The Determination of Alkali Extractable Organic Matter in Ash 1981

Methods for the Examination of Waters and Associated Materials

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Contents

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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 properly equipped laboratories. 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. 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 specifications. 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. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection,' Public Health Laboratory Service Monograph 6, HMSO, 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 emphasised 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 radio-chemical 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 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 the 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 part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have 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 the 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 nonmetallic 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.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

* These two working groups are in process of being wound up. Their tasks are being redistributed among the other Working Groups.

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

About these Methods

The presence of organic matter in ash is a significant factor in the formation of putrescence during storage and disposal of ash. Oxidizable organic matter and total organic carbon of an alkali extract (Procedures A and B respectively) have been found to be the most useful determinands in assessing ash putrescibility (1), (2).

Procedure for the Determination of Alkali Extractable Oxidizable Organic Matter in Ash (C_k)

A1 Performance Characteristics of the Procedure

A1.1	Substance determined	Oxidizable organic matter extractable from ash by sodium hydroxide.
A1.2	Type of sample	Ash from incineration of refuse, sewage, sludge, etc.
A1.3	Basis of Method	The alkali soluble organic matter is extracted by sodium hydroxide and oxidized with sulphuric acid and potassium dichromate; the residual dichromate is measured titrimetrically.
A1.4	Range of Application	Up to 0.25% m/m (nominal) organic matter oxidizable by acid potassium dichromate (C_k).
A1.5	Calibration Curve	Linear (for oxidation step).
A1.6	Precision*	See table below.
A1.7	Limit of Detection*	0.016% C_k. Assuming S_w of the low concentration sample (c) = S_w blank and using 5.18 S_w.
A1.8	Sensitivity**	1 ml 0.025M ferrous ammonium sulphate is equivalent to 0.075 mg C_k.
A1.9	Bias	No evidence of bias using potassium hydrogen phthalate.
A1.10	Interferences	Chloride interferes, though for many applications the effect will be unimportant. Inorganic reducing substances extracted from the ash give an apparent value for oxidizable organic matter.
A1.11	Time Required for analysis	Typical total time for the analysis of one to ten samples is approximately 5 hours.

A1.6 Precision*

	Mean% C_k	S_b	S_w	S_t
a.	0.120	Not significant at 95 percent confidence level	0.005	0.007
b.	0.182		0.004	0.007
c.	0.018	zero	0.003	0.003

* Obtained for Southern Division, Yorkshire Water Authority from three samples of ash from the incineration of sludge. Each determination has nine degrees of freedom.

** Reference 2

A.2 Principle

The alkali soluble organic matter is extracted into sodium hydroxide during a long period under reflux. The sample is then filtered and the chemical oxygen demand determined on an aliquot using a standard method of refluxing acid potassium dichromate [2].

A.3 Interferences

A3.1 Inorganic reducing agents such as nitrites, sulphites, ferrous iron, etc, will contribute to the oxidation reaction giving high results.

A3.2 Chloride causes positive interference, the magnitude of which depends on the concentration of chloride and the oxidizable organic carbon present [2]. The interference may be minimized by the addition of mercuric sulphate (see Section 9).

A.4 Hazards

Poisonous gases may be emitted from the sample on acidifying. This operation should be conducted in a fume cupboard. Hydrogen sulphide gas is highly toxic even at low concentrations and also impairs the sense of smell.

Addition of sulphuric acid (d_{20} 1.84) to water must always be carried out with care and gentle swirling of the contents of the flask.

The method involves the handling of boiling and strong solutions of sulphuric acid and dichromate. Protective clothing, gloves and full face protection are essential. In the event of spillage immediate copious washing with clean water is the simplest and most effective remedy.

Care is required when preparing and handling solutions containing silver sulphate and mercuric sulphate as these are toxic. In the event of either of these chemicals being swallowed give water to dilute and milk as a soothing and buffering agent. Do not delay seeking medical advice.

