

## focus on Laboratory Products

### Fast and Reliable TOC/TN<sub>b</sub> Determination in Saline Water Using the Multi N/C® Series

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In many areas of application – extending far beyond drinking and waste water analysis – a fast and reliable TOC/TN<sub>b</sub> determination is required. The catalytic high temperature combustion with subsequent selective and sensitive detection of the combustion products CO<sub>2</sub> and NO is an established determination method.

This measuring technique is used, for example, in the agricultural pedological area when determining the microbial biomass carbon or nitrogen in soil, using the fumigation extraction method. Soil samples are purged by chloroform to kill microorganisms as well as to destroy the cells and, subsequently, extracted with a 0.5 molar potassium sulphate solution. This highly saline solution is then directly analysed with a NPOC/TN method at the analyser.

Another application area is the process monitoring of chlorine alkali electrolysis in chemical industry. The used brines have a NaCl content of 26–28 percent by weight (saturation of 100°C), whereas the TOC content is process-crucial and must be monitored with measurement technology. This also applies to brines used in medical areas.

The concentrated acids and bases produced in chemical industry and used to various processes are analysed for contamination just as thoroughly, whereas the TOC parameter often must be monitored in the range of 1–10 ppm. Also for surface finishing industry, the TOC sum parameter is a guiding parameter for the quality of a galvanic bath. Due to the high metal salt concentrations, this matrix also implies a challenge for TOC analysers.

In the area of global ecosystem monitoring, the DOC and TDN content (Total Dissolved Nitrogen), amongst others, are of peculiar interest in different seawater levels and streams. Especially deep-sea samples from several hundred meters are taken which usually have DOC or TDN contents lower than 0.7 ppm and, thus, exclude the sample dilution to reduce the matrix load.

#### Selecting the Correct Digestion Method

According to DIN EN 1484, there are two digestion methods available for the various application areas of a TOC analyser, from environmental to process analysis.

For some of the application areas listed above, such as concentrated acids, bases or galvanic baths, the wet chemical UV digestion is a good alternative to reduce device wear and, thus, to keep operating costs low. As the wet chemical procedure implies a conversion of carbon compounds to CO<sub>2</sub> using an oxidation agent in combination with UV radiation, the problems regarding wear known of high-temperature combustion devices can be avoided. However, the wet chemical digestion has a limited oxidation capacity for particulate waters as well as for high chlorine contents.

Therefore, the selection of the digestion technique is often limited from the start to the catalytic high-temperature combustion, through the type of sample matrix or the combination of the analyses parameters TOC and TN<sub>b</sub>. The thermocatalytic digestion is preferably used in classical wastewater analysis. The influence of high temperatures, usually above 800°C, is here the crucial factor to ensure the complete oxidation, also of particles.

Most of the above mentioned matrices, if not for analytical regards either, represent an especially great challenge for thermocatalytic TOC measuring devices due to the high salt content of the sample matrix.

#### High Salt Contents – Where are the Limits?

For a complete conversion of nitrogen compounds to NO, DIN EN 12260 specifies a combustion temperature of at least 700°C in an oxygen-rich atmosphere. The TOC or DOC determination according to DIN EN 1484 presents no deviating digestion conditions and, thus, enables a simultaneous and time-saving measurement of the parameters TN<sub>b</sub> and TOC.

The high salt content of the sample matrix causes a high stress for the combustion tube and catalyst. Depending on chemical character and concentration, different salts can crystallise out in the combustion tube and agglomerate with the combustion tube filling. This will lead to system clogging, which results in an error message that stops the measuring sequence and requires a maintenance procedure. In addition, the alkali and earth alkali cations of the salts cause the quartz glass combustion tube to devitrificate, which requires combustion tube exchanges more often.

To extend the maintenance intervals when working with highly saline samples, the multi N/C® series by Analytik Jena AG offers various possibilities.

Through the freely adjustable combustion temperature of up to 950°C, the multi N/C® analysers ensure an optimised complete sample digestion, independent of the sample's matrix and particle content. This can be used in combination with an optimised combustion process control as well as combustion tube filling to create matrix-optimised NPOC/TN applications. Thus, maintenance cycles can be extended considerably with consistently stable analysis results.

