Thermalox™ TOC-TN

The modern alternative to COD and TKN

Thermal oxidation with unrivalled sensitivity

Aqueous matrices with a solids option

TOC, TC, TIC, NPOC, POC, TN_b

Total Organic Carbon: Total Carbon: Total Inorganic Carbon: Non-purgeable Organic Carbon: Purgeable Organic Carbon: Total Nitrogen

Total Organic Carbon, Total Nitrogen

Total Recovery

analytical sciences

Measuring Total Organic Carbon – methods – drawbacks – advantages

TOC (Total Organic Carbon) is a measurement widely used in a number of industries to assess the organic contamination of water. In wastewater TOC concentrations of many thousands of ppm are often found. At the other extreme, low ppb TOC levels must be measured in the Ultra-Pure water used by Pharmaceutical, Semiconductor and the Power Generation industries.

The basic techniques used to determine TOC are well established and suitable analytical equipment has been commercially available since the 60's. Essentially, the total carbon (TC) of a water sample is measured by oxidising all the carbon species to carbon dioxide (CO_2). The resulting CO_2 is then detected using well understood analytical techniques, including Non-dispersive Infrared.

The inorganic carbon in the sample (carbonate and bicarbonate) is either removed prior to the TC measurement, or the inorganic carbon is measured separately and this value is subtracted from the TC value to give TOC.

Various oxidation techniques are used. Firstly, chemical oxidation using a strong oxidising reagent such as TiO_3 or a persulfate. Oxidation may only be partial, so care should be exercised with samples containing particulate or difficult to oxidise materials. This method is therefore generally unsuitable for high level samples, such as wastewater.

A second method improves upon the wet chemical method by irradiating the sample with ultra-violet light after adding an oxidant such as persulfate. Photolysis of the persulfate and sample produces hydroxyl radicals and other strong oxidising agents which react with the organic carbon to produce CO_2.

This technique is widely used and offers precision and some advantages at very low levels. However it is now accepted that the oxidation of particulate and many commonly occurring organics is quite poor. Indeed the EN1484 standard for TOC specifically cautions against it where humic material or particulate need to be measured (In other words where you have to measure TOC as opposed to DOC).

The third technique, developed by Dow Chemicals in the 60's relies on introducing the sample into a furnace in the presence of a catalyst and oxygen. Thermal oxidation of the carbon produces CO_2. The method does not suffer from any of the incomplete oxidation problems of the methods previously described. However the furnace and catalyst can introduce contamination and because steam is produced this limits the flow of sample that can be introduced, restricting the detection limit of the method.

With all the methods described the CO_2 product is generally measured as a gas using a Non-dispersive Infrared detector. Although the technique is very accurate and selective, sensitivity is very much a function of cost and most vendors will compromise by trying to process larger amounts of sample to produce more CO_2. Inevitably larger sample volumes reduce catalyst life, slow down the analysis and challenge the oxidation.

At very low levels where the carbon oxidant will stay in solution as carbonate the carbon concentration can be determined by measuring the CO_3^{2-} ion, using selective conductivity methods. The major problem here is making the conductivity detector selective to carbonate. However, conductivity is a very sensitive technique and therefore capable of determining PPT levels.

The Thermalox employs the thermal catalytic oxidation technique to give near perfect oxidation, but combines this with the most sensitive detector manufactured anywhere in the world

Oxidation Method	Advantages	Disadvantages
Wet Chemical	**Inexpensive and robust.**	**Inefficient oxidation. Poor with particulate or hard to oxidise compounds. Slow. Only for low levels**
UV Persulfate	**Good Precision, Low detection limits. Ideal for DOC in pure waters.**	**Better than wet chemical, but still not good with particulate or humic material (i.e. natural waters)**
Thermal Catalytic Oxidation	**Near perfect recovery (oxidation). Fast.**	**Higher ownership costs. Trace catalyst contamination means sensitivity is compromised**

Thermalox™

TOC/TN_b

Why choose the Thermalox over other thermal oxidation systems?