In the event of an accident, expert medical advice should be obtained as quickly as possible.

A.5 Reagents

A5.1 Except where otherwise stated, analytical reagent grade chemicals are to be used. Reagents should be stored in glass bottles. All reagents, with the exception of ferrous ammonium sulphate solution, are stable for at least one month.

A5.2 **Water**

Either distilled or de-ionized water can be used provided the blank value remains acceptable (see steps A.3.2, A.3.3 and note 1).

A5.3 **Sulphuric Acid** (d_{20} 1.84)

Unacceptable blank values can be caused by minute amounts of contaminants in the reagents. The major cause is the sulphuric acid used — analytical reagent grade is not necessarily better than ordinary acid, and when a satisfactory batch has been found it should be reserved for COD use only.

A5.4 **1%m/V Silver sulphate solution**

Dissolve 10.0 ± 0.1 g of silver sulphate in 1 litre of sulphuric acid (d_{20} 1.84). To obtain a satisfactory solution the initial mixture should be shaken, allowed to stand overnight and then shaken again in order to dissolve all the silver sulphate. Store in a dark brown glass bottle out of direct sunlight.

A5.5 **20%m/V Mercuric sulphate solution**

Prepare 10% V/V sulphuric acid by adding cautiously, with swirling, 50 ± 2 ml of sulphuric acid (d_{20} 1.84) to 450 + 5 ml of water.
Dissolve 100 + 1 g of laboratory grade mercuric sulphate in 500 ± 5 ml of 10% V/V sulphuric acid. The micro analytical reagent grade of mercuric sulphate is advised when measuring very low COD values.

A5.6 **Standard reference solution of potassium dichromate,** 0.020833M (M/48)

Dissolve 6.129 g of potassium dichromate, previously dried for one hour at 140 — 150°C, in water and dilute with water to 1 litre in a calibrated flask.

A5.7 **1:10 phenanthroline ferrous complex** ('Ferroin')

This reagent is commercially available in either plastic or glass bottles; both are acceptable. If necessary a suitable indicator can be prepared as follows:

Dissolve 3.5 ± 0.1 g of ferrous sulphate heptahydrate in 500 ± 1 of water. Add 7.4 ± 0.1 g of 1:10 phenanthroline monohydrate and shake until dissolved.

A5.8 **Standard solution of ferrous ammonium sulphate** 0.025M

Dissolve 9.8 ± 0.1 g of ferrous ammonium sulphate hexahydrate in about 100 ml of water, cautious add 20.0 ± 0.5 ml of sulphuric acid (d_{20} 1.84), cool and dilute with water to 1 litre in a calibrated flask.

Standardize the solution, each day before use, againtst 0.020833M potassium dichromate solution as follows: take 5.00 ± 0.05 ml of 0.020833M potassium dichromate solution and dilute with water to approximately 60 ml; carefully add 15.0 ± 0.5 ml of sulphuric acid (d_{20} 1.84) and cool; add not more than two drops of 'Ferroin' indicator and titrate with the ferrous ammonium sulphate solution.
For a description of the end point see step A8.3.1, note i.

The molarity M of the ferrous ammonium sulphate solution is given by:

$$M = \frac{0.020833 \times 30}{V} \text{ or more exactly } M = \frac{5}{8V}$$

where V is the volume (in ml) of ferrous ammonium sulphate solution titrated

A5.9 **Sodium Hydroxide** 3%m/V

Dissolve 60.0 ± 0.5 g in 500 ml of distilled water. Allow the solution to cool and make up to 2 litres with water.

A5.10 **Sulphuric acid** 50%V/V

Add cautiously and slowly 100 ml of sulphuric acid (d_{20} 1.84) to 100 mls water in a cooled beaker.

A6 Apparatus

High blank values may be the result of minute amounts of contaminants in the oxidation flask, the reflux condenser or on the anti-bumping aid. Apparatus should be cleaned by repeatedly boiling fresh dichromate/sulphuric acid/silver sulphate mixture in the apparatus until low and consistent blank values are obtained. Apparatus should be reserved solely for COD determinations.

