The Instrumental Determination of Total Organic Carbon and Related Determinands 1995

Methods for the Examination of Waters and Associated Materials

HMSO

Standing order service

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This booklet consists of three main parts. Part A is an update of the review which comprised the 1979 booklet in this series and is now superseded. All reference to total oxygen demand included in the 1979 review has been deleted since there is no longer any interest in this determinand within the UK water industry.

Part B is a specimen analytical method for total organic carbon (TOC) determination based upon high temperature oxidation and carbon dioxide detection by infrared spectrometry.

Part C is a specimen analytical method based upon ultraviolet-persulphate oxidation using infrared detection as described in Part B.

The two methods have been included in the booklet since they are the most widely used systems amongst the many available.

Only limited performance data has been provided using these methods.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, groundwater, river and seawater, waste water and effluents as well as sewage sludges, sediments and biota. In addition, short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests reported for most parameters. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results encompassing at least ten degrees of freedom from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors), systematic error (bias), total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available. An indication of the status of the method is shown at the front of this publication on whether or not the method has undergone full performance testing.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets in the series 'Methods for the Examination of Waters and Associated Materials' and their continuous revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is managed by the Drinking Water Inspectorate. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are:

1.0 General principles of sampling and accuracy of results
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage treatment methods and biodegradability
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members associated with these methods are listed at the back of the booklet.

Publication of new or revised methods will be notified to the technical press. An index of methods and the more important parameters and topics is available from HMSO (ISBN 0 11 752669 X).

Every effort is made to avoid errors appearing in the published text. If, however, any are found please notify the Secretary.

Dr D WESTWOOD
Secretary

27 December 1994

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with The Health and Safety at Work etc Act 1974 and any regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 1988 SI 1988/1657. Where particular or exceptional hazards exist in carrying out the procedures described in this booklet then specific attention is noted. Numerous publications are available giving practical details on first aid and laboratory safety, and these should be consulted and be readily accessible to all analysts. Amongst such publications are those produced by the Royal Society of Chemistry, namely 'Safe Practices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', 5th edition, 1992; by Member Societies of the Microbiological Consultative Committee, 'Guidelines for Microbiological Safety', 1986, Portland Press, Colchester; and by the Public Health Laboratory Service 'Safety Precautions, Notes for Guidance'. Another useful publication is produced by the Department of Health entitled 'Good Laboratory Practice'.

Introduction

Review of method to date

The determination of organic carbon and its sub-components in various forms was believed to be straightforward, and it was the original intention of the Panel revising this Booklet to produce a reference method, or methods, for the determination of various forms of organic carbon. Discoveries since this booklet was first published in 1979 show that the analysis of total organic carbon is far more complex than was previously thought, particularly at low concentrations, and is currently undergoing a significant re-evaluation.

This booklet will concentrate upon providing information upon developments within this field highlighting, where necessary, their impact upon the water industry. Two methods for the determination of organic carbon are included; (i) using high temperature oxidation and (ii) low temperature ultraviolet (UV)-persulphate catalysed oxidation. These methods do not have the status of standard methods but can be used by analysts in conjunction with other information to form the basis of a method which an analyst can be confident produces data in which the analyst is interested.

The two major techniques for the determination of organic carbon have been divided generally in the following manner. High temperature oxidation has been used mainly where the sample contains particulate matter or the organic carbon content has been high, due to real or imagined problems with instrument stability at low concentrations. Such samples include sewages, effluents and trade effluents. Low temperature UV-persulphate catalysed oxidation has predominated where low concentrations, high dissolved solids and large through-put of samples are relevant, predominately in the areas of potable water, the semi-conductor industry, the nuclear industry and power generation.

In 1987 Sakamoto and Miyasaka (1) published an article comparing the efficiencies of the two methods on a wide range of samples and compounds, including humic and fulvic acids. This indicated that for some compounds, the low temperature/UV systems produced lower results than the high temperature combustion systems. This article was followed by a report by Svgimura and Suzuki (2), relating to the determination of dissolved organic carbon in seawater. Their conclusions confirmed those reported in Reference 1, and also indicated that there was a significant proportion of oceanic dissolved organic carbon (DOC) that was not being determined by the low temperature/UV method. Some of their conclusions were later retracted when re-evaluation of the results indicated that system and reagent blanks constituted a major problem (3).

The two earlier reports caused concern over the existing acceptance of the two types of instruments and techniques being used, and it was considered necessary to investigate whether the effects found for seawater were also applicable to riverine and potable waters. To determine this, it was proposed that a "round-robin" series of comparisons be made using standards in high purity water plus river and potable waters known to contain organic carbon. Manufacturers, water laboratories and academic establishments were approached for assistance in these trials and many generous offers were received.

Prior to running these round-robin trials, a series of small-scale trials were run to establish stability of the standards and samples in transit. The results obtained were such as to indicate that there was sufficient evidence that the true results of the instrument performance in the round-robin trials might be masked by problems resulting from sample stability. This resulted in the abandonment of the round-robin trials.

