TOC Determination in Wastewater

Figure 2: Shimadzu TOC-VCSH

> *"The TOC-V combustion analyser can directly analyse samples containing large concentrations of inorganic salts accurately and without dilution or other pre-treatment procedures"*

TOC DETERMINATION IN DIFFICULT MATRICES

The TOC content is a measure of the concentration of organically bound carbon and is therefore a direct indication of the pollution levels of organic compounds in different matrices. The application field for TOC analysis is quite broad, being used mainly in ultra pure water, surface water, drinking water applications and outlets of clarification plants. But nowadays, demand is increasing to measure TOC in more problematic matrices such as acids, bases and samples highly concentrated with salts. The question is which influence the matrix may have on TOC determination. This article indicates the diverse influences of matrix on the different TOC techniques and gives examples of how to avoid these influences.

TOC MEASURING METHOD

Two measuring methods are being applied successfully in TOC analysis:

- Catalytic combustion, which converts carbon compounds into CO_2 using high temperatures and a catalyst, with subsequent detection of the CO_2 formed using an NDIR detector
- Wet chemical oxidation, which uses a combination of UV irradiation and persulfate for oxidation. The CO_2 formed is detected either via NDIR or conductivity detector.

In environmental applications, TOC determination using catalytic combustion has been applied successfully – based on the higher oxidation potentials, especially for particles. The German Wastewater Ordinance, for instance, contains the following instruction on the TOC method: 'a TOC instrument with thermal-catalytic combustion (minimum temperature 670°C) must be used'.

An advantage of the wet-chemical oxidation is the use of a higher injection volume. This leads to lower detection limits and improved reproducibility in the ppb range, which is a basic requirement for ultrapure water analysis in the pharmaceutical and semiconductor industry.

INFLUENCE OF THE MATRIX

In TOC analytics, difficult matrices are considered to be those containing high concentrations of salts, acids or bases. The influence of the matrix can have a direct effect on the TOC measurement, or an indirect effect by increasing the need for maintenance. Substances which interfere with NDIR detection influence TOC measurement directly. They have similar bands, such as the detected CO_2, and can therefore lead to peak tailing and higher TOC values. An example is the measurement of sulphuric acid: concentrations higher than 1% sulphuric acid without further treatment cause peak tailing and higher measuring results. In the case of wet-chemical oxidation, higher concentrations of chloride lead to a decrease in oxidation potential and consequently, under certain conditions, to lower TOC recovery rates.

High concentrations of salts, acids and bases generally cause an increased maintenance need for TOC systems with catalytic combustion, as opposed to ultrapure water or drinking water applications. They do not directly influence TOC measurement but cause a higher wear of the catalyst and the combustion tube. Dissolved salts crystallise in the combustion tube on the catalyst. This influences its activity and, as a result, leads to a fast decrease in sensitivity. In this case, the catalyst must be replaced. In addition, the accumulation of salts in the combustion tube can lead to an increase in backpressure. In this case the salt must be removed from the combustion system.

The combustion tube usually consists of quartz. Certain salts and especially alkaline substances can attack the surface and cause corrosion whereby the combustion tube becomes brittle. Corrosive combustion gases can attack the detector cell and will cause additional maintenance complexity. For this reason, many TOC systems are equipped with a halogen scrubber that protects the detector cell. The scrubber must always be replaced promptly, as replacement of the detector cell leads to higher costs.

MEASURES TO REDUCE MATRIX INFLUENCES

Many manufacturers advise their customers, therefore, to keep the concentrations of salts, acids and bases as low as possible so as to prevent damage to the TOC system. Reality is, however, often different. What can be done when difficult matrices have to be determined using TOC? Shimadzu's TOC systems offer various possibilities to minimise the need for instrument maintenance when analysing highly contaminated samples. The combustion systems are operated with catalytic combustion at 680°C. This temperature is lower than the melting point of some salts (e.g. sodium chloride and potassium chloride), which avoids molten compounds deactivating the active centres of the catalyst. The use of a platinum catalyst ensures complete conversion of organic carbon to CO_2.

The highly sensitive NDIR detector enables small injection volumes (typically 20 – 50µL), keeping the absolute sample input onto the catalyst at a minimum. Additional dilution can be attained with the integrated dilution function. The IPS (Integrated Sample Dilution) module enables automated dilution of the sample. This can be affected on exceeding of the measuring values, or permanently. In this case, the user defines the dilution factor desired in the method and can thereby increase the lifetime of the catalyst.

APPLICATION EXAMPLES FOR TOC DETERMINATION IN DIFFICULT MATRICES

Measurement of TOC in Sulphuric Acid Solution

Sulphuric acid is an indispensable chemical product that is produced in large quantities to fulfil requirements in wide-ranging goods, medicines, fertilisers, fibres as well as in specialty applications such as electrolytic solutions for batteries. Since high-purity is required for sulphuric acid used as a raw material in various products, measurement of organic impurities in sulphuric acid may be necessary. The sulphuric acid ion could influence the measurement value when a TOC analyser is used for this purpose.

