The Permanganate Index and Permanganate Value Tests for Waters and Effluents 1983

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.75 net

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The Permanganate Index Test which forms the first part of this booklet was developed to meet the requirements of a European Community Directive[1]. Acknowledgment is also made of discussions which took place in ISO TC147 WG10. The differences between this test and the 4 hour 27°C Permanganate Value test which forms the second part of the booklet are given in the Introduction to the first method. The N/80 Permanganate 4 hour 27° Permanganate Value test which forms the second part of this booklet and the other Permanganate Value tests in the three short notes are still used for a variety of control purposes in the water and sewage industry and in related laboratories. They are a kind of Chemical Oxygen Demand test.

Contents

London Her Majesty's Stationery Office

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 whether for one's self, one's colleagues in the laboratory, outsiders or subsequently for maintenance workers. 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 emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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 both recommended methods for the determination of water quality, and in addition, 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 a committee of the Department of the Environment set up in 1972. Currently it has seven 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
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods.

The actual methods and review 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.

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 and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. 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 that booklet.

L R PITTWELL
Secretary

31 October 1983

General Introduction

The basis of both methods and the notes given in this booklet is the oxidation of oxidizable substances by permanganate ions in acid solution, in which reactions are very complex and very susceptible to the effects of minor variables. Most of the work on the use of permanganate ion as an oxidant has been on inorganic and oxalate determinations, which is well summarized in references 7, 8 and 9. The main points follow:

The oxidizing and reducing power of reagents and determinands is proportional to the concentration, falling as the concentration falls. Hence the ability to oxidize a substance requiring a strong oxidant may be governed by the amount of oxidant consumed by oxidizing any more readily oxidized substances also present in the sample. The reaction can also be affected considerably by the presence of ions which complex the various oxidation states of manganese (all valencies between seven and two are involved), so that while ions such as chloride, fluoride, phosphate, nitrate, thiocyanate and even oxalate and ammonia can cause interference in some circumstances under other conditions, or in the presence of other ligands, they have no effect. The reaction is also very pH and temperature dependent. Thus increase in pH to neutral or alkaline and reduction in temperature favours it stopping at intermediate manganese oxidation states usually IV or III. (The usual colours are VII purple-pink, VI green, V blue, IV red or black if insoluble, III brown or red, II colourless or very pale pink). Oxalate titrations that turn brown or black should be discarded and repeated using more sulphuric acid and at a slightly warmer temperature.

Boiling solutions of permanganate evolve oxygen, the amount being proportional to the acidity, but evolution can occur from boiling alkaline solution as well. This reaction is catalysed by manganese IV. If the solution becomes almost neutral or alkaline manganese II can reduce manganese VII to intermediate valencies. Although acid solutions have a higher Redox Potential than alkaline ones of the same strength and temperature, there are compounds such as amines which react more readily in alkaline solution. If the potassium permanganate contains insoluble black manganese dioxide this should be removed after solution by filtration through a fine all glass filter.

All glassware must be scrupulously clean and free from organic matter, including detergents, prior to use. Stains due to manganese compounds can be removed by soaking in a strong solution of a sodium bisulphite, followed by a thorough washing in water. Strong sodium hypochlorite may also be effective. Falsely high results have been traced to manganese IV absorbed on burettes and glassware.

If there is difficulty in obtaining water with a low blank, treat excess water by dissolving a few grains of potassium permanganate and sodium hydroxide in it. Then distil from an all glass apparatus, rejecting about the first 5% and stopping the distillation when about 80% of the water has distilled over.

Permanganate Index of Potable or Lightly Polluted Raw Waters (0.002M, 10 minute, Boiling Water Bath)

Introduction

The method has been prepared because of a requirement for a simple rapid procedure which also meets the requirements in the European Community Directive on drinking water[1] for a potassium permanganate oxidizability parameter.