At this time, the Panel was briefed about recently completed, but as yet unpublished, work by oceanographers that confirmed the original Japanese findings. This work indicated that there was a proportion of material containing organic carbon that was not being oxidised by the low temperature/UV systems. It was postulated that this material had a high molecular weight, was susceptible to biological attack and was not broken down by the combined effects of UV-persulphate at low temperatures. Further work in this area by a variety of groups have confirmed that this effect exists, but has shown that it is not consistent (3–8). Results reported show values of DOC obtained using the high temperature combustion methods are 0–30% greater than the low temperature UV-persulphate methods. These results have been obtained using both deep sea water and estuarine samples.

The Panel believed that in the absence of any data about this effect on waste, riverine and potable waters, its duty lay in alerting the industry to these developments. This information is not aimed at any specific group of analysts but is intended to highlight areas known to be problematical. In some instances the information is of a general nature, while in others, it is specific for either sample or method type. It would be difficult under these circumstances to propose exact methods that analysts could use to prove that the combination of instrument and methodology gives the correct result. It is for the analyst to determine the various ways in which this can be achieved.

There is no recommendation as to which method is the more correct. It may well be that the problems encountered by the oceanographers are specific to their medium. However, the determination of organic carbon is the final stage of some material testing and toxicological methods, and as the matrices involved in these methods are very complex, there is a reasonable probability that common problems do exist.

It is hoped that the work which will no doubt take place to confirm the applicability of existing methods will be reported to the Secretary of the Standing Committee of Analysts. This will then allow the Panel to produce an updated booklet in the future, containing complete definitive methods.

Areas of concern

The largest area of concern centres on the apparent variations that can arise by the use of the technique employing the difference between total inorganic carbon (TIC) and total carbon (TC). This difference gives a value for total organic carbon (TOC). Also of concern is the use of inappropriate standard conditions for the analysis of samples by the UV-persulphate method.

The two major techniques for oxidation, ie high temperature combustion or low temperature UV-persulphate oxidation, can produce results for total carbon that differ significantly. As the determination of inorganic carbon appears to show no difference between instruments, this will lead to the subtractive technique for determining total organic carbon giving a result that is highly dependent upon the method used. This effect will also be shown where the samples have the inorganic carbon removed prior to the determination of total organic carbon.

The types of sample presented to the more vigorous oxidative combustion technique appear not to show a reduction in conversion efficiency when pure standards and then samples which contain more complex or particulate material are analysed. It appears that the UV-persulphate method has difficulty in oxidising more complex compounds and particulate material under standard operating conditions.

This situation creates problems where the results are to be used for monitoring purposes, and specifically where legal implications of compliance monitoring are involved. It is not intended to state that one method is better or more correct than any other, but to highlight the potential problems involved with this determination. As in all cases of analysis, it is for the analyst to determine that the method used produces the correct result.

The Panel believe that the following are areas where the effects of the new information now available may be of interest to users. There are not sufficient data available to determine if some, or any, of these points relate specifically to any of the types of samples where total organic carbon, or its equivalent in other forms, is routinely used for absolute measurement or monitoring.

1 Sample stability

The work of Sugimura and Suzuki (2) shows that the instability of oceanic samples, even following acidification, is significant. The gradual loss of sample material can be slowed by storage at 4° C in the dark. It would appear that, where feasible, filtration of the sample followed by refrigeration offers the best solution to storage, but that this is applicable only when dissolved organic carbon (DOC) is being determined.

The filtration stage must not introduce any organic material into the sample. To achieve this, the use of a pre-ignited glass fibre paper is recommended, although if membrane filters are used they should be pre-washed with low carbon water until shown to be free of any contributing carbonaceous material. The pore size or filter grade must be quoted when reporting results as this affects particulate retention and consequently the final result. Abdel-Moati has shown that DOC can be retained on the filtration material (9).

Ideally, all samples should be analysed as soon as possible following sampling.

Whilst trying to determine if these techniques are instrument-dependent, the Panel carried out some preliminary trials using both artificial standards and real samples. These trials indicated that there were considerable problems which were attributable to the stability of these solutions when stored under different conditions. The results obtained in the trial are shown in Appendix 3.

The interpretation given to these results was that any intercomparison of instruments or methods should ideally be carried out at the same location, at the same time and under identical conditions to avoid sample stability problems masking the variance due to other factors. The "round-robin" exercise was thus cancelled as these conditions could not be met.

The Panel would like to thank everybody who volunteered to assist in this proposed exercise.

2 Stability of standards

From the results obtained it appeared that the stabilities of the standard solutions were similar to those of the samples. It is easier to control the conditions under which the standard solutions are prepared in order to minimise loss of organic carbon, as there is no reason why high purity water cannot be filtered to remove residual micro-organisms likely to utilise the standard. Additionally, this water can be subjected to any of the other forms of sterilization (heat, UV, etc) that does not involve the addition of chemicals which can contaminate the standard (refs 10–12). The sterilization of water in any manner must be carried out before the preparation of standards, if this course of action is followed.

To maintain stability, it is recommended that when standards are prepared, they are stored in amber glass and refrigerated at not more than 4° C.

Standard calibration material

There does not appear to be an accepted standard for total organic carbon. Phthalate, glucose and other compounds have all previously been used. Potassium hydrogen phthalate is recommended by the Panel as the primary standard, but there is the possibility of using alternative standard substances as secondary or quality control standards to ensure the optimisation of the equipment.