Reagent grade sulphuric acid was diluted 100-fold with ultra pure water to form a 1% sulphuric acid solution. First, TOC measurement of the 1% sulphuric acid solution was conducted. Next, different amounts of potassium hydrogen phthalate were added to the 1% sulphuric acid solution to form two solutions containing an organic substance with TOC concentrations of 2mg C/L and 5mg C/L. TOC measurement was then conducted as before and the results are shown in *Table 1*.

The instrument was calibrated using potassium hydrogen phthalate standard solutions with concentrations of 0 and 5mg C/L, respectively, and a calibration curve was generated. To eliminate the influence of any carbon content in the standard solutions, a correction was carried out by shifting the calibration curve to pass through the origin.

Higher concentration of sulphuric acid solution (up to 10%) can be measured with the help of a dedicated sulphur scrubber.

Table 1. Results of spiked sulfuric acid solutions.

Sample	TOC Result [mg C/L]
1 % sulphuric acid solution	0.109
1 % sulphuric acid solution + 2 mg C/L	2.081
1 % sulphuric acid solution + 5 mg C/L	5.037

TOC determination in hydrochloric acid

The use of hydrochloric acid is at least as varied as described above for sulphuric acid. Hydrochloric acid, unlike sulphuric acid, does not influence the integration in the detector directly. However, based on its etching properties, measurement of hydrochloric acid is a special challenge for the TOC instrument. In this example, low TOC concentrations in hydrochloric acid solutions are to be determined. This uncommon application requires both modification of the instrument and increased user awareness. The sample has a maximum HCL concentration of 6 molar.

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The TOC concentration is too low, and the solution cannot therefore be diluted prior to analysis. In order to measure this solution plastic parts must first replace all metal parts. In addition to the conventional halogen scrubber, others such as a wet-chemical halogen scrubber with tin-II chloride solution as well as copper spheres are installed to effectively prevent bleeding of HCL gas into the detector cell. These scrubbers also bind high concentrations of HCl and protect the detector cell. After modification, the TOC-V CPH/CSH is calibrated using potassium hydrogen phthalate *(Figure 2 – TOC-VCSH).*

Table 2. Calibration 0.5 - 2.0mg C/L.

Calibration point	Concentration [mg/L]	Area
1	0.5	12.2
2	1.0	23.0
3	2.0	24.0

*Injection volume 250µl

Slope: *21.171*
Intercept: *1.700*
r^2: *0.9999*

To assess the performance of this modified TOC system, the limits of detection and determination were verified using the blank value method. Seven hydrochloric acid solutions were measured and, based on the calculated standard deviation the limits of detection and determination were calculated.

Table 3. Results of blank value method.

Sample hydrochloric acid solution	Result [ppb]	Area
1	118	2.428
2	121	2.479
3	125	2.563
4	104	2.129
5	114	2.353
6	126	2.594
7	121	2.483

Mean value: *118.4*
SD: *7.547*
LOD: *15.65*
LOQ (3 x LOD): *46.95 ppb*

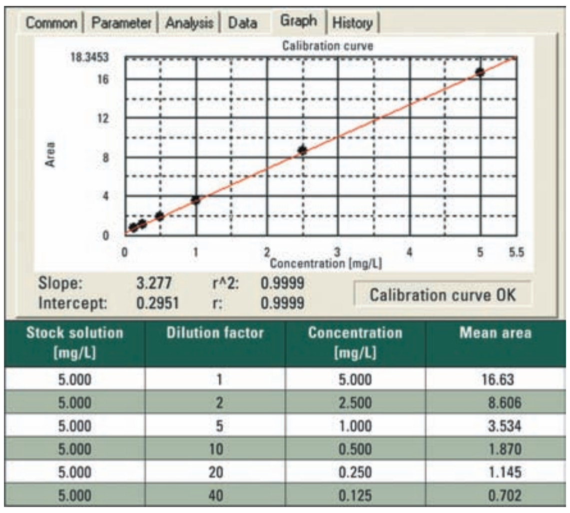
The results show that low TOC concentration can reliably be determined even in difficult matrices. Regardless of any modifications, contact between the hydrochloric acid solution and the instrument should be kept at a minimum.

After the final hydrochloric acid measurement, the instrument should be completely rinsed with ultrapure water in order to remove any hydrochloride acid residues including HCL gas.

TOC MEASUREMENT IN SEAWATER

Seawater contains large amounts of salts. The TOC-V combustion analyser can directly analyse samples containing large concentrations of inorganic salts accurately and without dilution or other pre-treatment procedures.

Table 1 shows the results of TOC analysis of four seawater samples. Three were spiked with 1mg C/L, 2mg C/L and 4mg C/L TOC. The instrument was calibrated up to 5mg C/L using potassium hydrogen phthalate as standard. All of the samples were accurately analysed without any pre-treatment such as dilution.