Analytical Sciences has made important advances in its techniques for measuring TOC and TN_b. Working with one of the world's leading NDIR analyser manufacturers, it has dramatically increased the sensitivity of its CO_2 detector. The Thermalox detector is now over ***twenty times*** more sensitive than its leading rival.

In addition, the furnace has been constructed to virtually eliminate trace carbon contamination within the reactor and catalyst, without compromising catalyst efficiency.

This allows lower injection volumes to be used leading to less catalyst contamination, more accuracy and faster measurements. It also provides a dramatic improvement in the detection limit for this method.

Some manufacturers use Pt coated quartz wool for low level work. This is fine with DI water, but rapidly blinds in natural waters. Other manufacturers' attempts to lower detection limits and increase the accuracy of their TOC and TN_b thermal oxidation analysers have centred on using larger injection volumes.

However this slows down measurements and shortens the operating life of the catalyst, particularly if contaminants – salts, for example, are present in the samples.

Our NO_x detector employs a number of features to ensure excellent sensitivity and stability. As well as heating the reaction under vacuum, we utilise an innovative $NO_x \rightarrow NO$ reduction furnace that remains efficient over an extended life. We use electronic vacuum flow control to maintain stable conditions inside the reactor. For safe operation of the detector, ozone is catalytically decomposed before any gases are vented

Another of the many benefits of using sensitive detectors is the long term stability of the calibration, which is exceptional.

With these improvements, the sophisticated but user-friendly software and excellent build quality, the THERMALOX™ Environmental has become recognized as probably the most cost-effective, powerful and robust tool for the analysis of TOC and TN_b anywhere in the world.

The Thermalox tolerates salts and suspended material without sacrificing detection limits

- Catalytic thermal oxidation. The only way to measure 'real' samples containing particulate or difficult to oxidise materials
- Standard Deviation better than 20ppb on low level Carbon
- Standard Deviation better than 10ppb on low level Nitrogen
- Upper Range Limit greater than 50,000ppm for TOC
- Detection Limit of better than 40ppb for TOC and 10ppb for TN_b
- Analysis time less than two minutes per replicate
- Complete recovery, including Suspended Solid fraction
- Handles salts and particulate easily
- Holds up to 88 samples
- Complete washing between samples ensures no carry over
- Totally software driven from a Windows™ based platform
- Automatic preparation of calibration standards

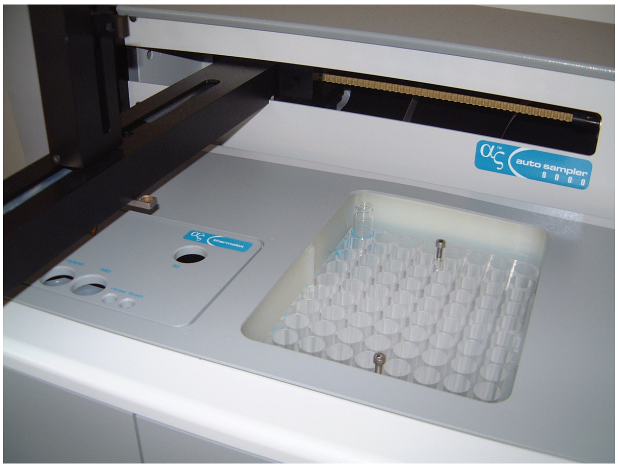
Remember – you can have stand alone TOC, stand alone TN_b or combination TOC/TN_b

The Thermalox is so well automated that you can mix high and low level samples on the same vial rack

Thermalox™

TOC/TN$_b$

The Thermalox™ Environmental is equipped, as standard, with features many manufacturers treat as extras – and you can measure solids