The oxidation conditions of the Permanganate Index method are more severe than for the Permanganate Value method[2] which uses a 4 hour incubation period at 27°C. Typically the Permanganate Index method yields higher oxygen demand results. Both procedures are empirical.

The method is intended for potable or lightly polluted raw waters. More highly polluted waters can be tested by utilizing sufficient pre-dilution of the sample. It is not recommended as a procedure for polluted samples.

1 Performance Characteristics of the method

1.1	Substance determined	Oxygen taken up by the heated acidified sample from permanganate, under the conditions of the test.
1.2	Type of Sample	Potable or lightly polluted water.
1.3	Basis of Method	Oxidation of acidified sample by heating with potassium permanganate for 10 minutes in a boiling water bath. The excess permanganate is determined by addition of excess sodium oxalate and back titration of the excess oxalate with potassium permanganate.
1.4	Range of Application	Up to 10 mg O_2/l. This is equivalent to a consumption of approximately 60% of added potassium permanganate. The range may be extended by predilution of the sample, but performance data (1.6;1.7) relates to concentrations up to 10 mg O_2/l.
1.5	Calibration Curve	Not applicable. However sodium oxalate, which is completely oxidized in the test, gave a linear relationship when concentration was plotted against the mean value of permanganate index.

Permanganate Index (mg O_2/l)

Sodium Oxalate (mg/l)	No. of Replicates	Mean	Max.	Min.	Std. Dev.
26.5	16	3.23	3.42	3.04	0.097
53.0	16	6.40	6.59	6.14	0.119
79.5	16	9.66	9.86	9.44	0.125

1.6 Standard Deviation

Within-batch standard deviation

Sample	Concentration Found (mg O_2/l)	Standard Deviation (mg O_2/l)	Degrees of Freedom	Note
Tap Water	1.28–1.94	0.06–0.21	10	(a)
Resorcinol (1.0 mg/l)	1.63–2.04	0.06–0.20	10	(b)
Resorcinol (6.0 mg/l)	9.32–10.28	0.07–0.27	10	(c)
Various raw and potable waters	0.23–8.17	0.05–0.60	Various up to 10	(d)

Total standard deviation

Sample	Concentration Found (mg O_2/l)	Standard Deviation (mg O_2/l)	Degrees of Freedom	Note
Resorcinol (1.0 mg/l)	1.83	0.10	20	(e)
Resorcinol (6.0 mg/l)	9.95	0.12	23	(e)

1.7	Limit of Detection	0.17–0.79 mg O_2/l with 10 degrees of freedom (Note (f)). 0.55 mg O_2/l with 40 degrees of freedom (Note (g)).
1.8	Sensitivity	1 ml of potassium permanganate (0.002M) consumed is equivalent to 3.2 mg/l oxygen demand as Permanganate Index.
1.9	Bias	(i) Not predictable as many organic compounds are only partially oxidized under the conditions of the test, to a degree which will vary between compounds. (ii) Any oxidizable material present in the water used for the blank determination will cause a negative bias. See section 2.4. (iii) Inter laboratory bias between participating laboratories was shown for both resorcinol standards. See section 1.6. The greatest difference between mean values being 1.63 to 2.04 mg O_2/l and 9.32 to 10.28 mg O_2/l for the lower and higher resorcinol concentration respectively. There is also evidence of non linearity of permanganate index with resorcinol concentration. However sodium oxalate, which is completely oxidized in the test, showed linearity of the mean value of permanganate index with a range of sodium oxalate concentrations. See section 1.5. This indicates the reason for non-linearity is not procedural. The reason is not known.
1.10	Interferences	Oxidizing and reducing agents may influence the permanganate index but are not classed as interferences. High chloride levels may cause an enhanced result and are regarded as an interference. See Section 3.