Purity of fulvic and humic acids

When comparative or efficiency studies are carried out fulvic and/or humic acids are frequently used. However, these complex mixtures cannot be obtained in high purity form and in most cases are extracted from natural sources. This can lead to other naturally occurring organic material being incorporated. This questionable purity will affect recovery and conversion values on an absolute basis.

It is important when carrying out such trials that common standards from the same stock solution are used.

Preparation environment

It is important that the environment where the standard solutions are prepared and stored is suitable. Many organic species are volatile, and it is possible that atmospheric organic carbon derived from volatile organic materials could dissolve in standard solutions to effectively increase the organic carbon content. This also applies to the collection and storage of the samples under test.

3 Pre-acidification

Acid is frequently added to remove inorganic carbon prior to analysis. Acidification can have the following effects upon samples:

(a) a lowering of pH may cause alteration of the sample by causing colloidal or dissolved material to coagulate as particulate material; by disrupting material that was particulate or colloidal and allowing it to dissolve, where previously it was not soluble;

(b) some acids may have a detrimental effect upon the fabric of the instrument. There seems to be a common use of phosphoric acid to overcome this effect; and

(c) the acid will dilute the sample and hence effectively alter the detection limit determined.

Effects (b) and (c) are particularly important where pre-acidification is used either as a mechanism for sample preservation, or where autosamplers are used. Particulate material may adhere to the container's inner surfaces and thus be made unavailable in subsequent analysis.

4 Use of autosamplers

Autosamplers are frequently offered as accessories to instruments. However, their use can cause the following problems.

(a) If the sample is not thoroughly mixed following acidification then some particulate material may fall to the base of the sample cup, whereas other material may be concentrated at the surface as a foam by the action of the purging gas; the positioning of a sample probe should be such that it takes a sample which is representative. Failure to achieve homogeneity will invalidate any result obtained. Where any doubt exists, a comparison between manual and automatic sample introduction should be undertaken.

(b) The use of purging gas may reduce the final value as any volatile material will be continuously removed while purging is taking place.

(c) Samples that contain particulate material, for example sewage and effluents, will cause problems both in sampling representatively and in potential for blockage; if these samples are sonicated to homogenise them, then care should be taken to prevent loss of volatile materials.

5 High temperature oxidation

All instruments that use this technique are not equally efficient in all uses. It has been shown that the material used for the oxidative catalysis of sample to carbon dioxide can have differing conversion efficiencies (6). This seems to relate to both the type and size of the packing material, the loading of the catalyst and the type of catalyst. It is recognised that the preparation of this material suffers from all the problems of inconsistency associated with the production of surface coated catalytic products and their susceptibility to poisoning. When new batches of material are used within the furnace these should be checked for conversion efficiencies before

being used for regular analysis. Additionally, the temperature of the furnace should be quoted—there appears to be an accepted operating temperature range of about 700–900° C outside of which no further oxidation occurs.

Prolonged use, or the introduction of samples with a high dissolved solids content, can help cause the breakdown and blockage of packing material. These effects will reduce the sensitivity of the instrument.

6 Low temperature UV-persulphate oxidation

It has been shown by oceanographers (2–8, 13) that there exists DOC material in their samples that is resistant to the combination of UV and persulphate oxidation but which is biodegradable. This material or group of compounds has not been characterised at present, but is likely to consist of large, complex naturally occurring macro-molecules. Despite the retraction by Suzuki (3), there is still interest in this material, as the large body of work generated by the initial paper supports its existence.

Similar material may occur in sewage, effluent from sewage treatment plants, river waters and possibly potable waters, and as such may or may not contribute to the analytical value obtained using this method. If this material is found in these types of samples it is not known if its presence is seasonal or if it is present all the time.

There is also concern that this technique may not achieve complete oxidation of particulate material consisting partially or totally of organic carbon.

It is in these areas in which the current debate about instrument dependency of results is occurring.

Information on comparative data between the low temperature UV-persulphate and high temperature combustion methods would be gratefully received.

7 Instrument geometry

There appears to be an effect of instrument geometry that enhances the performance of one instrument over that of another. This effect results purely from minor differences in piping, layout, injector siting, etc. The effect cannot be pre-determined but should be established by trial among selected instruments. The fact that one instrument uses one type of technique is not a sufficient reason to assume that all instruments using this technique are equivalent.

This effect should also be recognised when repairs or modifications are carried out to instruments in service, as they can enhance or reduce sensitivity dependent upon circumstances.

8 Solid material

The determination of organic carbon and its sub-components in samples which contain solid material can pose specific problems. These may be:

(a) representative sampling can be difficult due to possible non-homogeneity;

(b) there is an enhanced likelihood of blockage, either partial or total, occurring within the instrument; this will affect both sensitivity and reproducibility of the instrument; and

(c) solid/particulate material is unlikely to be fully converted to carbon dioxide in the low temperature/UV catalysed systems under normal conditions. Attempts to homogenise the sample will alter its characteristics and may result in the loss of volatile material.

9 Sample containers

Plastic material is to be avoided and glassware is the recommended material for sample containment, unless prior investigations show otherwise. In all cases, the containers should be thoroughly washed if previously used, and rinsed clean with water of a low organic carbon content. A representative sample of cleaned containers should be tested for cleanliness prior to sampling.

