Challenge

Avoidance of error influences due to DOC filter blank values as well as high suspended solids contents and fast and reliable determination of DOC/DN_b in carbonate-rich surface waters

Solution

Automatic filter blank deduction in the multi N/C series software and the NPOC plus method guarantee high sample throughput and precise results for TOC/DOC and TN_b/DN_b in surface waters

Determination of TOC/TN_b and DOC/DN_b in Surface Water According to DIN EN ISO 20236

Introduction

Surface water includes inland waters such as lakes, rivers, creeks, ponds, and dams as well as coastal waters and seawater, although the latter are not considered here. These waters are used for different purposes, either as service waters in various industries (e.g., as cooling waters in industrial processes or as boiler feed waters in power plants) or as raw waters for drinking water supply. Surface water is often rich in suspended solids and also contains dissolved substances. Since both, the suspended matter and the dissolved fraction, can contain pollutants, surface water can only be used as drinking water or as process water for industrial purposes after sufficient treatment.

Surface water is one of the most important resources that must be protected from scarcity and contamination. There are numerous laws and regulations in place that serve this protection. As an example, according to the European Union's water framework directive[1], for each national or international river basin district, management plans have to be in place for improvement and monitoring of surface water quality and corresponding status reports must be published[2]. In Germany, the surface water ordinance[3] specifies which parameters or pollutants in water must be monitored by states authorities. Monitoring is also necessary before surface water is put to further use, e.g., by drinking water suppliers. For the determination of individual pollutants, standard methods are used to ensure comparability of the results.

Sum parameters, such as TOC (total organic carbon) and TN_b (total bound nitrogen), are often used to assess the quality of surface waters. The international standard DIN EN ISO 20236[4] describes a procedure for the determination of these two parameters. In addition, it describes the determination of the parameters DOC (dissolved organic carbon) and DN_b (dissolved bound nitrogen). Also applicable are the individual standards for TOC (DIN EN 1484[5]) and TN_b (DIN EN 12260[6]) determination.

Since surface waters are often first freed from suspended solids before they are further utilized, the content of dissolved pollutants is often of greater importance. If DOC and DN_b are to be determined, the samples must be filtered before analysis. Membrane filters with a pore size of 0.45 µm should be used. If the suspended solids load is high, the membrane filters may clog quickly. In addition, the filter membranes often have a TOC blank value, which falsifies the DOC analysis result in particular. In both respects, polyethersulfone membranes proved advantageous in the application described. In addition, the multiWin software of the multi N/C series also provides support by automatically subtracting filter blank values from DOC/DN_b measurement results.

Together with organic contaminants, surface waters often contain a high carbonate/hydrogen carbonate content (by definition = TIC). This must be removed prior to TOC/DOC determination either by long purging times (during direct determination as NPOC) or it interferes with TOC/DOC determination according to the difference method (TOC = TC -TIC). This is the case if TIC ≥ TOC. The user is often faced with the question of which determination method should be used in such cases. Here, the so-called NPOC plus method is offered, which combines the advantages of both methods in a simple way and thus guarantees both, precise and correct results as well as reduction of long purging times to a minimum.

Materials and Methods

The determination of TOC/DOC was carried out on the multi N/C 3300 with the NPOC plus method. This method is especially suitable for the determination of low TOC contents in samples with high TIC contents or a high proportion of dissolved CO_2. In general, NPOC analysis is recommended for the analysis of such samples. However, for high and especially unknown TIC contents, sometimes very long times (t > 10 min) are required to completely remove/expel the CO_2. The NPOC plus method is a combination of the NPOC and the differential method.
As in NPOC analysis, the sample is acidified with 2 M HCl (pH 2). Immediately before the sample is analyzed, most of the carbon dioxide formed is automatically removed by purging; purging times of 60 s to 120 s are sufficient for this. The organic carbon (TOC) is then determined from the sample prepared this way using the difference method. The TIC value determined by this method is only a calculated value and has no analytical relevance.
Parallel to the TOC/DOC determination according to the described method, the determination of TN_b/DN_b is possible.

