Manganese in Raw and Potable Waters by Spectrophotometry (using formaldoxime) 1977

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £1 net

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Tentative Method

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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 a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. Where the Committee has 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 radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

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

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About this series

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

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

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

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

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

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

Manganese in Raw and Potable Waters by Spectrophotometry Tentative Method (1977 version)

Note: Throughout this method manganese is expressed as the element (Mn).

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series).

1.1	Substance determined	All forms of manganese (see Sections 2 and 8).		
1.2	Type of sample	Raw and potable waters.		
1.3	Basis of method	The reaction of manganese with formaldoxime to form a coloured complex whose concentration is measured spectrophotometrically.		
1.4	Range of application (a)	Up to 1.0 mg/l.		
1.5	Calibration curve (a)	Linear to at least 1.0 mg/l at 450 nm.		
1.6	Total standard deviation (a)	Manganese concentration (mg/l)	Total standard deviation (mg/l)	Degrees of freedom
	1.6.1 Without pretreatment:	0.05 (b)	0.003	14
		0.10 (b)	0.004	14
		0.20 (b)	0.009	14
		0.50 (b)	0.014	14
		1.00 (b)	0.020	14
	1.6.2 With pretreatment:	0.09 (c)	0.006	9
		0.19 (c)	0.010	9
		0.20 (b)	0.008	9
		0.50 (b)	0.016	9
1.7	Limit of detection (a)	0.005 mg/l (with 9 degrees of freedom).		
1.8	Sensitivity (a)	0.5 mg/l gives an absorbance of approximately 0.27.		
1.9	Bias (a)	No bias detected except when interferences occur (see Section 1.10).		
1.10	Interferences (a)	Cobalt, iron II and iron III may interfere (see Section 3).		
1.11	Time required for analysis (a)	The total analytical and operator times are the same. Typical times for 1 and 10 samples are approximately 60 and 90 minutes respectively excluding any pretreatment time.		

(a) These data were obtained by the Yorkshire Water Authority [1] [2] using a spectrophotometer with 40-mm cells at 450 nm.

(b) These data were obtained using distilled water spiked with the stated manganese concentration.

(c) River waters.

2 Principle

2.1 The method described is that used by the Yorkshire Water Authority[1]. It is based on experimental work carried out by the Water Research Centre (Medmenham Laboratory)[3] but with modifications to the procedure to enable the use of a mixed reagent for colour formation (see Section 5.6).

2.2 It is based on the spectrophotometric measurement of the coloured complex formed by the reaction between formaldoxime and manganese. All oxidation states of manganese are determined. Compensation for any natural colour and turbidity can be achieved by altering the order of addition of the reagents to a separate aliquot of the sample so as to prevent the formation of the coloured manganese-formaldoxime complex.

2.3 Tests on several types of raw water have indicated that pretreatment is not usually necessary. However, some samples may require pretreatment to convert manganese to forms capable of reacting with formaldoxime (see Section 8).

3 Interferences

The effect of other substances on the determination of manganese by the method described is shown in Table I. The data were obtained by the Yorkshire Water Authority[4]. Similar data were obtained by the Water Research Centre[3] using their own similar procedure.

Table I

Other substance	Concentration of other substance (mg/l)	Effect in mg/l Mn of other substances at a manganese concentration of (d)	
		0.000 mg/l	0.500 mg/l
Iron II (as Fe^{++})	2	+0.010	+0.009
,,	5	+0.022	+0.020
,,	20	+0.070	+0.060
Iron III (as Fe^{+++})	2	+0.010	+0.010
,,	5	+0.030	+0.030
,,	20	+0.100	+0.100
Calcium (as Ca^{++})	500	+0.015	+0.020
Magnesium (as Mg^{++})	100		
Calcium (as Ca^{++})	200	+0.004	+0.006
Magnesium (as Mg^{++})	100		
Orthophosphate (as P)	2	+0.007	+0.009
Hexametaphosphate (as P)	2		
Pyrophosphate (as P)	2		
Tripolyphosphate (as P)	2		
Dioctyl- sodium sulphosuccinate	10	0.000	+0.005
Humic acid (e)	10		
Sodium (as Na^{+})	200		
Potassium (as K^{+})	20		
Chloride (as Cl^{-})	40		
Sulphate (as SO_4^{2-})	40		
Nitrate (as N)	20		
Bicarbonate (as HCO_3^{-})	200		
Silica (as SiO_2)	20		
Nickel II (as Ni^{++})	2	+0.005	+0.006
Zinc II (as Zn^{++})	2		
Copper II (as Cu^{++})	2		
Aluminium III (as Al^{+++})	2		
Chromium III (as Cr^{+++})	2		
Tin II (as Sn^{++})	2		
Lead II (as Pb^{++})	2		
Cobalt II (as Co^{++})	2	+0.050	+0.055

(d) If the other substances did not interfere, the effect would be expected (95% confidence) to lie within the ranges 0.000 ±0.005 and 0.000 ±0.015 mg/l Mn at concentrations of 0.000 and 0.500 mg/l Mn respectively.

