A conductivity-based, batch-optimized system for analyzing the total of carbon parameter in water.

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Abstract

In cooperation with the company Purification Membranes Analytics GmbH (PMA), a prototype has been developed that analyzes the total organic carbon (TOC) content of water samples based on a complex conductivity measurement. In the process, a batch-optimized system was developed that delivers qualitative results even in highly polluted waters. This method requires small sample volumes and was assembled using an ultrapure water system, a sample mixing system, various electronic control units and a miniTOC system that uses a UV light source to decompose organic carbons and outputs differential values using two conductivity sensors. During the project, a fully automated prototype was developed and is ready for use. In the future, this method could support common methods and lead to more accurate statements on water quality in a cost-effective manner.

1. Introduction

All life is based on water. It is important in biological metabolic processes and also carries vital substances into the body. It is therefore of great relevance to examine the ingredients of water. A measurable sum parameter is the "Total Organic Carbon" (TOC) value, which has become increasingly important in recent years. It describes the total organic load of an examined water sample. [1]

Measuring instruments for the determination of the TOC content are based on different principles. In addition to the spectroscopic detection method in the infrared range (NDIR), there is also the detection method using conductivity, which was used in this project. Conductivity measurement is less expensive, but not as accurate as NDIR detection. [1, 2]

A mercury vapor lamp is used to generate high-energy UV-C light. This radiation breaks down carbonaceous organic particles, which are then emitted as CO2.

The principle used in the project improves the precision of the conductivity-based method in two ways. First, automated dilution is used to bring even highly contaminated samples into the measurable concentration range. In this case, the dilution was carried out using ultrapure water. Secondly, a recursive batch method has been tested, which is expected to increase the measuring accuracy. This prototype has been developed that can automatically take a water sample at predefined time intervals and analyze it for TOC content. In the process, highly polluted water samples are automatically diluted using ultrapure water. The values determined can be queried by the user via the internet. This System is called “boTOC”.

2. Theoretical basics

The theoretical basics refer to the explanation of the TOC analysis, the conductivity measuring procedure, the ultrapure water production and the UV denaturation.

2.1 Total Organic Carbon

Total Organic Carbon value, or TOC, is one of several sum parameters collected in aqueous samples and is used to estimate water quality. [2]

In this project, the conductivity-based method was used, which involves a complete oxidation of the total organic carbon. In this process, measurements are made before oxidation with the first conductivity sensor and after oxidation with a second conductivity sensor.

The TOC is calculated as follows [2]: TOC = TC - TIC

TIC = Total Inorganic Carbon, measured at the first sensor.

TC = Total Carbon - total carbon, sum of TOC and TIC. Is recorded at the second sensor.

TOC = Total Organic Carbon - total organic carbon, e.g. from biofilms and cells.

The temperature affects the conductivity and can lead to an increased susceptibility to errors in the measurements if it changes. This error can be reduced to a certain extent by software. This is done by continuously recording the temperature.

2.2 Electrical conductivity

The electrical conductivity of water is a measure of the total dissolved ions or conductive particles. To determine conductivity, the current flowing between two electrodes in the water is measured. Pure water is basically not electrically conductive, or only to an extremely small extent. Only dissolved ions such as magnesium, calcium, nitrogen, sulfur salts or chlorine make water more electrically conductive. Other substances, such as inorganic or organic particles, also affect the conductivity of water. [3, 4]

Electrical conductivity is expressed in micro siemens per centimeter (µS/cm). Seawater has a value of 56 mS/cm due to the high salt content. Drinking water in Germany about 300 to 800 µS/cm, whereas ultra-purified water has a value of about 0.05µS/cm. [3, 4]

Furthermore, conductivity is temperature dependent. As the temperature increases, the conductivity also increases. This can be explained by the increased ionic motion. [5] This circumstance must be considered in measurements and can be corrected by calculation if necessary.

2.3 UV Oxidation

The irradiation via UV light will break down molecules through the transfer of energy to the bonds between atoms. The higher the energy input, the stronger bonds can be broken. The lower the wavelength of electromagnetic radiation, the higher the energy that this radiation possesses. Therefore, wavelengths in the UV range are important for the breakup of organic carbon compounds; all wavelengths above 360 nm (visible light) are negligible for effective breakup. [6]

When organic carbon compounds are irradiated, they are broken down and converted into inorganic components such as CO2. In this project, a low-pressure mercury vapor lamp is used as the UV light-generating medium. These typically have emission peaks in the ranges: 184.95 nm, 248.3 nm, 253.65 nm, 280.4 nm, 296.73 nm, 312.56 nm, 334.15 nm and 365.01 nm. Wavelengths below 242 nm cause oxygen splitting, resulting in the formation of ozone. This ozone also has a reactive effect on various substances and promotes the decomposition of organic carbon. [6, 7]

2.4 Pure Water

In contrast to normal water, which contains e.g. minerals such as calcium and magnesium, ultrapure water is free of foreign substances. [8] Ultrapure water can be produced, for example, by reverse osmosis, ultrafiltration, photooxidation, or by means of ion exchangers. In some cases, such methods are also combined. Ultrapure water has an electrical conductivity of 0.055 µS/cm with a resistance of 18.2 MΩ/cm.