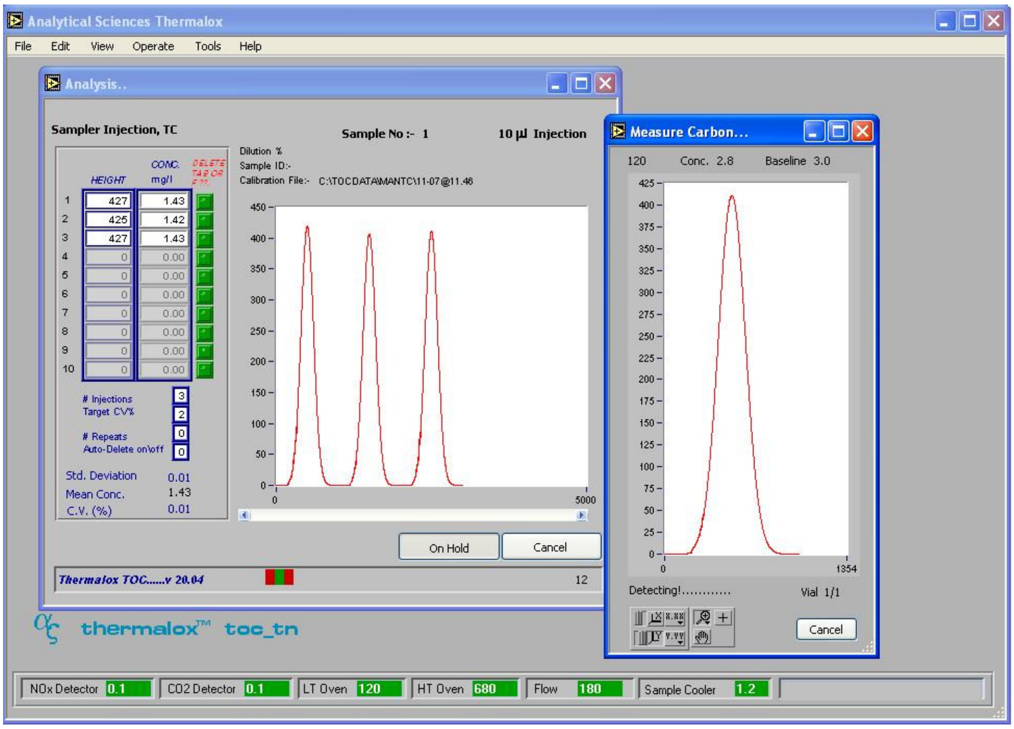


The Thermalox instruments utilize our Model 8000 XYZ autosampler. This gives maximum flexibility and allows a high degree of automation. Calibrants can be made up automatically; sparging, dilutions and sample agitation can easily be carried out.

The standard vial rack holds up to 88 glass or disposable plastic vials, with or without lids. It can be chilled and we are happy to provide racks to suit special requirements.