Samples and reagents

- 6 samples from different surface waters (3 x river water, 2 x creek water, 1 x pond water), all collected close to the shore
- 3 different membrane filter types (syringe filters), all with 0.45 µm pore size in different material design and size
- 2 M HCl for acidifying the samples
- Cellulose test suspension, 10 mg/L C (particle size between 20 µm and 100 µm) according to DIN EN ISO 20236
- 2 nicotinic acid solutions for system check according to DIN EN ISO 20236, solution 1: 1.0 mg/L N + 5.15 mg/L C and solution 2: 5.0 mg/LN + 25.7 mg/L C

Sample preparation and measurement

The samples were stored in the refrigerator at 4 °C until analysis. First, all unfiltered samples were analyzed for their TOC and TN_b content on the multi N/C 3300 in combination with the AS vario ER automatic sampler.
For this purpose, the samples were first homogenized for 2 min at about 15,000 RPM using a disperser, shaken up again, and immediately transferred to 40 mL sample vessels. A magnetic stir bar was added to each sample vial, then they were positioned on the 72 position sampler tray. For each sample, 2 vials were filled and subjected to the determination of TOC and TN_b.
For the determination of TOC/TN_b, a representative sample aliquot of 500 µL was injected into the combustion tube. To ensure a rapid and complete oxidation of all carbon compounds to CO_2, the reaction took place at 800 °C in the presence of a platinum catalyst. Pure oxygen was used as carrier gas (synthetic air, free of hydrocarbons and CO_2 is also possible). The sample gas was transferred to the detector after appropriate drying and purification. Quantification was performed using non-dispersive infrared spectrometry inside the Focus Radiation NDIR Detector.
The determination of the total bound nitrogen content TN_b was performed simultaneously with the TOC measurement. A chemiluminescence detector (CLD) was used for quantification of NO, which was formed during combustion; alternatively, an electrochemical detector (chemodetector) can also be used for this purpose in accordance with DIN EN ISO 20236, Annex C.
In a second series of sample measurements for the determination of DOC and DN_b, all samples were subjected to membrane filtration after homogenization, syringe filters were used for this purpose. In preliminary tests, three different filter types were investigated with regard to their

blank value contribution to DOC/DN_b and their filtration behavior at high suspended solids loads. A hydrophilic membrane made of polyethersulfone proved to be very suitable, showing the best filtration behavior at a filter diameter of 30 mm. Effortlessly, approximately 80 mL of highly suspended sample could be forced through the filter. The same membrane also showed very low DOC/DN_b blank values; after rinsing with approx. 10 mL ultrapure water, no more blank value could be detected for this filter.
When using filter materials with higher TOC blank values, it is recommended to use the automatic eluate blank value subtraction via a special function of the multiWin software. For this purpose, the residual blank value is determined from a small series of membrane filters pre-rinsed with ultrapure water by measuring a filtered ultrapure water (same volume as for standard DOC/DN_b sample preparation). The blank value determined there can be stored in the software as an eluate blank value and automatically subtracted in a special DOC/DN_b method according to the following calculation formula:

$$DOC_{eff} = DOC_{meas} - BV_{filter}$$

The measurement of the filtered samples was performed analog to the measurement of the unfiltered samples on the multi N/C 3300 in combination with the autosampler AS vario ER. Again, two vials were filled per sample. Magnetic stirring bars were not used in the sample vials.

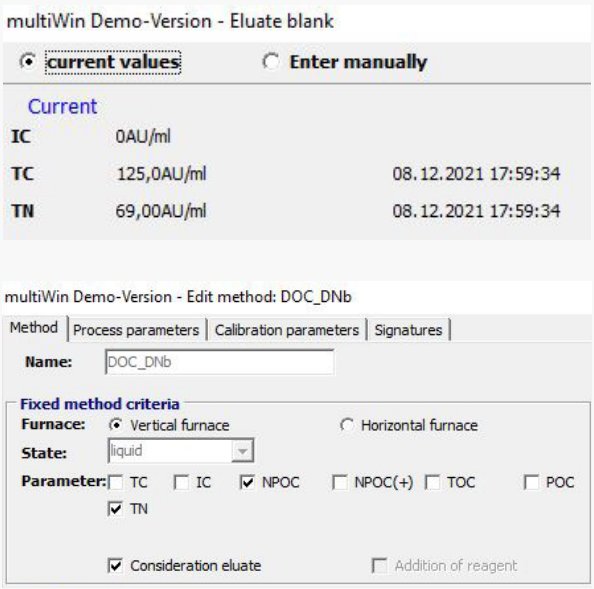


Figure 1a-b: Application of the automatic eluate blank value subtraction in the multiWin software.

Calibration

The multi N/C analyzer was calibrated between 1 and 100 mg/L with a mixed standard of potassium hydrogen phthalate and sodium carbonate/hydrogen carbonate and with a sodium carbonate/hydrogen carbonate solution in the range 1 to 10 mg/L for the parameter TC and TIC, respectively. For TN_b calibration, a mixed standard of ammonium sulfate and sodium nitrate was used in the range of 1 to 10 mg/L.
All calibration solutions were prepared according to DIN EN ISO 20236.

