The Instrumental Determination of Total Organic Carbon, Total Oxygen Demand and Related Determinands 1979

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2 net

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Contents

Grateful acknowledgement is made for information received from the instrument manufacturers listed in Table 1

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is *Code of Practice for Chemical Laboratories* issued by the Royal Institute of Chemistry, London. Another such publication, which includes biological hazards, is *Safety in Biological Laboratories* (editors E Hartree and V Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London.

Where the committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of the correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first aid, fire-fighting, and rescue equipment. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions rather, than to assume that no hazard exists until proved otherwise.

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About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in *Analysis of Raw, Potable and Waste Waters*. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

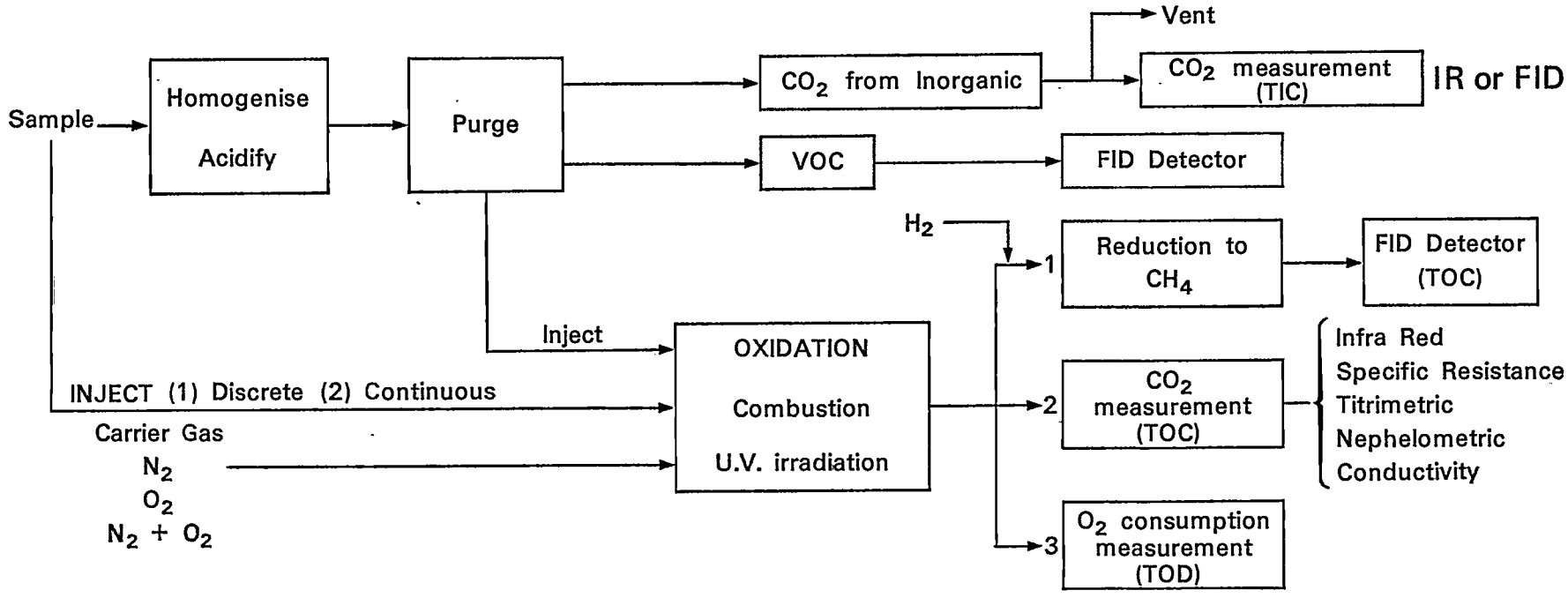
The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977



A TYPICAL SCHEMATIC DIAGRAM FOR TOC AND TOD MEASUREMENT

The Instrumental Determination Of Total Organic Carbon, Total Oxygen Demand and Related Determinands (1979 version)

Note: Oxygen Demand parameters expressed as mg/l O. Oxygen (O).
Carbon parameters expressed as mg/l C. Carbon (C).

1 Definition of Terms

A number of different procedures have been developed in recent years for automation of oxygen demand measurements (or their equivalent). Most of these techniques measure slightly different, although broadly related, parameters; these parameters are commonly referred to by initial letters. It is desirable to define them.

Biochemical Oxygen Demand (BOD)
Is that amount of oxygen consumed by aerobic microbial action in a sample under defined conditions over a specific period – normally 5 days at 20°C.

Chemical Oxygen Demand (COD)
Is the amount of oxygen consumed chemically by the sample from hot acid dichromate under standard arbitrary conditions – normally refluxing at 150 – 155°C for two hours. An alternative designation for this test is **Dichromate Value (DV).**

Total Carbon (TC)
Is that carbon present in all forms – organic compounds, inorganic carbonates ($CO_3^=$ and HCO_3^-), free carbon dioxide and other inorganic species such as HCN.

Total Inorganic Carbon (TIC)
Is that carbon present in all inorganic forms, principally as carbonates, bicarbonates and free carbon dioxide.

Total Organic Carbon (TOC)
Is that carbon present in all organic forms and is the difference between the total carbon and the total inorganic carbon.

Dissolved Organic Carbon (DOC)
Is that part of the total organic carbon present in the liquid phase of the sample after membrane filtration.

Volatile Organic Carbon (VOC)
Is that part of the total organic carbon which is volatile under specified conditions. An alternative nomenclature is **Purgeable Organic Carbon** – the possible confusion with the term Particulate Organic Carbon should be noted.

Particulate Organic Carbon (POC)
Is that part of the total organic carbon which is present in the suspended matter of a sample.

Residual Organic Carbon (ROC)
Is that part of the total organic carbon which is non-volatile under specified conditions and is the difference between TOC and VOC. An alternative nomenclature is 'Non-Purgeable Total Organic Carbon' (NPTOC).

Total Oxygen Demand (TOD)
Is the amount of oxygen consumed in the catalytic combustion of the sample. Some samples may contain materials which, on combustion, evolve oxygen leading to falsely low results (see Section 10).

2 General Introduction

Historically, an indication of the concentration of organic pollutants in waters has been evaluated either by Biochemical Oxygen Demand of Chemical Oxygen Demand measurements. The COD test usually correlates with the 5 day BOD test but still requires 2 hours and also suffers from drawbacks such as chloride interference and inability to oxidise some carbonaceous materials that could be present in an industrial effluent (for example benzene, pyridine, or acetone).

In recent years, alternative instrumented tests have been developed which by high temperature catalytic action, or other means, will very rapidly (a few minutes) oxidize waterborne organic pollutants. The basic principle of all these instruments is similar; the sample in a carrier gas stream is subjected to high temperature catalytic oxidation, the reaction being followed by one of the methods listed below. Most involve determining the amount of carbon dioxide produced.

2.1 The carbon dioxide is measured by non-dispersive infra-red analysis ('Combustion/ Infra Red' technique) (NDIR).

2.2 The carbon dioxide is catalytically reduced to methane which is then measured using a flame ionisation detector (FID).

2.3 The carbon dioxide is absorbed and measured by titration.

2.3 The carbon dioxide is absorbed and measured by titration.

2.4 The carbon dioxide is absorbed and determined by a nephelometric process.

2.5 The carbon dioxide is absorbed and measured by conductimetry.

2.6 The carbon dioxide is dissolved in pure water and the change in specific resistance is measured.

2.7 The quantity of oxygen consumed in the process is measured ('Total Oxygen Demand' technique).

Alternatively, instruments are available which employ high temperature wet oxidation using dichromate, peroxidisulphate or high energy ultra violet (UV) irradiation. The carbon dioxide produced by these techniques is measured by one of the above methods.

3 Hazards

The instrumental determination of organic carbon or TOD needs care and attention to detail to avoid a number of potential hazards.

The preparation of 'carbon free' water employs boiling alkaline potassium permanganate, concentrated sulphuric acid and potassium dichromate. Operators should wear gloves, protective clothing and full face protection. Spillages are best treated by copious dilution with water.