A6.1 Glassware should have standard ground glass joints where appropriate; grease must not be used.

A6.2 **150-ml and 500-ml boiling flasks** and a distillation tray capable of holding all the contents of the boiling flask in the event of breakage during the digestion stage.

A6.3 **Automatic dispensing pipette or burette** for the 1% m/V silver sulphate in sulphuric acid. (A tilt type dispenser is not suitable).

A6.4 **Water-cooled condenser,** a least 150 mm long, capable of being easily rinsed.

A6.5 **Water cooled condenser** to fit 500-ml boiling flask.

A6.6 **Protective cap for the reflux condenser** to keep dust out of the apparatus when not in use. A small beaker is satisfactory.

A6.7 **Predigested anti-bumping granules or an aid** made of glass and PTFE,* (see Ref 2, fig 1). The rod should be of sufficient length to keep the aid upright in the boiling flask. All anti-bumping granules and aids should be precleaned by digestion for 2 hours as described in Section A6.

* PTFE (Polytetrafluoroethylene).

A6.8 Uniform heating is essential to maintain gentle boiling. For safety reasons this is best achieved by using a heated sand tray. Point sources of heating are considered unsatisfactory. No part of the flask should be heated to a temperature in excess of the liquid boiling therein since decomposition of dichromate commences at a few degrees Celsius above the reflux temperature and will lead to high results.

A6.9 **25-ml burette,** grade B or better.

A6.10 250-ml calibrated flask.

A6.11 **10-ml pipette** grade B or better.

A.7 Sampling and Sample Preservation

The analysis should be carried out as soon as possible after sampling. The samples should be dried for 4 hours at 105°C and crushed before subsampling for analysis.

A.8 Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

All operations should be carried out with care.

Dangers of spillage obviously arise if the sample contains carbonate, or any other substance which will emit a gas. Poisonous gases may be emitted if, for example cyanide or sulphide is present; hence addition of sulphuric acid to the samples should be carried out in a fume cupboard. Caution in the initial mixing of sulphuric acid with unknown samples must always be the rule.

Step	Procedure	Notes
A8.1	Alkali Extraction	
A8.1.1	Weigh accurately (± 10 mg) about 15.0 g of dried sample and transfer it to a 500 ml round bottom flask.	
A8.1.2	Add 125 ± 1 ml of 3% M/V sodium hydroxide stopper and shake vigorously (Note a)	(a) It may be necessary to shake for a minute or longer to wet the sample entirely.
A8.1.3	Wash the flask down with the minimum quantity of water necessary to transfer all the material to the bottom.	
A8.1.4	Connect the condenser and reflux for three hours.	
A8.1.5	Remove the flask from the source of heat and allow to cool for approximately 10 minutes.	
A8.1.6	Rinse condenser with distilled water, remove flask, stopper it and cool in a cold water bath.	
A8.1.7	Vacuum filter the mixture with a Whatman GF/C paper or equivalent (Note b). Transfer filtrate to a 250-ml graduated flask. Rinse the filter flask several times, push the washings through the filter. Transfer the washings to the volumetric flask and make up to 250-ml.	