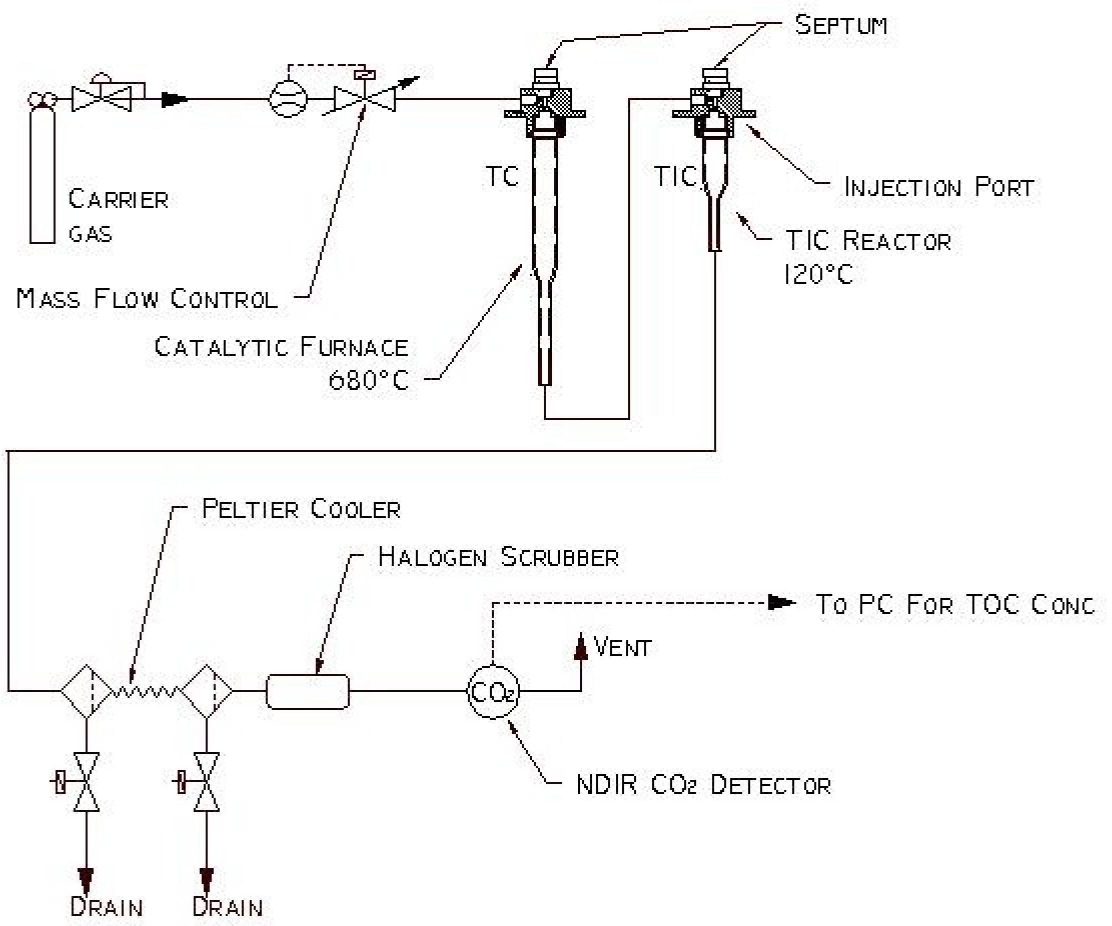
By using a special aspiration step, samples containing particulate can be automatically agitated, ensuring that a representative sample aliquot is aspirated from the vial.

- Both TOC by subtraction and by pre-stripping of inorganic carbon methods are fitted as standard
- Carrier gas generation fitted as standard on TOC – no need for bottled gases
- Automatically prepares its own calibrants – eliminates human error
- Peltier cooler for condensate removal - no desiccants
- Precise electronic mass flow control of the carrier gas – stable calibrations
- Highly sensitive detectors – prolongs catalyst life, lowers detection limit
- Stand-by Mode - limits carrier gas consumption and prolongs oven life
- Specially manufactured Carbon-free catalysis - virtually no blank carbon peak
- Direct Injection method - eliminates blockage or carryover contamination
- Options for adding the measurement of solids and sample sonication



Windows Platform software.

- Easy to learn
- Easy to use
- Secure
- Robust
- Tailored to suit you



Analysis begins by loading samples into a vial rack. The AS8000 XYZ autosampler handles up to 88 vials.

A sample aliquot from 3µl to 150µl is injected into the TC furnace through a special carbon free septum. CO_2 free Carrier gas sweeps the oxidant through to the CO_2 detector. Concentration is monitored by a PC and a characteristic asymmetric peak is plotted, the area of which is proportional to the CO_2 product of the oxidation. By calibration, TC is then determined from this peak area.

The inorganic carbon, carbonates, bicarbonates and dissolved CO_2 are either stripped from the sample prior to the TC measurement, or this fraction is measured separately by introducing an aliquot of sample into the TIC reactor. This reactor contains phosphoric acid heated to 120°C which reacts with the carbonate to form CO_2.

