

## A breakthrough in detection limits for $\delta^{13}\text{C}_{\text{DOC}}$ measurements of surface waters using thermal oxidation

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A system has been developed for stable isotope analysis of very low concentrations of dissolved organic carbon (DOC) in soil solutions using a catalytic combustion TOC analyser hyphenated with an isotope ratio mass spectrometer using a cryofocussing interface. This collaborative project between Purdue University, Thermalox and Sercon has allowed, for the first time, sub ppm measurements on water containing

refractory forms of carbon such as humic and fulvic acid. The system consists of a catalytic combustion TOC analyser (Thermalox TOC-TN, Analytical Sciences Ltd., UK) which converts DOC to  $\text{CO}_2$  via thermal oxidation, a cryo-trapping device (Cryoprep system, Sercon Ltd., UK) which traps the  $\text{CO}_2$  from the effluent gas stream of the TOC analyser, and a continuous-flow IRMS (20-20, Sercon Ltd., UK) which gives the isotopic ratio of DOC in the sample.

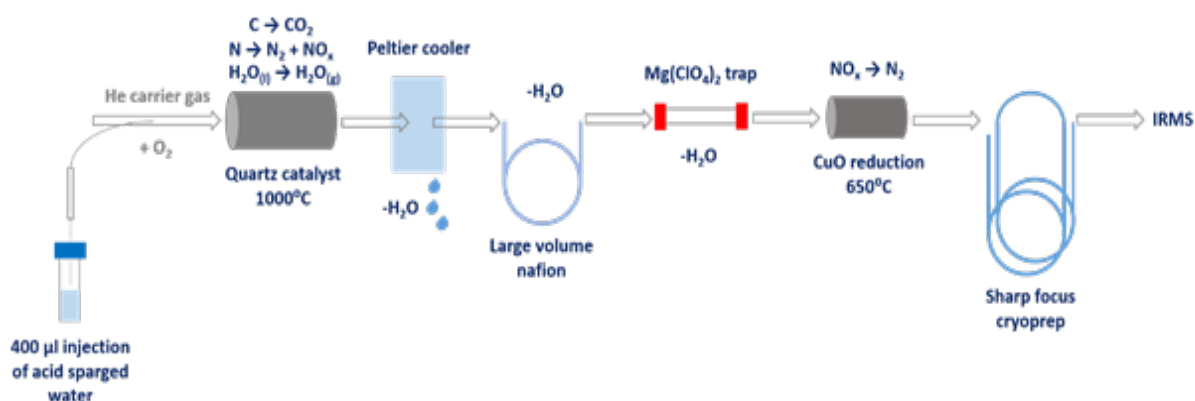


Catalytical combustion is the preferred method of oxidation of DOC to CO<sub>2</sub> when refractory forms of organic carbon such as humic and fulvic acids are the predominant dissolved carbon components, as found in waters from soils and peat. Refractory forms of carbon are difficult to oxidise via chemical oxidation of DOC which is routinely used for this type of analysis. Chemical oxidation techniques have traditionally shown higher sensitivity at low levels due to the large sample volumes which can be analysed, however recent modifications to our system have allowed us to get good precision (0.3‰) down to sub 1ppm C, the first time such measurements have been possible.

Before starting the analysis, inorganic carbon is removed from the samples by acid sparging. 400 µl of water is injected into the TOC and is carried through a high temperature combustion furnace by a mixture of helium and oxygen; water vapour and CO<sub>2</sub> are produced in the presence of a quartz catalyst, specially designed to give a low blank. The water vapour is removed via a condenser, a large volume nafion and finally a magnesium perchlorate trap. NO<sub>x</sub> is converted to N<sub>2</sub> in a reduction furnace. The CO<sub>2</sub> passes through an IR detector in the TOC, is cryogenically trapped in the modified "sharp focus" cryoprep and then transferred into the IRMS for δ<sup>13</sup>C analysis.

A schematic of the system is shown below and represents the TOCprep which is now available from Sercon. The TOCprep is a cryoprep system which has been specifically

designed for use as a TOC-IRMS interface for measurements of low concentrations of refractory carbon. With the same set-up δ<sup>13</sup>C ratios of TC and TIC can also be determined.

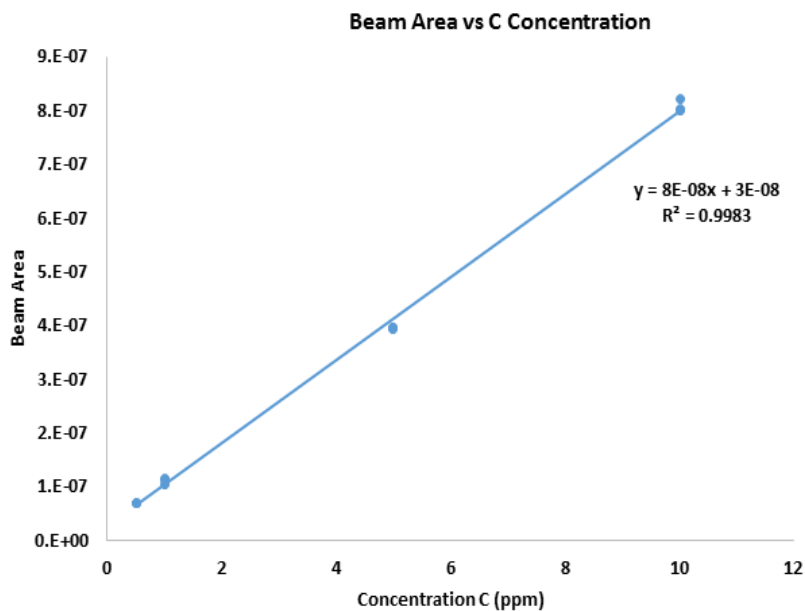


## Results

Data shown in table 1 shows the linear response of concentration to IRMS beam area, the <0.5ppm blank and the small change in δ<sup>13</sup>C across a range of concentrations.



Name	Conc (ppm)	Beam Area	$\delta^{13}\text{C}$ (SMOW)
BLANK_DI	0	3.60E-08	-22.5
BLANK_DI	0	3.90E-08	-23.1
BLANK_DI	0	3.90E-08	-24.5
BLANK_DI	0	3.00E-08	-27
BLANK_DI	0	3.20E-08	-26.5
BLANK_DI	0	3.30E-08	-26.1
Beet Sucrose 10ppm	10	8.00E-07	-21.0
Beet Sucrose 10ppm	10	8.00E-07	-21.2
Beet Sucrose 10ppm	10	8.20E-07	-21.3
Beet Sucrose 5ppm	5	3.90E-07	-21.7
Beet Sucrose 5ppm	5	4.00E-07	-21.7
Beet Sucrose 5ppm	5	4.00E-07	-21.6
Beet Sucrose 1ppm	1	1.00E-07	-20.7
Beet Sucrose 1ppm	1	1.10E-07	-20.4
Beet Sucrose 1ppm	1	1.10E-07	-20.1
Beet Sucrose 0_5ppm	0.5	6.90E-08	-20.8
Beet Sucrose 0_5ppm	0.5	7.10E-08	-20.3
Beet Sucrose 0_5ppm	0.5	6.90E-08	-19.7
BLANK_DI	0	4.40E-08	-18.7
BLANK_DI	0	4.60E-08	-18.2
BLANK_DI	0	4.60E-08	-18.0



This is a collaborative project between Purdue University, Thermalox and Sercon. All enquiries regarding this new system should be directed to [sales@sercongroup.com](mailto:sales@sercongroup.com)

