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 ® 2100S and multi N/C ® 3100?

Solution

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

Determination of TOC/TN_b Content in Soils After Potassium Sulfate Extraction

Introduction

In the case of site characterization of cultivation areas in agriculture, an important parameter is the determination of microbial biomass in soils, as well as dissolved organic matter (DOM), which are the basis of the microorganisms' diet.

For this purpose, the soil samples are extracted by aqueous salt solutions, e.g. to improve the extractability of ammonium compounds.

The EOC (extractable organic carbon) or EN (extractable nitrogen) is determined by means of a NPOC/ TN measurement. However, in order to also extract/ determine the microbial biomass, a second sample aliquot is fumigated by chloroform-fumigation extraction (CFE) with chloroform in order to lyse the microbial cells and thus to release the cell content for making it extractable.

Also here, the extraction is concluded by means of salt solutions (typically used: 0.01 M $CaCl_2$, 0.025-0.5 M K_2SO_4, 1 M KCl) and 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.

In the further course of this application, the instrumental analysis of the obtained soil extracts and their particular challenges to the analysis system are the focus.

Instrumentation

Table 1: Analyzer specifications: multi N/C® 2100S and mutli N/C® 3100

Parameter	Specification Analyzer
Parameter	TC, TOC, NPOC, POC, TIC and TN_b
Norm	DIN EN 1484, DIN EN 12260
Detection	Focus Radiation NDIR, Chemolumineszenz Detection (CLD) or electrochemical detection (ChD)
Digestion	Thermocatalytic up to 950 ° C
Sample feeding	Direct injection/ flow injection
User confidence and comfort	multiWin® control and evaluation software, VITA® technology, self-check system, etc.
Measuring range	multi N/C® 2100S: Carbon: 50 ppb-30000 ppm, multi N/C® 3100 Carbon: 4 ppb-30000 ppm Nitrogen: 5 ppb-200 ppm (CLD) or 50 ppb-100 ppm (ChD)
Injection volume	multi N/C® 2100: 50- 500 µl multi N/C® 3100: 100-1000 µl
Measuring time	appr. 3-5 min
Autosampler	AS 60 (8 ml or 2 ml vials) or AS Vario (40 ml, 20 ml or 12 ml vials)
Gas supply	Oxygen 4.5 or better, alternatively: HC- and CO_2-free synthetic air

Method settings

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

Table 2: Method settings

Parameter	multi N/C® 2100S, multi N/C® 3100
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