Various risks are associated with different stages of the determinations. Samples may be introduced by aspiration, which necessarily involves reduced pressures and the risk of implosion. Pressurized gases, including oxygen are used as carrier gases. Where hydrogen functions as a carrier gas in the reductive pyrolysis system, it is imperative that oxygen is not employed in the preceding oxidation because of the risk of an explosion.

The gaseous products of oxidation are hot, often corrosive and contain super-heated steam. Some detectors function with water saturated gases, thus presenting similar hazards.

Exposure of skin or eyes to high energy ultra violet (UV) radiation must be avoided.

Instrument maintenance, particularly of the electrical components, should be undertaken in accordance with the manufacturer's manual. Note that considerable static voltages may arise by induction from the furnaces used: proper earthing of equipment is, therefore, essential.

4 Sampling and Sample Preservation

The considerations and procedures to be used when collecting representative water samples are discussed more fully in the publication on 'General Principles of Sampling and Accuracy of Results' in this series.

It is essential that the sample is taken from a well-mixed zone of the liquid. If transfer of sample to the instrument is effected mechanically it is necessary to ensure that the suction lift to any pump used is minimal, so that volatile constituents are not lost. The rate of pumping must be such that suspended solids in the primary sample do not

settle before reaching the final point of sample acquisition (which may be an automatic analyser). While use of a pump is often unavoidable, it should be noted that vigorous mechanical action may modify the initial particle size distribution of suspended solids and also promote equilibrium in non-equilibrated water/solid systems.

Samples should be collected in glass bottles leaving an air space of 2 to 5 ml. Well fitting glass stoppers are preferred but if volatile components are significant then a screw cap of high density polyethylene should be used. It is wise to check the suitability of the caps by testing whether any absorption or desorption of organic compounds take place. Plastic or paper cap liners and plastic bottles are unacceptable.

Before use, bottles should be cleaned with chromic acid solution (see Section 3 – Hazards) and rinsed several times with carbon free water. Cleaning solutions containing organic compounds should be avoided.

For the highest accuracy, samples should be analysed within 2 hours of acquisition unless it is known that samples are stable for a longer time. If samples are to be held prior to analysis, they should be cooled to less than 5°C (but *not* frozen); acidification to pH 1–2 sometimes enhances the effectiveness of low temperature storage but cannot be used if *inorganic* carbonate is to be simultaneously determined.

When operating automated instruments in an 'on line' mode a continuous stream of the sample should flow near the instrument or may have to be pumped to the instrument in a loop system (figure 1). Discrete sample aliquots may then be taken from the sample stream (or loop) at short time intervals, and injected into the analyser. Such analysers often operate most satisfactorily in a particular working range (say 50–250µg/l TOC) and a scheme for achieving dilution may have to be incorporated as in figure 1.

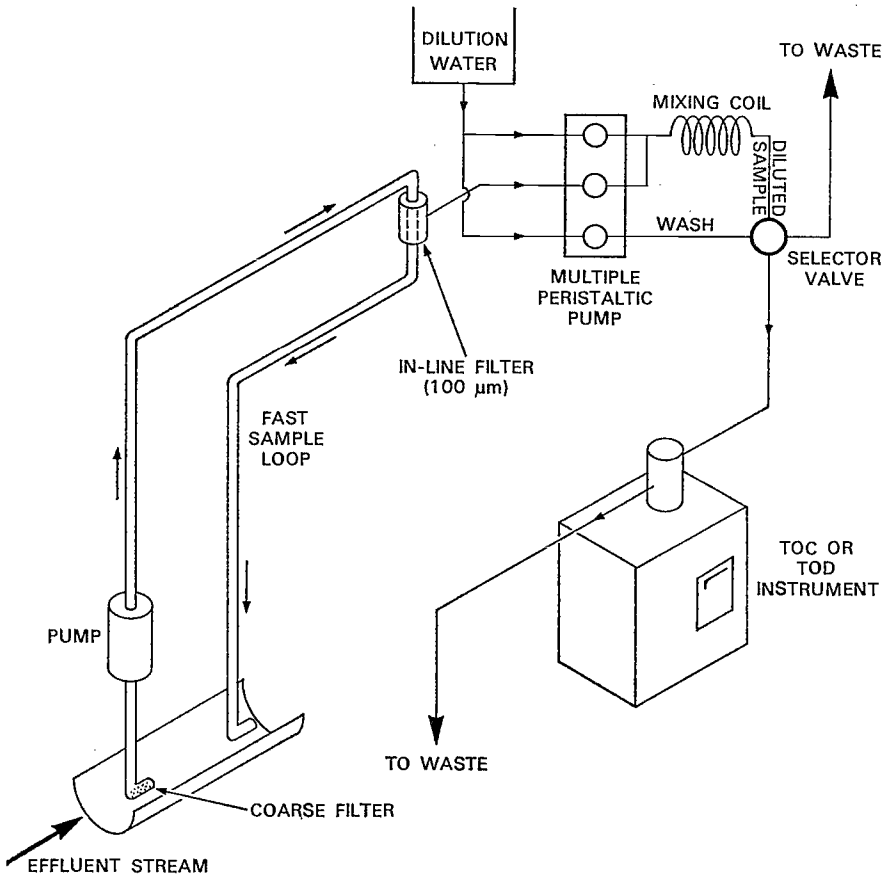


Figure 1 Automated sample acquisition

While it is possible, in principle, to feed samples continuously to the analyser, the presence of high concentrations of dissolved salts in the sample may result in loss of activity of the oxidation catalyst and blockage of the reaction chamber. The presence of surface active materials can give rise to long equilibration or response times where continuous injection systems are employed. Sparingly soluble organic solvents and emulsified oils may behave similarly. Free oil in the sample is likely to produce very erratic results and difficulties with subsequent samples. These problems, which are associated with absorption, arise from the use of peristaltic pump tubing.

In most cases, the sample injection system attached to the analyser will not handle suspended solid particles greater than about 100μm in diameter. It is, therefore, necessary either to remove suspended matter, see figure 1, from the sample prior to injection (recognizing, however, that organic and inorganic carbon may be associated with these solids) or, alternatively, to disperse the solids in the form of a stable suspension which can be accepted by the sampling valve on the analyser. This is discussed further in Section 5 on sample preparation. If much insoluble inorganic solid is fed to the analyser it is likely to deposit as an inert layer on the oxidation catalyst leading to rapid loss of activity and sometimes blockage of the system. Alternatively it may deposit in the injection system.

5 Sample (and 'Carbon-free' Water) Preparation

5.1 'Carbon-free' Water

Water that is extremely low in organic carbon is required for TOC determinations. Glassware used for the preparation and storage of 'carbon-free' water must be cleaned with chromic acid (see Section 3 – Hazards), and materials used should be analytical reagent grade.

'Carbon-free' water may be prepared by an alkaline potassium permanganate distillation of distilled or de-ionized water. The distillate is further distilled with sulphuric acid and potassium dichromate [6, 6a].

UV light can also be used to obtain 'carbon-free' water [9, 9a, 12].

For TOD analysis, care must be taken to remove dissolved oxygen from the product water; this may be done by boiling and allowing to cool in an atmosphere of oxygen-free nitrogen.

5.2 Total Carbon (TC) Determination

If the sample contains solid or particulate matter, it must be homogenized to such a degree that it is possible to present a representative aliquot to the instrument and not impair its operation (for example by blockage). Ultrasonic homogenization, if sufficiently powerful, is frequently adequate, but it will not deal with every type of organic material – pondweed, for example, and on occasions preliminary maceration may be necessary. The increase in temperature arising from homogenization or maceration may cause loss of volatile organic carbon (VOC). Dilution of the sample, if required, should be carried out after homogenization.