Step	Procedure	Notes
A8.2	Digestion	
A8.2.1	Insert the anti-bumping aid or granules into the boiling flask (Note c).	(c) Once in position they need not be removed between determinations.
A8.2.2	Measure 10.0 ± 0.1 ml of extract into the flask (Note d).	(d) If necessary, the extract should be diluted accurately and a 10 ml aliquot taken for oxidation, which equivalent to between 5 and 20 ml of 0.025M ferrous ammonium sulphate.
A8.2.3	Add slowly 3.0 ± 0.1 ml 50% v/v sulphuric acid (Note e)	(e) Do not pipette by mouth.
A8.2.4	Add 1.0 ± 0.2 ml of 20% m/V mercuric sulphate solution and swirl to mix; add 5.00 ± 0.03 ml of 0.020833M potassium dichromate. Using an automatic dispensing pipette or burette add 15.0 ± 0.5 ml of 1% m/V silver sulphate in concentrated sulphuric acid (Notes f and g)	(f) Run the acid down the side of the flask whilst gently swirling and cooling the flask under running cold water. This procedure minimizes loss of volatiles.
		(g) The amount of mercuric sulphate in this mixture will suppress, but not entirely eliminate, the effect of chloride ion. If the 10 ml taken for oxidation contains more than 5 mg of chloride ion see Section A9. For the determination of chloride see another publication in this series.
A8.2.5	Fit the condenser and swirl the flask and its contents, then boil gently under reflux for 2h ± 10 min (Note h).	(h) Excessive reflux times may result in high blank values.
A8.2.6	Remove the flask from the source of the heat and allow to cool for approximately 10 min, then add 25 ± 5 ml of water via the condenser in such a manner as to rinse residual dichromate from the condenser. Disconnect the flask from the condenser and cool the flask to room temperature in running water. Determine the residual dichromate by steps A8.3.1 to A8.3.4	
A8.3	Titrimetric determination of residual chromate	
A8.3.1	Add not more than two drops of 'Ferroin' indicator to the flask and titrate the residual dichromate with standardized ferrous ammonium sulphate (Note i).	(i) After the first addition of ferrous iron solution the indicator is blue-green in colour and the end point occurs when the colour changes sharply through deep blue to pink. The blue colour may reappear a few minutes later but this phenomenon should be ignored.
A8.3.2	*Blank determination* Ideally the blank value should be the mean of at least three determinations, but if any value differs by more than 0.5 ml from the mean value it must be rejected and a new mean recalculated from the acceptable blank values.	
A8.3.3	The blank test is carried out as described in steps A8.1.2 to A8.3.1 inclusive (Note j).	(j) An acceptable blank test should require at least 23.5 ml of 0.025M ferrous ammonium sulphate, or its equivalent, in the titration.

Step	Procedure	Notes

A8.3.4 *Calculation of results*

If it was necessary to pre-dilute the extract, the appropriate factor must be included in the calculation

$$\% C_k = \frac{M (V_B - V_s) \times 3 \times 250}{W \times 100}$$

Where V_B = average number of ml ferrous ammonium sulphate used in titrating the appropriate blank (step A8.3.3)

V_s = number of ml ferrous ammonium sulphate used in titrating the sample. (step A8.3.1)

M = Molarity of standard ferrous ammonium sulphate solution, as determined in Section A5.8.

W = Weight of sample taken in grammes

A9 Chloride Interference

(Aliquots containing in excess of 5 mg chloride per 10 ml)

It is recommended that, where possible, the chloride ion content of the sample aliquot taken for the test be limited to a maximum of 5 mg and in such cases the procedure given above is applicable. However, it may not always be possible to limit the chloride ion to this value because of the low organic content of the original sample and in these cases a special procedure can be used. This procedure is applicable to samples for which the aliquot taken for analysis contains more than 5 mg of chloride ion and employs additional mercuric sulphate in a ratio of 40 to 1 mercuric sulphate to chloride ion to suppress the effect of such high chloride concentrations.

Even after using this additional amount of mercuric sulphate, there may still be an enhancement of the true COD value, the magnitude of which will depend on the ratio of chloride to COD and the rate of oxidation of the organic material. The actual interference by chloride will be difficult to estimate.

A10 Removal of Silver and Mercury from Spent Test Solutions

In order to avoid risks to the environment, eg sewage treatment works and watercourses and to recover some of the cost of expensive reagents, the following procedures are recommended.

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE.

A10.1 **Removal of silver**

Place 40 ml of hydrochloric acid (d_{20} 1.18) in a Winchester bottle and add the spent test solutions to the acid. When the Winchester is full allow the silver chloride precipitate to settle overnight. Decant the supernatant liquid which contains mercury into a beaker.

