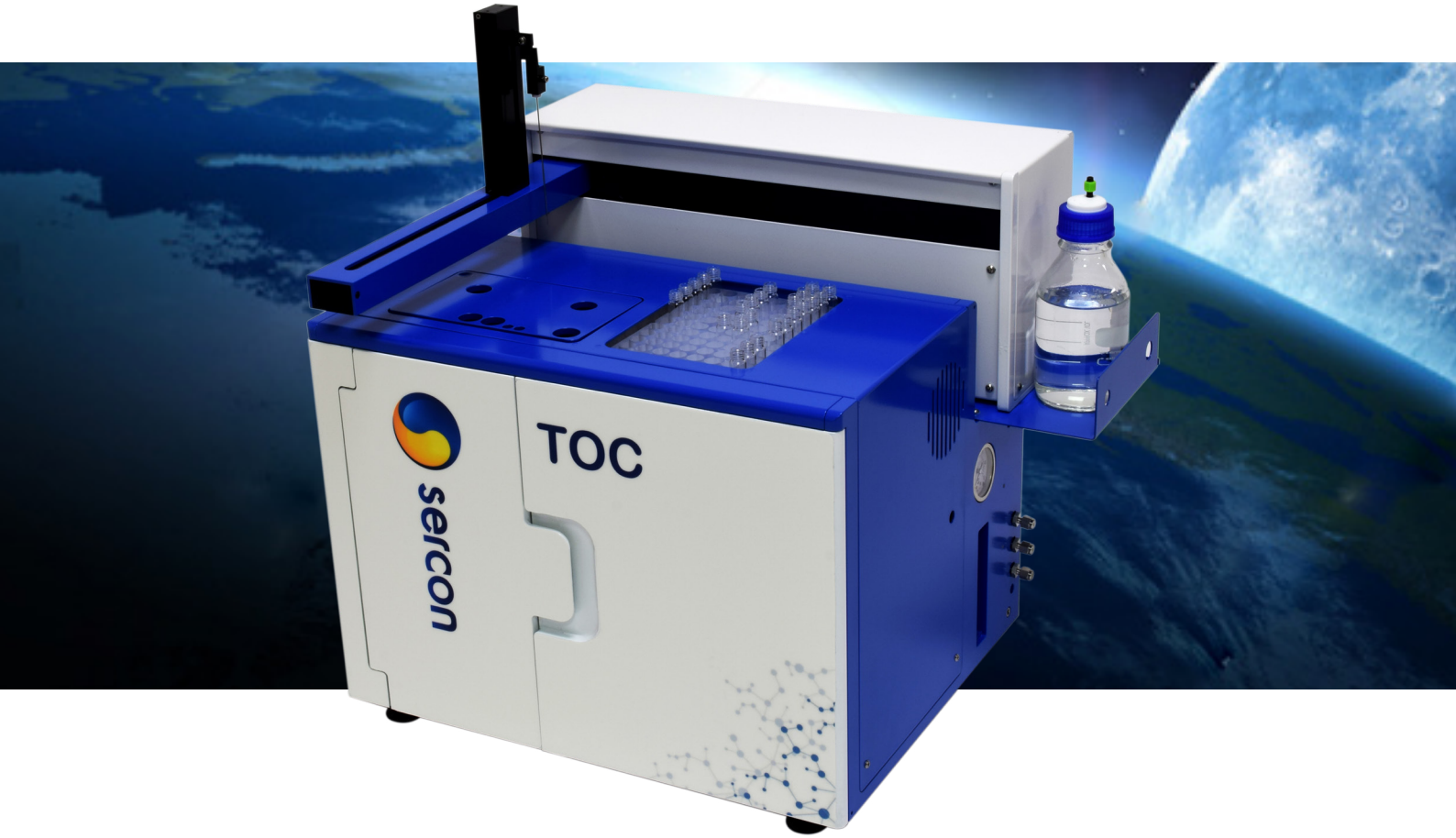
sercon
innovators in isotopes

Thermalox TOC-TN

The modern alternative to COD and TKN



COLLABORATE • CREATE • INNOVATE

THE SERCON THERMALOX TOC/TN_B

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.

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 a blank has to be controlled.

Why choose **The Sercon Thermalox** over other thermal oxidation systems?

Sercon 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 and faster analysis.