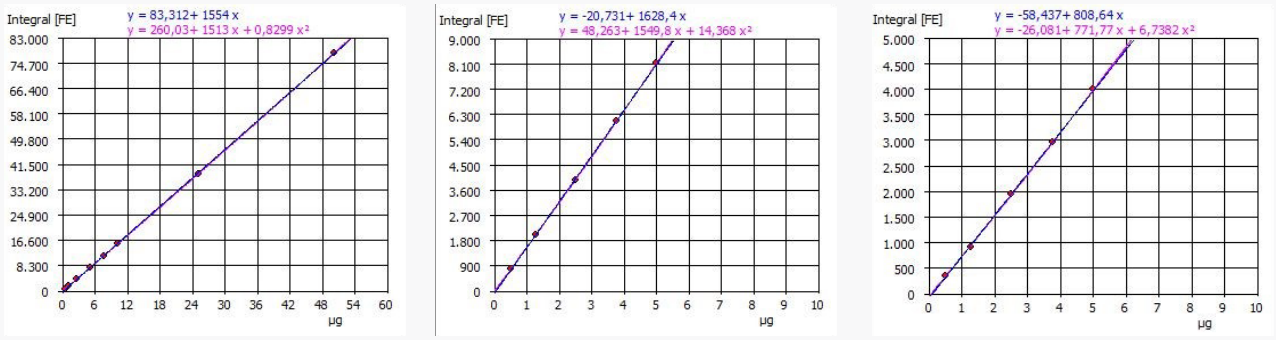


Figure 2a-c: Calibration curves for TC, TIC, and TN_b.

Table 1: Method settings

Parameter	multi N/C 3300
Method of determination	NPOC plus
Sample digestion	Catalytic high-temperature combustion (Pt) at 800 °C
Number of replicates	min. 3, max. 3
Autosampler, rack and vial size	AS vario ER, 72 positions rack, 40 mL sample vials
Rinse cycles with sample	3
Reverse rinse cycles with pure water	1
Injection volume of sample	500 µL
Stirring speed	7
Purge time (removal of TIC)	60 s

Results and Discussion

The analytical results of all samples, the system check solution (nicotinic acid) and the cellulose test suspension are summarized in Table 2. The measurements were each performed as a triplicate injection from one sample vessel. For both, the TOC/TN_b determination (unfiltered samples) and the DOC/DN_b determination (filtered samples), two sample vessels were filled and analyzed for each sample type.

Table 2: Results of different surface water samples, duplicate determination, each injected three times

Sample identification	No. of sample vessels	TOC [mg/L]	CV [%]	DOC after filtration PES, 30 mm [mg/L]	CV [%]	TN_b [mg/L]	CV [%]	DN_b after filtration PES, 30 mm [mg/L]	CV [%]
River water 1 (Saale)	1	4.79	0.9	4.02	0.7	3.25	0.0	3.19	0.0
	2	4.73		4.06		3.25		3.19	
River water 2 (Elster)	1	5.34	0.4	4.50	1.2	3.28	0.4	3.22	0.0
	2	5.37		4.58		3.30		3.22	
River water 3 (Werra)	1	2.62	4.9	2.24	3.6	2.06	1.7	1.97	1.1
	2	2.81		2.13		2.11		2.00	
Creek water 1 (Roda)	1	5.04	2.3	2.97	0.7	6.00	0.4	5.72	1.0
	2	4.88		2.94		6.03		5.80	
Creek water 2 (Leutra)	1	4.47	3.1	1.70	0.4	6.07	0.2	5.78	0.2
	2	4.67		1.71		6.09		5.80	
Pond water	1	6.28	0.8	5.35	0.0	5.25	0.1	4.99	0.4
	2	6.35		5.35		5.24		5.02	

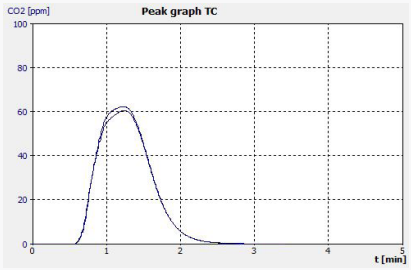
Table 2 (continued): Results of different surface water samples, duplicate determination, each injected three times

