Blank value determination

TOC trace analysis

TOC-V_{WP}

For the determination of low and trace concentrations, knowledge of blank values is indispensable. Blank values actually consist of different individual blank values. The instrument blank value is combined with residual concentration in the solvent and in the reagents used. In TOC analysis, these influences are particularly significant as carbon containing compounds are present everywhere and a widely distributed contribution of carbon cannot be prevented. During careful sample preparation and analysis, these blank values can be minimized and accurately determined.

This article presents an example of TOC determination in ultra-pure water, including the blank value determination as measured using a Shimadzu TOC-V_{WP} analyzer.

Analytical system and measuring method

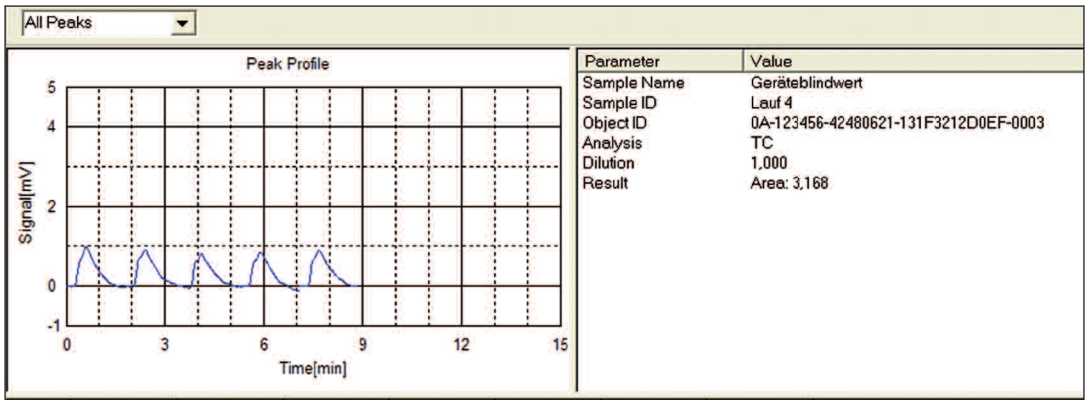
The principal technique of the TOC-$V_{WP/WS}$ analyzer is a powerful oxidation process via sodium persulfate and UV oxidation at 80 °C. These characteristics guarantee detection of all dissolved carbon compounds. An automatic reagent preparation function prevents possible contamination of the reagent solution and minimizes the blank value of the instrument. Using a combination of a high injection volume (up to 20.4 mL) and the highly sensitive NDIR detector, extremely low detection limits and excellent reproducibilities in the lower ppb-range can be attained. The TOC-$V_{WP/WS}$ system is therefore highly suitable for TOC determination in the ultra-trace concentration range.

The TOC-$V_{WP/WS}$ enables two methods of measuring the TOC content: the differential method (TOC = TC – IC) and the direct NPOC method. For ultra-pure measurements, the NPOC method is preferred since dissolved CO_2 present in air and adsorbed during sample preparation is eliminated shortly prior to TOC analysis. In this way, the blank value is not increased. In addition, volatile organic carbon compounds will not be present in ultra-pure water.

In the NPOC method, the sample is acidified with phosphoric acid (until the pH value 2 is reached) and subsequently sparged with carrier gas. In this way carbonates and hydrogen carbonates present in the sample are converted to CO_2 which is eliminated from the sample during sparging. The sample is subsequently injected into the TC reactor and mixed with persulfate solution, then irradiated with UV light. All remaining carbon compounds present in the sample are oxidized to CO_2 and detected via the NDIR detector.

Sample preparation and determination of the blank value

As mentioned, the blank value consists of several components, in this case the system blank value and the blank values of the reagents (persulfate solution and phosphoric acid). In comparison, the instrument produces a low blank value.



Parameter	Value
Sample Name	Geräteblindwert
Sample ID	Lauf 4
Object ID	0A-123456-42480621-131F3212D0EF-0003
Analysis	TC
Dilution	1,000
Result	Area: 3,168

	Spl. No.	Inj. No.	Area	Mean Area	SD Area	CV Area	Inj. Vol.	Date / Time
	1	1	3,355	3,168	0,1227	3,87	20400	21.07.2005 20:53:25
		2	3,218				20400	21.07.2005 20:58:32
		3	3,042				20400	21.07.2005 21:03:40
		4	3,093				20400	21.07.2005 21:08:51
		5	3,132				20400	21.07.2005 21:13:59

Figure 1: "Blank Check" of the TOC-V_{WP}

Standard concentration	Area (4 out of 6 injections)	CV
0.0 µg/L	11.51	1.03 %
10.0 µg/L	20.89	1.94 %
20.0 µg/L	30.20	0.42 %

Table 1: Measuring data of the calibration 20 µg/L

The determination of the system blank value ("Blank Check") can be carried out automatically in the TOC-V_{WP}. In this case, the persulfate solution is firstly injected into the TC reactor, possible contaminations of the reagent solution are removed to a large extent and 20.4 mL of ultra-pure water is subsequently added. After terminating the reaction, this solution is reused for the next measurement. Repeating this procedure several times leads to a virtually carbon-free solution. The measurements are documented and provide information on the extent of the instrument blank value. Figure 1 shows the "Blank Check" of the TOC-V_{WP}. The average system blank value is 2.7 area counts, calculated from 10 runs each of 5 injections.

