Overview of C.O.D., B.O.D., T.O.C. and UV absorbance in the measurement of the contamination of water.

There are a number of ways of measuring the overall level of contamination in water. Often used are - Biological Oxygen Demand (B.O.D.), Chemical Oxygen Demand (C.O.D.), Total Organic Carbon (T.O.C.) and UV absorbance. The underlying assumption is that the contamination is organic in origin, and carbon based. The methods were developed as laboratory methods over the last century or so and B.O.D., C.O.D. and T.O.C. have been described in the "Blue Book" series of Standard Methods. (Methods for the Examination of Waters and Associated Materials – created and maintained by the "Standing Committee of Analysts"). The existence and documentation of the methods opens up their use as legally supported consent limit parameters.

B.O.D.

B.O.D. is a test which in the original laboratory format takes a sample into a volume of water containing aerobic biological organisms and saturated with oxygen – 9mg/lt at 20°C. The mixture is sealed to eliminate oxygen ingress and held at 20°C for five days (this is usual in the UK – other times are used) and the resulting oxygen level is measured. The result is expressed as oxygen demand in mg/lt which means milligrams of oxygen used up per litre of sample.

This test is designed to measure the amount of organic material in a body of water. The more contamination - the more oxygen used to break it down biologically. The test was used as an indicator of the quality of treated waste water and is a very normal consent parameter for discharges to the environment.

The key advantage is that it measures the effect of water on the ecosystem into which it will be discharged. Taking the bugs from the local environment gives the test a direct relevance in that sense. Treatment of waste water using a biological process (which is overwhelmingly the case) again gives the test a direct relevance to the treatment process.

The key features of the test are

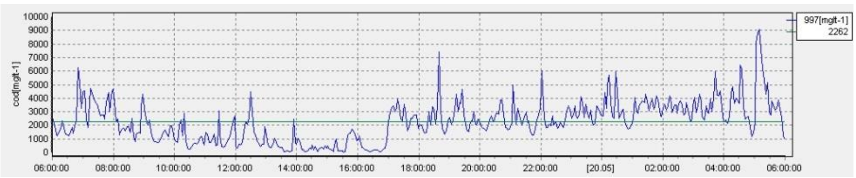
1. Reference method is described in the Standing Committee of Analysts series of Blue Books.
2. The biological nature of the test give it a relevance to environmental impact and treatment efficiency
3. the test result is dependent upon the biological organisms used
4. the temperature of the test is seldom the temperature of the environment
5. the results are not available in time to take any action
6. the test can involve high dilutions
7. the analyst needs to know approximately what the result will be in order to prepare the dilutions. The measured value after dilution should be 4 or 5 mg/lt and should not be too close to either 9 or 0 mg/lt O_2.
8. It is relatively labour intensive and expensive
9. It is not accurate or precise.
10. Toxic samples give low readings.
11. Used in consent limits for direct discharge to the environment.
12. The laboratory method is not easy to set up in an on-line analyser, however using a different approach allows continuous B.O.D. to be measured.

C.O.D.

The C.O.D. laboratory test was designed to provide a quicker assessment of oxygen demand. The test was based on readily available materials with aggressive oxidising power. There are standard methods described in the Blue Book "The Determination of Chemical Oxygen Demand in Waters and Effluents (2007)". In general the sample is mixed with the reagents – often in a ready to use test kit format – and heated to 148°C for 120 minutes. The result of the reaction can be measured photometrically or by titration with an indicator. The result is expressed in mg/lt – again mg of oxygen used up per litre of sample.

