



Challenge

Are the provided samples with high salt matrix (0.5 M of K_2SO_4 matrix) suitable for analysis on the multi N/C 2300 and multi N/C 3300?

Solution

Fast, safe and reproducible analysis with a high level of automation and very good long-term stability of the reactor filling

Determination of Soil Microbial Biomass by TOC/TN_b Measurement

Introduction

An important parameter in the site characterization of agricultural cultivation areas is the determination of microbial biomass in soils as well as dissolved organic matter (DOM), which are the basis of the diet of microorganisms. For this purpose, the soil samples are extracted by aqueous salt solutions according to DIN EN ISO 14240-2 "Determination of soil microbial biomass, Part 2: Fumigation-extraction method". The EOC (extractable organic carbon) or EN (extractable nitrogen) is determined by means of a NPOC/TN measurement according to DIN EN ISO 20236^[1].

For the determination of the microbial biomass, a second sample aliquot is fumigated according to the fumigation-extraction method with chloroform in order to lyse the microbial cells and thus to release the cell content, also making it available for the extraction. For this second step the extraction is conducted by means of salt solutions (typically used: 0.01 M $CaCl_2$, 0.025–0.5 M K_2SO_4 , 1 M KCl). From the difference calculation of the TOC/TN results of the fumigated and non-fumigated sample the soil content of microbial biomass can be determined. The focus of this application is the instrumental TOC/TN analysis of the obtained soil extracts and their particular challenges to the analysis system.

Materials and Methods

Samples and reagents

- Fumigation-extraction samples were received and stored in a refrigerator at 4 °C until analysis
- 2 M HCl was used for automatic sample acidification to a pH < 2