It should be policy to reduce the use of hazardous materials wherever possible in these methods. The use of chromic acid solution should be considered only when very low levels of organic carbon are being determined and then stringent safety precautions observed when handling this chemical and solutions containing it.

10 Blank values

The signal that arises from analysis of blank samples can be attributed to three main sources; the reagents, system and water. Reagent blanks can be minimised by using low carbon reagents, and will generally be constant. System blanks arise due to effects such as electrical noise, pressure surges, matrix, and carbon bleed from catalysts. Residual TOC in water blanks arise from the carbon that remains after pre-treating water which is used to prepare solutions and standards used in the analysis.

System and water blanks can lead to significant errors. Their effects should be fully investigated before routine use of the instrument and this information given when quoting results.

11 Further information

The above areas are those known to be contentious. If analysts know of or discover other areas where problems occur, then this additional information can be sent to the Secretary to the Standing Committee of Analysts at the address given at the back of this booklet. Any further information on existing problems or their solutions will also be gratefully received, and incorporated into the next update of this booklet.

Diagram 1   Relationship of the determinands described in this booklet

Total Carbon (TC)	= Total Organic Carbon (TOC)	+ Total Inorganic Carbon (TIC)
Total Organic Carbon (TOC)	= Volatile Organic Carbon (VOC)	+ Non-Volatile Organic Carbon (NVOC)
Non-Volatile Organic Carbon (NVOC)	= Dissolved Organic Carbon (DOC)	+ Insoluble Organic Carbon (IOC)

Alternative names are found for some sub-groups, these are:

Particulate Organic Carbon (POC) equivalent to IOC
Purgeable Organic Carbon (POC) equivalent to VOC
Residual Organic Carbon (ROC) and Non-Purgeable Organic Carbon (NPOC) equivalent to NVOC
Soluble Organic Carbon (SOC) and Filtered Organic Carbon (FOC) equivalent to DOC

Note the potential confusion over the abbreviations used for the alternative names used for particulate and purgeable organic carbon. For this reason these terms are not favoured.

A   Organic carbon measurements

Note: Throughout this booklet carbon parameters are expressed as mg C/l (ie milligrams (as carbon) per litre of solution).

For all references to persulphate in this booklet it is recognised that this is not the formal IUPAC nomenclature. The correct form should be "peroxodi-sulphate". This form is however rarely used.

A1   DEFINITION OF TERMS

A number of procedures have been developed for the instrumental, and in some cases automated, determination of organic carbon and related determinands. Individual techniques may measure slightly different, although broadly related, parameters. These parameters are defined as follows.

A1.1   Total Carbon (TC)

Total carbon is the quantity of carbon present in the form of organic, inorganic and elemental carbon.

A1.2   Total Inorganic Carbon (TIC)

Total inorganic carbon is the quantity of carbon present in the form of elemental carbon, total carbon dioxide, carbides, carbonates, cyanides, cyanates and thiocyanates.

A1.3   Total Organic Carbon (TOC)

Total organic carbon is the quantity of carbon present as organic matter which is dissolved and suspended. TOC equates to the difference between total carbon and total inorganic carbon. The species concerned may be simple molecules containing C-C or C-H bonds (for example CH_4, C_2H_6, etc); relatively simple or more complex compounds composed of the elements C, H, O, N, P and/or S; compounds comprising the above elements but in addition containing one or more of a very wide range of "hetero-atoms" within the molecule.

Note: TOC is generally non-specific. Specific identification of pollutants would require the application of such techniques as gas chromatography-mass spectrometry (GC-MS). Methods for many trace organic pollutants are available in this series.

A1.4   Dissolved Organic Carbon (DOC)

Dissolved organic carbon is the quantity of organic carbon present in solution or suspension following filtration.

A1.5   Insoluble Organic Carbon (IOC)

Insoluble organic carbon is that part of the total organic carbon present in suspended, settled or floating material within any sample. It is effectively defined by the separation technique employed to differentiate the sample (see DOC above). An alternative designation for this parameter is particulate organic carbon (POC).

A1.6 Volatile Organic Carbon (VOC)

Volatile organic carbon is that part of the total organic carbon which is volatile under specified conditions. An alternative nomenclature is purgeable organic carbon (POC). The possible confusion with particulate organic carbon (POC) should be noted.

A1.7 Non-Volatile Organic Carbon (NVOC)

Non-volatile organic carbon is that part of the total organic carbon in a sample which is non-volatile under specified conditions. It is the difference between total organic carbon and volatile organic carbon.

Alternative designations are residual organic carbon (ROC) and non-purgeable organic carbon (NPOC).

A2 GENERAL INTRODUCTION

The need for the monitoring of water quality is manifest in most areas of public, industrial and environmental situations. This ranges through the entire spectrum from environmental pollution studies to the production of very high purity water, for example pyrogen-free water. Included in this spectrum of uses are the very important areas of potable water, waste water treatment and disposal, and a whole host of widely varied industrial applications.

The availability of rapid measurements of total organic carbon in waters can give a useful indication to the functioning of treatment plants, the onset of pollution incidents, the quality of potable/industrial waters, etc. Over the years a wide range of instrumental methods for organic carbon determinations have appeared. In the past decade there has been a strong move towards the use of automated methods of TOC determination based on "low temperature" (room temperature to about 100° C) UV-persulphate chemical oxidation and "high temperature" combustion of the organic carbon present. Both techniques produce carbon dioxide which is usually measured by infrared (IR) spectrophotometry, with the entire analyser system under micro-processor control.