This is swept to the CO_2 detector and measured in the same way as the TC fraction. Both of these methods, TOC by difference and TOC by acid stripping (sometimes known as NPOC – non purgeable organic carbon) are available on the Thermalox Instrument as standard.

The disadvantage of the difference method is that if most of the carbon present is inorganic, the inaccuracy of the difference value, TC-TIC, will be too large.

The disadvantage of the acid stripping method is that there is a risk of stripping out purgeable organic material and at low levels contaminating the sample.

To handle samples with high levels of suspended solids, such as effluents, large bore needles – up to 1.0mm - may be fitted to the autosampler.

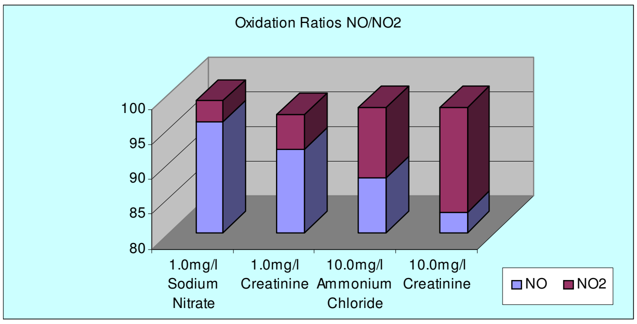
Thermalox™

Nitrogen

Total Nitrogen (TN) determination may be added to the Thermalox TOC analyser to give TOC and TN measurements from the same vial. We also manufacture the Thermalox TN_b analyser where only this analyte is required.

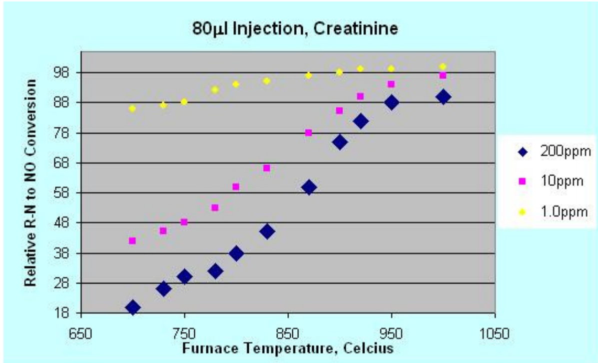
In the same way as TC measurements are performed, a sample aliquot is injected into a catalytic furnace. Carrier gas (oxygen) sweeps the oxidant, in this case NO_x gases, through to the NO_x detector.

The detector utilizes the chemiluminescent reaction between NO and O_3 to determine the NO concentration. Because NO_2 is also present as an oxidant, this is reduced in a special reduction furnace to NO – a step many of our competitors omit. The importance of this reduction step is illustrated by the different NO/NO_2 splits of the various compounds shown below.