5.3 Total Organic Carbon (TOC) Determination

To determine the TOC the sample must be treated so as to remove the total inorganic carbon (TIC). This is normally done by acidification and purging with an inert gas. The gas may be freed from carbon dioxide by passage through a column filled with a molecular sieve or other suitable absorbant. The rate and duration of purging must be determined according to aliquot size and nature of sample. Any tendency for particulate matter either to settle out or float in froth should be minimized by stirring. This sample purging technique is not suitable if an appreciable amount of the TOC content is volatile, or is rendered volatile by acidification (for example, cyanides). Whereas no appreciable loss of methanol or acetic acid has been found at low concentrations, loss of acetone is significant [1], and volatile organic compounds which are sparingly soluble in water, exert a higher partial vapour pressure and are more volatile than expected [2]. A technique has been reported for removing trace quantities of diesel oil from water by purging [3].

Some instruments measure the TOC only after acidification and purging of the sample as described, while another can determine the TC and the TIC separately by injecting the original sample on to columns placed side by side at 900°C and 150°C respectively and thus obtains the TOC by difference. Certain instruments can determine both the TIC and the TOC sequentially by acidification and purging of the sample, followed by measurement of the evolved carbon dioxide (TIC), before the stripped sample is passed into a combustion tube at 900°C (TOC). Other instruments acidify and purge the sample but then either vent the evolved carbon dioxide to atmosphere and absorb the evolved volatile organic fractions (VOC) on a column from which they can be later released for measurement, or absorb the evolved carbon dioxide and allow the VOC to pass through for immediate measurement. Such instruments then measure what is sometimes classed as the residual organic carbon (ROC).

Then ROC + VOC = TOC (See also Sections 5.5 and 5.6.)

5.4 Total Inorganic Carbon (TIC) Determination

Sample injection on to a column containing phosphoric acid on an inert support at 150°C and measurement of the evolved carbon dioxide using a non-dispersive infra-red analyser provides a direct method for TIC measurement.

Another approach is to acidify the sample, purge with carbon dioxide-free carrier gas and measure that gas subsequently for entrained carbon dioxide. Alternatively, the TIC may be estimated as the difference between TC and TOC, but loss of volatile organic compounds in either determination could lead to errors. If cyanides are present they will be included in the result for TC but not in the result for TOC (see Section 5.3). If cyanides are absent the TIC could be obtained from the difference in values which are obtained by measurement of the carbon content of the sample after purging with and without acidification:

For example

Sample injected without acid or purging	=	TC
Sample purged without acidification	=	TC when volatiles absent
Sample purged without acidification	=	(TC–VOC) when volatiles present
Sample acidified and purged	=	TOC when volatiles absent
Sample acidified and purged	=	(TOC–VOC) when volatiles present

Hence TIC = TC–TOC when volatiles absent.
or TIC = (TC–VOC) – (TOC–VOC) when volatiles present.

5.5 Dissolved Organic Carbon (DOC) Determination

It is necessary to remove both inorganic carbon (see Section 5.3) and particulate matter (see Section 5.6) from the sample. The method of filtration is dictated by the desired cut-off point of particle size, which in turn depends on the sample. Membrane filters, silver frits and some glass fibre papers are suitable but ordinary filter paper may introduce organic contamination. Any filtration system should be checked to ensure that sample contamination or carbon absorption does not cocur and this is extremely important at low levels of organic carbon measurement. Water soluble matter should be eluted from membrane filters by passing 1 litre of water through up to 10 filters in series held in a suitable filtration apparatus at an internal pressure of 2·6 to 3·3 kPa. A similar procedure is advised for glass fibre filter papers.

Filtration of the sample should be carried out before sample dilution or purging. Samples for DOC measurement should not be homogenized since this treatment can cause dissolution of particulate material (see Section 5.6). It should also be kept in mind that, at reduced pressure, filtration of a sample is likely to cause loss of volatile organic carbon, and filtration at atmospheric pressure is recommended for samples believed to contain volatile material. Determination of the dissolved organic carbon should *not* then contain a purging procedure (see also Sections 5.3 and 5.4).

Total DOC = Dissolved, non-volatile organic carbon (DNVOC) + VOC,
and TOC = total DOC + POC.

In many cases the volatile fraction can be assumed to be negligible and
DOC = TOC – POC = (TC – TIC) – POC.

5.6 Particulate Organic Carbon (POC) Determination

This can be estimated only by difference between TOC and DOC determinations and is normally obtained by filtration of the original sample (see Section 5.5). Samples should not be homogenized prior to filtration since this can cause dissolution of some particulate material. Filtration may also cause loss of volatile organic carbon (see Section 5.5). However, if the TOC and DOC are both measured by the same procedure (for example acidification and purging), the loss of volatiles will not matter, and

POC = TOC – DOC.
Also POC + DOC = ROC = TOC – VOC (see Section 5.8).

5.7 Volatile Organic Carbon (VOC) Determination

VOC is that part of the carbon content of a sample which can be removed by exhaustive purging at a defined temperature, with an inert gas. Certain instruments are said to be capable of determining VOC by measuring the carbon content of the pure gas (see Section 5.4) before the sample is introduced into the combustion area at 900°C or the UV

irradiation area (see Section 8.5). Alternatively VOC may be estimated by the determination of the total carbon before and after purging but this is subject to errors of difference measurements. Thus:

Original sample injected with no acidification or purging = TC .....(1)
Sample purged with inert gas and injected = TC–VOC .....(2)
Sample acidified and purged and injected = (TC–VOC–TIC) .....(3)

Then VOC = (1) – (2)
TIC = (2) – (3)
ROC = (3)

5.8 Residual Organic Carbon (ROC) Determination

This term usually refers to (TOC–VOC) which can be measured by presenting an acidified and purged sample to the instrument. Certain instruments, however, can distinguish between volatile and non-volatile components automatically and provide a print-out of both VOC and ROC results.

Then TOC = VOC + ROC (see Section 5.3).
and where ROC contains POC + DOC.

5.9 Total Oxygen Demand (TOD) Determination

The sample must be sufficiently homogeneous to present a representative aliquot to the instrument, (see Section 5.2). However, apart from the risk of loss of volatile oxidizable material, there is an additional possibility of atmospheric oxidation during homogenization. This can be avoided by homogenizing the sample under nitrogen.

6 Sample Injection Systems for Total Organic Carbon and Total Oxygen Demand Analysis Methods

6.1 Introduction

For these measurements a discrete small sample or a continuous flow of sample for a period of several minutes is required. Only the former can be performed manually, but both can be used in automated equipment. Generally it is easier to inject downwards into a vertical combustion tube using gravity to assist the direction of movement.

In the laboratory, samples from a 'turntable' system can be used in conjunction with an automated analyser to produce a series of results from different samples.

For total organic carbon measurement an on-line instrument usually incorporates a two-stage sampling system. The first stage involves continuous pumping of the sample stream, at a rate sufficient to give a linear velocity of 100 to 150 cm/sec, to a constant level device. Solids separation, acidification and gas sparging may be carried out at this stage. The second stage feeds the sample forward to the injection system from a constant level device.

6.2 Manual Injection of a Discrete Sample

A syringe to deliver 10 µl to 5 ml of sample can be used. The sample size is dependent on the instrument design and the concentration range being examined. When the injection is to be made into a horizontal combustion furnace a spring-loaded syringe which will release the sample in one rapid movement is sometimes to be preferred.

The syringe is best used to introduce the sample through an open tube which is stoppered before and after injection. Introduction of the syringe can be carried out through a septum cap but care must be taken if errors resulting from small pieces of the septum cap breaking off and entering the combustion tube are to be avoided. Syringe injection into a small 'boat' containing the catalyst, can be used with the advantage that measurement of both volatile and non-volatile components can be made and any poisoning of the catalyst is restricted to the one sample. The boat is advanced horizontally into an oxidation furnace. In one system, up to 10 ml of sample is placed in a borosilicate ampoule, potassium persulphate is added, the sample is acidified and purged with purified oxygen to remove carbonate ions. The ampoule is then sealed and autoclaved. Generally manual injection cannot be carried out with the same reproducibility as automated methods of injection.

6.3 Automated Injection of a Discrete Sample

6.3.1. *Use of a 'Slide Valve'*

The 'slide valve' can be used to inject a sample of 10 to 40 ml preferably into a vertical furnace. The sample is fed to the valve by suction using an air aspirator or by a metering or peristaltic pump (see figure 2). Air pressure is then used to move the slide, usually constructed in polytetrafluoroethylene, such that a discrete sample is injected into the combustion tube. The sequence of events can be carried out by a cam and timer or an electronically controlled system.

