007; Zheng et al., 2009, 2010). SEC-OCD was found to be equally interesting for quality control of technical waters which are supposed to be NOM-free, like waters used for turbine steam (Heijboer et al., 2006), water for injection (Woiwode and Huber, 2000) or in the semiconductor industry (Huber, 2003, 2005).

With this paper we describe the SEC-OCD technique based on Gräntzel, called LC-OCD-OND, covering all improvements of past years. This includes refined fraction assignment, the implementation of an organic nitrogen detector and an improved diagram for the characterisation of aquatic humic matter.

2. Materials and methods

2.1. Physical description of the LC-OCD-OND system (Fig. 1)

On-line purified mobile phase (a phosphate buffer exposed to UV-irradiation in an annular UV-reactor) is delivered with an HPLC pump (S-100, Knauer, Berlin, Germany) at a flow rate of 1.1 mL/min to an autosampler (MLE, Dresden, Germany, 1 mL injection volume) and the chromatographic column (250 mm × 20 mm, TSK HW 50S, 3000 theoretical plates, Tosoh, Japan). The chromatographic column is a weak cation exchange column on polymethacrylate basis. Prior to chromatographic separation, samples are made particle-free by passing a 0.45 µm PES-filter (Sartorius, Germany, # 16537). The first detector after chromatographic separation is non-destructive, fixed wavelength UV-detection (UVD 254 nm, type S-200, Knauer, Berlin, Germany) and thereafter the organic carbon detector (OCD, Huber and Frimmel, 1991). At the inlet of the OCD, the solution is acidified at a flow rate of 0.2 mL/min (gravity-driven) to convert carbonates to carbonic acid. The column is bypassed with a restricted flow (flow rate 0.1 mL/min, back pressure-driven) to obtain a DOC value at the dead volume time of each chromatographic run. For nitrogen detection (Section 2.2) a side stream is diverted after UVD with

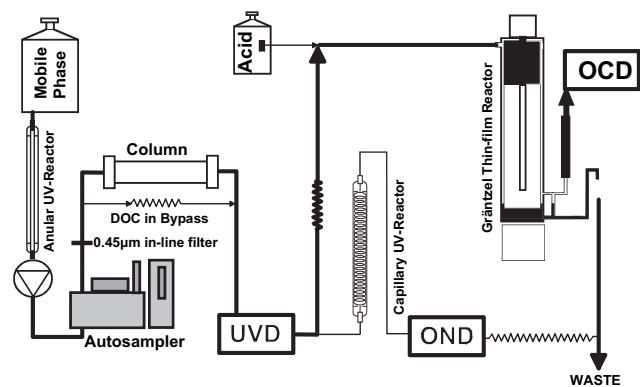


Fig. 1 – Flow scheme of the liquid chromatographic SEC-OCD system.

a restricted flow rate 0.1 mL/min (back pressure-driven) for nitrogen analysis (see Section 2.3).

OCD and UVD calibration was based on potassium hydrogen phthalate. Its carbon mass was used to calibrate the OCD and its extinction coefficient (ϵ) at 254 nm was used to calibrate the UVD. The extinction coefficient ($\epsilon = 1.683 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) was determined with a UV-spectrometer following the law of Lambert Beer. OND calibration was based on potassium nitrate.

For data acquisition and data processing a customised software program was used (ChromCALC, DOC-LABOR, Karlsruhe, Germany).

2.2. Novel organic nitrogen detector (OND, Fig. 1)

The diverted side stream after UVD enters a helical, fused silica capillary of about 4 m length and 1 mm inner diameter. The helix is fused into the electric discharge arc of a low-pressure mercury lamp (80 cm length, 18 mm diameter) emitting at 185 nm and 254 nm (DOC-LABOR, Karlsruhe, Germany). In this UV-reactor, organic carbon (OC) is converted to carbonic acid (which remains unstripped in the aqueous phase) while organically bound nitrogen (e.g. bound to humic substances or biopolymers) and inorganically bound nitrogen (ammonium, nitrite and urea) is converted to nitrate while primary nitrate remains unaltered. Nitrate absorbs strongly in the deep UV-range. This property was used to quantify nitrate in a UV-detector at 220 nm (K-2001, Knauer, Berlin, Germany).

2.3. Chemicals and samples

Mobile phase is a phosphate buffer of pH of 6.85 (2.5 g KH_2PO_4 + 1.5 g $\text{Na}_2\text{HPO}_4 \times 2\text{H}_2\text{O}$ to 1 L, Fluka, #30407 + #30412). The acidification solution was prepared by adding 4 mL o-phosphoric acid (85%, Fluka #79620) and 0.5 g potassium peroxodisulfate (Fluka, #60489) to 1 L of demineralised water. For calibration of detectors, potassium hydrogen phthalate (Fluka, # 60359) and potassium nitrate (Fluka, #31263) was used. For calibration of HS molecular weights Suwannee river Standard II humic (HA) and fulvic (FA) acids from the International Humic Substances Society (IHSS) were used (Perdue, 2008). Nominal average molecular weights (M_n -values) for IHSS-FA and IHSS-HA were determined to be 711 and 1066 Da based on published data (Aiken et al., 1989). A river water sample was taken from the River Pfinz near Karlsruhe, Germany.

3. Results and discussion (see also Supplementary materials)

3.1. LC-OCD-OND fingerprint and fraction assignment

Meaningful interpretation of SEC-OCD fingerprints requires specific software because a full separation of individual peaks of NOM cannot be achieved. Here we introduce our approach which is based on an HS peak fit.

As an example for fraction assignment we show first the fingerprints of a surface water (river Pfinz) for all three detectors OCD, UVD and OND (Fig. 2) and later the same figure with fitted fractions (Fig. 5). Peaks up to 60 min show responses in all detectors, except for peak “A” which does not appear in

Download English Version:

<https://daneshyari.com/en/article/6368031>

Download Persian Version:

<https://daneshyari.com/article/6368031>

[Daneshyari.com](https://daneshyari.com)