Based on this procedure, the system blank value also includes the blank value for the persulfate solution.

The ultra-pure water used in these measurements originated from a Millipore Simplicity 185 system. For the NPOC method, a 1 % phosphoric acid solution was added for acidification. Determination of the phosphoric acid blank value was carried out using the standard addition method, in this case 5.9 area counts with a coefficient of variation of 1.2 %.

The glassware used was cleaned with a persulfate solution and subsequently rinsed 5 times with ultra-pure water.

Calibration

For trace analysis the TOC-V_{WP} was calibrated in the lower ppb-range.

Method parameters:

Method: NPOC
Acid addition: 1 % phosphoric acid
Sparging time: 3 minutes
Oxidizing agent: 3 mL persulfate solution
Injection volume: 20.4 mL

Sample measurement

Taking into account the determined blank values, these are now subtracted from the measuring value of the sample.

Measuring value
– Blank value$_{system}$
– Blank value$_{phosphoric\ acid}$
= End result (area counts)

To illustrate, a sample of ultra-pure water obtained from the Millipore Simplicity 185 system was measured (Figure 3).

The ultra-pure water sample was injected six times and four measurement results were used in the calculation. The average value was 10.4 area counts. Corrected with the blank value, a value of 1.8 area counts is obtained, corresponding to a concentration value of 1.9 ppb.

It is interesting to note that the result is lower than the blank value. The final result is 18 % of the original measured value. As the standard deviation of the blank value is very small, this calculation is legitimate. Based on this calculation, higher coefficients of variation for the end result are being obtained.

These experiments show that the influence of the total blank value on the measuring results in the trace concentrations (lower ppb range) is quite significant. In the middle ppb range the influence of the blank values becomes less critical.

The excellent performance (sensitivity and reproducibility) of the TOC-$V_{WP/WS}$ enables accurate TOC determinations in ultra-trace concentration ranges.

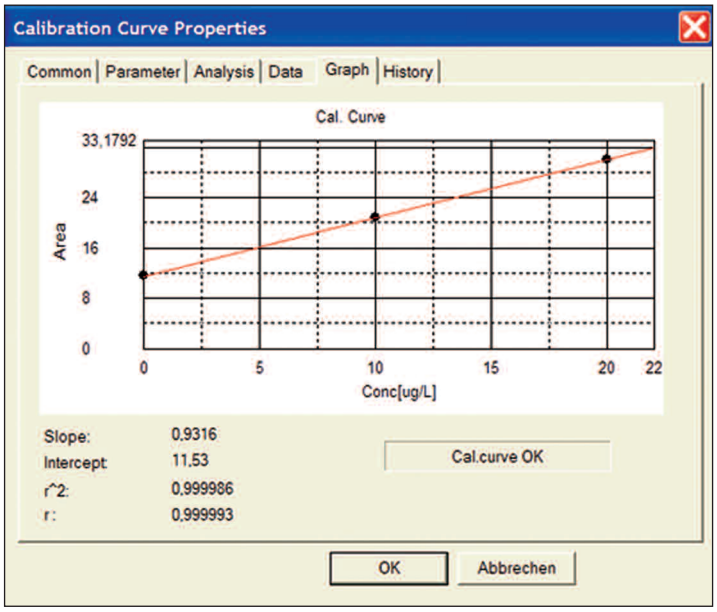


Figure 2: Calibration curve 20 µg/L
Slope of calibration curve: 0.9316
Linear regression: 0.99999

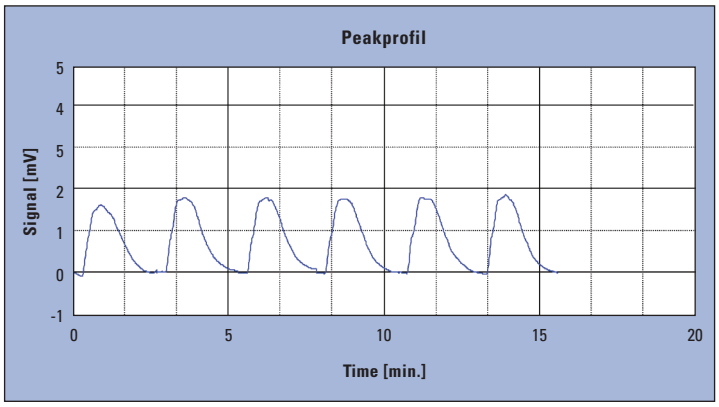


Figure 3: Peak graph of an ultra-pure water measurement