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 NOx detector employs a number of features to ensure excellent sensitivity and stability. As well as heating the reaction under vacuum, we utilise an innovative NOx ➔ 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 SERCON 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
- Upper Range Limit greater than 50,000ppm for TOC
- Analysis time less than two minutes per replicate
- Complete recovery, including Suspended Solid fraction
- Handles salts and particulate easily
- Vial trays hold up to 155 samples
- Complete washing between samples ensures no carry over
- Totally software driven from a WindowsTM based platform
- Automatic preparation of calibration standards
- Automatic dilution of high concentration samples in under five seconds

REMEMBER – YOU CAN HAVE STAND ALONE TOC, STAND ALONE TNB OR COMBINATION TOC/TN_B

THE SERCON THERMALOX IS SO WELL AUTOMATED THAT YOU CAN MIX HIGH AND LOW LEVEL SAMPLES ON THE SAME VIAL RACK

THE SERCON THERMALOX TOC/TN$_B$

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

The Sercon 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.

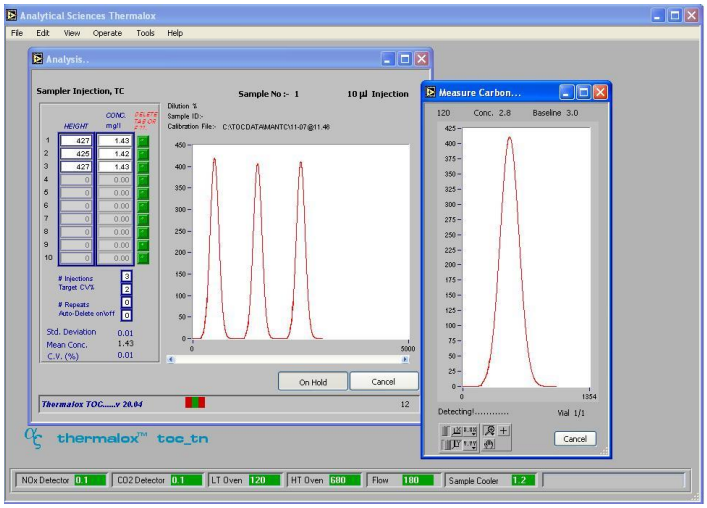
The standard vial rack holds up to 155 glass or disposable plastic vials, with or without lids. It can be chilled and we are happy to provide racks to suit special requirements.

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



Analytical Description

Analysis begins by loading samples into a vial rack. The AS8000 XYZ autosampler handles up to 155 vials.

A sample aliquot from 3µl to 350µl 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.

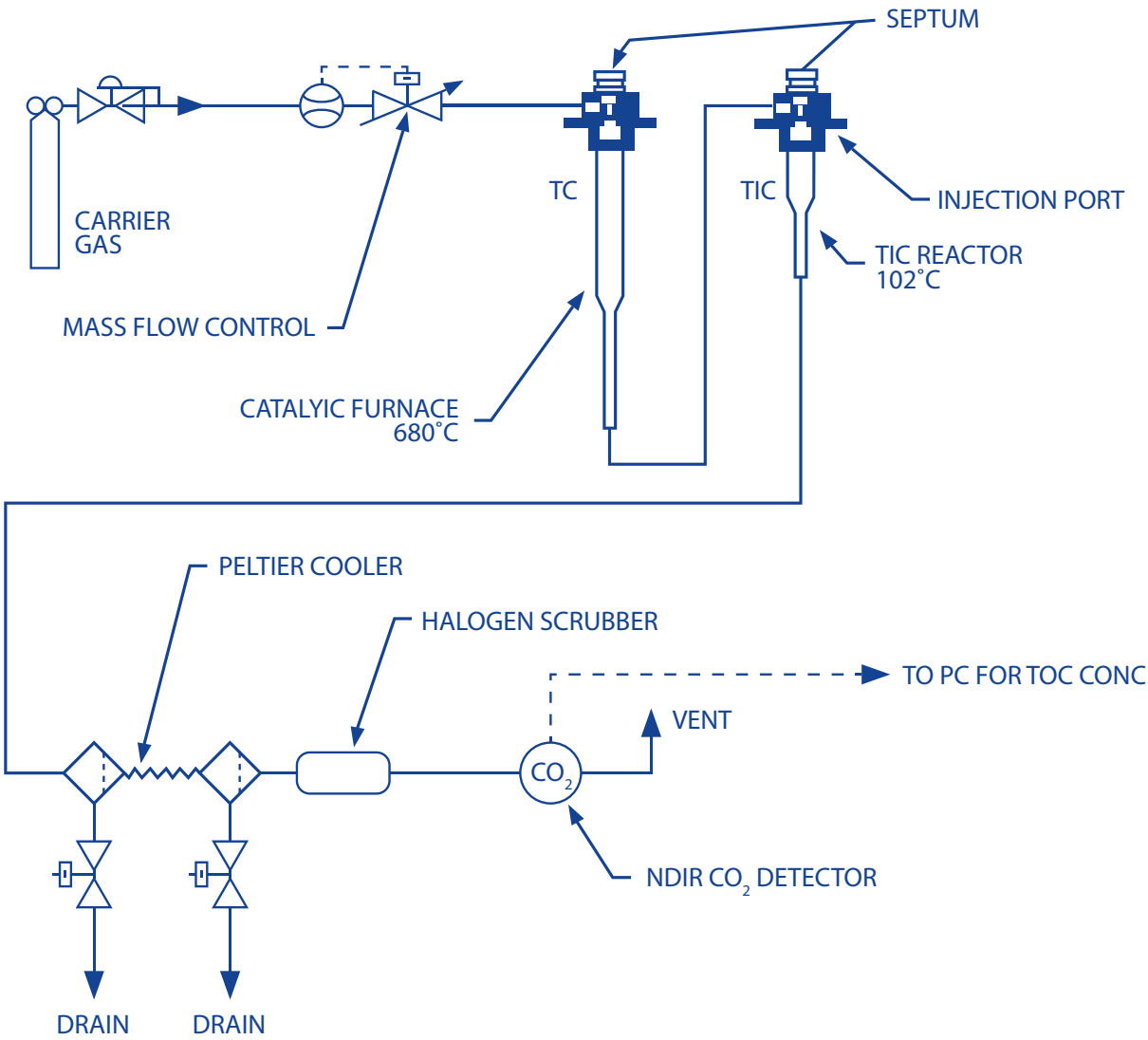
The inorganic carbon, carbonates, bicarbonates and dissolved CO_2 are either stripped from the sample prior to the TC measurement, or this fraction is measured separately by introducing an aliquot of sample into the TIC reactor. This reactor contains phosphoric acid heated to 120°C which reacts with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