A10.2 **Removal of mercury**

NOTE:

The hydrogen sulphide evolved during this precipitation process is poisonous. All operations, including the decantation of the supernatant liquid should be carried out under a fume hood.

Add between 1 and 3 g of stick ferrous sulphide to the decanted liquid from the silver recovery step. Allow to stand at least 24 hours, occasionally swirling or stirring the solution to disperse the hydrogen sulphide, and finally allow the precipitated mercuric sulphide to settle. Decant the supernatant liquid.

A10.3 **SILVER CHLORIDE AND MERCURIC SULPHIDE ARE NOTIFIABLE WASTES AND MUST NOT BE DISPOSED TO LAND WITHOUT CONSENT**

A10.4 The supernatant liquid from step B10.2 contains a relatively high concentration of sulphide. The liquid should be oxidized or diluted 500 to 1 before disposal. Precious metal refiners may accept silver and possibly mercury for ultimate recovery. For more detailed information on silver and mercury recovery, see the booklet of methods for chloride published in this series [6].

A11 Checking the Validity of Analytical Results

Once the method has been put into normal routine operation many factors may subsequently affect the validity of the analytical results. It is recommended that experimental tests of the validity should be made regularly.

As a minimum, however, it is suggested that a typical sample be analysed in duplicate at the same time and in exactly the same way as normal samples, such checks will be facilitated by plotting results obtained on quality control charts which will detect inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

B Procedure for the Determination of Alkali Extractable Total Organic Carbon (C_T)

B1 Performance Characteristics of the Procedure

B1.1	Substances determined	Total organic carbon in the liquid phase left after a prolonged reflux of a solid sample with alkali.
B1.2	Types of sample	Ash from the incineration of refuse, sewage sludge, etc.
B1.3	Basis of method	The alkali soluble organic matter is extracted by sodium hydroxide and oxidised catalytically in a furnace. The resulting carbon dioxide is either determined directly or converted into methane (see another publication in this series[5].
B1.4	Range of application	Up to 0.25% m/m alkali soluble organic carbon (C_T).
B1.5	Calibration curve	Linear over range of application.
B1.6	Precision* Potassium hydrogen phthalate standard solutions using copper oxide and nickel catalysts and determining the methane produced by gas chromatography[4].	(i) Instrumental procedure: C_I mg/l / Standard Deviation: 0.5 / 0.015; 5.0 / 0.030; 50.0 / 0.35 (ii) Total procedure: 0.5 / 0.035; 5.0 / 0.075; 50.0 / 0.85 with 9 degrees of freedom.
B1.7	Limit of detection**	0.18 mg/l on final solution.
B1.8	Sensitivity	See references 4 and 5, none given in references 1 and 3.
B1.9	Bias	Volatile organic compounds may be lost by acidification and air stripping.
B1.10	Interferences	None known.
B1.11	Time for analysis	Typical time is approximately four hours per sample.

* (References 1 and 2)

** Based on 5.18 S_W of 0.5 mg/l standard solution through total procedure.

B.2 Principle

B2.1 The alkali-soluble organic matter is extracted into strong alkali during a long period under reflux. The sample is then filtered and an aliquot, suitably diluted, is acidified with nitric acid.
After the pH of the sample has been reduced to less than 1.0 it is stripped of inorganic carbon by bubbling carbon dioxide-free air through it. The total soluble organic carbon is then oxidized catalytically. The resulting carbon dioxide is then determined directly or by conversion to methane (see another publication in this series [5]).

B2.2 For comparison, standards with a known concentration of a total organic carbon are analysed.

B2.3 Samples can be run on an auto-analyser sample turntable with the air stripper synchronised with the sample probe in the turntable position immediately before the sample being analysed.

B2.4 The usual operating pattern is eight minutes of sample followed by eight minutes of water run as a blank.