Slope: 3.277 r^2: 0.9999
Intercept: 0.2951 r: 0.9999

Stock solution [mg/L]	Dilution factor	Concentration [mg/L]	Mean area
5.000	1	5.000	16.63
5.000	2	2.500	8.606
5.000	5	1.000	3.534
5.000	10	0.500	1.870
5.000	20	0.250	1.145
5.000	40	0.125	0.702

Figure 1: NPOC calibration curve 5mg/L

Calibration curve

NPOC calibration curve is up to 5mg/L. This calibration curve was performed with auto dilution function from a 5mg/L TOC (potassium hydrogen phthalate) standard solution. *(see Figure 1)*

Measurement conditions:

Method: NPOC
Acidification: 1.5%
Sparging: 1.5min
Sample: Natural sea water
Potassium hydrogen phthalate used for spiking

Table 4. Results of spiked seawater samples.

Sample	TOC as NPOC [mg/L]	RSD [%]
Sea water	0.72 ± 0.01	1.36
Sea water + 1 mg/L TOC	1.77 ± 0.02	1.25
Sea water + 2 mg/L TOC	2.80 ± 0.05	1.78
Sea water + 4 mg/L TOC	4.85 ± 0.05	1.08

Due to the high salt content, analysis of seawater samples requires higher maintenance compared with other applications such as analysis of drinking water. Nevertheless, 700 injections of seawater samples can be conducted before maintenance is required (injection volume 50µl).

The salt in the seawater accumulates on the catalyst. The catalyst can therefore be regenerated externally and used again. Cracked balls and dust must be removed. Afterwards, a small amount of new catalyst balls is required to reach the recommended filling height. Depending on the condition of the combustion, it can be used again for several fillings.

CONCLUSION

TOC determination is subject to various matrix influences. However, special measures are available to minimise these effects. The application examples show the wide range of applications where modern TOC analytical systems can be deployed.

Newly Designed 21-Model Water Bath Range

Grant Instruments has unveiled a newly designed, precision engineered, 21-model range of high quality, competitively priced unstirred, shaking and boiling water baths - the Aqua Plus series. The Aqua Plus series is marketed in four distinct families - SUB Aqua Plus digital unstirred baths, JB Aqua Plus analogue unstirred baths, GLS Aqua Plus series linear shaking baths and SBB Aqua Plus series boiling baths. The new models are unbeatable for everyday use, offer exceptional value-for-money, and come with Grant's renowned high quality and reliability built-in.

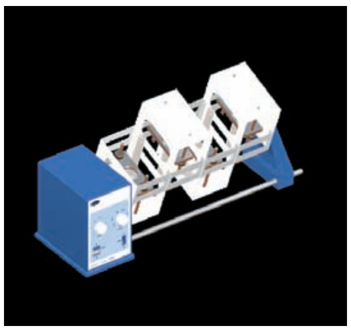
Boasting new usability features such as drain taps, temperature presets, front panel lockout, countdown timers and non-drip polycarbonate lids and bases, the new, easy-to-use, robust and reliable baths are designed to meet the ever changing needs of laboratories worldwide, including life sciences and educational establishments.

Like all Grant products, the new water baths are built to last. They meet CE and CSA standards (Grant has its own CSA accredited test facility). The baths are manufactured in Grant's UK production facility, using only the highest quality materials and come with a 3-year warranty as standard.

Ludo Chapman, Managing Director of Grant Instruments, said: "We have listened to our global customers and distributors, and we have managed - despite the current economic downturn - to design a new, feature-rich range of precision engineered water baths without compromising the great quality, service and support and competitive price for which we are renowned."

Circle no. 86

Rotator Keeps Statutory Fertiliser Analysis Work Turning Over



Kent Scientific Services, a Public Analyst Laboratory, selected a **Stuart** STR4 rotator to meet the requirements of its fertiliser enforcement analysis work. The prescribed analysis methods for checking the nitrogen and phosphorus content in fertiliser samples require flasks to be mixed end-over-end at 35–40rpm, faster than many other rotators can achieve.

Nitrogen (N), Phosphorus (P) and Potassium (K) are the three primary nutrients needed in large quantities by plants. Manufactured fertilisers, used to supply crops with nutrients the soil lacks, have to be labelled with three figures indicating their NPK content. The Fertilisers (Sampling and Analysis) Regulations 1996 require the figures to be checked by standardised analysis techniques. Kent Scientific Services, one of 18 Public Analyst Laboratories in England, provides scientific and calibration services for local authority enforcement agencies, including analysis of fertiliser samples collected by local Trading Standards officers from manufacturers' premises or at the point of sale.

David Heath, Quality Manager/Toxicology Manager at Kent Scientific Services, commented: "The prescribed analysis methods for soluble N and P require fertiliser samples to be mixed with 400ml of water in a volumetric flask and mixed by end-over-end rotation at 35–40rpm. The speed we needed was well within the range offered by the STR4. The Bibby Scientific engineering department were very helpful to us, adjusting the bracket on the rotator so that it would work with the large 500ml flasks we need to use." The Stuart STR4 drive unit is highly versatile, accepting a choice of five drums designed to take test-tube holders, plates, racks of microcentrifuge tubes, conical flasks, reagent bottles, or jars and paint tins up to 200mm in length and 120mm diameter. The rotation speed is variable from 6 to 60rpm for a range of mixing applications, and the unit can be run in continuous operation mode or with the analogue timer set for 10 to 60 minutes.

Circle no. 87