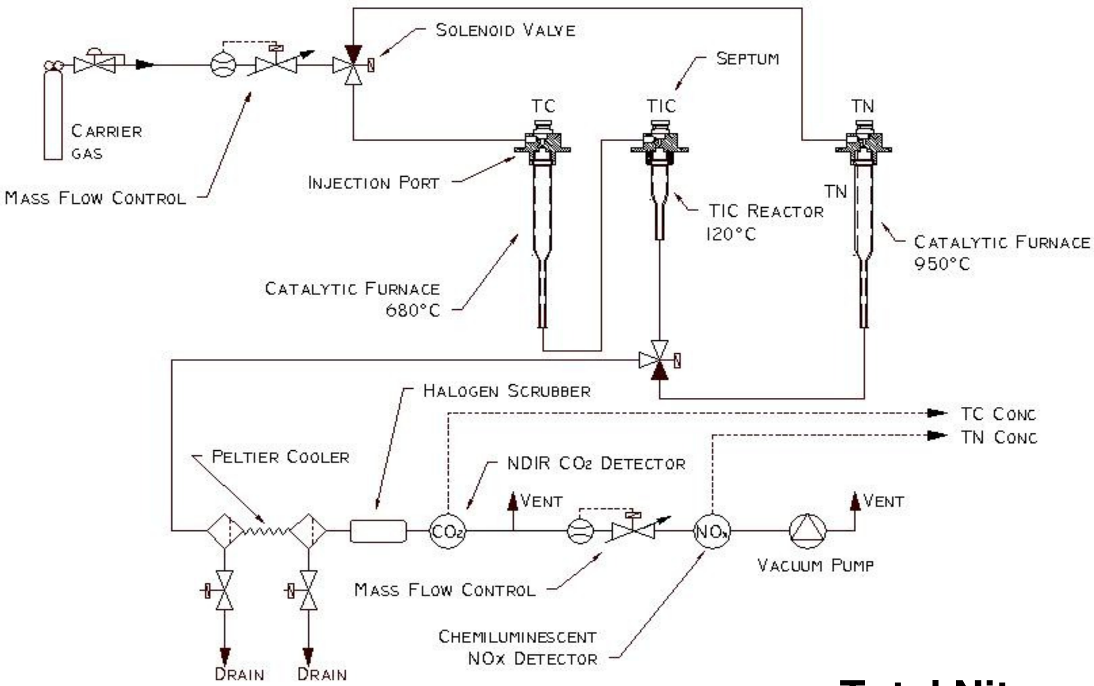
Unlike most vendors, our chemiluminescent reaction is performed under vacuum in a heated chamber. This gives the Thermalox TN analyser its remarkable sensitivity; at least an order of magnitude more than its main rivals.

The NO concentration is monitored by the PC controller and a characteristic asymmetric peak is plotted, the area of which is proportional to the NO_x product of the decomposition. By calibration, TN_b is determined from this peak area. As can be seen from the graph below, temperature, concentration and injection volume have a critical effect on the conversion of R-N to NO.



For most applications the TC catalytic furnace can be modified to allow it to perform both the TC and TN decompositions. However for higher level TN applications – up to 200mg/l – or highly particulated samples, a specialised TN oven is added.

This oven runs at up to 1000°C and has a larger internal volume and special catalyst. This overcomes the quenching effects experienced on many TN applications where larger sample volumes are needed or higher concentrations of TN are measured - for example effluent samples. Large bore needles may be used to aspirate particulated samples representatively.



Total Nitrogen

Total Recovery

Thermalox™

TOC/TN$_b$

Rangeability…

Calibration – from two to 7 points may be automatically defined in the method set-up. The software then uses regression mathematics to generate a best fit curve. This may be a linear or an n-order polynomial function to give unrivalled rangeability.

Automation…

Users can select a method which includes automatically preparing calibrants from a stock solution, calibration, acid stripping and measurement of TOC and TN all in one operation. The principals of FDA21 CFR11 are applied to ensure that the data is tamperproof and auditable.

Sensitivity and precision…

It's very hard to beat the sensitivity and precision of the Thermalox range of elemental analysers. The following results were obtained on the Thermalox TOC/TN Environmental.

Accuracy…

TOC/TN$_b$ Test	TC µg/l KHP	TC mg/l KHP	TC mg/l KHP	TN µg/l NH_4Cl	TN mg/l NH_4Cl	TN mg/l NH_4Cl
Concentration	145	1.97	10,108	101	1.03	201.6
	138	1.99	10,023	98	1.02	200.8
	143	2.00	10,098	98	0.98	199.4
Mean	142	1.99	10,076	99	1.01	200.6
Nominal Concentration	140	2.00	10,000	100	1.00	200.0
SD	2.9µg/l	0.01 mg/l	37.93 mg/l	1.25 µg/l	0.02 mg/l	0.91 mg/l
CV	2.1 %	0.5 %	0.38 %	1.25 %	2.0 %	0.45 %