A2.1 The techniques for carbon dioxide measurement include:

(i) Infrared analysis (for example the "combustion/infrared technique") It has been found that better detection limits can generally be achieved using "non-dispersive infrared" (NDIR) analytical systems.

(ii) Catalytic reduction of carbon dioxide to methane, which is then determined using flame ionisation detection (FID).

(iii) Absorption and titrimetric measurement.

(iv) Absorption and nephelometric determination.

(v) Absorption into water, sodium hydroxide solution or barium hydroxide solution; determination is by conductivity or specific resistance measurement.

A2.2 The systems outlined above cover a dynamic range from 0.01 to 30000 mg/l measured with a high degree of precision, claimed at ±2% of the measured value.

The more modern equipment is very adaptable and variations are capable of handling samples with high dissolved solids, highly caustic waters and solid samples.

A2.3 Four key areas within the water industry where knowledge of the concentration of organic carbon is of value are:

(i) a measure of pollution potential;

(ii) a rapid means of assessing treatment-plant performance;

(iii) a measure of biodegradation in the biodegradability testing of chemicals, especially when specific tests are not available, or when a measure of the total organic residual is required and not the residual of a specific compound; and

(iv) a readily available identifier, and as such, a warning test for unusual quality of river water or effluent monitoring.

Other valuable uses of the determination of organic carbon include:

(i) the determination of organic pollution in sea water due to the inherent difficulties associated with the biochemical oxygen demand (BOD) and chemical oxygen demand (COD) tests, the former with its inhibitory problems associated with toxic substances and the latter with the problem of chloride interference; and

(ii) a knowledge of the TOC content of a sample can be a valuable guide to the selection of the volume of sample for the BOD test, in effect a screening test.

A2.4 Typical levels of TOC encountered in various situations are: —

Sample	Concentration mg C/l
(a) River monitoring	1 – 10
(b) Potable water treatment:	
intake	5 – 20
output	2 – 10
(c) Sewage treatment:	
inlet	100 – 1,000
outlet	20 – 100
(d) High purity industrial	
process waters	0 – 1
(e) Industrial waste waters	500 – 30,000

A3 HAZARDS

In order to avoid potential hazards, the instrumental determination of organic carbon requires care and attention to detail. 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. Pressurised 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 ultraviolet (UV) radiation must be avoided. UV light is a hazardous radiation and the source should not be operated without correct screening to remove this hazard.

Instrument maintenance, particularly of the electrical components, should be undertaken in accordance with the manufacturers' instructions. Note that considerable static voltages may arise in induction from furnaces used, and proper earthing of equipment is, therefore, essential. Maintenance should be undertaken only by staff who are fully conversant with equipment.

A4 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 should be such that suspended solids in the primary sample do not settle before reaching the point of sample draw off (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 equilibration 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 to minimise their loss. It is wise to check the suitability of the caps by testing whether any adsorption or desorption of organic compounds take place. Paper cap liners, waxed or otherwise treated, should not be used.

Before use, bottles that are to be used for sampling very low concentrations may be cleaned with chromic acid. This presents a hazardous risk and should be avoided where possible. Soaking and rinsing with water having a very low carbon content is an alternative.

For the highest accuracy, samples should be analysed within 2 hours of sampling unless it is known that they are stable for a longer period. If samples are to be held prior to analysis, they should be cooled to 2–4° C and stored in the dark (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 in a particular working range (say 50–250 µg/l TOC) and a scheme for achieving dilution should be incorporated as in Figure 1.

Dilution of flowing streams may be carried out using an ejector pump, whereby one stream automatically ratios the other at reasonable rates of flow; this is an alternative to a peristaltic pump.

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 adsorption, can arise from the use of peristaltic pump tubing.

The growth of algae in translucent tubes may also cause problems.

Adsorption of organic compounds by sample tubes is likely to be a problem only at low levels and low flow rates. In general, deposits do not adhere easily to PTFE tubing. Overall, it is best to use water to flush the whole system at regular intervals and to take samples during the 'cleaning stage' for off-line analysis to establish the system zero.

In most cases, the sample injection system attached to the analyser will not handle suspended solid particles greater than about 100 µm in diameter. It is, therefore, necessary to remove suspended matter, from the sample prior to injection, see Figure 1, recognising, however, that organic and inorganic carbon may be associated with these solids. Alternatively, it is possible 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 A6. 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. It may also deposit in the injection system (14,15).

A5 CARBON-FREE WATER PREPARATION

A5.1 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 should be cleaned with chromic acid (see section A3), 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 (16).

UV light can also be used to obtain carbon-free water (10, 11, 12).

Hydrogen peroxide combined with UV light has been shown (17) to produce water which contains a low carbon content.

For routine use modern "point of use" water purification systems are capable of producing water with a very low carbon content. These rely on reverse osmosis, ion exchange, activated carbon and/or membrane filtration in combination to produce very high purity water with a low carbon content.

A6 SAMPLE PREPARATION

A6.1 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 will not deal with every type of organic material, 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.