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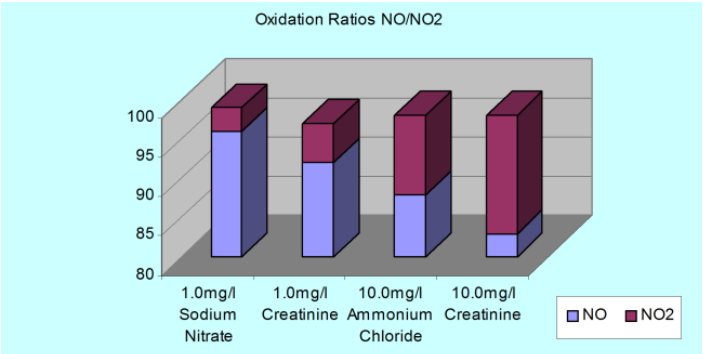
THE SERCON THERMALOX NITROGEN

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 TNb analyser where only this one analyte is required.

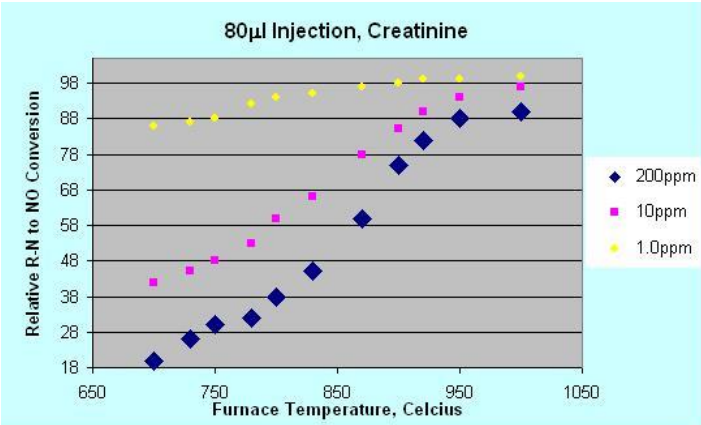
In the same way as TC measurements are performed, a sample aliquot is injected into a catalytic furnace. Carrier gas (oxygen) sweeps the oxidant, in this case NOx gases, through to the NOx detector.

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.