B3 Field of Application and Interferences

B3.1 Chemical oxidation of heterogeneous organic matter will not result in the complete determination of the total amount of organic carbon present. However, combustion analysis will result in complete oxidation of organic matter and thus the total amount of organic carbon present can be determined.

B3.2 This test does not necessarily make any assessment as to the ease with which the organic matter will undergo chemical or biochemical oxidation. However good correlation is obtained between this method and chemical and biological oxidation tests [1].

B3.3 As only organic carbon is to be determined, inorganic carbon compounds such as carbonates etc must be stripped by acidifying and aerating the samples.

B4 Hazards

See another publication in this series,

The instrumental determination of TOC and TOD needs care and attention to detail to avoid a number of potential hazards. [5]

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 radiation must be avoided.

Instrument maintenance, particularly of the electrical components, is best undertaken in accordance with the manufacturer's manual. Note that considerable static voltages may arise by induction from the furnace: proper earthing of equipment is, therefore, most necessary.

B5 Reagents

B5.1 Except where otherwise stated, analytical reagent grade chemicals are to be used. Reagents should be stored in glass bottles. All reagents, are stable for a least one month.

B5.2 **Water**

Either distilled or de-ionized water can be used provided the blank value remains acceptable. Prepare water for blank determinations by redistilling laboratory distilled water first from alkaline permanganate and then from acid dichromate.

B5.3 **Sodium Hydroxide 3% m/V**

Dissolve 60.0 ± 0.5 g sodium hydroxide in 500 ml of distilled water. Allow the solution to cool and make up to 2 litres.

B4 **Nitric Acid** (d_{20} 1.42)

B5.5 **Carbon dioxide free air.**

B5.6 **Carbon dioxide free nitrogen.**

B5.7 **Potassium hydrogen phthalate** dried at 120°C for one hour and stored in a desiccator.

B5.8 **Standard Solution A**

Weigh accurately 212 ± 1 mg of potassium hydrogen phthalate and transfer quantitatively to a 200 ml graduated flask and make up to volume with distilled water.

B5.9 **Standard Solution B** (50 mg l^{-1} total organic carbon as potassium hydrogen phthalate)

Transfer 25.0 ± 0.1 ml of solution A to a 250 ml graduated flask and make up to volume with distilled water.

B.6 Apparatus

High blank values may be the result of minute amounts of contaminants in the flask, the reflux condenser or on the anti-bumping granules. Apparatus can be cleaned by repeatedly boiling fresh dichromate/sulphuric acid mixture until low and consistent blanks are obtained. If possible apparatus should be reserved solely for this determination.

B6.1 Glassware should have standard ground-glass joints where appropriate; grease must not be used.

B6.2 **500 ml round bottom flask** and a distillation tray capable of holding all the contents of the boiling flask in the event of breakage.

B6.3 **Water-cooled condenser** of adequate size to fit the 500 ml flask and capable of being rinsed easily.

B6.4 **Protective cap** for the reflux condenser to keep dust out of the apparatus when not in use. A small beaker is satisfactory.

B6.5 **Predigested anti-bumping granules** which should be precleaned by digestion for 2 hours.

B6.6 Uniform heating is essential to maintain gentle boiling. This can be achieved by using a heated sand tray or electric mantle.

B6.7 **Apparatus for the determination of total organic carbon** (see a publication in this series [5].

B.7 Sampling and Sample Preservation

The analysis should be carried out as soon as possible after sampling. The samples should be dried for 4 hours at 105°C and crushed before subsampling for analysis.