A6.2 Total Organic Carbon (TOC) Determination

To determine TOC the sample must be treated so as to remove total inorganic carbon (TIC). This can be achieved by acidification and purging with an inert gas which may be separated from carbon dioxide by passage through a column filled with a molecular sieve or other suitable absorbent. The rate and duration of purging should be determined according to aliquot size and nature of sample. Any tendency for particulate matter to settle out or float should be minimised by stirring. This sample purging technique is not suitable if an appreciable amount of 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 (18) and volatile organic compounds which are sparingly soluble in water, exert a higher partial vapour pressure and are more volatile than expected (19). A technique has been reported for removing trace quantities of diesel oil from water by purging (20).

Some instruments measure TOC only after acidification and purging of the sample as described, while others can determine TC and TIC separately by injecting the original sample on to columns placed side by side at approximately 900° C and 150° C respectively. This technique allows TOC to be determined by difference. Certain instruments can determine both TIC and TOC sequentially by acidification and purging of the sample, followed by measurement of the evolved carbon dioxide for TIC, before the stripped sample is passed into a combustion tube at 900° C for determination of TOC. Other instruments acidify and purge the sample but 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. Alternatively, they absorb the evolved carbon dioxide and allow the VOC to pass through for immediate measurement. These instruments allow non-volatile organic carbon (NVOC) to be determined.

$$NVOC + VOC = TOC$$

A6.3 Total Inorganic Carbon (TIC) Determination

The sample injection on to a column, containing phosphoric acid on an inert support at 100–150° C, and subsequent measurement of the evolved carbon dioxide, using a non-dispersive infrared analyser, provides a direct method for TIC measurement.

An alternative approach is to acidify the sample with sulphuric acid, purge with inert carrier gas (carbon dioxide-free) and measure the resulting gas for entrained carbon dioxide. TIC may be estimated as the difference between TC and TOC, but loss of volatile organic compounds in either determination will lead to significant errors. If cyanides are present they may be included in the result for TC but not in the result for TOC. 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
Sample, filtered, acidified and purged	= DOC when volatiles absent
Sample, filtered, acidified and purged	= (DOC-VOC) when volatiles present

Hence TIC = TC − TOC when volatiles absent

or TIC = (TC-VOC) − (TOC-VOC) when volatiles present.

A6.4 Dissolved Organic Carbon (DOC) Determination

For this determination it is necessary to remove both inorganic carbon and particulate matter from the sample. Filtration is the accepted method of removing particulate matter, and the type and pore size of the filter should be indicated clearly with the result. Membrane filters offer the most consistent pore size, but are known to contribute DOC to the sample from component material or added wetting/surfactant compounds. Pre-ignited glass fibre papers are unlikely to contribute DOC to the sample. It is important to check that before procedures are used routinely, any material used for filtration does not contribute carbon to the sample. This can be assessed by running system blanks using low carbon water before and after filtration. It should also be confirmed that DOC is not retained by the filter. Reference 9 indicates that up to 20% DOC can be lost during filtration, and that the loss is increased with increasing filter diameter.

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. It should also be kept in mind that, under reduced pressure, filtration of a sample is likely to cause loss of volatile organic carbon, if present. Filtration at atmospheric or positive pressure is recommended for samples believed to contain volatile material. Determination of the DOC should not contain a purging procedure.

$$TOC = DOC + IOC + VOC$$

In many cases, the volatile fraction can be assumed to be negligible and

$$DOC = (TC − TIC) − IOC.$$

A6.5 Insoluble Organic Carbon (IOC) Determination

IOC can be estimated by difference between TOC and DOC determinations and is normally obtained by filtration of the original sample. 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 and the pore-size of the filter medium can also influence the result. 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

$$IOC = TOC − DOC$$

A6.6 Volatile Organic Carbon (VOC) Determination

VOC is that part of the carbon content of a sample which can be removed by exhaustive purging with an inert gas at a defined temperature. Certain instruments are capable of determining VOC by measuring the carbon content of the pure gas before the sample is introduced into the combustion area at 900°C or the UV irradiation area. 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)
       NVOC = (3)

A6.7 Non-Volatile Organic Carbon (NVOC)

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

Hence TOC = VOC + NVOC

where NVOC contains contributions from both IOC and DOC.

Note: NVOC represents the non-volatile organic carbon content of the unfiltered sample.

A7.1 Introduction

For the measurement of TOC a discrete sample or continuous flow of sample is required. 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.

For TOC measurement, an on-line instrument usually incorporates a two-stage sampling system. The first stage involves continuous pumping of the sample stream, to a constant level device, at a rate sufficient to give a linear velocity of 100 to 150 cm/sec. Gross solids separation, acidification and gas sparging may be carried out at this stage. The second stage feeds sample forward from a constant level device to the injection system. For further details see Appendix 1.

A7.2 Manual introduction of a discrete sample

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

A7 SAMPLE INJECTION SYSTEMS

The syringe is best used to introduce the sample through an open tube which is stoppered before and after injection, either by a septum or mechanical valves. When a septum cap is used, care should be taken if errors are to be avoided as a result of small pieces of the septum cap breaking off and entering the combustion tube. 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 and 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, automated injection systems are more reproducible than manual methods.