(e) Compensation for colour carried out.

In this table the brackets indicate that the specified substances were present simultaneously in the test solutions.

4 Hazards

4.1 The reagents described in Sections 5.3, 5.5 and 5.6 should be regarded as special hazards. Hazardous operations should be carried out in a fume cupboard. Care must be taken to avoid ingestion, inhalation of vapours and to protect the hands, eyes and face. Gloves and goggles must be worn and any suspected skin contamination washed off immediately.

4.2 Formaldehyde and formaldoxime are severe skin irritants. Inhalation of the vapours will result in severe irritation and oedema of the upper respiratory tract. Hydroxyammonium salts and solutions are severe irritants and burn the eyes. Contact with the skin must be avoided. Continued contact may cause dermatitis. Systemically, methaemoglobinaemia may occur. Also formaldehyde and hydrochloric acid vapours may combine to form a carcinogen.

5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified.

5.1 Water

The water used for blank determinations and for preparing standard and reagent solutions should have a manganese content that is negligible compared with the smallest concentration to be determined in samples. Distilled water is normally suitable. Determine the manganese content of the water to be used for blanks as described in steps 9.11 to 9.13.

5.2 5M Hydrochloric acid

Add 445±5 ml of hydrochloric acid (d_{20} 1.18) to approximately 400 ml of water in a 1-litre calibrated flask, mix, allow to cool, and dilute with water to the mark. Check the molarity of this solution by titration with a standard alkali solution and adjust, if necessary, to 5.0±0.1M. Store in a polyethylene bottle.

5.3 Formaldoxime solution

This reagent is hazardous (see Section 4). Dissolve 50±1 g of hydroxyammonium chloride in approximately 200 ml of water and dilute with water to 500 ml in a calibrated flask. Transfer to a glass bottle and add 25±1 ml of nominal 40% m/V formaldehyde solution and mix well. This solution is stable for at least four months.

5.4 Ethanolamine buffer solution

Add 80±1 ml of hydrochloric acid (d_{20} 1.18) to approximately 450 ml of water. Cool, add slowly 450±5 ml of ethanolamine, mix and transfer to a 1-litre calibrated flask and dilute with water to the mark. Store in a polyethylene bottle. This solution is stable for at least four months.

5.5 Ethylenediamine tetra-acetic acid (EDTA)/hydroxyammonium chloride solution

This reagent is hazardous (see Section 4). Dissolve 250±2 g of hydroxyammonium chloride in approximately 300 ml of water and transfer to a 1-litre calibrated flask. Dissolve 46.5±0.5 g of ethylenediamine tetra-acetic acid disodium salt in approximately 300 ml of water. Transfer this solution to the calibrated flask, mix and dilute with water to the mark. Store in a glass bottle. This solution is stable for at least four months.

5.6 Mixed reagent

This reagent is hazardous (see Section 4). It should be prepared immediately before use. Dissolve 4.2±0.1 g ascorbic acid in 70±1 ml ethanolamine buffer solution and add 30±1 ml of formaldoxime solution. Mix well.

5.7 5M Sulphuric acid (Approximately)

Add slowly and cautiously with constant stirring 265±5 ml of sulphuric acid (d_{20} 1.84) to about 600 ml of water in a 2-litre beaker immersed in cold water. Cool and dilute with water to 1 litre in a measuring cylinder.

5.8 **Nitric acid** (d_{20} 1.42)

5.8.1 10% *V/V Nitric acid*

Dilute 100±5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder.

5.9 **Standard manganese solutions**

5.9.1 *Solution A* 1 ml contains 500 µg of manganese

Dissolve 0.500±0.002 g of manganese flake (99.9% purity) in approximately 200 ml of water containing 20±1 ml of 5M sulphuric acid. When all the metal has dissolved transfer the solution quantitatively to a 1-litre calibrated flask and dilute with water to the mark. Store this solution in a glass bottle; it is stable for at least twelve months. As it may be difficult to weigh exactly this quantity of manganese flake, it may be advantageous to use a commercially available standard manganese solution. Alternatively weigh exactly a little more than 0.500 g, prepare the solution, dilute to 1 litre and then add the required extra water from a burette.

5.9.2 *Solution B* 1 ml contains 5 µg of manganese

Prepare this solution freshly on the day of use. Pipette 10.00±0.02 ml of *solution A* into a 1-litre calibrated flask and dilute with water to the mark.

