Challenge

Reproducible and reliable determination of total organic carbon (TOC) content in drinking water providing a high inorganic-carbon matrix.

Solution

Reliable TOC determination by NPOC method with TIC control measurement, realizing a high sample throughput by parallel purging and analyzing.

TOC Determination in Raw and Drinking Water

Introduction

Clean drinking water is the most important food for humans, and measures to ensure its healthiness and purity are therefore highly regulated by law. For instance, in the EU, the European drinking water directive[1] defines purity requirements, cleanup and disinfection methods, and sampling and measurement intervals. This directive applies to water for human consumption, which has to meet minimum requirements regarding microbiological, chemical, and further indicator parameters, expressed in limit values. In addition to color, taste, and conductivity, oxidizability and TOC are also mentioned. Whereas for TOC there is no limit value assigned, the oxidizability (determined as permanganate index) is limited to 5.0 mg/L O_2. Since the oxidizability is proportional to total organic carbon, note 4 clearly states that the oxidizability "need[] not be measured if the parameter TOC is analyzed." Furthermore, for TOC, an uncertainty of measurement of ≤ 30% at a level of 3 mg/L is given (SD ≤ ± 0.9 mg/l), and the standard norm EN 1484 for total organic carbon and dissolved organic carbon (DOC) measurement has to be followed.

The biggest issue of TOC determination in drinking water is the fact that, typically, TOC represents only a fraction of about less than 5% of total carbon content of the sample. Furthermore, EN 1484 strongly recommends that the difference method (TOC = TC – TIC) should only be used if the expected TIC (total inorganic carbon) value is equal to or less than the TOC value in the sample.

Example:

TC = 125 mg/l, TIC = 123 mg/l with a considered RSD of 1%

SD (TC) = ± 1.25 mg/l, SD (TIC) = ± 1.23 mg/l, resulting in a total error of ± 2.48 mg/l

TOC (calc.) = 2 mg/l ± 2.48 mg/l (-0.48 – 4.48 mg/l)

Thus, the NPOC method with automatic acidification of the sample followed by automated purging of the TIC by the analyzer carrier gas provides the method of choice. Furthermore, the multi N/C® analyzers offer a TIC control measurement option, which provides a measurement result of residual TIC after the purge process. This can easily be used for method optimization regarding purge time and acid strength used, as well as a means of quality assurance of the obtained NPOC results.

Materials and Methods

Samples and Reagents

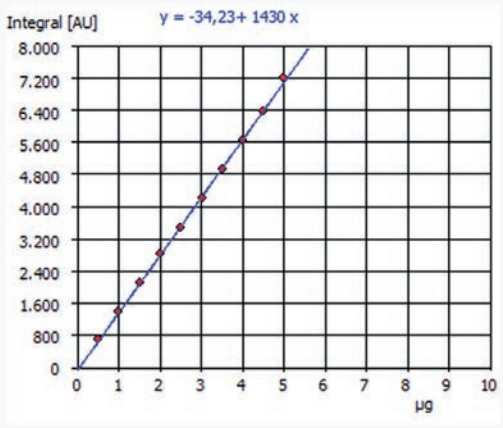
Drinking water samples from different origins and inorganic carbon content as well as reference standards were analyzed.

Sample Preparation

The samples were stored in a refridgerator at 4 degrees Celsius until analysis. For measurement, the samples were transferred into suitable autosampler vials.

Calibration

The multi N/C® analyzer was calibrated for NPOC using a 1 mg/L standard solution of potassium hydrogen phthalate. A multi-point calibration was carried out by variation of the injection volume from 2 – 20 mL on the multi N/C® UV HS to evaluate the results of the NPOC measurement. This refers to an actual working range of 0.4 – 4 mg/L when using a 5 mL injection volume for sample measurements. The identical working range can be covered for multi N/C® 3100 utilizing the EasyCal function with a 2 mg/L standard solution and the variation of injection volume from 100 – 1000 µL and running the samples with a 500 µL injection volume.



Residual SD:	45,761AU	Linearity:	OK
Method SD:	0,032001µg	Variance homogeneity:	OK
Method VC:	1,1637%	Detection limit:	0,059µg
Qual. of rep.:	0,9996	Identification limit:	0,117µg
Correl. coeff.:	0,9998	Quantification limit:	0,213µg

Fig. 1: Example of NPOC calibration and method characteristics for an EasyCal function carried out by multi N/C® 3100

Instrumentation

The analysis were run on the multi N/C® UV HS and multi N/C® 3100. Both models are equipped with the Focus Radiation NDIR detector for sensitive CO_2 detection.
For automated sample introduction an AS vario (with 72 sample positions) was applied.

Method Parameters

For NPOC determination the samples were adjusted to pH < 2 by automatic acidification and subsequently purged with carrier gas for TIC removal. After the purge step a first sample aliquot was injected into the TIC reactor for subsequent determination of residual TIC by TIC control measurement. A second aliquot was then injected into the main reactor, where organic compounds were completely oxidized to carbon dioxide either by catalytic high-temperature combustion at 800 degrees Celsius in an oxygen atmosphere or by UV/persulfate wet chemical digestion. After purification of the reaction gases, the formed CO_2 was transferred to the detector by the carrier gas. The quantification of TOC was carried out by non-dispersive infrared spectrometry in the Focus Radiation NDIR detector.

