



TOC Monitoring in Boiler Feed and Cooling Water of Fossil-Fuel-Fired and Nuclear Power Plants

Challenge

Reproducible and precise determination of total organic carbon (TOC) in the trace range in boiler feed and cooling water for the monitoring of corrosion-influencing parameters in power plants.

Solution

Fully automated and sensitive NPOC measurement by wet chemical UV oxidation providing the most cost-effective and robust analytical routine method.

Introduction

Water within power plants, and particularly boiler feed water, is subject to strict analytical control. Organic impurities in the boiler feed water can easily oxidize under high pressure and high temperatures and may lead to the formation of corrosive organic acids and carbonic acid. State-of-the-art feed water production therefore uses reverse osmosis or ultrafiltration membranes and ion exchangers to reduce and control the corrosion potential of the final feed water. Rule of thumb: the higher the operating pressure of the boiler system, the lower the recommended contaminant levels set, e.g., TOC < 0.5 mg/L at pressures above 31 bar, or TOC < 0.2 mg/L above 62 bar *).

The condensate return has to be checked for TOC levels as well to monitor for contamination, for example contamination caused by leakages in the steam pipes or heat exchangers. In addition salts are often added as oxygen scavengers, as are neutralizing amines or boric acid to regulate pressurized-water reactors in nuclear power plants.

Wet chemical UV digestion is particularly suited for TOC determination within the ppb concentration range accompanied by specific additive sample matrix. multi N/C 4300 UV was used for the sample measurements. Various types of autosamplers, such as AS 10e, AS 21hp and AS vario, which offer different sample rack capacities, provide a high degree of automation.

*) published by APAVE (Association of electrical and steam unit owners)

multi N/C UV 4300 UV offers the possibility of injecting very large volumes up to 20 mL and hence highest measurement sensitivity. The integrated high-power UV reactor utilizing two hard UV wavelengths (185 nm and 254 nm) simultaneously ensures powerful sample oxidation even for salt matrices. There is no need for TOC blank loaded oxidation reagents allowing unspoiled/unadulterated direct TOC readings in the trace range.

Materials and Methods

Samples and Reagents

- Boiler feed water samples
- Synthetic cooling water solution
- 2 M H_2SO_4 for automatic sample acidification

Sample Preparation and Measurement

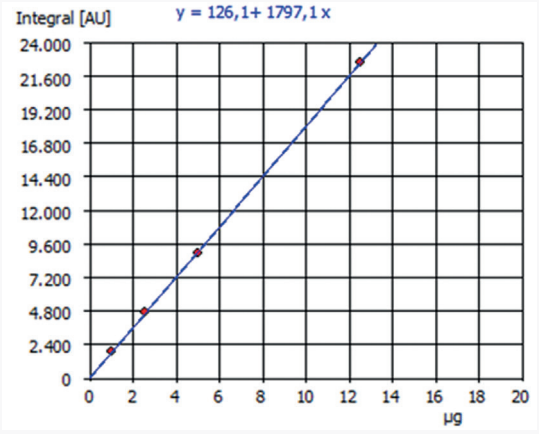
Feed water samples were stored in the refrigerator at 4 °C until analysis. Furthermore a synthetic cooling water as usually found in nuclear power plants was prepared and spiked with defined TOC contents. The solution was prepared as follows:

- 7 g/L boric acid
- 1 mg/L sodium
- 7 mg/L potassium
- 2 mg/L lithium
- 7 mg/L ammonium

A 300 µg/L and a 1000 µg/L TOC-standard (potassium hydrogen phthalate) were added to this synthetic solution. After several rinse steps, the samples were filled into 40 mL autosampler vials, sealed with aluminum foil and placed into the AS vario sample rack. Before measurement the samples were automatically acidified with 2 M H_2SO_4 to a pH below 2 and subsequently purged by carrier gas. This was done by the autosampler according to the method settings for complete TIC removal prior to NPOC measurement.
During the oxidation process in the high-power long-life UV reactor, all carbon compounds were quantitatively converted to CO_2. The wide-range Focus Radiation NDIR detector was used for quantitative determination of the CO_2 content in the measurement gas. A TIC control measurement ensured that inorganic carbon and dissolved carbon dioxide were removed completely.

Calibration

The system was calibrated for non-purgeable organic carbon (NPOC) measurement with standard solutions prepared from a 1000 mg/L potassium hydrogen phthalate stock solution. For the trace range a single-point-calibration at 500 µg/L was performed. A second multi-point calibration covered a working range from 0.5 to 2 mg/L. A calibration curve and its characteristics are presented in Figure 1.