1.11	Time Required	Total and operator analytical time for up to 10 samples is typically in the range 40 to 60 minutes.
		(a) Range of results obtained for a distributed tap water analysed in 6 laboratories. N.B. The range of concentrations found should not be taken to indicate the presence of inter-laboratory bias, because of possible sample instability. (b) Range of results obtained by 7 laboratories for a 1.0 mg/l solution of resorcinol in water, made up by the individual laboratories from a distributed resorcinol sample. (c) As (b), but for a 6.0 mg/l solution. (d) Range of standard deviations for a variety of raw and potable waters; data obtained from 5 laboratories. (e) Total standard deviations obtained by a single laboratory. (f) Range of data from 6 laboratories.

2 Principle

2.1 The test is empirical.

2.2 In hot acid solution chemical oxidation by potassium permanganate results in the reduction of the permanganate Mn (VII) ion to the manganous Mn (II) ion.

2.3 The remaining unreduced permanganate is determined by addition of excess sodium oxalate and back titration with potassium permanganate.

2.4 The following may contribute to the blank
(i) Autoreduction of $KMnO_4$ to Mn^{2+} during the test.
(ii) Reagents.
(iii) Determinand in the blank water.
Any contribution from (iii) will give a negative bias to the results for samples. Typically blank titrations obtained experimentally did not exceed 0.3 ml which is equivalent to a permanganate index of about 1 mg O_2/1. If derived solely from the blank water this would be the amount of negative bias which is large in relation to the limits of detection achieved experimentally.

The blank water quality is not entirely responsible for any blank value as there is evidence from similar analytical procedures [3][4][9] of autoreduction of $KMnO_4$ to Mn^{2+}. This is supported by results from one laboratory (Water Research Centre) when closely similar blanks were obtained from eight blank waters prepared by eight different procedures. The interference was drawn that the determinand in the different blank waters did not represent the major contributor to the blank values found.

It is not possible to assess the individual contributions to overall blank value and therefore impossible to determine the bias. For practicable purposes a blank value of 0.3 ml is proposed as a working maximum for the test. Where this value is exceeded or where there is poor duplication of blanks the cause(s) should be investigated. See section 8.8.

2.5 Reactions:—

2.5.1 Oxidation reaction:—

$$MnO_4^- + 8H^+ + 5e = Mn^{2+} + 4H_2O$$

2.5.2 The permanganate/oxalate reaction

$$8MnO_4^- + 6H^+ + 5H_2C_2O_4 = 2Mn^{2+} + 1OCO_2 + 8H_2O$$

3 Field of application and Interferences

Inorganic reducing agents such as nitrite, and ferrous iron will contribute to the permanganate index. Oxidizing agents may also contribute and possibly give negative results. There is little possibility of either being present in sufficient quantity in potable or lightly polluted water to affect the result appreciably.

The effect of chloride is to increase the observed permanganate index. This effect is regarded as an interference, but is unimportant at the chloride concentrations of most, if not all, potable waters.

The effect of a number of the above substances on the determination of the permanganate index has been investigated by one laboratory and the results are reported below. Table 1.

Table 1

Other Substance	Added as	Concentration of other substance (mg/l)	Effect in mg O_2/l of the other substance on results for resorcinol solutions at concentrations of:— 1.0 mg/l	6.0 mg/l
Nitrite as N	$NaNO_2$	0.5	−0.32	−0.54
Ferrous Iron	$FeSO_4$	0.5	−0.02	+0.08
Chloride	NaCl	400	+0.07	+0.04
Chloride	NaCl	500	+0.11	+0.25

If the other substance did not interfere the effect would be expected to lie (95% confidence) between ±0.16 mg/l at 1.0 mg/l resorcinol and ±0.20 mg/l at 6.0 mg/l. resorcinol. (1.0 mg/l of resorcinol gave a permanganate index of approximately 1.8 mg/l O_2/l, and 6.0 mg/l of resorcinol gave a permanganate index of approximately 10 mg O_2/l).

4 Hazards

Sodium oxalate is harmful and copious amounts of water should be used to remove this chemical from the eyes or skin. If ingested, large quantities of water/milk should be drunk and expert medical treatment sought.[5]

Addition of sulphuric acid (d_{20}1.84) to water must always be carried out with care and with gentle swirling to ensure mixing and to avoid localized concentration of acid.