A7.3   Automated injection of a discrete sample

Automated injection of a sample into an instrument is usually achieved by the use of a syringe, or slide or rotary valves. In the latter cases, the valve isolates a precise volume of the sample stream flowing through it and automatically redirects this volume into a gas or liquid stream flowing into the instrument. Further details are given in Appendix 2.

A7.4   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. The technique also yields lower limits of detection, and overcomes the problem of particulate matter clogging narrow bore needles.

A8   CARRIER GAS SYSTEMS

A8.1   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 factors influencing 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 piece of apparatus and determination. Three types of gas system can be used, namely those utilising:

(i)   inert gas;
(ii)   oxygen; and
(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 carbon dioxide to methane in a hydrogen carrier gas over a nickel catalyst. In this type of process, injected water is usually condensed out between the oxidation and reduction stages.

A8.2   Reduction stage

Where the carbon dioxide is reduced to methane, and the methane measured using a flame ionization detector (FID), 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.

A9   OXIDATION SYSTEMS

A9.1   Introduction

The next stage in the determination of TOC and its sub-groups is the oxidation of carbonaceous components to carbon dioxide. It is the procedure for doing this that has recently become contentious, as previously explained.

The three main processes are:

(a)   High temperature/combustion oxidation (21, 22, 23);
(b)   Low temperature UV-persulphate oxidation (10, 12, 24, 25, 26);
(c)   Elevated temperature persulphate oxidation
(d)   Low temperature UV oxidation.

The benefits and disadvantages of each method have been previously discussed and the analyst should ensure that the instrument used is compatible with both sample and determinand.

A9.2   High temperature combustion furnaces

The sizes and shapes of combustion furnace 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 tube exist, from the simple straight and "U-shaped" tubes to a more complicated chamber with internal baffles which increase oxidation efficiency. Common materials of construction are glass, fused silica, nickel alloy and ceramic material. Fused silica 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.

Furnace tubes can be mounted vertically or horizontally, and both arrangements have certain advantages and 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 causing blocking. Horizontally mounted tubes are prone to the gases channelling through the catalyst leading to incomplete oxidation.

A9.3   Catalytic systems

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

(i)   platinum;
(ii)   platinum-rhodium;
(iii)   palladium;
(iv)   cobalt oxide; and
(v)   copper oxide.

The precious metal catalysts, of which platinum is the most popular, are commonly used in the form of gauze, usually in conjunction with oxygen or oxygen/inert gas mixtures. Copper oxide (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 deposited as the nitrate. The catalyst is used with oxygen or nitrogen carrier gas systems. Supported catalysts have proven unsatisfactory because of a tendency to settle in use and cause blockages, but considerable development work is being undertaken in this area to improve their performance.

Different loadings of catalytic compounds on alternative support materials have been shown to give significantly different results when used with real samples (6).

The production methods for the catalytic material are likely to give batches which have different efficiencies in terms of oxidation ability. This should be checked by the use of known standard solutions at standard instrument settings. This can also

be used to check the efficiency of catalysis in the combustion tube, as mechanical damage or poisoning of the catalyst will lead to reduced response under standard conditions.

A9.4 Chemical oxidation systems

A technique has been published that utilises the resulting carbon dioxide from the chemical oxygen demand (boiling dichromate + sulphuric acid) test. The gas is swept from the reaction vessel for measurement (21). Another reported technique uses persulphate oxidation at high temperature and pressures (25). Neither system is favoured by instrument makers.

The use of elevated temperature (100 °C) persulphate oxidation is employed in several commercially available instruments. This technique has been combined with a system which traps the resultant carbon dioxide and subsequently thermally desorbs the gas and presents the detector with a concentrated 'plug' of carbon dioxide. However, the same problems associated with the UV-persulphate system are also encountered.

A9.5 Photochemical oxidation systems

The use of UV-promoted oxidation in the presence of persulphate is well established. There are many instrument types that use this system of oxidation. However, there appear to be certain samples which resist these conditions in the time taken for the sample to flow through the reaction vessel. Such samples are likely to contain particulate material or complex organic material, both of which can resist oxidation. In the case of particulate material, reduced oxidation is due to physical barrier action slowing the availability of carbon to the oxidant, while complex molecules take longer to undergo the oxidative reactions required to cleave them into more easily oxidised chemical units.

The UV radiation is usually obtained by using mercury vapour lamps set around, or in proximity to, the reaction vessel. This vessel is a simple or coiled tube, and its internal volume, divided by the total flow through it, will enable the residence time to be determined. In some situations, it has been proposed that increasing the residence time will enable more resistant material to be oxidised.

The reactions involve the formation of persulphate and hydroxyl free radicals and a comprehensive study of these free radical systems has been reported by Peyton (27). Very powerful oxidising agents chemically attack the available organic material oxidising it to carbon dioxide. In all cases, the resultant carbon dioxide is gas-stripped from the reaction stream, dried and then detected.

The reaction tube is normally constructed of fused silicon to allow the transmission of the UV radiation into the flowing reaction stream.