In this project, a device is used that uses the principle of reverse osmosis process. This is a "counteracting" against the osmotic pressure by a membrane, which retains all particles except water molecules. [9]

3. Materials & Methods

<u>Components:</u>

- Commercial polypropylene tubing with diameters of 3.1 mm / 1.3 mm, and 6.4 mm / 4 mm and 8 mm / 5.5mm.
- Transparent Plexiglas (PMMA) discs in the thickness of 1 cm.
- Opaque UV protection Plexiglas (PMMA) panes in the thickness of 0.3 mm.
- Item profiles (aluminum) for the frame
- Various sliding blocks (M6 & M8) and screws (M6 & M8), and washers in the appropriate size
- 4 swivel casters
- Various electrical cables, including a distribution socket, control box

In addition to the components, ready-made systems for individual applications were used. These are as follows:

<u>Hardware & Systems:</u>

- miniTOC analyzer from membraPure, measuring range 0.5 - 1000 ppb
- Astacus^2 ultrapure water system from membraPure, production rate 2 l/h ultrapure water,
- Air compressor from Schneider Druckluft, SN 0051431533
- Symax double stroke syringe pump from Spetec.

Software:

- miniTOC Onboard Operating System - Windows 10, membraPure miniTOC Measuring Software Version 1.212b W 10 M
- SolidWorks Dassault Systems, Version 2022

3.1 Basic Procedures

The entire system was first functionally set up and tested on a grid plate wall and put into operation before it was installed in the final housing. All systems were independently tested before each step. The validation was done by measuring a calibration series with glucose and samples of river water. The basic structure was designed in SolidWorks beforehand.

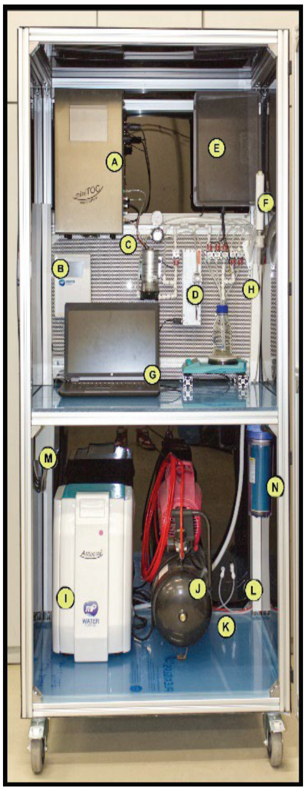
4. Results & Discussion

Within the project duration, the overall system (see Figure 1 left) was completely built and validated.

The main unit of the system is the control board, which is located behind the letter E in Figure 1. This controls every step of the process, from sample collection to automatic dilution to the examination unit (A) and ultimately to the discarding of the sample. The control board also stores the data obtained which can be retrieved via various systems (direct connection, Internet). When the system is used, the sample is automatically taken from the river and first coarsely cleaned via a prefilter (Figure 1 letter N). Afterwards the sample is prediluted with a factor of 1:10. The prediluted sample is then analyzed by the miniTOC system. The TOC content is determined by a conductivity-based difference method. The system contains a low-pressure vapor lamp as standard, which is used as the UV-generating medium. The data measurement units are ppm and µS/cm. A range of 0 - 1000 ppm TOC is the limit of the miniTOC test system. If the value is exceeded, a higher dilution of the same sample is automatically applied in the next measuring step until the sample concentration is within the range that can be evaluated. he software calculates the dilution level with the measured values to obtain the actual sample load. Measurement data is stored locally on the hard disk and can be sent to a server if required. They can also be retrieved directly. An example measurement is shown in Figure 1 on the right. Here a dilution series measured by the boTOC system is shown. A dilution level below 1:100 and lower could no longer be detected by the system and was output as "Signal Overflow". Dilutions above 1:108 could no longer be measured unambiguously, since carbon containing substances were introduced by the system itself via connections and hoses, as well as the pump. Here, it will be necessary to replace the connections and hoses with more inert and dense materials for more precise investigations. However, for the intended goal of the project, this range was completely sufficient. At full power and maximum water flow, the prototype consumes approximately 370 watts and up to 120 liters of water per hour. The main voltage here is 230 V.

4.1 Recursive batch system

The recursive batch system was outlined and tested in this project. The basic idea was to treat a water sample several times by a UV light source. This should result in even more accurate measurement results. Basic findings of this procedure could be obtained. A stronger oxidation within a certain period of time up to 7 Minutes was recorded. However, this was negated by the intrinsic input of TOC through the system itself, through hoses and presumably the pump, which continuously brought an input of carbonaceous substances into the sample. This "background noise" could not be suppressed during the project. Further investigation of this principle is planned after the project period.