The method involves the handling of hot acidified solutions and care is essential. In the event of a spillage immediate washings with copious volumes of water is advised as a simple effective remedy.

5 Reagents

5.1 Analytical reagent grade chemicals should be used for all solutions. With the exception of the 0.005M sodium oxalate, all are stable for a period of at least one month. All reagents should be stored in glass.

5.2 Water.

Distilled water or deionized water can be used provided the blank value is acceptable. See Section 8.8 note (i), Section 2.4 and the General Introduction.

5.3 Potassium permanganate solution 0.002M.

Weigh out 0.316±0.001g of potassium permanganate. Dissolve in water, filter through a glass fibre paper and make up to one litre in a volumetric flask. Store the solution in a dark bottle.

This solution should be standardized as described under sections 8.14 to 8.16 each time an analytical batch is run.

5.4 Sulphuric Acid 2M.

Add with caution one volume of concentrated sulphuric acid (d_{20} 1.84) to 8 volumes of water. Whilst still hot add just sufficient 0.002M potassium permanganate solution to give a faint permanent pink coloration to the solution.

5.5 Sodium oxalate stock solution 0.05M (Primary Standard).

Dry a sufficient quantity of sodium oxalate $Na_2C_2O_4$ in an oven at 120°C for 2 hours. Remove and allow to cool in a desiccator. Weigh out 6.70±0.01g, dissolve in distilled water and make up to one litre in a volumetric flask.

5.6 Sodium oxalate working solution 0.005M.

Pipette out 100±0.25 ml of sodium oxalate stock solution (0.05M) and dilute to one litre with water in a volumetric flask. This solution is stable for approximately 2 weeks and should be discarded after this period. Reference 6 states oxalate solutions attack glass and solutions should not be stored more than a few days. Tests by a number of analysts have confirmed the sodium oxalate solution 5.5 and 5.6 are stable for the periods stated. If in doubt analysts should check the stability of these reagents under their own storage conditions.

6 Apparatus

6.1 Boiling water bath, fitted with a perforated tray and containing polypropylene spheres to minimize heat losses. The heater should be situated in the base of the bath covering as much of the area as possible and should have a heating capacity of at least 1.5 watts per sq. cm. working area.

6.1.1 Water bath heating will typically raise the test tube contents to between 96 and 98°C provided the bath has sufficient heating capacity. Baths with a stirrer/heater at one end show temperature gradations and are not satisfactory.

6.1.2 For analysis of large numbers of samples, a water bath is most suitable. For individual or small numbers of samples a beaker of boiling water is a suitable alternative. In either case the surface of the liquid in the test tube must be below the surface of the boiling water.

6.1.3 Maximum temperature should be reached within five minutes of immersion for all test tube contents with the maximum number of tubes to be heated at any one time present. This indicates that the heating system is of sufficient capacity.

6.2 Borosilicate test tubes between 150 x 25 mm and 200 x 32 mm in size have been tested and found suitable for this test. The tubes must be thoroughly pre-cleaned with hot acidified permanganate and reserved for this test. See Section 2.4. If high blanks are found or tubes are unused for long periods, repeated pre-cleaning is advised. Conical flasks are not recommended as an alternative to test tubes. Experimentally, lower temperatures are found for solutions contained in the flasks when both are heated simultaneously in boiling water.

6.3 Tube rack, preferably stainless steel, to fit inside the bath, and designed to hold a sufficient number of tubes in an upright position.

6.4 Pipettes, 5 ml. An automatic pipette or dispenser capable of dispensing to an accuracy of 5± 0.05 ml is convenient for multiple analyses. Alternatively a bulb pipette may be used.

6.5 Micro-burette, 5 ml, reading to 0.02 ml.

6.6 Stop clock.

7 Sampling and Sample Preservation

A representative sample should be taken into a clean glass bottle fitted with a ground glass stopper. A plastic stopper may be used provided tests have shown that the plastic does not affect the result.