B.8 Procedure

Step	Procedure	Notes
B8.1	Extraction	
B8.1.1	Weigh accurately (± 10 mg) about 50.0 g of dried sample, and transfer it to a 500 ml round bottom flask. Note the weight Wg.	
B8.1.2	Add 125 ± 1 ml of 3% m/v NaOH, stopper flask and shake vigorously (Note a)	(a) It may be necessary to shake for a minute or longer to wet the sample entirely.
B8.1.3	Wash the flask down with the minimum quantity of water necessary to transfer all the material to the bottom.	
B8.1.4	Connect condenser and reflux for 3 hours (note b).	(b) Studies on shorter reflux periods indicated lower results.
B8.1.5	Remove the flask from the source of heat and allow to cool for approximately 10 mins.	
B8.1.6	Rinse condenser with distilled water, remove flask, stopper it and cool in a cold water bath.	
B8.1.7	Vacuum filter the mixture with Whatman GF/C paper (note c). Transfer filtrate to a 250 ml volumetric flask. The filter flask is then rinsed several times the rinse water being filtered and added to the filtrate.	(c) Whatman No. 1 can be used as a backing.
B8.2	Oxidation and Reduction	(d) The dilution is assessed from C_K. (See Method A). If C_K is substantially different from C_T, then a different dilution might be necessary.
B8.2.1	Add nitric acid to produce a pH value of less than 1. Cool and dilute to 250 ml. It may be necessary to dilute the extract to give a final strength of below 50 mg ml^{-1} total carbon (Note d). The pH of the diluted extract should be maintained below 1. Note the dilution D.	
B8.2.2	Transfer 100 ± 1 ml of the acidified extract into a suitable container and bubble carbon dioxide free air through the sample.	
B8.2.3	Determine the total soluble organic carbon using an appropriate apparatus [5] (Note e). Note the peak height H_1 of the response on the chart recorder.	(e) Work reported on the determination of total organic carbon (1), (2) employed copper oxide and nickel catalysts and the determination of the methane produced, by gas chromatography [4].
B8.2.4	Repeat steps B8.1.2 – B8.2.3 with standard solution B, 50 mg $^{-1}$ C_T as potassium hydrogen phthalate. Note peak height H_2.	
B8.2.5	Repeat steps B8.1.2 – B8.2.3 to determine a blank value H_B.	

Step	Procedure	Notes
B8.2.5	*Calculation of Results*	

$$\% C_T = \frac{H_1 - H_B) \times 50 \times D}{H_2 - H_B) \times W \times 4 \times 10}$$

where W is the weight of sample taken in grammes.

B.9 Checking the Linearity of the Calibration Curve

The procedure in this section must be carried out on at least two independent occasions before application of this method to any samples and occasionally thereafter.

B9.1 To a series of 100 ml calibrated flasks pipette 0.00, 2.00, 5.00 and 10.00 ml of standard solution A acidify to below pH 1 with nitric acid and dilute to volume with nitric solution acid at a pH value of 1. These solutions contain respectively 0, 10, 20 and 50 mg l^{-1} potassium hydrogen phthalate. Repeat steps B8.2.2 – B8.2.3 in the Experimental Procedure for each of these solutions. Plot the peak heights against mg l^{-1}.

B9.3 A variety of other carbon compounds can also be used to calibrate the total organic carbon analyser [1], [3], [4] and [5].

B.10 Checking the Validity of Analytical Results

Once the method had been put into normal routine operation many factors may subsequently affect the validity of the analytical results. It is recommended that experimental tests of the validity should be made regularly. As a minimum, however, it is suggested that a typical sample be analysed in duplicate at the same time and in exactly the same way as normal samples, such checks will be facilitated by plotting results obtained on quality control charts which will detect inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

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(1) Hrudey S. E., Perry R. Assessment of organic content of incinerator residues. *Environ. Sci. Tech. 1973,* **13** (7), 1140–1147.

(2) Department of the environment/National Water Council – Standing Committee of Analysts. *Chemical oxygen demand (Dichromate Value) of Polluted and Waste Waters 1977*; H.M.S.O. London 1978.

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(5) Department of the Environment/National Water Council. Standing Committee of Analysts. *The Instrumental Determination of Total Organic Carbon, Total Oxygen Demand and Related Determinations 1979.* HMSO. London.

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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:

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