The extremely sensitive Focus Radiation NDIR detector (FR-NDIR) allows to reduce the sample injection volume in order to decrease the absolute amount of the critical sample matrix entered into the combustion tube or to measure pre-diluted samples at a higher sensitivity, with the same effect. The robust design of the FR-NDIR detector (see Figure 1), independent of reflection, provides application solutions for extreme matrices with minimised device wear and notably extended operating times, thanks to the multi N/C® series.

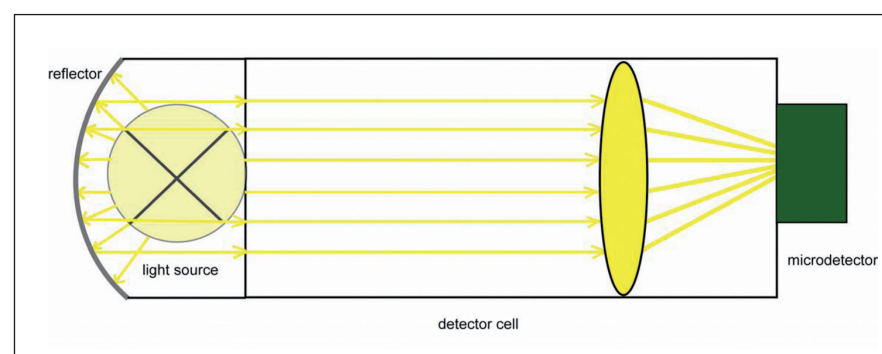


Figure 1. Schematic layout of the FR-NDIR detector: Extremely robust design, as the radiation yield in the part measuring gas flows through is completely independent of reflection. Thus, there is no loss of sensitivity through possible wall deposits and the construction is practically corrosion-free due to inert materials.

#### Experimental Part

The multi N/C® 2100 coupled with a chemiluminescence detector (CLD) was used for the measurement within the framework of these researches. The multi N/C® 2100 as direct injection device features small injection volumes (50–500 µl), short sample paths (without valves and long tube paths), small space requirement and the optimum particle handling with an internal canula diameter of 0.7mm (see Figure 2).

Due to matrix influences, especially of salt and pH value, there are higher deviations within an analysis sequence of the TN<sub>b</sub> recovery of mixed standards (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>) and nicotinic acid as organic nitrogen compound. Aim of the researches was to optimise the application of the NPOC/TN method to reduce these deviations and receive 100% recovery rates for different nitrogen compounds over an extended period without maintenance. The NPOC parameter was analysed as well, ensuring that the optimisation of nitrogen would have no negative effects.