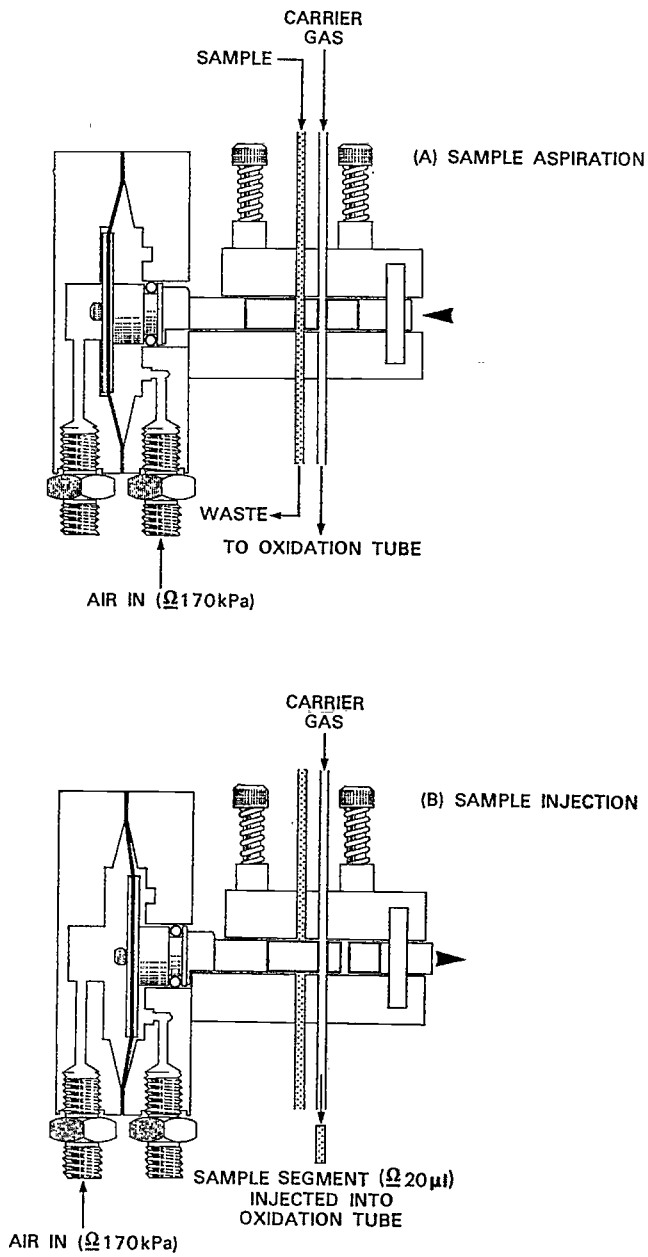


Figure 2 Slide valve

6.3.2. *Use of 'Rotary Valve'*

The 'rotary valve' is more complex than the slide valve as it makes use of rotation to control the sequence of events rather than employing a separate cam and timer or other control system. The sample stream flows continuously through a channel in the valve from a pumped system (see figure 3). A sample for analysis is aspirated from the flow channel through a 0·033 mm diameter injection port by means of a mechanical syringe assembly that is activated by a circular cam and cam follower. The syringe and cam follower are mounted in the rotating sample transfer assembly that is driven at a fixed rate by a motor. When the cam follower drops down the step in the cam, the sample is injected into the oxidation furnace. The overall sequence of events is usually controlled electronically.

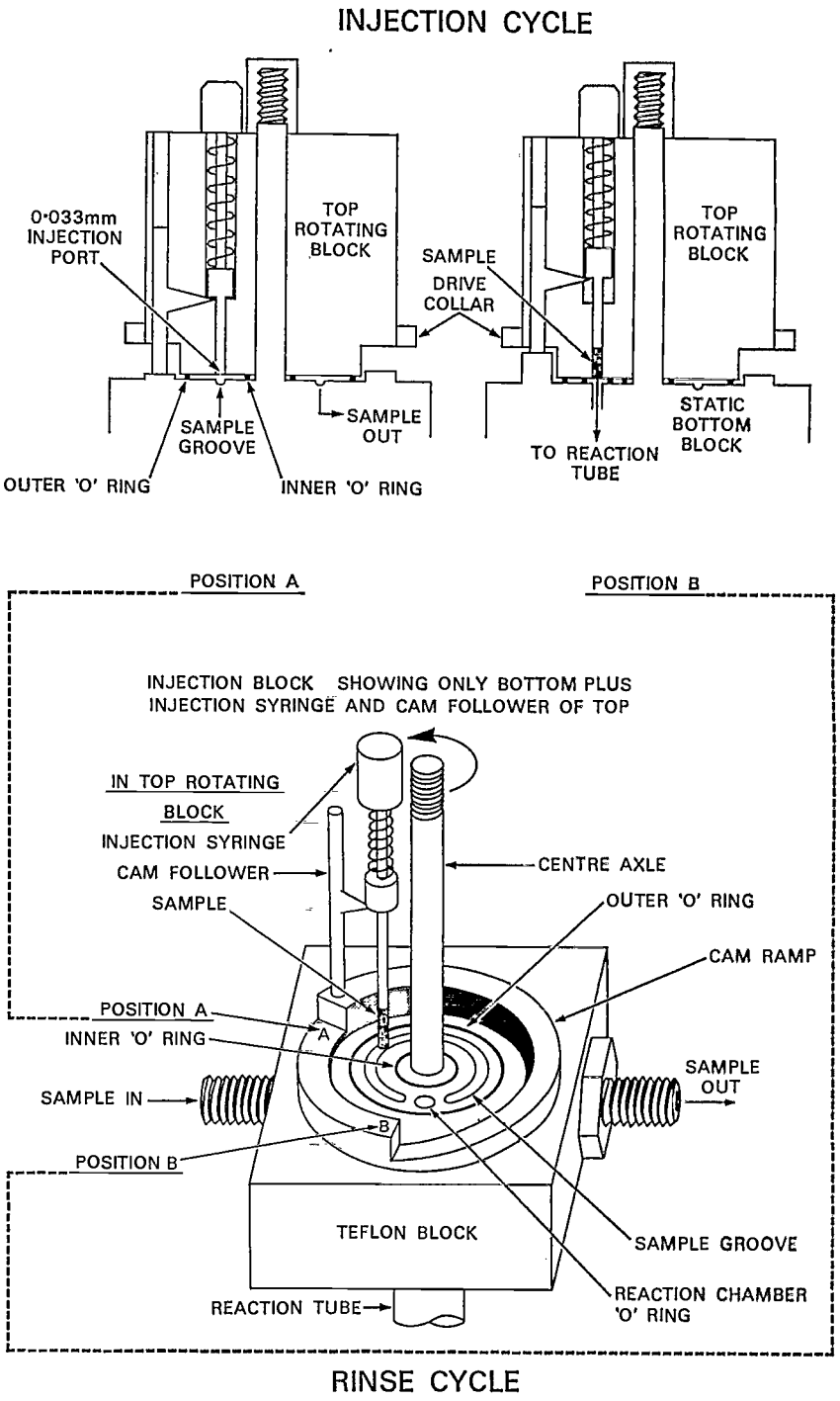


Figure 3 Rotary valve

6.4 Use of a Continuous Flow of Sample

Whilst a discrete sample will give a 'peak' for measurement purposes a continuous flow of sample is used to arrive at an equilibrium response. The limits of detection using discrete sampling systems are governed by the variability of the response to blank water. A continuous flow of sample produces lower, more reproducible, blank values than does discrete sampling. It gives lower limits of detection.