Analysis should be carried out as soon as possible after sampling. Whilst complete and unequivocal preservation of samples is not practicable, changes can be retarded by refrigerating the sample at 4°C in the dark.

8 Analytical Procedure

Step	Procedure	Notes
8.1	Add 25± 0.25 ml of well mixed or pre-diluted sample to a test tube (Note a).	(a) See Section 6.2.
8.2	Add to the test tube 5± 0.5 ml of 2M sulphuric acid and mix by swirling gently.	
8.3	Preheat the test tube for a period of 10± 2 mins. in the water bath which has previously been raised to boiling. (Notes b and c).	(b) Alternatively place in a beaker of water. See Section 6.1.2. (c) The preheat period must be sufficient for the test tube contents to reach maximum temperature. See Section 6.1.3.
8.4	Add 5± 0.05 ml of 0.002M potassium permanganate reagent and commence timing. (Note d)	(d) For the reagent additions in steps 8.4 to 8.5 it is recommended that automatic pipettes or dispensers are used for multiple analysis to ensure compliance with time requirements.
8.5	10 minutes ±15 seconds after the addition of the potassium permanganate reagent add 5±0.05 ml of 0.005M sodium oxalate reagent.	(e) The test tubes should be left in the hot water prior to titration to maintain the solution temperature as high as possible before titration starts. The temperature of the solution must remain above 60°C throughout the titrations.
8.6	Remove the tube from the water bath and titrate the contents, whilst still hot, with 0.002M potassium permanganate reagent to a faint pink colour which persists for 30 seconds (Notes e, f, g).	(f) Care must be exercised in handling the hot test tubes. (g) It is left to the individual analyst to either titrate the test tube contents directly or to transfer them to an alternative titration vessel prior to titration. Any transfer must be quantitative and the solution temperature maintained as per note (e) above.
8.7	Record the titre (t ml) (Note h).	(h) See Section 1.4.

Procedure for duplicated blank value

8.8	Add 25±0.25 ml of water (reagent 5.2) to a test tube. (Note i).	(i) Blank determination should be carried out in duplicate and should agree to within 0.1 ml and the mean value used for t_B. Typically the Blank value should not exceed 0.3 ml. See Section 2.4.
8.9	Carry out steps 8.2–8.6.	
8.10	Record the first blank titre (t_{B1} ml).	
8.11	Repeat steps 8.8–8.9.	
8.12	Record the second blank titre (t_{B2} ml).	
8.13	Retain the titrated solution for standardization of the potassium permanganate solution.	

Standardization of the Potassium Permanganate Reagent (see Section 5.3)

8.14	To the solution retained from steps 8.13 add 5±0.05 ml of 0.005M sodium oxalate reagent.	
8.15	Titrate the contents of the tube with the 0.002M potassium permanganate reagent to a faint pink colour which persists for 30 seconds (Note j).	(j) Reheat prior to titration if necessary. The temperature of the solution must remain above 60°C throughout the titrations.

Step	Procedure	Notes
8.16	Record the titre ($t_s$ml).	

Calculation

Permanganate Index (Boiling Water Bath)

$$= \frac{1000}{25} \times \frac{5}{t_s} \times \frac{80}{1000} \times (t - t_B)$$

$$= 16 \times \frac{t - t_B}{t_s} \text{ mg oxygen/litre}$$

Where t_B = mean blank = $\frac{t_{B1} + t_{B2}}{2}$

Pre-diluted Sample

Permanganate Index (Boiling Water bath)

$$= 16 \times \frac{t - t_B}{t_s} \times D \text{ mg oxygen/litre}$$

Where D = dilution factor = $\frac{\text{Volume (ml.) of diluted solution}}{\text{Volume (ml.) of original sample}}$

Permanganate Value (N/80, 4 hr, 27°C)

1 Performance Characteristics of the Method

1.1	Substance determined	Oxygen taken up by the acidified sample under the conditions of the test.
1.2	Type of Sample	All waters and effluents.
1.3	Basis of the Method	Oxidation of the acidified sample, the excess permanganate being determined by liberation of iodine followed by titration with thiosulphate.
1.4	Range of Application	Up to about 500 mg O_2/l. Substantially higher values can be analysed by dilution.