6 Apparatus

6.1 **Glassware**

If possible, apparatus should be reserved solely for manganese determinations. All residual manganese from previous determinations must be removed. Clean all glass and polyethylene ware by filling or soaking in 10% V/V nitric acid overnight. Rinse thoroughly with water.

6.2 A spectrophotometer of prism or grating type or using a narrow band pass optical filter having its maximum transmission at 450 nm and 40-mm cells.

7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure given in Section 6.1, add to the empty bottle 20±1 ml of 5M hydrochloric acid per litre of sample to be collected and collect the sample. The acidification minimizes the absorption of manganese on the walls of the bottle and assists in the dissolution of colloidal and particulate forms of manganese. The dilution of the sample by the acid must be allowed for when calculating the final result (see step 9.15).

8 Sample Pretreatment

8.1 Samples containing suspended or organically bound manganese may require pretreatment to convert manganese to a form capable of reacting with formaldoxime. For most waters pretreatment has not been found necessary, but experience will indicate to analysts whether pretreatment is necessary for their particular water samples. It is recommended that analysts should check their particular water samples by comparing the results obtained by carrying out the procedure in Section 9, along with those obtained using the procedures in both Section 8.4 and Section 9.

8.2 **Additional reagents**

8.2.1 *Sulphuric acid* (d_{20} 1·84)

8.2.2 50% *V/V Ammonia solution.*

Add 50±5 ml of ammonia solution (d_{20} 0.880) to 50±1 ml of water. Mix well and store in a polyethylene bottle.

8.3 **Additional apparatus**

8.3.1 100-ml graduated borosilicate glass beakers and suitably sized watch glasses to cover them. This glassware is cleaned by the procedure given in Section 6.1.

8.3.2 pH meter.

Step	Experimental Procedure	Notes
	Pretreatment Procedure (notes a and b)	
8.4.1	Pipette 40.0 ml of the well mixed sample to a 100-ml graduated borosilicate glass beaker and cautiously add 2.0 ± 0.1 ml of sulphuric acid (d_{20} 1.84) and mix carefully. Cover the beaker with a watch glass supported on a glass saddle and heat on a hot plate until white fumes begin to be evolved. Remove from the hot plate and cool.	(a) If pretreatment is carried out a calibration curve must be prepared with calibration standards which have been put through this pretreatment procedure (see Section 11.1). (b) A quality control solution containing 0.5 mg/l manganese should be included with each batch of samples (see Section 14).
8.4.2	Without removing the watch glass add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42) dropwise. Heat until *all* brown fumes cease to be evolved.	
8.4.3	Cautiously wash down the watch glass, glass saddle and sides of the beaker with water until a volume of approximately 25 ml is in the beaker. Replace the watch glass and cool.	
8.4.4	Add, with stirring, 50% V/V ammonia solution until the solution has a pH of 1.5 ± 0.2 (as measured with a pH meter).	
8.4.5	Transfer the solution quantitatively to a 50-ml calibrated flask, dilute with water to 35 ± 5 ml (note c) and proceed as in step 9.2.	(c) It is convenient to make a mark on the flask corresponding to a volume of 35 ml.
	Blank determination	
8.4.6	A blank must be included with each batch (eg up to 10 samples) of determinations for which pretreatment is required using the same batch of reagents as for the samples. Add 0.80 ± 0.05 ml of 5M hydrochloric acid and 40 ± 1 ml of water to a 100-ml graduated borosilicate glass beaker. Carry out steps 8.4.1 to 8.4.4. inclusive beginning with the addition of the sulphuric acid. Transfer the solution quantitatively to a 50-ml calibrated flask, dilute with water to 35 ± 5 ml (note c) and proceed as in step 9.6.	
	Compensation for colour and turbidity in the sample (note d)	
8.4.7	A sample compensation solution must be included with each sample for which pretreatment is required and for which a colour/turbidity correction is necessary using the same batch of reagents as for samples. Carry out steps 8.4.1 to 8.4.4 inclusive. Transfer the solution quantitatively to a 50-ml calibrated flask, dilute with water to 35 ± 5 ml and proceed as in step 9.8.	(d) The steps 8.4.7. and 8.4.8. may be omitted if the analyst, due to his experience, judges them to be unnecessary.
	Compensation for colour and turbidity in the water used for reagent blanks (note d)	
8.4.8	A blank compensation solution should be included with each batch of samples in which a sample compensation solution is run (step 8.4.7) using the same batch of reagents as for samples. Carry out step 8.4.6. except finally proceed as in step 9.8 instead of step 9.6.	