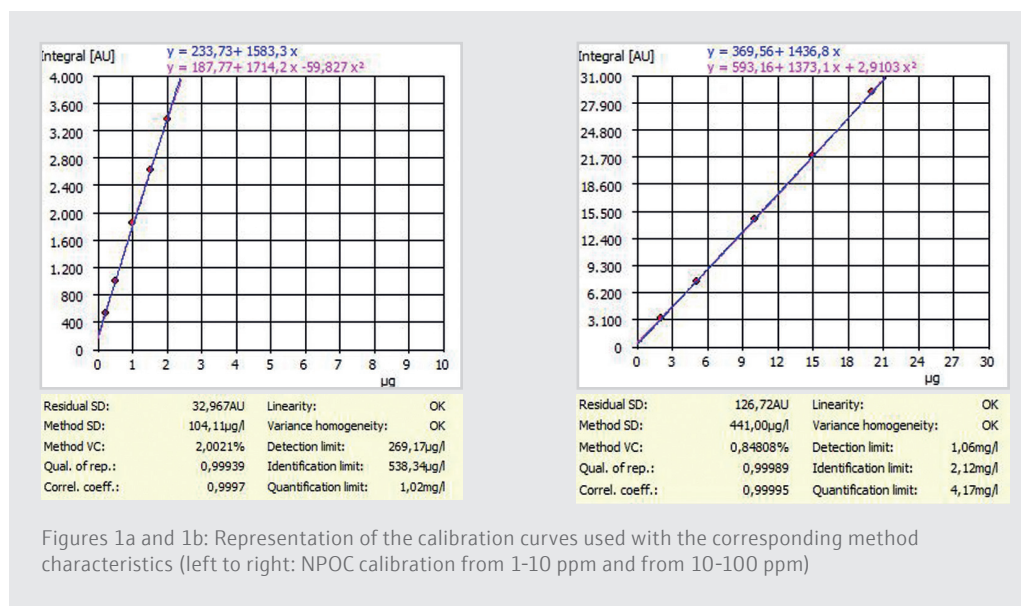
Sample preparation

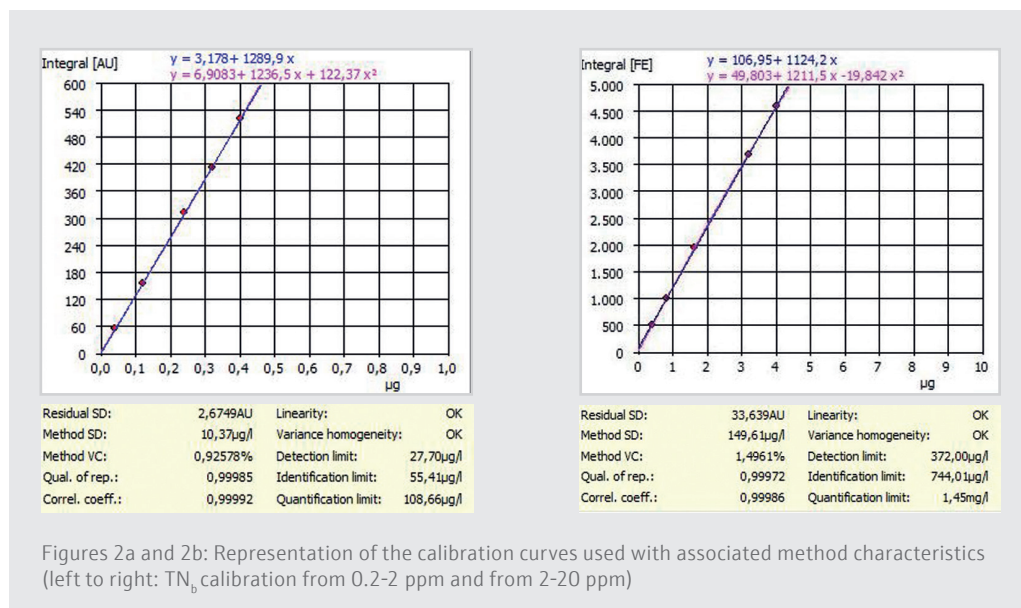
For measurement the samples were transferred into suitable autosampler vials. All samples were analyzed by NPOC/TN method. For this purpose, the pH was adjusted to < 2 by adding 2N HCl. This can be carried out manually during sample preparation / sampling or automatically by the autosampler. This pH provides the conversion of the inorganic carbon species (carbonates and bicarbonates) into CO₂, which is present in the sample in dissolved form. This CO₂ was automatically purged out by the autosampler with the aid of the used carrier gas and thus removed from the sample. Subsequently, a sample aliquot of 200 µL was injected directly into the combustion tube. The carbon compounds were completely oxidized to CO₂ at 800 °C by means of a platinum catalyst. The CO₂ was transported to the detector using a carrier gas stream. The quantification

was carried out with the aid of non-dispersive infrared spectroscopy in the focus radiation NDIR detector. The determination of the total bound nitrogen (TN_b) was performed simultaneously for each NPOC measurement. The NO gas generated by the catalytic combustion was transferred into a CLD (chemiluminescent detector) and evaluated there. Alternatively an electrochemical Detector (ChD) can be used for NO quantification.

Calibration

The NPOC/TN calibration was performed with mixed standards of different concentrations. For NPOC, the classical TOC calibration standard potassium hydrogen phthalate and for nitrogen a mixed standard consisting of ammonium sulfate and sodium nitrate was used. In the method the multiWin software can store up to three calibration ranges per parameter, which are automatically used to evaluate the measuring signals depending on the integrated peak area. Figures 1a–1b and 2a–2b summarize the individual calibration curves including the corresponding method characteristics..





Instrumentation

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

Table 1: Method settings

Parameter	multi N/C 2300, multi N/C 3300
Measurement parameters	NPOC/ TN
Digestion	High temperature digestion at 800 °C with platinum catalyst
Number of single repetitions	min. 4, max. 5
Rinse with sample before injection	3 times
Injektion volume	200 μL
Dilution	1:1

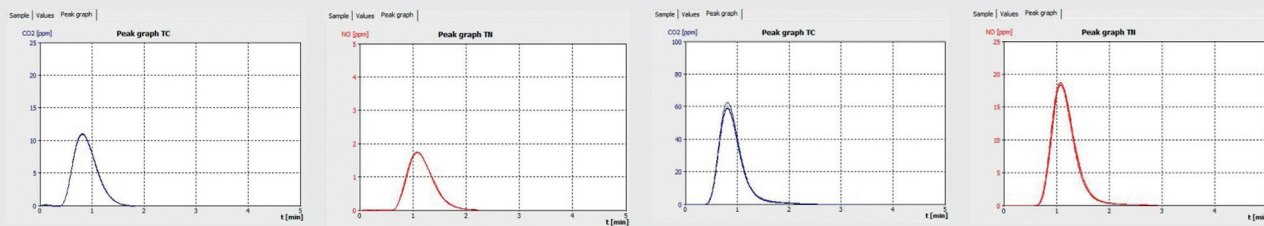
Results and Discussion

Two different customer samples were measured in an endurance test using the NPOC/TN method.

After each 5th sample, a vial containing ultrapure water was inserted into the sequence to reduce the salt deposits in the combustion tube by means of regular flushing. The measurement results are shown exemplified in Table 2. Examples for typical measuring curves are shown in Figures 3a–3d for both samples.

Table 2: Measurement results

Sample name	NPOC [mg/L]	NPOC RSD [%]	TN [mg/L]	TN RSD [%]
Sample 1	1.56	2.2	0.497	1.1
Sample 2	11.6	1.3	4.8	0.9



Figures 3a–3d: Typical curves for the parameters NPOC and TN of samples 1 and 2

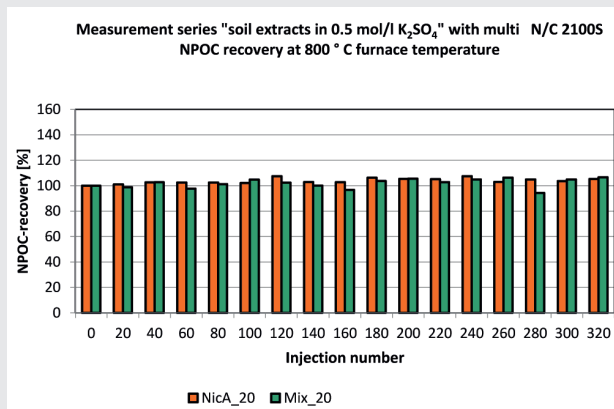


Figure 4: NPOC recovery comparing nicotinic acid to KHP/ NH₄/ NO₃ mixing standard over 320 injections