A10 DETECTION SYSTEMS

The gases emerging from the combustion tubes, which are an inherent part of many TOC instruments, are hot and highly corrosive. Water and oxides of carbon may be accompanied by halogens and the oxides of nitrogen, sulphur and phosphorus. It is undesirable for these acidic gases to pass into the detector system and usually they are removed from the gas stream by condensing the water vapour which 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 hydroacids and sulphur dioxide. Gas lines carrying these corrosive vapours should be constructed in suitable materials. Scrubbed gases may be passed directly to many detectors (for example a platinum/lead fuel cell) without further treatment but, in the case of FID, should be dried. The self-indicating silica gel used for drying also removes ammonia which may be present and which would have an adverse effect on the performance of certain designs of FID.

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

A10.1 Flame Ionization Detection

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

A10.2 Non-Dispersive Infrared Detection (NDIR)

The mode of operation of this type of detector is described in references 10 and 29. 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, at selected wavelengths, prevent significant interference due to the presence of other substances in the gases leaving the oxidation furnace; the absorbance maxima of such gases are as follows: —

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

Most detectors can tolerate the cooled gases from the combustion furnace containing up to 1% of water by volume.

A new type of detector has been developed using solid state electronics. This detector shows greater stability and is less prone to vibration. It is reported (17) to give increased signal to noise ratio and increased precision.

A10.3 Titrimetric method

For titrimetry, the gases leaving the combustion zone should be free of halogens and oxides of elements other than carbon. The carbon dioxide is absorbed in standard barium hydroxide solution and determined by back-titration with standard hydrochloric acid, or absorbed in alkaline barium perchlorate which is back-titrated with barium hydroxide (29). Greater sensitivity is claimed if the carbon dioxide is absorbed in monoethanolamine dissolved in dimethylformamide. 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.

A10.4 Nephelometric method

This procedure 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 enables a value for the carbon content of the original sample to be determined.

A10.5 Electrical Conductivity and Specific Resistance methods

Descriptions of these methods can be found in References 26 and 30 respectively. Gases emerging from the combustion zone should be free of oxides of nitrogen, sulphur and phosphorus, before being passed into a solution of barium hydroxide, sodium hydroxide or low conductivity carbon-free water. The change in electrical

conductivity or specific resistance of the resulting solution is found to be linearly related to the amount of carbon dioxide absorbed. The conductivity cell should be thermostatically controlled as conductivity is influenced by temperature (2 to 2.5% per degree C).

A10.6 Spectrophotometric method

This technique can be used in an automated procedure where carbon dioxide, produced by persulphate and/or UV oxidation (31), is passed through a gas-permeable dialyser membrane into a weakly buffered phenolphthalein solution. The decrease in absorbance due to the real colour is proportional to the carbon dioxide concentration and hence to the initial organic carbon.

A11 INTERFERENCES AND SOURCES OF ERROR

A11.1 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, will interfere.

Inorganic carbonate, bicarbonate and dissolved carbon dioxide, are eliminated by methods already discussed in sections A6.3 and A6.4. By supplying the instrument with aliquots of sample, which have been pre-treated, it is possible to determine the amount of the various forms of carbon present in a sample.

A11.2 Sulphur compounds

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

A11.3 High salt contents

Samples with a chloride content exceeding 0.1% are treated by adding mercury(II) salts to the potassium persulphate oxidant. Mercury(II) salts can however cause corrosion in the apparatus and reduce sensitivity and oxidation with sodium persulphate may be preferred in view of its higher solubility. Salinities in excess of this can be diluted, but are otherwise difficult to accommodate, especially if low TOC levels are being investigated.

A11.4 Instrument effects

As described earlier, differing results can be obtained in some circumstances by the use of the alternative oxidation techniques available.

B The determination of organic carbon in raw, potable and waste waters using high temperature catalytic oxidation with infrared detection

B1 Performance characteristics of the method		
B1.1	Determinand	Organic carbon.
B1.2	Type of sample	Raw and potable waters.
B1.3	Basis of the method	High temperature combustion and catalytic oxidation to carbon dioxide. Detection is by non-dispersive infrared spectrometry.
B1.4	Range of application	Nominally 0.1–50,000 mg/l, but instrument dependent.
B1.5	Standard deviation[1] (within batch, on a 1 ml sample size)	See Table B1.
B1.6	Limit of detection	Nominally 0.2 mg/l, but instrument dependent.
B1.7	Sensitivity	Instrument dependent.
B1.8	Bias	Instrument dependent.
B1.9	Interferences	None specific.
B1.10	Time required for analysis	Instrument dependent. Nominally 3 minutes.

Table B1 Performance data

Solution	Concentration mg/l	Standard Deviation mg/l	Degrees of Freedom
Raw water	4.10	0.44	13
Standard	0.5	0.09	16
Standard	4.5	0.20	13

[1] Based on Dohrman DC 180, results provided by Thames Water Utilities Ltd.

B2 Field of application

See appropriate sections in Part A.

B3 Principle

The organic carbon content of the sample is oxidised over a catalyst at 700-900°C in an atmosphere of oxygen. The resulting gaseous mixture, containing the carbon dioxide formed, is dried and neutralised prior to analysis by non-dispersive infrared (NDIR) detection. Liquid samples are introduced into a sample loop system using a microsyringe. Samples with high solids contents can be analysed by introducing the sample into the furnace in a platinum boat. Analysis of the different organic carbon species can be made by pre-treatment of the sample and reconfiguration of the analytical system.