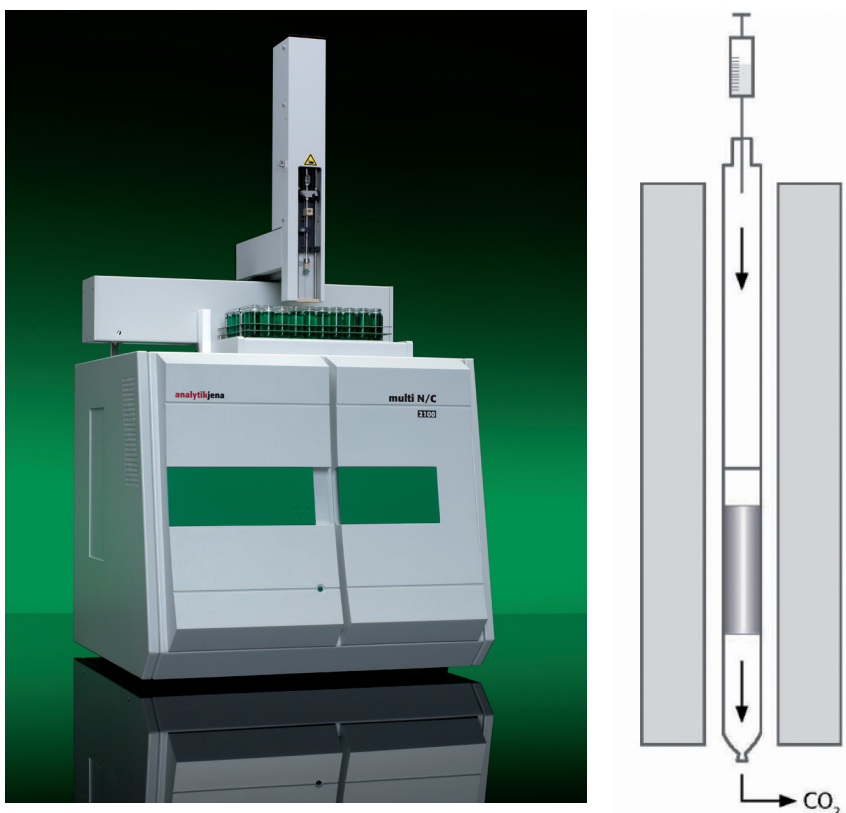


Figure 2. multi N/C® 2100 with APG 60 and injection scheme

For the analysis series, the NPOC/TN method was used to measure 0.5 molar potassium sulphate solutions in the form of soil extracts, as it is usually received with the fumigation extraction method. The method was calibrated using a mixed standard of potassium hydrogen phthalate, ammonium sulphate and sodium nitrate prepared in a 0.5 molar potassium sulphate solution. As control standards, a mixed standard as well as nicotinic acid with 20 ppm in 0.5 molar potassium sulphate solution were measured.

A platinum catalyst with a combustion temperature of 800°C was used and an autosampler equipped with a 250µl syringe and a 112 positions tray à 2mL was applied. The injection volume was 100µl and each 20th injection was performed with ultrapure water to check the system blank value.

The following recovery rates are related to the first measurement of the 20mg/L mixed standard. The system blank values were all below the detection limit of 50 ppb for NPOC and below 0.1 ppm for TN<sub>b</sub>.

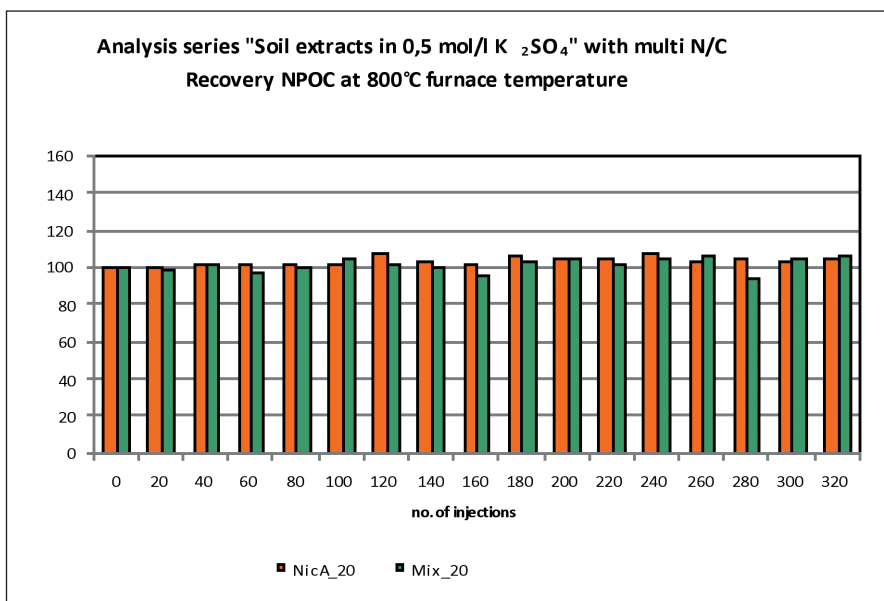


Figure 3. NPOC recovery rates of mixed standard and nicotinic acid standard in 0.5 molar potassium sulphate solution

As clearly visible at the trend of the recovery rates, mixed standard as well as nicotinic acid standard show a high level of reproducibility and stability for the NPOC parameter, throughout 320 injections.

