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Application News

Total Organic Carbon Analyzer TOC-LCPH and SSM-5000A

Total Organic Carbon in Soil: A Comparison between Solid Sample Combustion and Suspension Methods

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User Benefits

- High Suspension Kit to improve precision of injection.
- External Sparging Kit to reduce analysis time.

■ Introduction

An important parameter for the environmental status estimation of terrestrial and aquatic ecosystem is the total organic carbon (TOC) content in soils and sediments. The soil and sediments organic carbon are mainly derived by decomposition of the plants and animals or plankton or anthropogenic sources such as chemical contaminants, fertilizers or organic rich waste. The organic carbon concentrations in sediments and soils also correlate very well with organic contaminants and for this reason can be used to estimate the level of contamination and toxicity [1].

The established regulations to determine TOC in solid samples is known as the Solid Sample Combustion (SSC) method. Here, a weighed solid sample is combusted in a stream of air or oxygen [2] to produce carbon dioxide which is then detected and quantified using a calibration curve. The Shimadzu TOC solid sample measurement system has been used to evaluate the differences in the total carbon content in soil and compost without extraction or other pretreatment procedures [3]. However, the inhomogeneity of the soils has a direct effect on the results as each weighed solid sample can only be combusted once. This method is also labour-intensive and time-consuming.

Another established regulation is the Suspension (SP) method [2] where the soil sample is suspended in diluted acid solution to break down carbonate compounds and homogenized to produce small soil particles. This method is simpler and enables the possibility of statistically reliable multiple injections within a single sample batch [4].

This application news compares the results obtained using both the SSC and SP methods.

■ Experimental

The soil samples, AgroMAT-Clay Soil (AG-1) and AgroMAT-Sandy Soil (AG-2) were from SCP Science, Canada. The chemical reagents were purchased from Merck, Germany. Type E-1 ultra-pure water (Milli-Q® Millipore system, Germany) was used in this analysis.

Solid Sample Combustion (SSC) Method

The soil samples were used without further pre-treatment since the samples were dried and less than 200 mesh size. The NPOC method was used where the sample was mixed with 2 M HCl in a ceramic sample boat before measurement (Figure 1). The measurement conditions are shown in Table 1.

Table 1 Instrument and Analytical Conditions for SSC Method

Instruments	: TOC-LCSH TOC analyzer and SSM-5000A solid sample combustion unit
Cell length	: Short cell
SSM Carrier Gas	: Oxygen, 500 mL/min
Oxidation Method	: Cobalt Oxide/Platinum catalytic combustion, 980 °C
Method	: NPOC
Calibration Curve	: 2 % TC standard solution prepared from Glucose ($C_6H_{12}O_6$)

Suspension (SP) Method

The soil suspension was prepared as in BS EN 15936 [2]. About 200 mg of soil sample was placed in a 250 mL Erlenmeyer/conical flask and mixed with 200 mL of 0.22 M HCl gradually to form a suspension. The suspension was dispersed and homogenized using a T 18 digital ULTRA-TURRAX® (IKA Works, USA) dispersion device for 3 minutes at 18,000 rpm. The TOC-LCSH (Figure 1) measurement conditions are shown in Table 2. The suspension was stirred with magnetic stirrer during TOC measurement.

Table 2 Instrument and Analytical Conditions for SP Method

Instruments	: TOC-LCSH TOC analyzer
Accessory	: High Suspension Kit (High Conc TC) External Sparging Kit
Oxidation Method	: Standard Platinum catalyst, combustion, 680 °C
Method	: NPOC
Calibration Curve	: 2-20 mg/L NPOC standard solution prepared from Potassium Hydrogen Phthalate ($C_8H_5KO_4$)

Fig. 1 TOC-LCSH TOC analyzer (left) and SSM-5000A solid sample combustion unit (right)

■ High Suspension Kit

The TOC-L series could be used to measure solid suspension with good precision. However, in some samples, the suspended solids are heavy and can precipitate over time in the syringe of the TOC instrument. Hence, the measured sample concentration would not be uniform. The precipitated samples can also contaminate the syringe and plunger, resulting in carryover to the next sample. The High Suspension Kit minimizes the effect of the precipitation of suspended solids through a different sampling sequence and injection motion so that high precision measurements could be carried out (Figure 2). This makes it possible to measure samples that contains suspended solids with high sedimentation rates.