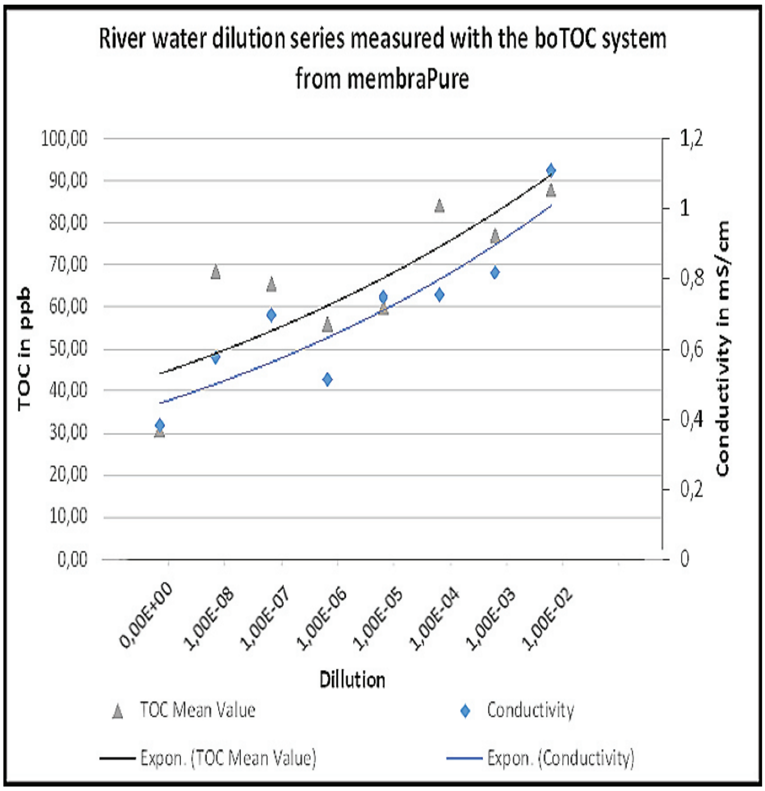


Figure 1: Left - The complete system, A miniTOC system; B Control & monitoring ultrapure water module; C Water pump; D Pro-bend dosing unit, mixing chamber with magnetic stirrer; E Automation electronics in control box F Ultrapure water connection; G (optional) computer for reading out, setting and controlling the prototype; H Cable ducts (electronics on the right) (water guide on the left) for connection in the lower part. Bottom right: Components of the prototype systematized in the lower part of the prototype. I Ultrapure water system; J Compressed air system; K Connections to the outer wall of the housing; L Cable ducts (electronics on the right) (water guide on the left) for the connection to the upper part of the system; M Central power supply and control box; N Prefilter for water inlets; Right - Dilution series of river water measured with the boTOC system at dilution levels 1:10^{8} - 1:10^{2} and ultrapure water.

5. Outlook

Once the entire system was set up, other improvements were planned. For example, to replace the tubing, fittings and various connectors. It is also planned to use a pump other than a peristaltic pump to reduce the system's inherent TOC load. The whole system will also be made more compact and economical.

The method used here is chemical-free and automated. This developed system is a further step towards the monitoring of water systems such as rivers. Even highly polluted water samples can be automatically analyzed for their carbon content.

The principle around the recursive batch system is also being pursued and will be further investigated in the future with an inert setup.

The measurement principle can be applied to other projects in the future and thus supplement the basic water quality testing with higher precision.

6. References

[1] Bernie B. Bernard, Heather Bernard, James M. Brooks: Determination of TC, TOC, and TIC in Sediments [Internet Received 26.03.2023 12:00]

[2] Roger Schmid, SWAN Analytische Instrumente AG, Hinwil, Schweiz: Verfahren in der TOC-Messung, Pharm. Ind. 75, Nr. 11, 1840 – 1848 (2013)

[3] https://www.test-wasser.de/elektrische-leitfaehigkeit-wasser [Internet Received 26.03.2023 14:00]

[4] Kurt Marquardt u. a: Rein- und Reinstwasseraufbereitung. Expert-Verlag, 1994

[5] https://info.hannainst.de/parameter/leitfaehigkeit-erklaert [Internet Received 27.03.2023 14:00]

[6] Prof. Dr. T. Jüstel, Florian Baur, Desinfektion mit UV-Strahlung – Status Quo und zukünftige Entwicklungen, Institut für Optische Technologien FH Münster, Auszug aus der Zoom Konferenz am 02.09.2020

[7] https://www.oekorecherche.de/de/1-das-natuerliche-ozongleichgewicht [Internet Received 27.03.2023 15:00]

[8] https://www.chemie.de/lexikon/Reinstwasser.html [Internet Received 27.03.2023 16:00]

[9] Melin, Thomas und Rautenbach, Robert: Membranverfahren, S. 264 f., Springer, 2007, ISBN 3-540-00071-2