Sample identification	No. of sample vessels	TOC [mg/L]	CV [%]	DOC after filtration PES, 30 mm [mg/L]	CV [%]	TN_b [mg/L]	CV [%]	DN_b after filtration PES, 30 mm [mg/L]	CV [%]
Nicotinic acid test solutions:									
Solution 1: 5.15 mg/L C	At start and end of the measurement sequence	5.10	1.2	-	-	4.98	1.4	-	-
		5.19		-		4.88		-	
Solution 2: 5.0 mg/L N	At start and end of the measurement sequence	5.20	1.0	-	-	5.15	0.6	-	-
		5.13		-		5.11		-	
Cellulose test suspension 10 mg/L TOC	1	9.88	0.5	-	-	< LOQ	-	-	-
	2	9.91		-		< LOQ		-	
	3	9.81		-		< LOQ		-	

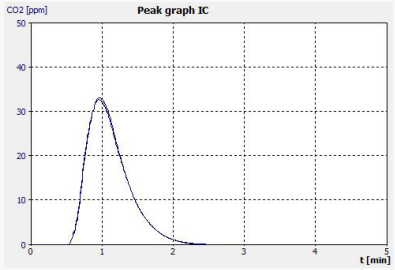
The results of the duplicate determinations of TOC and TN_b in the unfiltered samples show only very slight deviations from each other. The maximum coefficient of variation (CV) of the TOC determination is 4.9% (river water 3). For the majority of the samples investigated, a CV of < 3% is obtained. For TN_b, very small deviations of the duplicate determinations could be observed for all samples, the highest CV being only 1.7%. These very homogeneous results for waters rich in particles and at the same time rich in carbonates prove the very good particle management in the analyzer itself. Additionally, the good agreement of the results illustrates that the selected determination method, the NPOC plus method, is ideally suited for this type of samples.

For the determination of DOC and DN_b in the membrane-filtered samples, the agreement of the duplicates is even higher, which underlines the performance of the TOC analyzer. These results also clearly demonstrate that the selected filter material is very well suited for this application. For the duplicate determination, the same filter was used, which was pre-rinsed with approx. 10 mL of sample before filling the first sample vial. With this pre-rinse volume, the filter could effectively be rinsed blank-free. Any blank value still present would have been noticeable during the first determination (first sample vial) with higher results compared to the second determination (second vial).

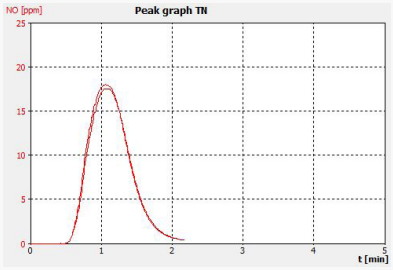
The system check required by DIN EN ISO 20236 using a nicotinic acid standard was performed at the beginning and at the end of the sample series. The recoveries obtained are in the specified range of ± 5% or ± 1 mg/L deviation from the theoretical value and also the coefficient of variation clearly meets the expectations of < 5%. Furthermore, a cellulose test suspension prepared according to DIN EN ISO 20236 was analyzed, the TOC measurement for the same was carried out at the beginning, in the middle and at the end of the sample sequence. Again, the results significantly exceed the specified value for recovery (± 10% of the theoretical value and ≤ 10% CV). The particle processing capability of the analyzer for TOC and TN_b is considered to be proven with the determination of TOC in this test suspension in compliance with the limits for recovery and CV.