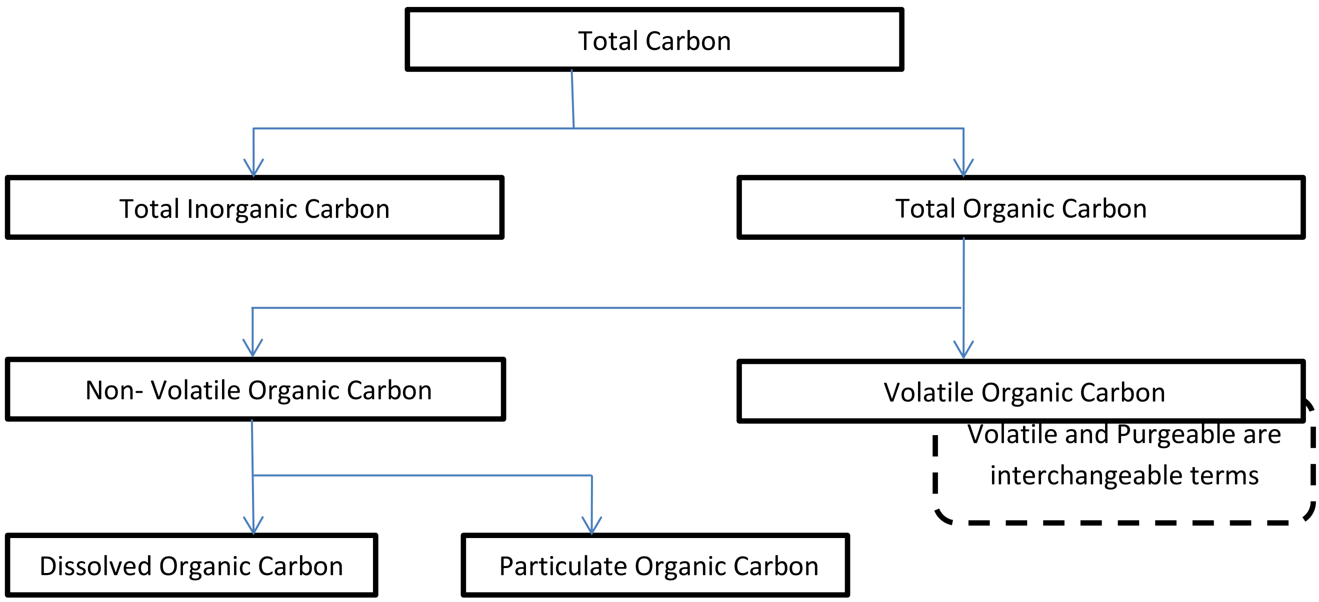
The features of the test are

1. Reference methods are described in the Standing Committee of Analysts series of Blue Books.
2. Defined chemical reaction conditions which give good precision.
3. The test is an overall measure under defined conditions rather than an absolute measure of any particular chemical species.
4. The reaction conditions oxidise a wide range of organic compounds, usually but not always completely.
5. The extent of oxidation is consistent for each particular organic molecule.
6. Results are available in 3 hours or so.
7. Hazardous chemical reagents used.
8. The analyst needs an approximate idea of the value before the test is started.
9. The test is normally used to give a view of organic contamination however the conditions will oxidise other materials.
10. The test can be configured as a batch analysis to give a continuous analyser based on the reference method.
11. Alternative technologies can give C.O.D. readings.



T.O.C

This test looks at the organic carbon content of water samples. Carbon can be present in various forms in aqueous solutions. These are shown in the following diagram.



Various acronyms are used – TC, TIC, TOC, NPOC, VOC, POC, DOC. The Standing Committee of Analysts does not use them in the "Blue Book" as they are seen as a possible source of confusion.

To measure T.O.C. it is important to ensure that inorganic carbon does not introduce significant errors and that volatile organic compounds are captured. Any procedure which vents CO2 derived from acidification of inorganic carbon runs the risk of losing the volatile organic compounds.

There are two approaches to measuring T.O.C.

1. The inorganic carbon and total carbon can both be measured . Total Organic Carbon is then calculated as the total carbon minus the inorganic carbon.
2. Inorganic carbon is removed from the sample and the remaining carbon is measured as Total Organic Carbon.

The analysis will inevitably involve a digestion of the sample to produce CO2 which is then measured. The extent of digestion and oxidation of the organic carbon will depend upon the nature of the organic molecule and whether the molecule is dissolved or suspended in particulate form.

Unlike the reference C.O.D. method (which uses an arbitrary and consistent set of reference conditions) there are several methods for measuring T.O.C. These methods will each have their own performance characteristics. In practice this means that they will all have sample streams for which they are appropriate and those where they are not appropriate.