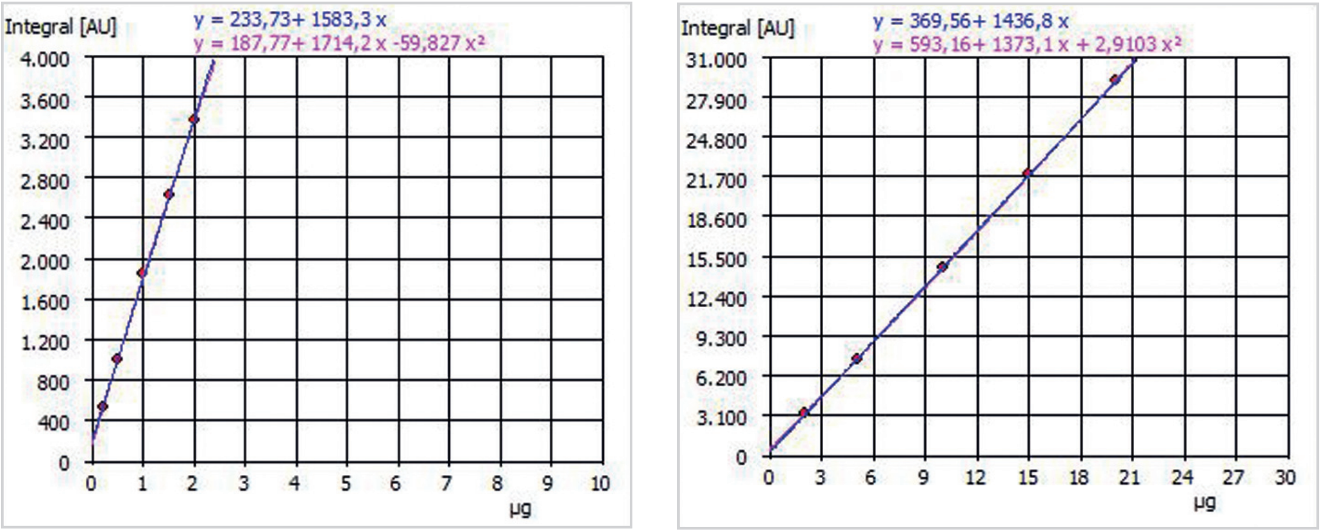
Samples and Reagents

The samples were stored in a refrigerator at 4 °C until analysis. For measurement these 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 CO_2, which is present in the sample in dissolved form. This CO_2 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 CO_2 at 800 ° C. by means of a platinum catalyst. The CO_2 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.

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 3 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 summarizes the individual calibration curves including the corresponding method characteristics.

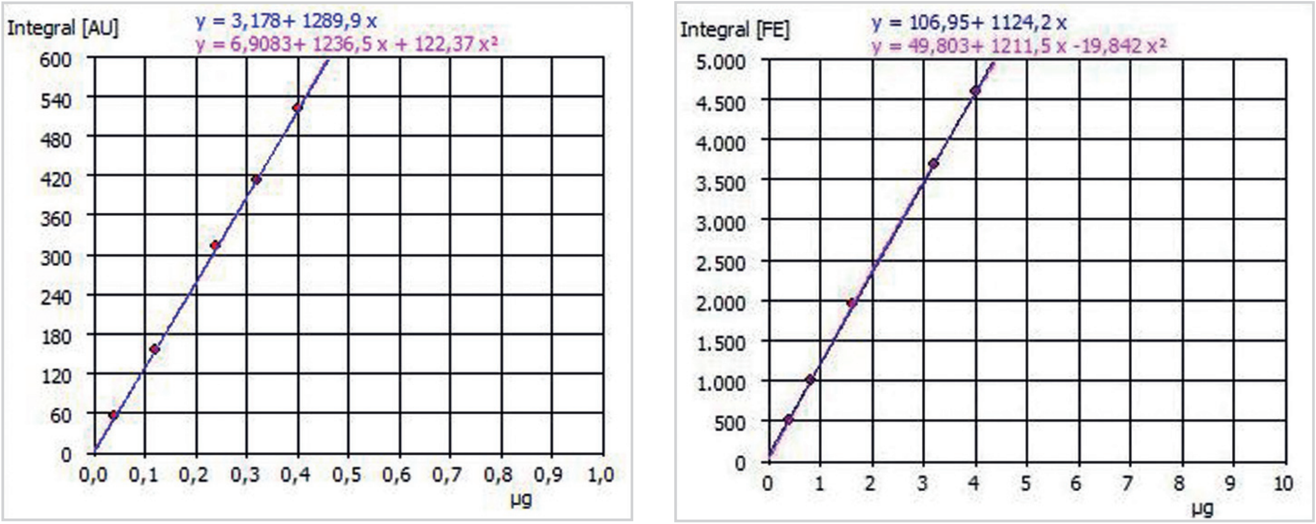
Calibration Currves



Residual SD:	32,967AU	Linearity:	OK
Method SD:	104,11µg/l	Variance homogeneity:	OK
Method VC:	2,0021%	Detection limit:	269,17µg/l
Qual. of rep.:	0,99939	Identification limit:	538,34µg/l
Correl. coeff.:	0,9997	Quantification limit:	1,02mg/l

Residual SD:	126,72AU	Linearity:	OK
Method SD:	441,00µg/l	Variance homogeneity:	OK
Method VC:	0,84808%	Detection limit:	1,06mg/l
Qual. of rep.:	0,99989	Identification limit:	2,12mg/l
Correl. coeff.:	0,99995	Quantification limit:	4,17mg/l

Figures 1a and 1b: Representation of the calibration curves used with the corresponding method characteristics (left to right: NPOC calibration from 1-10ppm and from 10-100ppm)