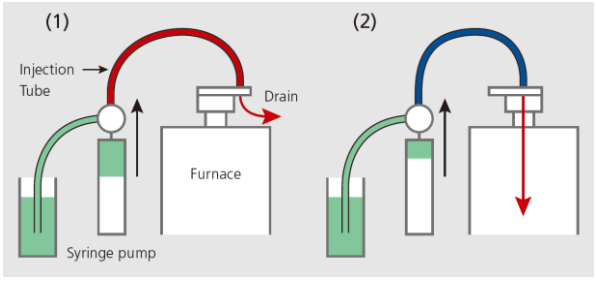

Fig. 2 Measurement Sequence of High Suspension Kit [5]

Step (1) - The sample is pushed out of the injection tube immediately after being transferred to the syringe. The injection tube is rinsed and filled with a highly suspended sample (red flowline).

Step (2) - The injection slider is moved to the injection position and the sample is injected using the syringe pump. The injection volume is adjusted exactly to the inner volume of the injection tube (blue flowline). This sequence enables precise injection of the entire sample in the injection tube to the furnace.

The High Suspension Kit has been used to measure microscopic algae biomass suspensions with high precision results [6]. To determine if the High Suspension Kit could be used to measure soil suspension accurately, the same soil samples were also measured with the more established SSC system.

■ Results and Discussion

Both the calibration curves used in the SSC and SP methods have good linearity as shown in Figures 3 and 4.

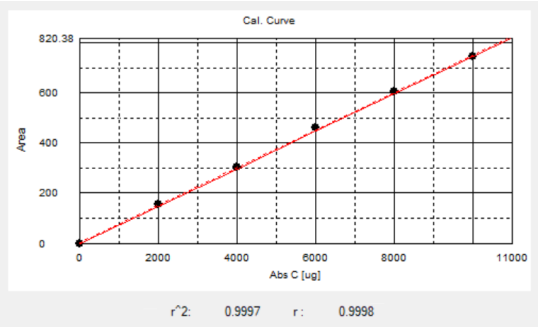

Fig. 3 Calibration Curve for SSC Method

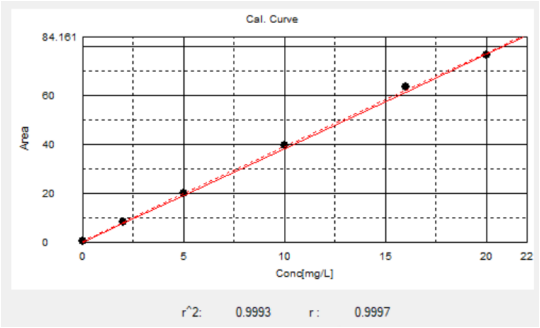

Fig. 4 Calibration Curve for SP Method

The TOC content for the soil samples measured with SSC and SP Methods are summarized in Table 3.

Table 3 TOC Content Results in Soil Samples with SSC and SP Methods

Sample	TOC Content with SSC Method (A)	TOC Content with SP Method (B)	% Difference between SSC and SP Methods (B/A x 100 %)
AgroMAT-Clay Soil (AG-1)	1.074 % wt (1.22 % RSD for 3 repetitions)	1.083 % wt (1.02 % RSD for 4 repetitions)	100.8 %
AgroMAT-Sandy Soil (AG-2)	1.446 % wt (0.46 % RSD for 3 repetitions)	1.493 % wt (0.73 % RSD for 4 repetitions)	103.3 %

The TOC results measured with SSC and SP Methods are comparable as the percentage difference between these two methods was less than 5 %. With the High Suspension Kit, good precision was achieved in the SP method as the precision was less than 2 % RSD.

■ Conclusion

The High Suspension Kit can be used to measure soil suspensions with heavy particles using SP method. Good precision was obtained, and the results were comparable with the SSC method. With autosampler, the analysis can also be automated, unlike the SSC method.

■ References

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