1.5 Standard Deviation

	Mean	Range	mg O_2/l S.D.	Degrees of Freedom	Notes
Chalk derived drinking water	0.18–0.23		0.03–0.04	6	(a)
River derived drinking water	0.97–1.04		0.03–0.07	6	(a)
Drinking Water	0.25	0.21– 0.28	0.028	4	(b)
Filtered Water	1.64		0.033	4	(c)
Raw Water	2.20		0.033	4	(d)
Standard Sample	10.07	9.6 –10.5	0.19	49	(e)
Various Reservoir Waters	1.12	0.5 – 1.8	0.24	49	(f)
	1.13	0.6 – 2.2	0.27	49	(f)
	1.16	0.6 – 1.9	0.22	49	(f)
	1.18	0.6 – 2.8	0.33	49	(f)
	1.20	0.7 – 2.6	0.29	49	(f)
	1.78	1.0 – 3.0	0.32	49	(f)
	1.96	1.1 – 3.0	0.41	39	(f)
	1.99	1.2 – 2.7	0.34	39	(f)
	2.41	1.6 – 3.1	0.33	49	(f)
Sewage Effluents	4.7	4.6 – 4.8	0.10	10	(g)
	6.7	6.2 – 7.0	0.93	10	(h)
	9.01	8.8 – 9.2	0.16	10	(g)
	9.8	9.6 –10.0	0.13	10	(i)
	12.1	10.8 –14.4	1.03	7	(j)
	18.1	15.4 –20.4	1.40	7	(j)
Treated Cheddar Lake Water	0.23	0.20– 0.32	0.02	7	(k)

1.6	Limit of Detection	Very dependent on sample type. For very clean waters it can be as low as 0.1 mg O_2/l to 0.2 mg O_2/l, rising for waters with non oxidizable suspended matter and colour.
1.7	Bias	Variable. Causes of both positive and negative bias are reported in the literature, such as easily oxidized material lowering the oxidation potential before difficulty oxidized materials can react and loss of free oxygen respectively.

1.8	Interferences	See General Introduction at the beginning of this booklet.
1.9	Time Required	Approximately 6 hrs for up to 10 samples of which about 1 hr at the beginning and the end is operator time.

Notes

(a) Lee Valley Water Co. 3 hr, 37°C variant (see Section 2.1), each batch had 6 degrees of freedom. Ranges indicate operator variation.
(b) Colne Valley Water Co. 3 hr, 37°C variant (see Section 2.1).
(c) Essex Water Co., Hanningfield Laboratory.
(d) Essex Water Co., Langford Laboratory.
(e) Central Scotland Water Development Board, Balmore Laboratory. Data from preliminary standardization tests, hence minimum error expected.
(f) Central Scotland Water Development Board, Balmore Laboratory. Data based on repeated sampling over one year, deviations are therefore larger than the truth due to slight sample variation affecting the value of the mean thus increasing the error beyond that for the actual analysis.
(g) Clyde River Purification Board.
(h) Solway River Purification Board.
(i) Tweed River Purification Board.
(j) Data from a joint Analytical Quality Control exercise organized by the seven Scottish River Purification Boards. Sample stability problems will have contributed to the error.
(k) Bristol Water Works Co process control data from a period when other determinands were virtually constant. 3 hr, 37°C variant (see Section 2.1).

2 Principle

A suitable volume of sample to approximately half consume 50 ml of N/80 potassium permanganate is acidified with sulphuric acid and the permanganate and allowed to react at 27°C for four hours. Excess potassium iodide is then added to liberate iodine, which is titrated with sodium thiosulphate with a starch indicator end point.

