Fine, finer, finest

The European Pharmacopoeia (EP) requires a measuring range from 50 - 500 µg/L using TOC analyses. However, various application areas, such as semiconductor production or water purification unit manufacturing require that this measuring range be extended. The TOC-$V_{WP/WS}$ has been developed especially for these applications. The excellent performance of the TOC-$V_{WP/WS}$ is described here using calibration and measuring data as an example.

TOC-$V_{WP/WS}$

The fundamental technique of the TOC-$V_{WP/WS}$ analyser is powerful oxidation via the combination of sodium persulphate and UV oxidation at 80 °C. These features guarantee that all dissolved carbon species will be detected. An automatic reagent preparation function eliminates possible contamination of the reagent solution and minimises the blank value of the instrument. These features, together with the high injection volume (up to 20.4 mL) and the highly sensitive NDIR detector, result in extremely low detection limits and excellent reproducibilities in the low ppb-range. This is why the TOC-$V_{WP/WS}$ is especially suitable for TOC determination in the ultra-trace range.

TOC determination in the ultra-trace range

In addition to the instrument performance and measuring method, sample preparation plays a significant role when carrying out low ppb-range analyses. Exceptional care has to be taken when cleaning the glassware and preparing the reagents and standard solutions. In addition, the quality of the acids and the purified water has a pronounced effect on the measurements.

With the TOC-$V_{WP/WS}$ it is possible to determine TOC content in two ways: via the difference method (TOC = TC – IC) or via the direct NPOC method. For purified water determination, where no volatile organic carbon compounds are expected, the NPOC method is preferred.

In the NPOC method, the sample is acidified (up to a pH-value of 2) and subsequently sparged with carrier gas. In this way the carbonates and hydrogen carbonates are converted into CO_2 and removed from the sample during sparging. Dissolved CO_2 which is adsorbed from the ambient air during sample preparation is eliminated shortly before measurement and therefore does not lead to an increase in blank values.

TOC-V – developed for the most sensitive measurements, for example in the semiconductor industry

In this illustration, the glassware was cleaned with diluted phosphoric acid and subsequently rinsed 5 times using ultra pure water. The ultra pure water was obtained from a Millipore water purification unit. The flasks for the standard solutions were filled with ultra pure water and the TOC-content was measured. An aliquot of the stock solution was pipetted into the flasks only when its TOC-content did not surpass that of the ultra pure water.

The flasks containing the prepared standard solutions were measured according to the method described below. The goal was to obtain a 6-point calibration curve up to 200 µg/L and to determine the detection limit, determination limit and correlation coefficient.

Measuring method: NPOC (3 % acid, 3 min sparging)
Oxidant: 1.5 mL
Injection volume: 5.1 mL
The offline port was used for the calibration curve.

Standard concentration	Area (5 injections)	CV
0 µg/L	3.61 ± 0.125	3.5 %
20 µg/L	9.31 ± 0.38	4.1 %
40 µg/L	15.33 ± 0.18	1.2 %
80 µg/L	27.20 ± 0.34	1.3 %
100 µg/L	31.73 ± 0.66	2.1 %
200 µg/L	62.62 ± 0.73	0.8 %

Measuring data for the 200 µg/L calibration (see figure 2)

TOC determination in ultra pure water

The data show that the reproducibility is excellent for each concentration point. In each case the coefficient of variation is below 5 % and at concentrations over 20 µg/L even around 2 %.

When plotted on a graph (figure 2), the calibration curve shows excellent linearity in the lower concentration range. The excellent performance of the calibration curve is confirmed via a correlation coefficient of 0.9992.

The detection limit and determination limit was calculated from the calibration curve according to the DIN 32645 Standard. The following values were obtained:

Detection limit: 3.3 µg/L NPOC
Determination limit: 12.3 µg/L NPOC

For the second measuring sequence, the maximum injection volume of 20.4 mL was used. The goal here was to determine the detection limit, determination limit and correlation coefficient in the lower concentration range (down to 20 µg/L).

Standard concentration	Area (5 injections)	CV
0 µg/L	7.53 ± 0.004	0.05 %
10 µg/L	18.39 ± 0.31	1.7 %
20 µg/L	29.39 ± 0.14	0.5 %

Measuring data for the calibration curve 20 µg/L (see figure 3)

By using a higher injection volume, a reproducibility of less than 2 % could be obtained.

From the calibration curve, the following parameters were calculated:

Correlation coefficient: 0.99999
Detection limit: 0.4 µg/LNPOC
Determination limit: 2.2 µg/L NPOC

After the calibration curves were obtained, a sample of Milli-Q-water was measured. The result was 2.44 ± 0.42 µg/L TOC (NPOC).

The results shown here confirm the excellent specifications of the TOC-$V_{WP/WS}$, which allow TOC determination also in the trace concentration range.

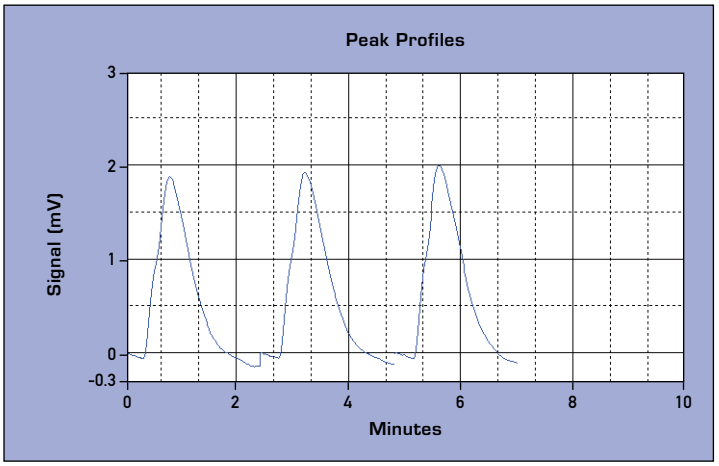

Figure 1: Sample 2 µg/L

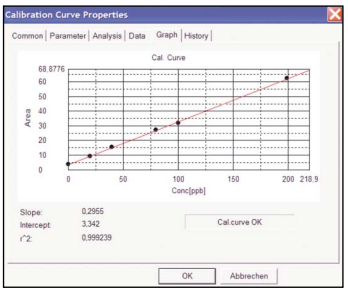

Figure 2: Calibration curve 200 µg/L

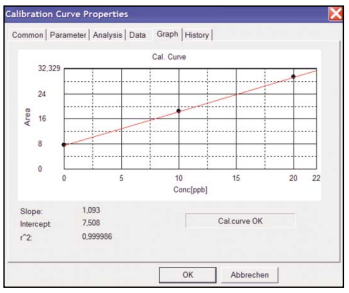

Figure 3: Calibration curve 20 µg/L