Residual SD:	143,47AU	Linearity:	OK
Method SD:	15,97µg/l	Variance homogeneity:	OK
Method VC:	1,5207%	Detection limit:	45,10µg/l
Qual. of rep.:	0,99984	Identification limit:	90,19µg/l
Correl. coeff.:	0,99992	Quantification limit:	190,1µg/l

Figure 1: Example of a NPOC multi-point calibration curve and characteristics

The software of the multi N/C analyzer allows the combination of one measuring method and up to three calibration ranges. The analyzer automatically selects the most suitable calibration curve for calculating the results, based on the signal area integrals. This ensures that the optimal calibration range is selected. This is particularly user-friendly and guarantees highest accuracy and precision of the measured values.

Instrumentation

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

Table 1: Method parameters

Parameter	multi N/C 4300 UV
Measurement parameter	NPOC (with TIC control)
Digestion	UV radiation, no oxidizing reagent
Number of repetitions	min. 3, max. 4
NPOC purge time	360 sec
Rinse with sample before injection	3 times
Injection volume	5 mL

Results and Discussion

The following table shows the mean values of the NPOC measurements calculated from at least three replicate injections as well as the relative standard deviation. The spiked synthetic cooling water samples were run as sample type “QC standard”. The multiWin pro software automatically subtracted the previously determined preparation water TOC blank of the synthetic solution (matrix blank, determined at 113.9 AU/mL) from the QC measurements.

Table 2: Results

Sample ID	NPOC Average [µg/L]	RSD [%]
matrix + 300 ppb KHP	326.2	1.25
matrix + 1000 ppb KHP	1060	0.89
boiler feed water 1	129.0	2.8
boiler feed water 2	55.2	3.3

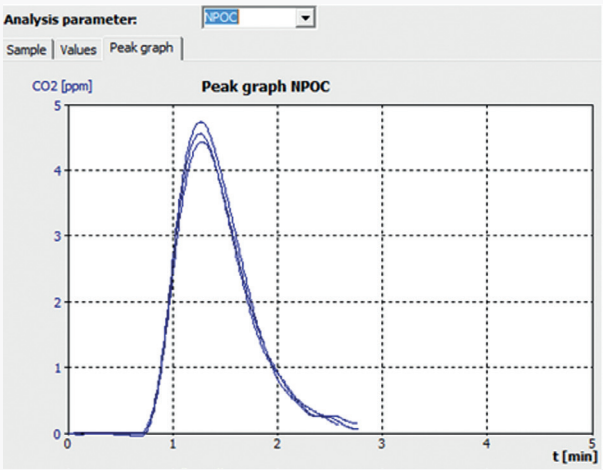


Figure 2: Measurement curves “boiler feed water 2”

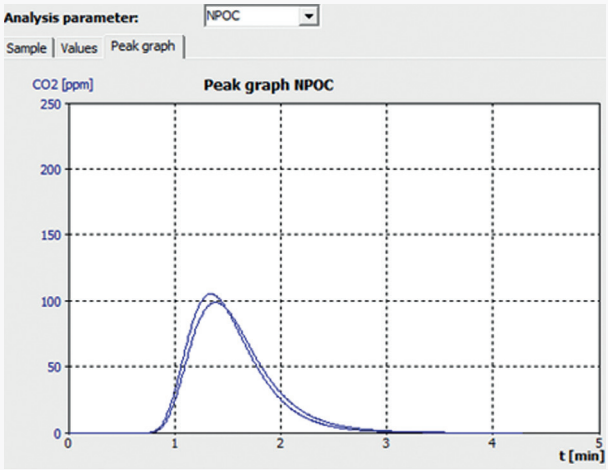


Figure 3: Measurement curves “matrix + 1000 ppb KHP”

Conclusion

The results of the spiked synthetic boric acid samples clearly show that there is no need to add an oxidizing agent for complete oxidation to TOC compounds. Hence the use of sodium peroxodisulfate, which always adds a significant TOC blank value to the sample reading, and which has to be handled carefully, can be omitted. The UV radiation and the dissolved oxygen in the sample are sufficient to convert all organic compounds into CO_2. The achieved results are extremely reliable for TOC measurements in the boiler feed and cooling water in power plants.

The applied multi N/C 4300 UV offers the most comfortable solution for TOC monitoring tasks in power industries. With its high-power long-life UV reactor, it reduces cost of ownership. The UV lamp typically serves for significantly more than three years of operation. Furthermore, required chemicals can be purchased from local suppliers and can easily be prepared by the user. A high degree of automation can be achieved by using the autosampler AS vario, which offers high sample throughput and cost-efficiency in routine quality control labs.

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