2.1 Some laboratories use a minor varient — 3 hrs at 37°C and use a bacteriological incubator instead of a water bath.

3 Hazards

In addition to the usual laboratory hazards of sulphuric acid and iodine, care should be taken when acidifying the sample and when adding the permanganate. For effluents and contaminated waters, these operations should be carried out in a fume hood and wearing safety glasses and any similar protection deemed necessary.

4 Reagents

4.1 Distilled deionized water giving a low blank (see General Introduction)

4.2 Potassium Permanganate 0.0025 M(N/80).

Weigh out 0.395± 0.001 g of potassium permanganate (reject any having a dull brown colour instead of a deep purple sheen). Dissolve in water, filter through a glass filter into a 1-litre volumetric flask and make up to the mark with water and mix.

4.3 Sulphuric acid 2M

See Permanganate Index Section 5.4.

4.4 Potassium iodide, crystals.

4.5 Sodium thiosulphate 0.0125M.

4.5.1 Prepare a master 0.125M solution by dissolving 31.2± 0.05 g of sodium thiosulphate pentahydrate in about 2.00 ml of water, transfer quantitatively to a 1-litre volumetric flask dilute to the mark and mix. Shelf life is limited and variable. Store in an amber glass bottle. Turbid solutions should be discarded.

4.5.2 As required, pipette 50.00 ml of the 0.125M master solution into a 500-ml volumetric flask, dilute with water to the mark and mix. Standardize as detailed in reference 10. Use a factor $F = \frac{10}{V_1}$ to correct the strength in subsequent calculations. (For V_1 see reference 10). The dilute solution should be used the same day and not stored.

4.6 Starch Solution

Grind 0.5± 0.1 g of soluble starch into a smooth paste with a little cold water and pour into 1.00± 10 ml of boiling water stirring constantly. Boil for one minute and allow to cool before use. The reagent remains stable for up to one week if stored in a refrigerator, otherwise prepare fresh solutions as required.

5 Apparatus

5.1 350 ml glass-stoppered bottles.

5.2 Water bath set at 27± 0.5°C. (see also Section 2.1).

5.3 Stop clock or timer capable of timing 4 hrs.

6 Sampling and Sample Preservation

See Permanganate Index Section 7.

7 Analytical Procedure (a)

Step	Procedure	Notes
	Sample Procedure	
7.1	Pipette into a clean 350 ml glass-stoppered bottle 10 ml of 2M Sulphuric acid and 50 ml of 0.0125M Potassium permanganate and swirl to mix.	(a) All glassware must be absolutely free from reducing substances and organic matter before use.
7.2	First shake or homogenize the sample thoroughly diluting if necessary (see table 1) and then dependent on the expected permanganate value, measure out the volume of sample indicated in Table 1 below note b).	(b) If samples are homogenized do not use a bottom bladed device as there is a risk of contaminating the sample thereby.

Table 1 Sample volumes and dilutions

Expected Permanganate Value mg O_2/l	Volume of Sample Aliquot (V_2 but see Section 8) ml	Dilution
<25	100	none
50	50	none
100	25	If the sample contains much suspended solid, such that the volume to be taken is not likely to be representative, quantitatively dilute the sample prior to taking the aliquot such that the volume taken is 50 or 100 ml as seems best
125	20	
250	10	If the sample contains any suspended matter dilute as above such that the volume taken is at least 20 ml, preferably 50 or 100 ml.
>500		Dilute the sample quantitatively such that the sample aliquot is 20 to 50 ml.