7 The Carrier Gas System for Total Organic Carbon and Total Oxygen Demand Analysis Methods

7.1 Oxidation Stage

After the sample has been introduced into the system a carbon dioxide-free carrier gas sweeps it into an oxidation furnace. The carrier gas type and flow-rate are important influences on both the sensitivity and reproducibility which can be achieved. The gas mixture, flow-rate and sample size can only be optimized, as far as response is concerned, for a given apparatus and determination. Three types of gas system can be used, namely:

i. an inert gas
ii. oxygen
iii. mixtures of inert gas and oxygen

For TOC determinations all three types of gas systems have been used. The inert gas system, usually nitrogen, is used when the oxidation stage is followed by a reduction of the carbon dioxide produced to methane in a hydrogen carrier gas over a nickel catalyst (see Section 9.1.1). In this type of process, injected water is usually condensed out between the oxidation and reduction stages.

Oxygen is a preferred carrier gas for TOC systems where catalytic oxidation is a first stage followed by measurement using non-dispersive infra-red analysis.

A mixture of oxygen and inert gas is the only system used for TOD measurements. In this case carbon dioxide-free nitrogen is used with a measured quantity of oxygen. The oxygen is metered either via a known length of semi-permeable silicone tube held in a constant temperature enclosure, or by using a zirconia cell at 640°C where an applied voltage can be used to control the amount of oxygen passing through it. This is more fully explained in Section 9.2.1. The latter method does enable the measurement of oxygen consumed to be electronically linked to the oxygen introduced [21, 23] (see figure 4).

7.2 Detection Stage

Where the carbon dioxide formed is reduced to methane, and the methane measured using a flame ionization detector, hydrogen is introduced and, together with any inert gas from the oxidation stage, forms the carrier gas for the reduction stage. In this case it is imperative that oxygen is not used in the first stage.

8 Oxidation Systems

8.1 Introduction

When the sample has been introduced into the system, oxidation of carbonaceous components to carbon dioxide is the next stage in both TOC and TOD determinations. The most widely used oxidation stage is carried out at high temperature, 850°C to 950°C, using a catalyst [4, 5, 6] but alternative methods, such as dichromate oxidation at 140°C to 160°C [7] and ultra violet oxidation [8, 9, 10, 11, 12] in the presence of persulphate or oxygen can be used with some limitations.

8.2 Combustion Tubes

The size and shape of combustion tubes are dictated by the sample size and the flow rate through them; tubes range in length from 200 to 400 mm and in width from 15 to 50 mm. Various designs of combustion tubes exist, from the simple straight tube to a more complicated chamber with internal baffles to increase the oxidation efficiency. The common materials of construction are quartz, nickel alloy and ceramic material. Quartz eventually devitrifies and needs replacing more frequently than the more robust metal (nickel alloy) tubes. The latter, however, can corrode if subjected to acidic gases. Ceramic tubes, which are resistant to acidic gas corrosion, have been successfully used.

Tubes can be mounted vertically or horizontally, but both arrangements have disadvantages. Sample introduction to a vertical tube is easier to automate and the catalyst packing is likely to remain intact. On the other hand, oxide catalysts tend to powder and the fines accumulate at the bottom of vertical tubes with resultant blocking. Horizontally mounted tubes are prone to the gases channelling through the catalyst with resultant incomplete oxidation.

8.3 Catalytic Systems

Although several catalytic systems have been used, the differences, if any, have not been defined in detail. The following are in general use:

i. Platinum
ii. Platinum-Rhodium
iii. Palladium
iv. Cobalt Oxide
v. Copper Oxide

The precious metal catalysts, of which platinum is the most popular, are most commonly used in the form of gauze, usually in conjunction with oxygen or oxygen-inert gas mixtures. Copper oxide, invariably the wire form, can be employed as an oxidation catalyst

when inert gas is used. Cobalt oxide is commonly used on an inert support, such as pumice, on which it is initially added as the nitrate. It is used with oxygen or nitrogen carrier gas systems. Catalysts supported on asbestos have been unsatisfactory because of a tendency to consolidate in use and cause blockages.

8.4 Chemical Oxidation Systems

Two processes have been developed for wet chemical oxidation. It is important to note that neither may give complete oxidation of all organic materials.

In the first, a conventional dichromate oxidation in sulphuric acid is carried out in a flow system using peristaltic pump techniques and temperature as a variable. As well as measuring the dichromate consumed under the experimental conditions (COD), the carbon dioxide formed is swept out and measured by conductimetry (TOC) [7].

In the second process, the sample is placed in a borosilicate ampoule, potassium persulphate is added and carbonate is removed by acidifying the sample and purging with oxygen. The ampoule is sealed, subjected to oxidation by autoclaving for 2–4 hours at 140°C, then broken and the carbon dioxide formed is released into the instrument where it is measured by an IR gas analyser (TOC) [13, 14].

8.5 Photochemical Oxidation Systems

UV oxidation has been shown to be particularly applicable to DOC determinations in river, lake and sea waters. Again, two systems are encountered.

In the first [12, 15] the filtered sample (up to 20 ml) is injected into a vessel where inorganic carbon is removed by acidifying and purging with carbon dioxide-free air or helium. The sample is then subjected to irradiation from a mercury-vapour lamp placed inside the vessel for a period of 3–10 minutes. The resulting carbon dioxide is led through a condenser and filter, to be measured by an IR gas analyser [15], a flame ionization detector after conversion to methane [12] or by a resistivity detector [33].

The alternative procedure [8 9, 9a] is to pass the samples continuously through silica coils wound round the UV source. The carbon dioxide is separated from the liquid phase by stripping with nitrogen and finally measured by an IR gas analyser [8, 9, 9a] or spectrophotometrically using phenolphthalein [11].

9 Detection Systems

The gases emerging from the combustion tubes, which are an inherent part of many TOC or TOD instruments, are hot and highly corrosive. Water and carbon oxides may be accompanied by halogens and the oxides of nitrogen, sulphur and phosphorus. It is undesirable that these acidic gases should pass forward into the detector systems and usually they are removed from the gas stream by condensing the water vapour which, in liquid form, then acts as a scrubbing system. Following this, a plug of manganese dioxide may on occasion be used to remove nitrogen oxides and a plug of silver wool to remove halogens, halogen hydracids and sulphur dioxide. Gas lines carrying these corrosive vapours should be constructed in AISI type 316-S12 or 316-S16 stainless steel or in glass. The scrubbed gases are saturated with water vapour. They may be passed directly to many detectors (for example platinum/lead fuel cell, Section 9.2.2) without further treatment but, in the case of the flame ionization detector (FID), they should be dried. The self-indicating silica gel used for drying simultaneously removes any ammonia present which would have an adverse effect on the performance of certain designs of FID.

Titrimetric, nephelometric and spectrophotometric procedures can only be operated with larger sample volumes than is conventional in other forms of detector (most systems operated with 2–50 ml samples). Larger samples are an advantage where a representative sample is difficult to achieve.

The various detector systems that have been incorporated into commercially available instruments are conveniently discussed under the two main headings of sections 9.1 and 9.2.

9.1 Detectors used in TOC Instruments

9.1.1 *The Flame Ionization Detector*

The mode of operation of this detector is well described in reference 16. It is insensitive to the carbon dioxide normally produced in the oxidation furnace of a TOC apparatus, so that the gases from the furnace are passed, with added hydrogen, through a nickel catalyst at 450°C. The resulting methane is readily detected by the FID and is a direct measure of the concentration of carbon compounds in the initial sample.

9.1.2 *Non-dispersive Infra Red Detector (NDIR)*

The mode of operation of this type of detector is described in reference 17. In modern instruments, narrow band pass optical filters are used to select the analytical wavelength. Carbon dioxide is the product of combustion most commonly measured but carbon monoxide may also be measured. The optical filters prevent significant interference at the selected wavelength due to the presence of other likely components of the gases leaving the oxidation furnace; the absorbance maxima of such gases are as follows:

Carbon monoxide	4.6, 4.7 μm
Carbon dioxide	4.4 μm
Nitrogen dioxide	5.7, 6.2, 7.9 μm
Sulphur dioxide	7.4, 8.6 μm
Hydrogen chloride	3.4, 3.5 μm

The detector accepts the cooled gases containing up to 1% water by volume from the oxidation furnace.

