

A new and powerful analytical technique combining the Thermalox TOC/TN analyser with Sercon's 20-20 Isotope Mass Spectrometer to provide a powerful new method for the stable isotope analysis of dissolved organic carbon in soil solutions and environmental water samples.

TOC-IRMS

Existing Methods

Automated systems for analysis of ^{13}C DOC have previously been developed which couple commercially available wet chemical TOC instruments with a continuous-flow IRMS. These automated systems have been used successfully to determine the ^{13}C / ^{12}C isotope ratio of DOC and DIC in freshwater samples and of DOC in marine water samples. However their suitability for soil solution samples and leachates has not been examined or reported.

The drawback of the wet chemical DOC method is that oxidation is not completely efficient and can become incomplete with samples contain high concentrations of more refractory organic carbon such as humic and fulvic acids. In addition relatively large sample volumes are required.

For TOC analysis of environmental samples containing materials which are difficult to oxidise, the much preferred method is to use high temperature catalytic oxidation (HTC) to completely convert all of the carbon present to CO_2 .

Attempts have previously been made to use an HTC TOC analyser. Two published attempts are firstly Lang et al, who measured the ^{13}C of seawater's DOC with an error of $\pm 0.8\%$. However, this technique was not completely automated and quite time consuming due to the necessity of many rinses to minimise the errors.

Secondly Panetta et al. also used an HTC TOC instrument with an IRMS. With their set-up, samples could be analyzed with a ^{13}C DOC accuracy of $<0.2\%$ and precision of $<0.3\%$; but the analysis of one sample, rinsing included, required an aliquot of around 7 mL.

Also both systems were specifically set-up for the analysis of marine and freshwater samples with DOC concentrations at natural abundance levels.

Our Method

Before starting the analysis, inorganic carbon is removed from the samples by acid sparging. The sample is injected in the TC reactor, which is filled with Pt catalyst and heated at 680°C . The He/O_2 carrier gas flows through the reactors and sweeps the CO_2 resulting from the sample combustion to an NDIR CO_2 detector. The effluent of the TOC instrument flows to the Sercon CRYOPREP interface. The gas stream is first cryogenically trapped by immersing the flow path in liquid N_2 . The CO_2 will condense while He and O_2 will flow away to vent. Once the CO_2 has been effectively

trapped from the sample, the CO_2 is transferred through a GC column in order to separate CO_2 from N_2O to the Sercon 20-20 IRMS.

The analysis of one sample, pulse of monitoring gas included, takes around 25 minutes in total, but the entire procedure is completely automated.

System Blank

Previously the main drawback of working with HTC TOC analyzers is the contribution of a significant blank which is the result of an instrument/system blank and a blank caused by the reagents used. However, blank correction seemed not to be necessary for samples exceeding 7 mg/L C with our method.

The contribution of the blank in our hyphenated set-up was measured directly. For sample volumes of 160 μL , the system blank accounted for 0.21 μg C and the dissolved CO_2 and carbon in the milliQ water for an extra 0.08 μg C.

Tracer Experiments

Dissolved Organic Matter (DOM) plays an important role in soil genesis and in the transport of soil pollutants with a high affinity for organic matter. The origin and dynamics of organic carbon in soil are frequently studied with tracer experiments. In ^{13}C tracer experiments at natural abundance level as well as with enriched samples, the ^{13}C / ^{12}C ratios of soil organic carbon and CO_2 have been measured routinely. However a direct analysis of the ^{13}C / ^{12}C isotope ratio in the DOC of a soil solution has remained more elusive until now. In a ^{13}C tracer experiment, we observed that mixing plant residues with soil caused a release of plant derived DOC, which was degraded or sorbed during incubation. Based on these results, we are confident that this approach can become a relatively simple alternative method for ^{13}C / ^{12}C ratio analysis of DOC in soil solutions.

Conclusion

Based on the results of the performance tests, we concluded that ^{13}C / ^{12}C ratios of TOC in solutions with concentrations ranging from 1 to 100 mg/L C could be measured with an acceptable precision and accuracy. Within this range, the system showed good linearity and the overall standard deviation between the measurements was 0.4‰. Carry-over, which is known to be a problem in dry combustion systems, was tested for natural abundance as well as enriched samples and no significant memory-effect was observed.

Performance Specification

Cycle time	Typically 25 minutes including acid sparging to remove TIC
Lower detection limit	Better than 1.0 mg/l C
Upper detection limit	More than 1,000 mg/l C
Accuracy	Better than 0.4%
Repeatability	Standard deviation: $\leq 2\%$ of full scale