Step	Procedure	Notes
7.3	Subtract the sample aliquot volume taken from 100 ml and add this volume of water to the acidified permanganate in the bottle to keep the reaction volume and initial permanganate concentration constant.	
7.4	Put the bottle into the water bath and allow it to come up to temperature.	
7.5	Add the selected volume of sample (pre-diluted if necessary) to the bottle in the water bath, stopper loosely, swirl gently to mix and start the timer immediately.	
7.6	After 4 hrs± 5 minutes, remove the stopper from the bottle, add about 0.5 g of potassium iodide crystals, remove the bottle from the bath and swirl to dissolve and mix the iodide.	
7.7	Titrate immediately with 0.0125M sodium thiosulphate solution, adding about 1 ml of starch solution when the mixture is a pale brown colour. Continue titrating until the blue colour formed just disappears (V_3ml) (note c).	(c) The blue colour may return on standing due to oxidation by air. This should be ignored.
	Blank Procedure	
7.8	Carry out steps 7.1 and 7.4 above (omitting steps 7.2 and 7.3). Then add 100 ml of water at step 7.5 and continue with steps 7.6 and 7.7, thus obtaining the blank titration (V_4ml). (note d and e)	(d) The blank should be included in with each batch of samples on the water bath and analysed at the same time to ensure identical treatment. (e) See also Section 9 on Analytical Quality Control.

8 Calculation

8.1 If the sample was pre-diluted in step 7.1 calculate the actual volume of undiluted sample present in the diluted aliquot under V_2 ml, otherwise use the sample volume taken directly (V_2 ml).

8.2 Permanganate Value is $\frac{(V_4 - V_3) \times F \times 100}{V_2}$ mg O_2/l

where V_4 is defined in step 7.8.
V_3 is defined in step 7.7.
V_2 is defined in 8.1 above and table 1.
F is defined in Section 4.5.2.
(If F is determined, V_1 used to calculate F is defined in reference 10).

9 Analytical Quality Control

Users report that under one percent of determinations are erroneous. As an absolute minimum, it is suggested that a quality control chart be kept of the blank values. As analytical results are usually used for proces control any erratic analyses should be repeated immediately.

Other Permanganate Value Tests (Test data not available except on 3 which is fully tested)

Four other Permanganate Value Tests are known to be in current use. One which is very similar to the foregoing method is included therein. The old "Royal Commission" test using the foregoing procedure, but with all reagents at ten times the strengths given in the second part of this booklet appears to be obsolete.

The other tests known still be be in use are:

1 Permanganate Value (N/80, 3 min, 27°C)

This test sometimes used for assessing the dilution to be made in BOD tests is as the foregoing procedure but the samples are removed from the bath, treated with iodide and titrated after 3 minutes ± 5 seconds.

2 Permanganate Value (N/8, 1 min. boiling)

This test is sometimes used for assessing the dilution to be made in the foregoing Permanganate Value (N/80, 4 hr, 27°C) test. The procedure is as in the foregoing test, without any dilution, using 25 ml of sample, reagents at ten times the strength given and the sample is heated on a boiling water bath for 1 minute.

3 Organic Carbon (Permanganate Value) Test

100 ml of sample is boiled with 5 ml of 15% W/V sodium hydroxide and 15.00 ± 0.01 ml of 0.01N potassium permanganate for 16 minutes, acidified with 7 ml of 50% V/V Sulphuric acid and boiled for a further 14 minutes. It is then titrated immediately, without cooling with 0.01N oxalic acid. The method was developed for use with samples containing amines.

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(6) Vogel A. I. *A textbook of Quantitative Inorganic Analysis,* Longmans 3rd Edition, p. 284.

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(10) *Chemical Disinfecting Agents in Water and Effluents, and Chlorine Demand 1980,* p 13 (Steps B 8.1 and B 8.2).

(11) CEGB Manual *"Methods of Sampling and Analysis",* (Volume 1A (Steam and Water) Section 13. Central Electricity Generating Board, 1966.

Address for Correspondence

However thoroughly a method may have been tested there is always the chance of a user discovering a hitherto unreported problem. While the method given in the second part of this book has been used routinely for at least half a century very little quantitative data on precision is available and most of the information given has been obtained by inference from work elsewhere. However the Main Committee decided that the method should continue to be made available. Users with problems or data on either of the two main methods, but especially on the second, are asked to write to:

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