9.1.3 *Titrimetric Method*

Gases coming from the combustion zone must again be completely freed from halogens and oxides of elements other than carbon.

The carbon dioxide is either absorbed in standard barium hydroxide solution and determined by back-titration with standard hydrochloric acid solution, or absorbed in alkaline barium perchlorate which is back-titrated with barium hydroxide produced as required by electrolysis [18].

Greater sensitivity is claimed if the evolved carbon dioxide is absorbed in monoethanolamine dissolved in dimethylformamide. [19] Automatic titration of the resulting ammonium carbamate is carried out with standard tetrabutyl ammonium hydroxide solution, using thymolphthalein as indicator and photometric detection of the end point.

9.1.4 *Nephelometric Method* [20]

This procedure has been introduced quite recently and involves passing the gaseous products from the combustion furnace into barium hydroxide solution. The only pretreatment necessary is to cool the gas stream to condense out the majority of the water. Measurement of the turbidity produced by the carbon dioxide then provides a value for the carbon content of the original sample.

9.1.5 *Electrical Conductivity Method* [10]

If the gases emerging from the combustion zone are freed of the oxides of nitrogen, sulphur and phosphorus, and passed into a solution of barium hydroxide or sodium hydroxide, the change in electrical conductivity of this solution is found to be linearly related to the amount of carbon dioxide absorbed.

9.1.6 *Spectrophotometric Method* [11]

This is used in an automated procedure where carbon dioxide is produced by persulphate and/or UV oxidation and is then passed through a gas permeable dialyser membrane into a weakly buffered phenolphthalein solution. The decrease in colour is proportional to the carbon dioxide concentration and hence to the initial organic carbon.

9.1.7 *Resistivity Method* [33]

An air stream carries the carbon dioxide produced by UV oxidation to a measuring chamber which contains 'carbon free' water with a conductivity of about 0·055 μS/cm. The carbon dioxide dissolves in the water and the resultant change in the specific resistance of the water is measured.

9.2 Detectors used on TOD Instruments

9.2.1 *Measurement using Zirconium Oxide Cells* (21)

This system of measurement is based on the high-temperature electro-chemical properties of zirconium oxide which, at about 600°C, are:

i. Permeable to oxygen when an electrical potential difference is applied across the oxide layer and the quantity of oxygen transported is directly proportional to the current passing.

ii. If a difference in oxygen partial pressure exists across the zirconium oxide, this results in the establishment of a potential difference between the two surfaces exposed to the two different gaseous atmospheres (Nernstian behaviour).

iii. Acts as a typical semiconductor and exhibits a negative temperature coefficient of resistance. This property can be utilized in accurately controlling the temperature of zirconium oxide elements used for the present purposes.

In a common form of the instrument, one zirconium oxide measuring cell is used. The carrier gas to the oxidation furnace is purified nitrogen in which a controlled oxygen concentration is established by diffusion of air through a length of silicone rubber tubing.

When aqueous samples containing organic matter are fed to the oxidation furnace, the oxygen content of the effluent gas from the furnace falls. The decrease is measured by the zirconium oxide detector cell and is recorded as a measure of the TOD value of the sample. With this system, the gases leaving the oxidation zone are scrubbed free of acid constituents and simultaneously rehumidified by bubbling through water.

In another form of TOD instrument, the zirconium oxide is used in the form of a cylindrical tube (figure 4b) and two such cells are arranged, one on each side of a combustion furnace containing platinum catalyst at 900°C (figure 4a). Both cells are exposed to the air on their external surfaces and purified nitrogen carrier gas passes internally through the dosing cell. The dosing electrodes supply a constant current to this cell, thus introducing a closely controlled oxygen content into the carrier. Step changes in the current permit range changes on this type of instrument.

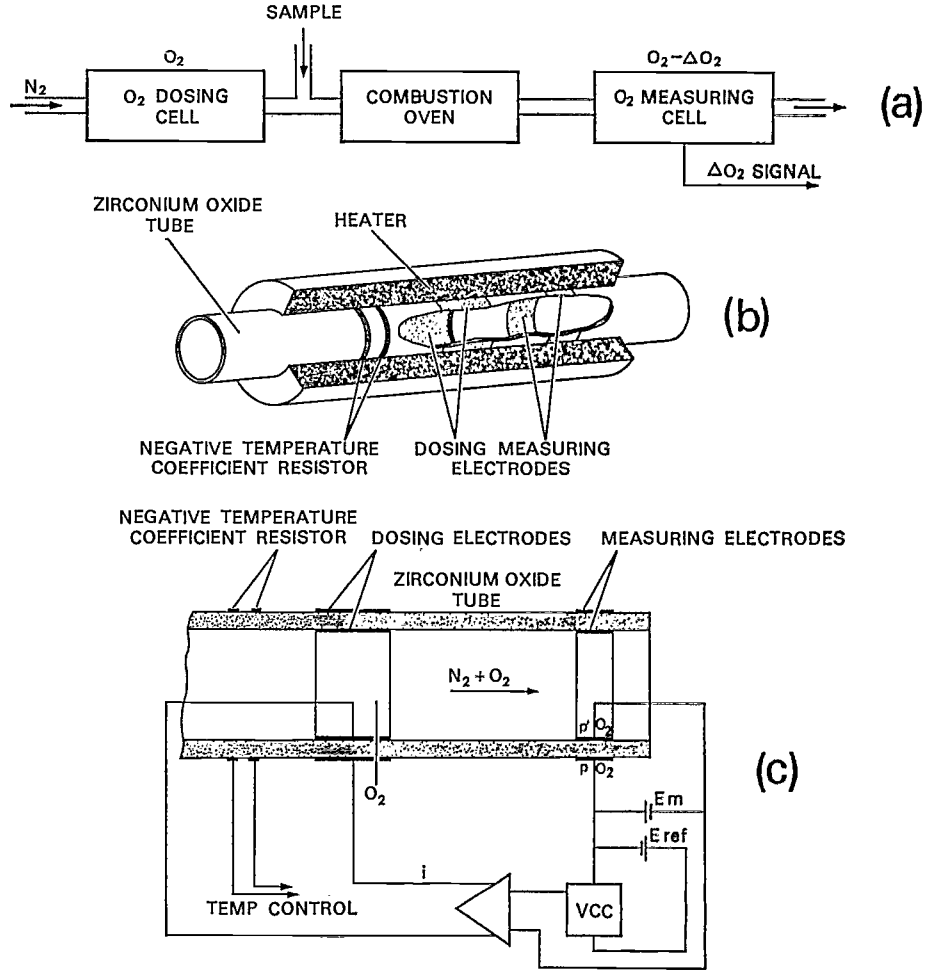


Figure 4 The zirconium oxide detector

The gases emerging from the combustion zone are dried and passed through the measuring cell. The Nernst potential difference E_m, across the measuring electrodes is balanced by a reference potential E_{ref} (figure 4c). When combustion of an aqueous sample occurs, the oxygen partial pressure in the measuring cell drops, the potential increases and an out of balance potential (E_{ref}–E_m) appears at the voltage convertor VCC. The current output of VCC is amplified and applied to the dosing electrodes in the measuring cell, thus transporting oxygen from the atmosphere into this cell until electrical balance is restored, and transport ceases. The dosing current of the measuring cell is integrated with respect to time to give the amount of oxygen transported and hence the TOD value of the sample.

9.2.2 *Measurement by Electrochemical Cell* (22)

The other commonly used detector system for TOD measurement makes use of an electrochemical cell often referred to as a platinum/lead fuel cell which has an electrical output proportional to the partial pressure of oxygen in the gas passing through it. A closely controlled level of oxygen is maintained in the nitrogen carrier gas by a diffusion system of the type described in section 9.2.1. Aqueous samples, injected into this carrier gas, are swept into an oxidation furnace containing platinum gauze at 900°C. Gases leaving the furnace are scrubbed in potassium hydroxide solution and then passed into the oxygen-measuring cell, which has a lead anode and a platinum cathode partially immersed in a solution of potassium hydroxide. The electrical potential difference between the electrodes is dependent on the partial pressure of oxygen in the gaseous atmosphere in equilibrium with the electrolyte solution as given by the Nernst equation:

$$E = E_o + \frac{RT}{2F} \log pO_2$$

The change in electrical potential brought about by injection of an aqueous sample into the oxidation furnace is thus a measure of the TOD value of the sample. When a discrete sample is injected, the detector output on a chart recorder is a sharp peak (reflecting the reduction of oxygen content in the emerging gas as the sample burns) and its height is proportional to the TOD value of the sample. Range changes on this instrument are accomplished by altering the level of the cell electrolyte.