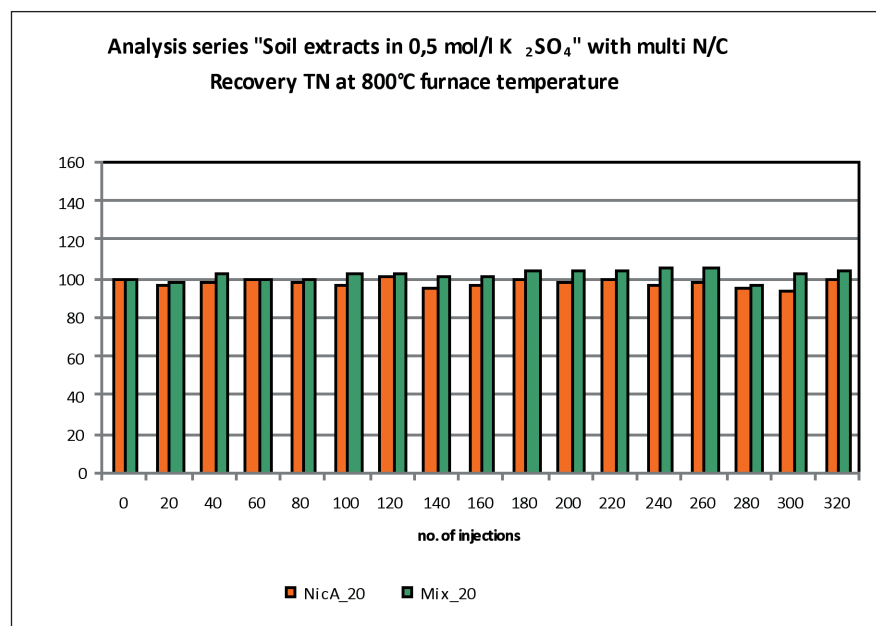


Figure 4. TN<sub>b</sub> recovery rates of mixed standard and nicotinic acid standard in 0.5 molar potassium sulphate solution

Also for the TN<sub>b</sub> parameter, the selected method settings resulted in a stable recovery close to 100% for mixed standard and nicotinic acid, over the entire measurement cycle.

During the entire measurement period, there was no need to adjust the calibration or to maintain the analyser. The measurements were not continued further, after a long-term stability could be proven which ensured the processing of an entire 112 pos. rack with a method setting of 2–3 injections. The combustion tube was removed after completed test. It showed no unusual signs of wear, only the catalyst cover had to be replaced and the catalyst fill had to be flushed with ultrapure water for continuous use of the tube.

A further test series with ultrapure brine was performed using the multi N/C® 3100. The sample was pre-diluted 1:10, the injection volume was 500µl and the combustion temperature 800°C, and a platinum catalyst was used.

As visible in Figure 5, the reproducibilities for a 5 way determination were excellent.

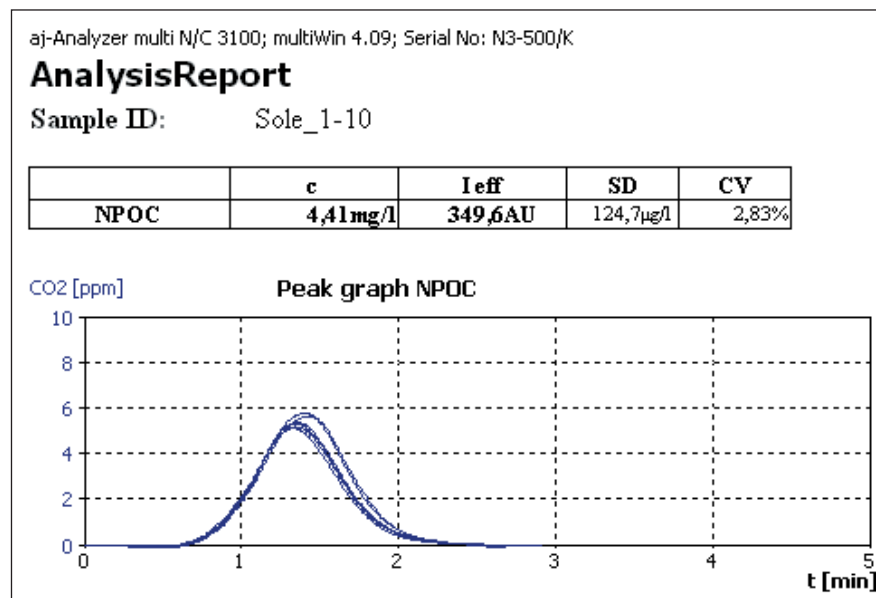


Figure 5. 5 way injection to check the purity of an ultrapure brine – results and curve shape

### Summary

The measuring devices of the multi N/C® series with their high flexibility and the robust design of the device components provide optimised application solutions for the thermocatalytic digestion of highly contaminated samples, with minimised device wear and notably extended operating times.

The analysers of the multi N/C® series by Analytik Jena AG can help you to increase the productivity in your laboratory significantly and reduce the operating costs accordingly.

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