

## DOC Characterisation of Condensate Return

**Your proj.-ID/ our proj.-ID:**

**Project Partner/ contact:**

**# and type of samples:** 1 (water)

**Measuring conditions:** column: 50710 / 015 flows: 1.0 / 0.3 / Ø buffer: STD

**Sampling date:** 2009-Jul-

STD

MC

**Incoming date:** 2009-Jul-21

report: Y

N

**Measuring date:** 2009-Jul-21

**data processing:** Dr. M. Abert

**Date of Report:** 2009-Jul-22

**report:** Dr. M. Abert

**Disclaimer:** We guarantee the correctness of analytical data according to the actual state or standard of science and technology. All interpretations are based on the assumption that samples are representative for a situation under investigation. We do not take responsibility for any action that is taken on the basis of our reports, irrespective of whether such action has been recommended by us or not. Reports are treated confidentially and are exclusive property of customer. Anonymized data may be used for scientific purposes if no additional agreements are made.

**Technical note:** LC-OCD stands for "Liquid Chromatography – Organic Carbon Detection". Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV-absorbance at 254 nm (UVD) and organic bound nitrogen (OND). All concentration values refer to mass of organic bound carbon (OC). As a „rule-of-thumb“ compound mass is about twice (for acids threefold) the value of OC. Chromatograms are processed on the basis of area integration using the program ChromCALC. In many samples the acid fraction contains low-molecular mass humic acids which are subtracted by ChromRES on the basis of SAC/OC ratio for HS. Thus, despite the visible presence of an acid peak there may no LMW acids be present.

### SUMMARIC PARAMETERS:

**DOC (Dissolved OC):** Determined in the column bypass after in-line 0.45 µm filtration.

**HOC (Hydrophobic OC):** Difference DOC minus CDOC, thus all OC retained on the column is defined as „hydrophobic“. This could be natural hydrocarbons or sparingly soluble "humins" of the humic substances family.

**INORGANIC COLLOIDS** (respond only in UV-Chromatograms): Negatively charged **inorganic** polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si are detected by UV light-scattering (Raleigh-effect).

**CDOC (Chromatographic DOC):** This is the OC value obtained by area integration of the total chromatogram. Chromatographic subfractions of CDOC are:

#### **ROM = Refractory Organic Matter:**

**A: Humics (HS):** In LC-OCD measurements there is a tight definition for HS based on retention time, peak shape and SAC. Calibration on the basis of „Suwannee River“ Standard IHSS-FA and IHSS-HA. In addition, statistical data are given, like number-averaged molecular mass (Mn) and aromaticity (SAC/OC).

**B: Building Blocks (BB):** The HS-fraction is accompanied by shoulders, shape, concentration and UV-activity varies. This are sub-units of HS with molecular weights of 300-450 g/mol. Building Blocks are considered to be natural breakdown products of humics. They cannot be removed in flocculation processes.

#### **BOM = Biogenic Organic Matter:**

**C: Biopolymers (BP):** This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), hydrophilic, not UV-absorbing. BP are typically polysaccharides but may also contain proteinic matter (this is quantified on basis of OND). BP exist only in surface waters.

**D: LMW Organic Acids (OA):** In this fraction all aliphatic, low-molecular weight (LMW) organic acids co-elute due to an ion chromatographic effect. A small amount of HS may fall into this fraction and is subtracted on the basis of SAC/OC ratios.

**E: LMW Neutrals (NEU):** Low-molecular weight (LMW weakly or uncharged hydrophilic or slightly hydrophobic ("amphiphilic") compounds appear in this fraction. This includes alcohols, aldehydes, ketones and amino acids. The hydrophobic character increases with retention time, e. g. pentanol appears at 120 min, octanol at 240 min. NEU may be in part refractory.