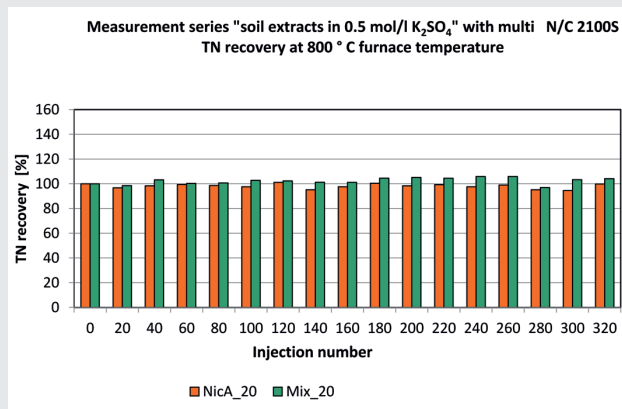


Figure 5: TN recovery comparing nicotinic acid to KHP/ NH₄/ NO₃ mixing standard over 320 injections

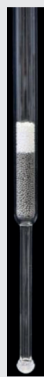


Figure 6a



Figure 6b



Figure 6c

Figure 6a: Newly filled combustion tube (high-temperature mat, Pt catalyst and Pt net)

Figure 6b: Combustion tube after 320 injections (salt deposits on the colder outlet part of the combustion tube)

Figure 6c: Deposits of salt crystals at the combustion tube outlet can be easily removed by immersion in water

The photos above illustrate the salt permeability of the combustion tube filling. Salt aerosols which are formed during the sample oxidation are transported through the combustion tube filling by aid of the carrier gas enriched with water vapor and then condensate at the colder outlet part of the combustion tube where they can then be easily removed. As a result, the blocking of the gas path by accumulating salt deposits in the combustion tube can be avoided and extended maintenance cycles can be achieved.

Summary

Both the long-term tests with customer samples as well as with the synthetically prepared spiked potassium sulfate solutions have shown a very good long-term stability and reproducibility of the measured values in the NPOC/TN analysis of soil extract samples. The used 16 mm quartz combustion tube shows a good throughput behavior for the injected salt load. The only maintenance after completion of the measured sample sequence is the replacement of the catalyst cover (high-temperature mat) and the washout of the salt crystals at the outlet part of the combustion tube.

Both, multi N/C 2300 and multi N/C 3300, are ideally suited for the required measurement task. The small amounts of catalyst and additional filling materials in the 16 mm combustion tube contribute significantly to the reduction of running costs for this basically challenging sample matrix.

Both analyzers can optionally be equipped with the chemiluminescence detector or chemodetector for simultaneous TN determination. The AS 60 and AS vario also offer powerful automatic sample homogenization, automatic acidification and purge of the TIC and a smooth and high sample throughput.

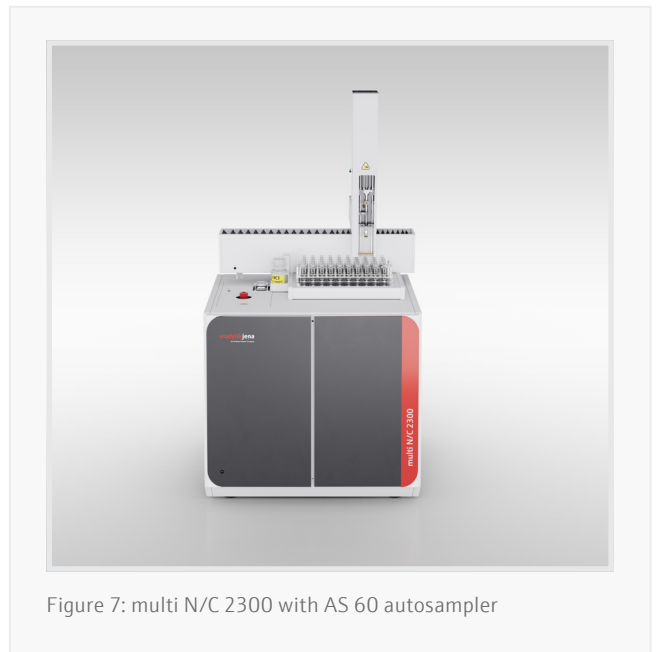


Figure 7: multi N/C 2300 with AS 60 autosampler

References

- [1] DIN EN ISO 20236:2023-04 „Water quality - Determination of total organic carbon (TOC), dissolved organic carbon (DOC), bound nitrogen (TN_b) and dissolved bound nitrogen (DN_b) after catalytic oxidative high-temperature combustion (ISO 20236:2018)“

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