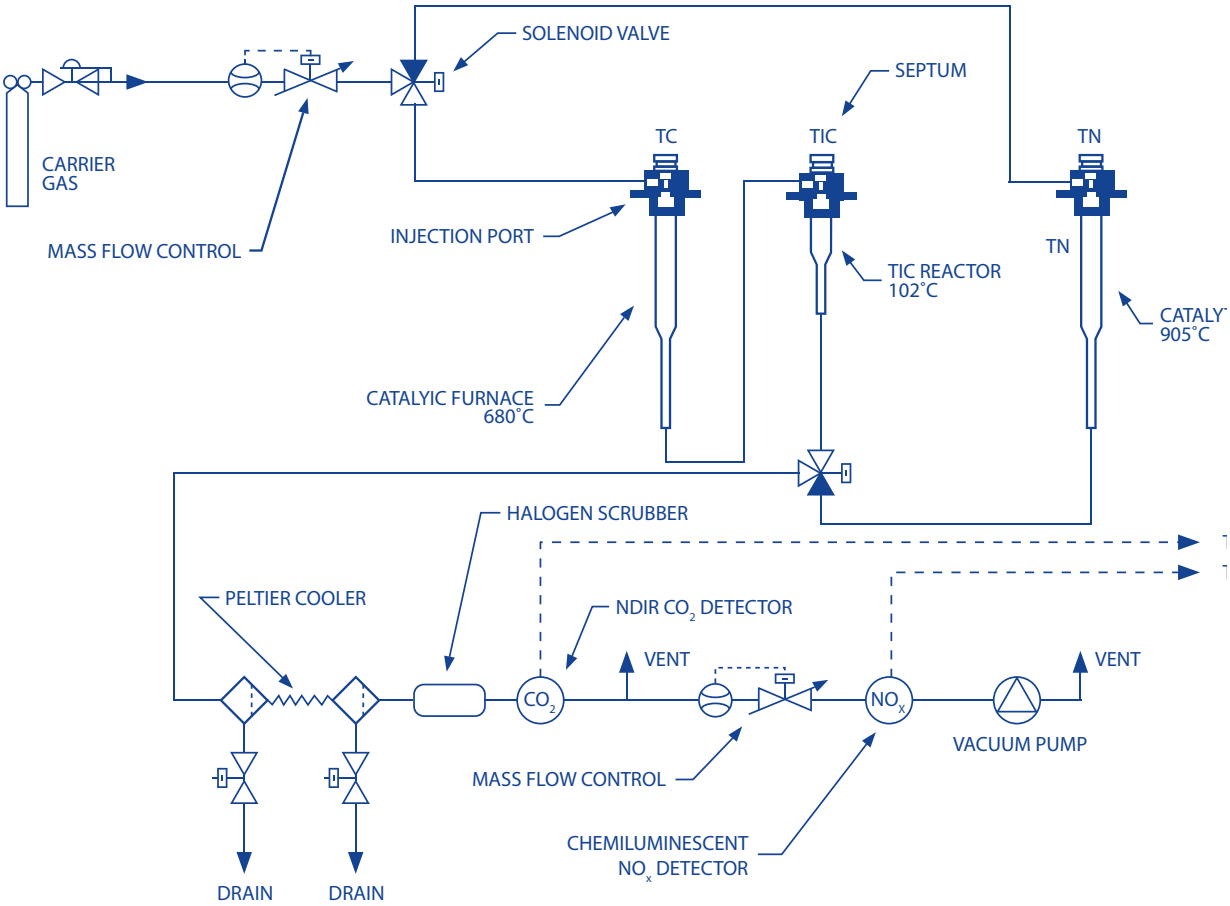


Unlike most vendors, our chemiluminescent reaction is performed under vacuum in a heated chamber. This gives the Sercon Thermalox TN analyser its remarkable sensitivity; at least an order of magnitude more than its main rivals.

The NO concentration is monitored by the PC controller and a characteristic asymmetric peak is plotted, the area of which is proportional to the NOx product of the decomposition. By calibration, TNb 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 used to perform both the TC and TN decompositions. However, for higher level TN applications – up to 400mg/l – with highly particulated samples, a specialised TN oven may be used.



THE SERCON 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. Our unique auto-dilution feature means we can measure two orders of magnitude in a single calibration curve.

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

It's very hard to beat the sensitivity and precision of the Thermalox range of elemental analysers. Our hi-sense detectors, low leak construction and low blank combustion makes for a very sensitive and versatile analyser.

PRECISION

It's very hard to beat the sensitivity and precision of the Thermalox range of elemental analysers. Standard deviation is best in class for carbon and nitrogen.

SPEED

The Thermalox works quickly using small aliquots to preserve catalyst longevity, carrier gas and minimise sparge times.

RECOVERY

Excellent recoveries are achieved when measuring TN concentrations of different chemical species containing molecularly bound nitrogen.

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ISO 9001:2015 Certified
ISO 13485:2016 Certified

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