#### **SOM = Synthetic Organic Matter**

With LC-OCD all water-soluble synthetic organic compounds can be quantified and identified (after comparison with model compound) down to the low ppb-range. However, chromatographic resolution in SEC is moderate (about 15000 theoretical plates/metre). Typical examples for SOM are flocculant polymers, antiscalants, org. additives like amines, resin leaching products like polysulfonic acids (PSS) or trimethyl amine (TMA).

**Inorganic Colloids (only visible in UV-detection):** Inorganic colloidal or particulate matter eluting slightly before the biopolymer fraction becomes visible by Raleigh light scattering. This material could be iron oxid hydrates or colloidal sulfur.

**SUVA (SAC/DOC):** Additional parameter derived from the ratio of DOC and SAC.



Results

Table 1

Project:	DOC			Approx. Molecular Weights in g/mol:										Inorg. Colloid. SAC (m <sup>-1</sup> )	SUVA (SAC/DOC) L/(mg*m)			
	DOC	HOC		>>20.000			~1000 (see separate HS-Diagram)					300-500	<350			<350		
	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	N/C µg/µg	% Proteins in BIOPol.*	Humic Subst. (HS)	DON (Norg)	N/C µg/µg	Aromaticity (SUVA-HS)	Mol-Weight (Mn) g/mol	Position in HS diagram			Building Blocks	LMW Neutrals	LMW Acids
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOPol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--			ppb-C	ppb-C	ppb-C
% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC			
Condensate return	627	79	548	n.q.	n.q.	--	--	n.q.	n.q.	--	--	--	--	137	393	17		
	100%	12,5%	87,5%	--	--	--	--	--	--	--	--	--	21,9%	62,8%	2,7%			

LMW = low-molecular weight

DON = Dissolved organic nitrogen

n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)

n.m. = not measured

\*:under the presumption that all org. N in the BIOPolymer fraction is bound to proteinic matter

"Biopolymers" = Polysaccharides, Proteins, Aminosugars

"Building Blocks" = mostly breakdown products of humics

"Neutrals" include mono-oligosaccharides, alcohols, aldehydes, ketones and amino sugars

"Acids" = Summaric value for monoprotic organic acids < 350 Da

<b>Sample</b>	<b>Condensate return</b>
<i>Treatment Scheme</i>	<i>Condensate</i>
<b>Humics (HS) quantitative</b>	Not found (as expected).
<b>Humics (HS) qualitative</b>	
<b>Building Blocks (BB)</b>	An OCD signal in retention window of BB is found, but absence of UVD signal indicates that an organic compound other than BB elutes here (formally assigned to BB). Compound should have a molar mass of 300-500 Da (according to its retention time).
<b>Biopolymers (BP)</b>	Not found.
<b>Neutrals (NEU)</b>	Contains a biogenic compound "X1" (263 ppb C).
<b>LMW Acids</b>	17 ppb C as free acids found, which leads - as a rule of thumb – to an additional electric conductivity of 0.17 $\mu\text{S/cm}$ .
<b>Other Compounds</b>	Ammonium found (88 ppb $\text{NH}_4^+\text{-N}$ ).
<b>Comments</b>	

(Void boxes = no peculiarities)

## Discussion

TOC value is 632 ppb. DOC value is 623 ppb. Proportion of particular organic carbon (POC) is negligible. However, the sample shows some coloration. SAC (254 nm) for filtered sample (DOC) is  $0.28 \text{ m}^{-1}$ , for the unfiltered sample (TOC) is  $2.84 \text{ m}^{-1}$ . Therefore, coloration is caused mainly by an (colloidal) inorganic compound.

The OCD-chromatogram shape is unusual. Identity and origin of organic compound in BB fraction is unclear.

Second unknown compound X1 does not show a UVD signal, too. Retention time of X1 is identical to ethanol.

Presumably both organic compounds are decomposition products of added amines (together with ammonium found).

Concentration of low molecular weight acids is comparably low (17 ppb C).