10 Interferences and Sources of Error

10.1 Interferences in TOC Analysis

10.1.1 *Dissolved Carbon Dioxide, Inorganic Carbonate and Bicarbonate*

Since the measurement of TOC is essentially based upon the determination of carbon dioxide produced during combustion of the sample, any sources of carbon dioxide other than organic carbon compounds clearly will interfere.

Inorganic carbonate, bicarbonate and dissolved carbon dioxide, are eliminated by methods already discussed in Section 5.3 and 5.4. By feeding the instrument with aliquots of sample, which have been pretreated in several different ways, it should be possible to determine the amount of the various carbon forms present in the sample.

10.1.2 *Oxidising Agents*

Certain oxidising agents (such as hydrogen peroxide, nitric acid, hypochlorous acid) if added in sufficient quantity to a sample may give rise to increased TOC response. This may be due to oxidation of traces of residual carbonaceous material in such compounds. The effect can be important if operating the instrument in the 0·05–5·0 mg/l C range.

10.1.3 *Sulphur Compounds*

Some sulphur compounds may poison the reduction catalyst thereby reducing its effective life.

10.2 Interferences in TOD Analysis

Many of the effects commented upon in this subsection are not true interferences. They are included so that the reader can derive a better understanding of the TOD process.

10.2.1 *Dissolved Oxygen*

Since TOD analysis involves the measurement of residual oxygen, any dissolved oxygen in the sample as presented to the instrument will proportionately reduce the TOD value. An aqueous sample at ordinary temperatures in equilibrium with the air will have a dissolved oxygen content of about 9 mg/l.

Dissolved oxygen in all samples and standards should either be measured and the respective TOD values corrected, or alternatively removed by aspiration of nitrogen through the sample prior to presentation. If this latter course is taken, volatile compounds may be lost from the sample resulting in low TOD values.

10.2.2 *Ammonia*

In COD analyses, free and saline ammonia is converted to ammonium sulphate. Under the more rigorous conditions of TOD, the fate of ammoniacal nitrogen depends on the amount of oxygen available. Where oxygen is present in large excess. ammoniacal nitrogen is oxidised to nitric oxide:

$$NH_3 + \frac{5}{4}O_2 \longrightarrow NO + \frac{3}{2}H_2O \quad ^{(22)}$$

Under these conditions every 1 mg/l of ammoniacal nitrogen present in a sample should contribute to the TOD by 2·9 mg/l. Values of 2·5 mg/l [23] and 2·9 mg/l [22] have been reported.

When instruments are operated in such a manner that the available oxygen is strictly controlled to avoid large excess, then either the ammoniacal nitrogen is not oxidised at all, or partial non-reproducible oxidation occurs, giving rise to erratic TOD results [21].

Other unoxidised forms of nitrogen (eg. organic nitrogen) behave similarly to ammonia [21, 24, 25].

10.2.3 *Nitrate*

Nitrates under the test conditions may decompose giving up oxygen and reducing TOD values. The equation usually quoted is as follows but supporting evidence is lacking.

$$2\,NaNO_3 \xrightarrow[900°C]{Pt} Na_2O + 2\,NO + \frac{3}{2}O_2 \quad ^{(26)}$$

However, under conditions where oxygen is available in excess, there is evidence for an alternative:

$$2\,NaNO_3 \xrightarrow[900°C]{Pt} Na_2O + NO + \frac{1}{2}N_2 + 2O_2$$

Thus each mg/l of nitrate nitrogen in a sample should depress the TOD value by 2·3 mg/l and this figure has been reported [22].

When no large excess of oxygen is present further evidence would indicate yet another equation:

$$2\,NaNO_3 \xrightarrow[900°C]{Pt} Na_2O + N_2 + \frac{5}{2}O_2$$

with each mg/l nitrate nitrogen depressing values by 2·9 mg/l TOD. A value of 2·8 mg/l has been reported [23].

10.2.4 *Nitrite*

It is unlikely that nitrite concentrations in any real waste water sample would be of such magnitude as to contribute significant interferences in TOD measurement. However,

it may be assumed that like nitrite, nitrate would break down under TOD conditions via a number of routes dependent upon the availability of free oxygen in the system:

$$2\,NaNO_2 \xrightarrow[900°C]{Pt} Na_2O + 2NO + \frac{1}{2}O_2$$

$$2\,NaNO_2 \xrightarrow[900°C]{Pt} Na_2O + NO + \frac{1}{2}N_2 + O_2$$

$$2\,NaNO_2 \xrightarrow[900°C]{Pt} Na_2O + N_2 + \frac{3}{2}O_2$$

Thus every 1 mg/l of nitrite nitrogen in a sample would be expected to depress TOD values by 0·6, 1·1 and 1·7 mg/l respectively.

The limited evidence available indicates a figure of ca. 1·5 mg/l TOD depression for each mg/l nitrite nitrogen [23].

10.2.5 *Sulphate*

Free sulphuric acid is reported to decompose as follows, depressing TOD values [23]:

$$H_2SO_4 \xrightarrow[900°C]{Pt} H_2O + SO_2 + \frac{1}{2}O_2$$

Alkali metal sulphates do not decompose in a similar manner [26].

10.2.6 *Heavy Metals*

As with any high temperature platinum catalysed system there can be a problem of a catalyst poisoning by heavy metals [24, 26].

10.2.7 *High Salt Concentrations*

It has been observed that TOD instruments receiving many samples with high salt concentrations such as sea water, rapidly begin to give erratic readings. This has been attributed to the catalyst becoming coated with molten sodium chloride (meling point 804°C). It is reported that reduction of the furnace operating temperature to 770°C will overcome this problem.

10.2.8 *Other compounds which will yield oxygen under TOD conditions*

It should be recognised that certain types of sample may contain compounds such as peroxides and hypocholorites which will decompose under TOD conditions yielding oxygen and thus depressing TOD values.

11 Performance and Reliability

11.1 Introduction

Methods for the instrumental determination of total organic carbon or total oxygen demand consist basically of three stages, firstly, sample introduction, secondly oxidation and finally detection of carbon dioxide or oxygen consumed. The systems which have been used for these determinations are listed at the left of Table 1. With the exception of instrument type Nos. 12, 13 and 15 and that described in reference No. 8 all the systems are available commercially.

Relatively little has been published on the performance characteristics of the systems and much of the information in Table 1 is gleaned from the generalized data in manufacturers' literature. The only systems for which a reasonable quantity of well defined independent performance data are available are instrument types Nos. 1, 5, 6, 12, 13, 14, 20 and 22.

11.2 Applicability of Different Types of Instrument

The limitations of the various injection systems and the efficiencies of oxidation systems are discussed in the relevant chapters of this document. These two stages limit the performance of all the current instruments. The detection stage is generally not critical.

The applicability of the various types of instrument is summarized in Table 2. In using the table it should be noted that samples having high concentrations of carbon compounds may be diluted for those instruments having restricted oxidation capacity. Similarly saline waters may be diluted where sufficient instrument sensitivity is available. Wet oxidation systems (instrument types Nos. 11, 12 and 19), although known to give less than 100% oxidation efficiencies with some organic compounds have been shown to give greater than 90% oxidation of organics in natural waters.

11.3 **Reliability**

The only commercially available instruments with long term wide user experience are instrument types Nos. 1, 5, 6, 19, 20 and 22 (Tables 1 and 2). All the instruments have had problems of electrical faults and failure of high temperature tubes and catalyst packings. These problems can be resolved by carrying out a regular maintenance schedule. The continuous injection system has had problems of inlet pipe blockage; these can be resolved by the use of suitable operating conditions and procedures. All the other instruments have proved reliable to some users, but further data are lacking.