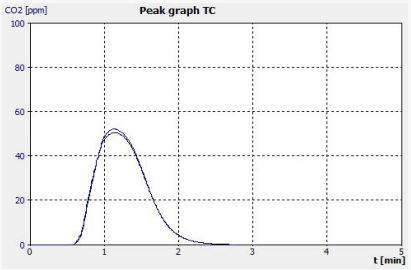
River water 2: TC



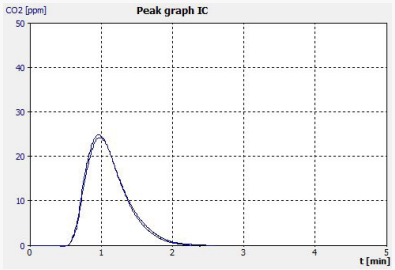
River water 2: TIC



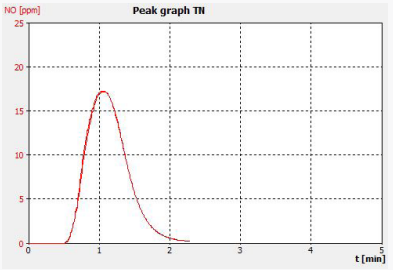
River water 2: TN_b



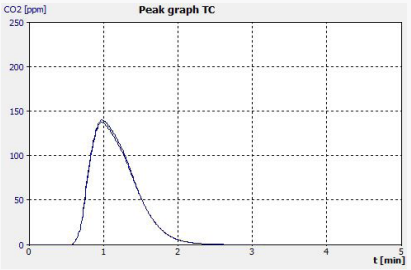
River water 2: DC



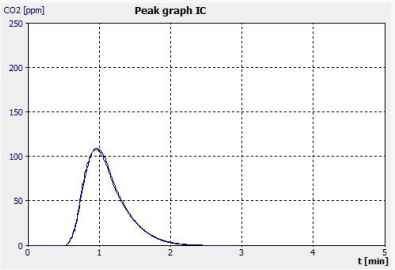
River water 2: DIC



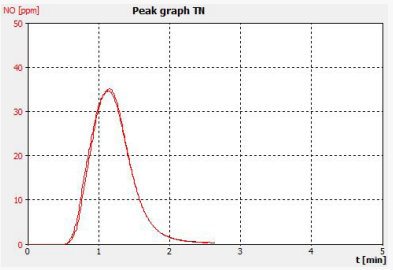
River water 2: DN_b



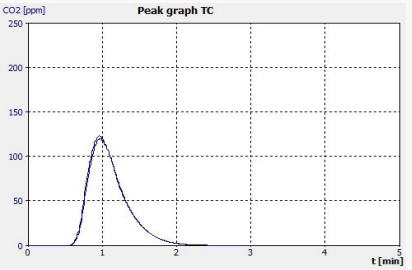
Creek water 2: TC



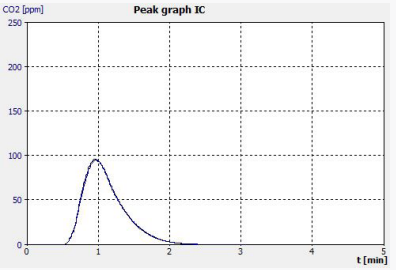
Creek water 2: TIC



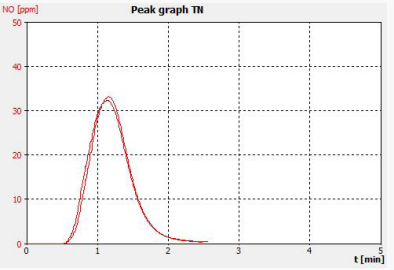
Creek water 2: TN_b



Creek water 2: DC



Creek water 2: DIC



Creek water 2: DN_b

Figure 4a-l: Measurement curves for the samples river water 2 and creek water 2.

The example measurement curves illustrate the excellent reproducibility of the measured values within a multiple injection from one sample vessel.

Conclusion

The multi N/C 3300 is a universally applicable TOC/TN_b analyzer that is ideally suited for the determination of different sample matrices. Both, very low and very high TOC concentrations can be determined effortlessly, even without internal or external sample dilution. The multi N/C 3300 is characterized in particular by its efficient particle processing and its flexibility in selecting the most suitable TOC determination method. Particle-rich samples can be easily analyzed after prior homogenization and clogging inside the analyzer is reliably prevented by large internal tube diameters and effective rinsing processes. Carbonate-rich waters can be analyzed for TOC using the NPOC plus method in a time-saving manner and with very good reproducibility. For less carbonate-rich waters, the classic NPOC method is available, which, supplemented by an optional TIC control measurement, enables an even higher sample throughput, especially in the parallel purge and analysis mode, with simultaneous good result assurance of the NPOC readings. With the available eluate blank value subtraction for DOC/DN_b results, the multiWin software supports youto get a better grip on result-relevant filter blank values.

Figure 3: multi N/C 3300 with autosampler

The multi N/C 3300 is ideally suited for the determination of TOC/TN_b as well as DOC/DN_b according to DIN EN ISO 20236 in surface waters. Fast, reliable, and standard-compliant routine analysis is guaranteed at all times.

References

[1] DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy

[2] Water Framework Directive - The status of German waters 2015, 09-2016

[3] Ordinance on the protection of surface waters (Surface Water Ordinance - OGewV)

[4] DIN EN ISO 20236 Water quality — Determination of total organic carbon (TOC), dissolved organic carbon (DOC) total bound nitrogen (TN_b) and dissolved bound nitrogen (DN_b) after high temperature catalytic oxidative combustion

[5] DIN EN 1484 Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)

[6] DIN EN 12260 Water quality - Determination of nitrogen - Determination of bound nitrogen (TN_b), following oxidation to nitrogen oxides

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