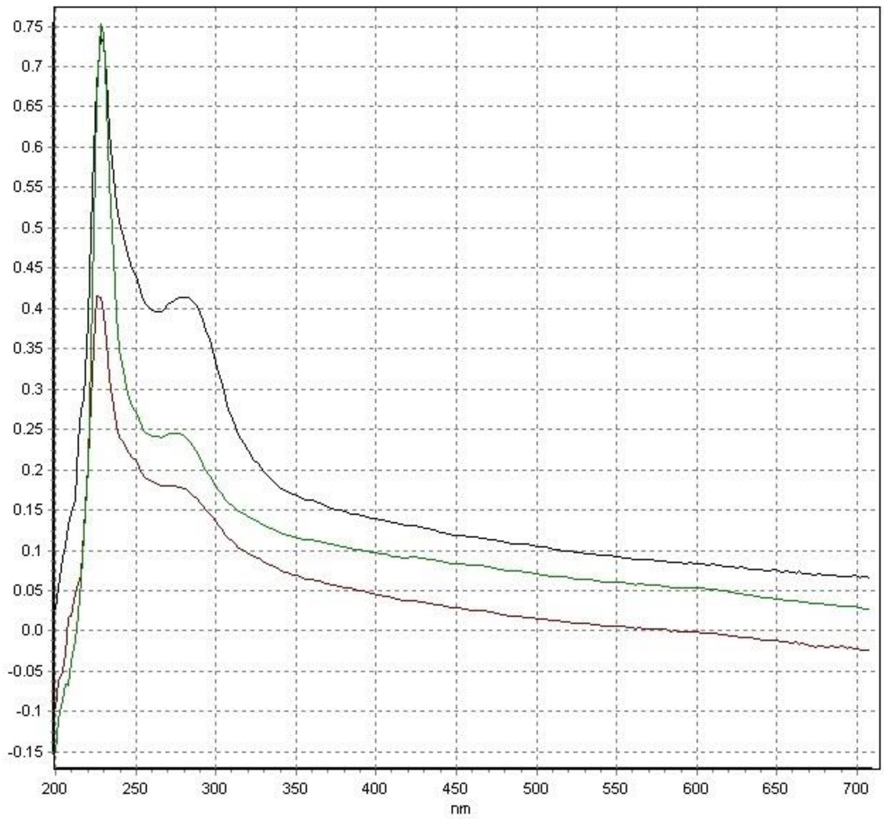
The results are expressed in mg of carbon per litre of sample.

The features of T.O.C. measurement are

1. Reference methods are described in the Standing Committee of Analysts series of Blue Books.
2. Clear chemically defined parameter.
3. Variety of methods to measure it with a variety of performance characteristics.
4. The results should be expressed with a note of the method used.
5. Aggressive oxidation conditions – using some combination of any of the following :- heat, catalysts and oxidising agents.
6. Results can take a range of time depending on the oxidation process.
7. Hazardous reagents may be used.
8. Sample characteristics (e.g. the presence of particulate and volatile carbon) need to be understood and verified as part of the analysis.
9. The range of methods available allows different technologies to be used in building on-line monitors for T.O.C.

UV absorbance.

Methods are available which use the absorbance spectrum of the sample. Carbon compounds will create spectra which may exhibit absorbance in the ultra violet region of the spectrum. The shape of the spectrum will depend on the particular molecule, although there is a general pattern of molecules containing carbon to carbon double bonds and benzene ring type structures (aromatic carbon molecules) absorbing between 240 and 300 nm. (254nm is a wavelength which is very often used in analysers which detect organic content) This means that it may be possible to calibrate the spectrum against C.O.D. or T.O.C. The following diagram shows spectra from a typical waste water stream from food production where there is a mix of a vast range of organic material.



This is an example of a situation where a useful calibration against C.O.D. can be made and cost effective process control can be implemented. Each case needs to be assessed individually to see what information is required and whether or not that information can be obtained using this technology.

The calculation of C.O.D. is made using the Beer Lambert Law. This is a powerful analytical technique which results in a simple calculation of

concentration = Abs λ 1 x Factor1 + Abs λ N x FactorN +Factor

The number of wavelengths (λ) can vary from 1 to 10 or more theoretically. In practice it is rare that going beyond 2 or 3 wavelengths makes any significant difference to the quality of the result.

The features of optically based measurement of carbon content are

1. No reference method is available
2. Instantaneous measurement.
3. Relatively low cost continuous analysers.
4. Low running costs compared with wet chemistry analysers.
5. Site specific calibration required.
6. Not universally suitable – for example it would not be recommended for batch production in the chemical industry.
7. Not normally a laboratory technique – optical methods lend themselves to continuous measurement formats.