Recovery…

TN Digestion Efficiency 40µl Injection	Creatinine	NH_4Cl (Calibrant)	$NaNO_3$
Concentration (mg/ℓ N)	98.8	100.3	102.0
	98.2	99.8	101.8
	98.7	100.1	101.7
Mean (mg/ℓ N)	98.62	100.10	101.87
Nominal Concentration	100.00	100.00	100.00
SD (mg/ℓ N)	0.26	0.20	0.13
Digestion Efficiency	98.6%	100.1%	101.9%

The above samples were prepared by adding each of the chemicals in the nominal concentrations to deionised water. The digestion efficiency represents the ratio of nitrogen measured compared to the amount of chemically bound nitrogen contained in the sample. Oven Temperature was 950°C. Lower oven temperatures give a wider spread of recoveries at higher concentrations, but have some advantages with some matrices at low levels.

Thermalox™

TOC/TN$_b$

Thermalox TOC/TN	
Analyte	TC, TIC, TOC, NPOC, POC with options for measuring TN and TP
Applications	Drinking water, pharmaceutical cleaning in place water, ground water, surface water, saline waters, domestic, and industrial wastewater
Method	Total substance: Thermal catalytic oxidation at 680ºC (1000ºC for TN). Inorganic substance: acid stripping or injection into low temperature acid reactor (120ºC)
Range	Carbon: Various from less than a range of 40-150µg/l to greater than a range of 100-40,000mg/l: Nitrogen: From 20-100µg/l to 1.0-200mg/l
Cycle time	Typically 120 – 180 seconds
Precision	Standard deviation: ≤ 5% of full scale for ranges to 3mg/l; ≤ 3% of full scale for ranges up to 500mg/l and ≤ 2% of full scale for ranges up to 40,000mg/l
Sample matrix	Aqueous samples including those containing suspended solids and salts. Acids, slurries, sludges and organics by special application. A solids option is available
Injection volume	3 to 150µl. Needle diameters up to 1.0mm are available for particulated samples
Sample injection	Automatically from an 88 position vial tray, or manually.
Carrier gas	A carrier gas generator is fitted as standard for TOC, except for very low level measurements. For TN, oxygen (grade 5.5 or better) is required; flow rate is 15 litres per hour or less.
Power supply	230V AC ± 10%, 50Hz ± 1%; or 115V AC ± 10%, 60 Hz ± 1%
Ambient temperature	5 – 35ºC
Dimension and weight	645^W x 505^D x 650^H mm footprint (WDH) ; weight 50kg; (figures include sampler)
Protection Class	EMI class Euro 50081/50082.
TOC and TN method compliance	BS and DIN EN 1484 of 1997; ISO 8245, AOAC973.47, Standard Methods 5310B, Environmental Protection Agency (EPA) Methods 415.1, EPA SW-846 Method 9060A, ASTM D2579-85. TN according to DIN38409 part 27, ENV 12260 and ISO/TR11905-2.

Solids Option	
Analyte	TC, TIC, TOC
Method	TC by Thermal catalytic oxidation at 950ºC. TIC by acid decomposition at 120ºC. TOC by difference
Range	From 50µg C to 150mg C per sample
Cycle time	Typically 5 minutes for TC, 8-31 minutes for TOC
Precision	Greater of +/-15% or 15µg per sample
Sample matrix	Soils, Sludge, Slurries, Sediments, Polymers
Sample size	Maximum 1.0 gm
Sample introduction	Semi-Automatically
Carrier gas	12 litres per hour Oxygen, 5.5 grade. Also 18 litres hour dry compressed air for actuators.
Power supply	230V AC ± 10%, 50Hz ± 1%; or 115V AC ± 10%, 60 Hz ± 1%. 950VA
Ambient temperature	10 – 40ºC
Dimension and weight	585^H x 178^W x 406^D; weight 12kg;

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