Residual SD:	2,6749AU	Linearity:	OK
Method SD:	10,37µg/l	Variance homogeneity:	OK
Method VC:	0,92578%	Detection limit:	27,70µg/l
Qual. of rep.:	0,99985	Identification limit:	55,41µg/l
Correl. coeff.:	0,99992	Quantification limit:	108,66µg/l

Residual SD:	33,639AU	Linearity:	OK
Method SD:	149,61µg/l	Variance homogeneity:	OK
Method VC:	1,4961%	Detection limit:	372,00µg/l
Qual. of rep.:	0,99972	Identification limit:	744,01µg/l
Correl. coeff.:	0,99986	Quantification limit:	1,45mg/l

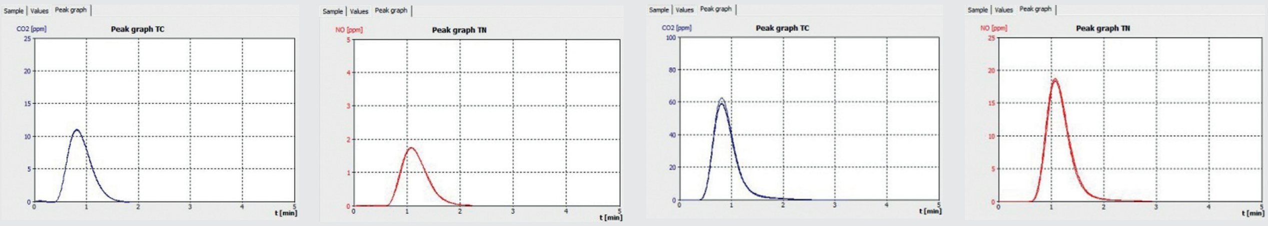
Figures 2a and 2b: Representation of the calibration curves used with associated method characteristics (left to right: TN$_b$ calibration from 0.2-2 ppm and from 2-20 ppm)

Results and Discussions

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 3. Examples for typical measuring curves are shown in Figures 3a-3d for both samples.

Table 3: 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

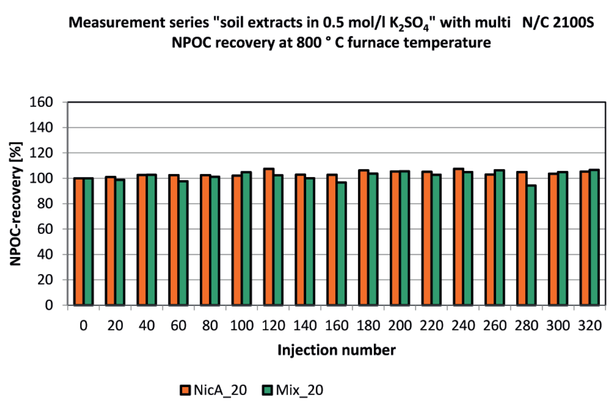


Figure 4: NPOC recovery comparing nicotinic acid to KHP/ NH_4/ NO_3 mixing standard over 320 injections

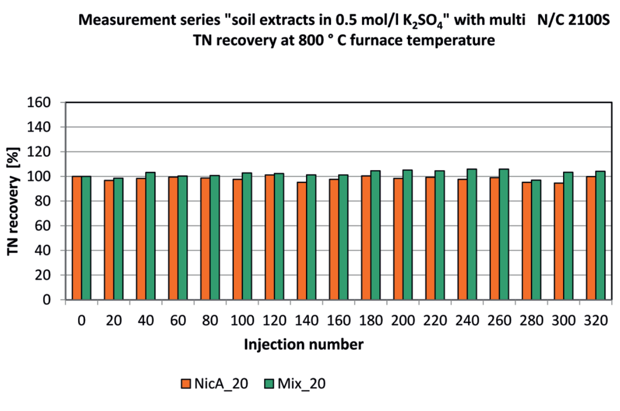


Figure 5: TN recovery comparing nicotinic acid to KHP/ NH_4/ NO_3 mixing standard over 320 injections

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. Saltaerosols, which are formed during the sample oxidation, are transported through the combustion gas charge enriched with water vapor, 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.

Conclusion

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® 2100S and multi N/C® 3100, 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 autosamplers for automatic sample homogenization, automatic acidification and purge of the TIC and a smooth and high sample throughput.

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