End of Report

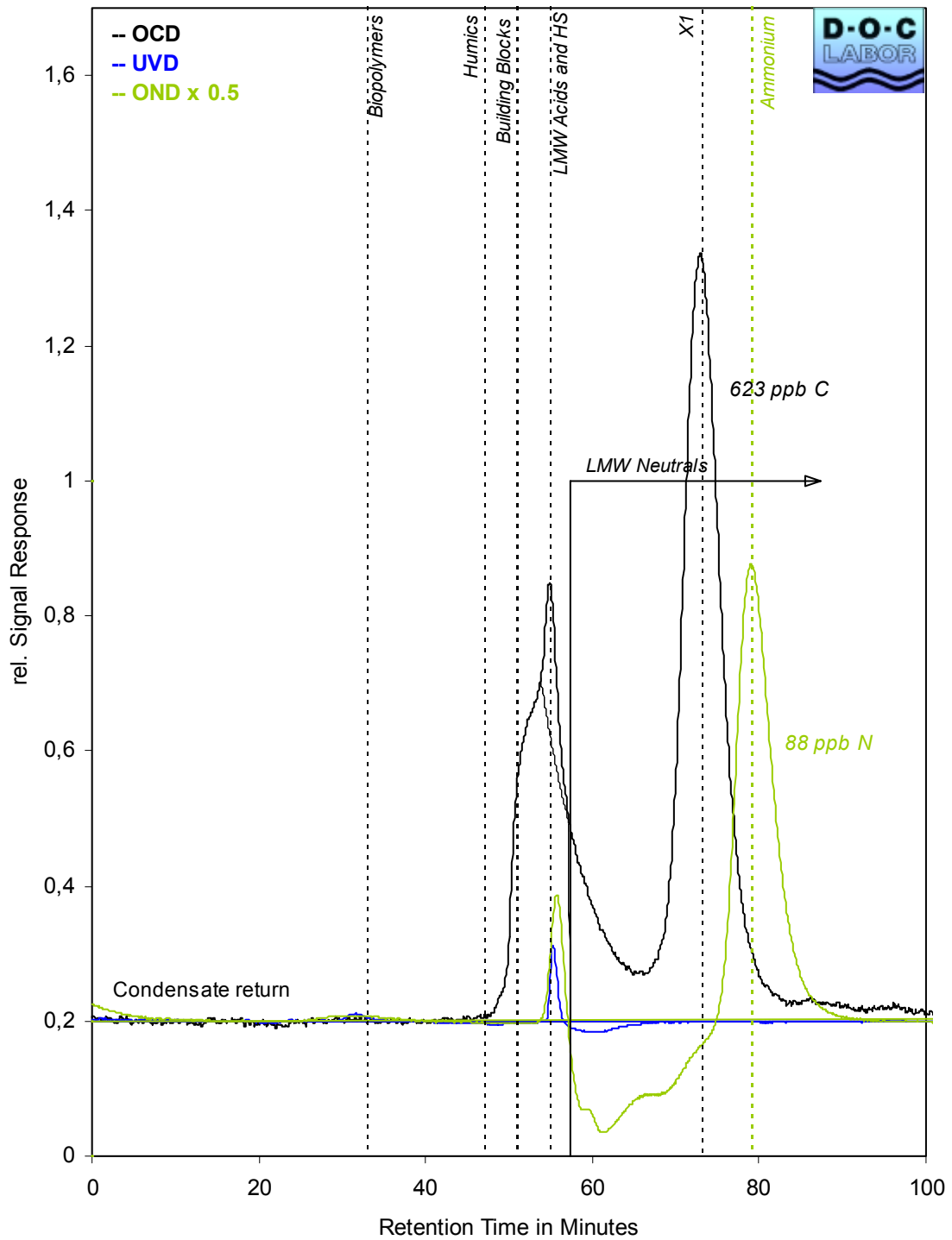


Fig. 1: LC-OCD chromatograms