Table 1 Types of instruments, ranges, detection limits and repeatabilities

Instrument Type No and Manufacturer	Ref	Instrument Type			Upper limit of ranges mgC/l (TOC) mgO_2/l (TOD)	Detection Limits mgC/l (TOC) mgO_2/l (TOD)	Relative 95% Confidence intervals of replicate analysis of Standards. Std. level ±Confidence interval
		Oxidation System	Detector	Injection System			
TOC							
1. Phase Separations	6	High temp	FID	Continuous	500 and 1500*	0·02 to 0·1*	50±2·8%
2. Phase Separations	—	High temp	FID	Discrete†	—	—	—
3. Carlo Erba	—	High temp	FID	Discrete	600*	0·1*	0–5±4%
4. Dohrmann DC52	28	High temp	FID	Boat	200 and 6000	0·1*–8·0	2000±2%
5. Maihak	29	High temp	NDIR	Continuous	1000	0·05	—
6. Beckman	4 30	High temp	NDIR	Discrete	20 and 4000	1·0–4·0	100±0·8%
7. Strohlein Coulomat	18	High temp	Coulometric	Boat	—	0·1*	—
8. Hereaus	19	High temp	Titrimetric	Discrete	2000	0·2	800±0·5%
9. Delta Scientific	20	High temp	Nephelometric	Discrete/ on line	10 and 5000*	0·4*	± 2% f.s.d.
10. Oceanography Int Corp	—	High temp wire	NDIR	Discrete	250*	—	± 0·5% to 2%
11. Oceanography Int Corp	13 14	Persulphate	NDIR	Ampoules	10	0·02	0·1±5%
12. Not available commercially	9	Persulphate	NDIR	Continuous	5	0·01	5·0±1·2%
13. Not available commercially	8 9	UV	NDIR	Continuous	5 and 25	0·01 to 0·001	5·0±2%
14. Maihak	15	UV	NDIR	Discrete	—	—	—
15. Not available commercially	10	UV	Conductimetry	Continuous	10	<0·1	10±1·2%
16. Technicon	11	UV	Spectrophotometric		20 and 1000	0·2 and 2	2·3±5%
17. Dohrmann DC 54	12	UV	FID	Discrete	10*	0·02*	± 2%*
18. Sybron/Barnstead	33	UV	Specific resistance	Discrete		No other information	
19. Wösthoff	7	Dichromate	Conductimetry	Continuous	—	—	—
TOD							
20. Ionics	22 24	High temp	Fuel Cell	Discrete	1000*	12·0	200±2·3%
21. Ionics	32	High temp	Zirconia	On-line	1000 and 6000	23·0	
22. Philips	23	High temp	Zirconia	Discrete/ auto inject	100 to 10000	8·0	250±2%
23. Aquarator (Precision Scient)	31	High temp (CO_2)	NDIR (CO)	Discrete	300	8·0	250±2%

* Manufacturer's data † Attachment for saline samples

A new range of on-line and laboratory instruments are now available from Ionics Ltd for TOC, TOD and TOC/TOD determinations. (UK Agents – Techmation Ltd).

The above information is not exhaustive and was based on that available at the time of going to press.

Table 2 Applicability of systems

Instrument Type No and Manufacturer (refer to Table 1)	Oxidation and Detection Systems	Type of Sample					
		Particulates 100 mμ	Low Level 1mg C/l	Natural Waters 2–20 mgC/l	High Level 20 mgC/l eg Wastes Sewages etc	Undiluted Sea Water	Volatile Organics
TOC							
1. Phase Separations	High Temp/FID		✓	✓	✓		*
2. Phase Separations	High Temp/FID					✓	
3. Carlo-Erba	High Temp/FID		✓	✓	✓		✓
4. Dohrmann DC52	High Temp/FID	✓		✓	✓	✓	✓
5. Maihak	High Temp/NDIR			✓	✓		✓
6. Beckman	High Temp/NDIR			✓	✓		*
7. Strohlein Coulomat	High Temp/ Coulometric	✓	✓	✓	✓	✓	*
8. Hereaus	High Temp/ Titrimetric	✓		✓	✓		*
9. Delta Scientific	High Temp/ Nephelometric	✓		✓	✓		✓
10. Oceanog. Int. Corp.	Hot Wire/NDIR	✓		✓	✓		✓
11. Oceanog. Int. Corp.	Persulphate ampoules/NDIR		✓	✓		✓	
12. Private	Persulphate/NDIR		✓	✓			✓
13. Private	UV/NDIR		✓	✓		✓	
14. Maihak	UV/NDIR		✓	✓		✓	✓
15. Private	UV/Conductimetric		✓	✓		✓	
16. Technicon	UV/Spectrophotometric		✓	✓	✓	✓	
17. Dohrmann DC54	UV/FID		✓	✓		✓	✓
18. Sybron Barnstead	UV/resistivity		✓	✓	✓		✓
19. Wösthoff	Dichromate/ Conductimetric			✓	✓		
TOD							
20. Ionics	High Temp/Fuel cell				✓	✓	✓
21. Ionics	High Temp/Zirconia				✓	✓	✓
22. Philips	High Temp/Zirconia				✓	✓	✓
23. Aquarator (Precision Scientific)	High Temp (CO_2)/ NDIR (CO)				✓	✓	✓

✓ The presence of a tick shows a *particular* suitability for the application.
The absence of a tick does not necessarily imply that the instrument cannot be used for these applications.

* Can be done indirectly.

11.4 Performance

The published performance data on the various types of instrument are given in Table 1. Limits of detection have been calculated as recommended by Wilson [27] (about 5 × standard deviation of blank). Where reproducibility figures have been quoted as a percentage of full scale deflection, the reproducibility claimed has been assumed to be at the 95% confidence level and the limits of detection have been calculated from this figure for the most sensitive range of the instrument. All the detection limits quoted are the concentrations of carbon detectable above the instrument blank. All the instruments give a background reading on the most rigourously prepared 'carbon-free' water the lowest values recorded being between 0·05 and 0·10 mg/l C. Although this level is thought to arise from contamination from the materials of construction of the apparatus, or dynamic instrument factors, it cannot be proved that it does not originate from the blank water and, therefore, results may be biased by the apparent carbon content of the blank water.

The time taken for a single analysis varies from 2 to 10 minutes except for the wet oxidation systems which may take at least 2 hours. The disadvantage of the latter is somewhat offset by oxidising several samples simultaneously. Generally those instruments giving similar performance have very similar response times. The repeatability of all the systems for which data is available is given in Table 1.

The most sensitive systems for TOC analysis are those employing continuous injection. With the exception of persulphate oxidation using ampoules, and a UV/FID procedure, all instruments giving limits of detection less than 0·1 mg/l C employ this system. Apart from certain boat-type injectors, discrete injection systems using high temperature combustion have limits of detection ranging from 0·2 to 4·0 mg/l C. They are, therefore, more suited to sewage and effluent samples while their generally shorter response times may also be advantageous.

Only high temperature oxidation systems are available for TOD analysis. The usual oxidant gas is oxygen but carbon dioxide has been used (instrument No. 23, Table 1); the two systems should probably be regarded as providing different measurements, but no comparative data are available. The systems employing oxygen as oxidant are much more widely used than that employing carbon dioxide. Both oxygen detector systems give very similar performance. The ranges of all commercially available systems except instrument type Nos. 11 to 17 are sufficiently large to deal with a diversity of samples. For instrument type Nos. 11 to 17 the range is limited by the oxygen available either from an added oxidant solution or from the sample itself and these systems are most suited to the analysis of natural and high purity waters.

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Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

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Mr B Rhodes	3	from July 1978
Prof JP Riley	3	
Mr GS Sayers	1	
Mr CC Scott	2	
Mr R Sinar	3	(since Deceased)
Mr FJ Whitby	1, 2	
Mr BT Whitham	3	
Mr AL Wilson	3	
Mr R Wood	3	to July 1978

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