The following method settings were used to determine the NPOC content:

Table 1: Method settings

Parameter	multi N/C® UV HS	multi N/C® 3100
Measurement parameter	NPOC + TIC control	NPOC + TIC control
Acid used for sample acidification	2 M H_2SO_4	4 M HCl
Digestion	UV oxidation at 185 nm and 254 nm + peroxo disulphate	High temperature digestion at 800° C with platinum catalyst
Number of repetitions	min. 3, max. 4	min. 3, max. 4
Rinse with sample before injection	3 times	3 times
Sample purge time	600 sec.	600 sec.
Injection volume	5000 µL	500 µL
Measuring time per injection	3 – 5 min	3 – 5 min

Results and Discussion

The following table shows the mean values of the NPOC measurements calculated from at least 3 replicate injections as well as the relative standard deviation. Check standards were run as sample type "AQA standard" and the previously determined preparation water TOC blank determined at 154 AU/mL was automatically subtracted by multiWin software from the AQA measurements.

Table 2: Results

Sample ID	NPOC Average [mg/L]	RSD [%]	TIC control level [µg/L]
tab water - Malmö	2.46	0.32	0.12
tab water - Oslo	3.23	0.81	0.19
tab water - Helsinki	2.14	0.60	0.09
tab water - Jena	0.85	0.95	0.07
AQA-Std – 1,0 mg/L	0.98	0.31	0.04

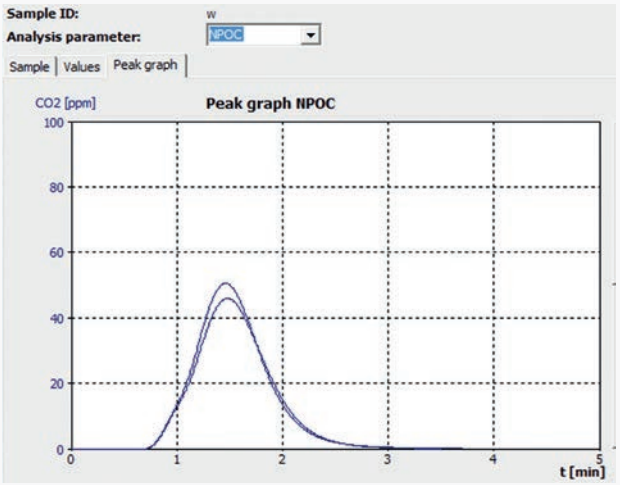


Fig. 2: NPOC measurement curve "tap water - Helsinki"

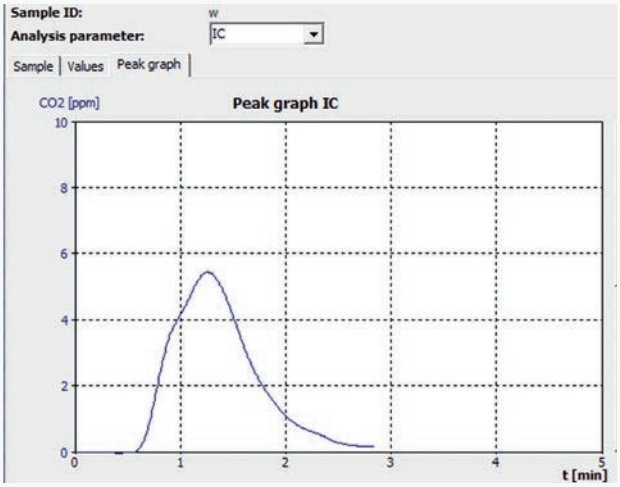


Fig. 3: TIC control measurement curve "tap water - Helsinki"

Conclusion

The presented data show that tap water from different origins can be measured precisely and reliably using an optimized NPOC method. For this purpose, the TIC control feature in the multiWin software was applied and purge times and acid strength used for automatic acidification were adapted accordingly. The results show very low RSD values and that the TIC control reading for each sample was at an acceptably low level (far below 10% of the NPOC reading). By applying the parallel purge and analyses feature of multi N/C® analyzers in combination with the high throughput autosampler AS vario, long purge times don't add up to long sequence runtimes. The TIC purge is already finished during triplicate injection of the previous sample, and the subsequent sample is analyzed straightaway.

Calibration effort is reduced to a minimum using the multiWin Easy Cal feature. This feature allows calibrations to be conducted with only one stock solution on a stable calibration level above or equal to one ppm and while injecting different volumes. This way, the drinking-water range can be calibrated from the sub-ppm up to several ppm TOC.

A high degree of automation combined with the well-proven Self Check System for trouble-free unattended system operation makes TOC analyses by multi N/C® systems the most comfortable parameter in your lab. Flow fluctuations inside the system caused by sample evaporation are completely compensated by the patented VITA flow-management system, which gives you TOC calibration stability for up to one year, saving valuable time for your sample runs.

References

[1] Council directive 98/83/EC (03.11.1998), latest amended by Commission Directive (EU) 2015/1787 of 6 October 2015

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