9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples (note e)	
9.1	Adjust the temperature of the sample to 18 – 27 C (see Section 11.3) and pipette 40.0 ml of the well mixed sample to a 50-ml calibrated flask (note f).	(e) A quality control solution containing 0.5 mg/l manganese should be run with each batch of samples (see Section 14).
9.2	Add 5.0 ± 0.1 ml of mixed reagent. Mix well by swirling.	(f) See Section 12 for the concentration range of the method.
9.3	Allow to stand between 2 and 10 minutes. Add 2.0 ± 0.1 ml of EDTA/hydroxyammonium chloride reagent and mix by swirling. Dilute with water to the mark and mix well by repeated inversion of the flask. Allow to stand for 15 ± 5 minutes.	
9.4	Meanwhile set up the spectrophotometer (see Section 6.2) according to the manufacturer's instructions. Adjust the zero of the instrument with water in the reference cell. Measure the absorbance (see Section 10) of the well mixed solution at 450 nm using 40-mm cells (note g). Recheck the instrument zero. Let the absorbance of the sample be S.	(g) Other sizes of cells may be used but the performance characteristics quoted in Section 1 would no longer apply.
	Blank determination (if pretreatment not used)	
9.5	A blank must be included with each batch (eg up to 10 samples) of determinations for which pretreatment was not required using the same batch of reagents as for samples. Add 40 ± 1 ml of water and 0.8 ± 0.1 ml of 5M hydrochloric acid to a 50-ml calibrated flask and mix by swirling.	
9.6	Carry out steps 9.2 to 9.4 inclusive. Let the absorbance of the blank be B.	
	Compensation for colour and turbidity in the sample (note h)	
9.7	A sample compensation solution should be included with each sample for which a colour/turbidity correction is necessary (see Section 13.1) using the same batch of reagents as for samples. Carry out step 9.1.	(h) The steps 9.7 to 9.10 may be omitted if the analyst, due to his experience judges them to be unnecessary.
9.8	Add 2.0 ± 0.1 ml of the EDTA/hydroxyammonium chloride reagent and mix by swirling. Add 5.0 ± 1.0 ml of the mixed reagent. Dilute with water to the mark and mix well. Allow to stand for 15 ± 5 minutes. Carry out step 9.4. Let the absorbance of the sample compensation solution be S_1.	
	Compensation for colour and turbidity in the water used for reagent blanks (note h)	
9.9	A blank compensation solution should be included with each batch of samples for which a sample compensation solution is used using the same batch of reagents as for the samples. Carry out step 9.5.	
9.10	Carry out step 9.8. Let the absorbance of the blank compensation solution be B_1.	

Step	Experimental Procedure	Notes
	Determination of manganese in the water used for the blank (notes i and j)	
9.11	Add 10.0 ± 0.2 ml of water and 0.8 ± 0.1 ml of 5M hydrochloric acid to a 50-ml calibrated flask and mix by swirling.	(i) This determination is not necessary if the manganese content of the water used for the blank is known or is negligible (see Section 13.2). (j) All reagents must be from the same batch as for the samples.
9.12	Carry out steps 9.2 to 9.4 inclusive. Let the absorbance be M. Calculate the absorbance, W, due to manganese in 30 ml of water from $W = B - M.$	
9.13	Determine the apparent manganese concentration, C_{aw}, in the water, from W and the calibration curve. (see Section 11). Obtain the true manganese concentration, C_w, in the water from $C_w = 1.33\ C_{aw}$ mg/l (note k).	(k) The factor 1.33 allows for the fact that the calibration curve is for 40 ml samples whereas W was obtained for an effective 30 ml sample.
	Calculation of results	
9.14	Calculate the apparent absorbance due to manganese in the sample, R, from $R = S - B$ or when a correction for colour and turbidity is made from $R = (S - S_1) - (B - B_1)$	
9.15	Determine the apparent manganese concentration, C_a, in the sample from R and the calibration curve (see Section 11). Calculate the manganese concentration, C, in the original sample from $C = 1.02\ (C_a + C_w)$ mg/l (note l).	(l) The factor 1.02 allows for the dilution of the sample by the acid into which it was collected. (See Section 7).

10 Measurement of Absorbance

The exact instrument setting for the wavelength of the absorption peak must be checked for each instrument and then used in all future work. The procedure used for measuring absorbance should be rigorously controlled to ensure satisfactory precision. The same cells should always be used and should not be interchanged between the reference and sample. They should always be placed in the same position in the cell holder with the same face towards the light source.

It is difficult to ensure reproducible alignment of cells with chipped corners, and therefore they should be discarded. Similarly, the slide of the cell holder should be kept scrupulously clean. Before every set of measurements the absorbance of the sample cell should be measured against the reference cell when both are filled with water. This will also enable the true absorbance of the blank to be determined.

11 Preparation of Calibration Curve

11.1 When pretreatment is carried out

Make a mark on a series of 100-ml graduated borosilicate glass beakers corresponding to a volume of 40 ± 1 ml. Pipette into these beakers 0.0, 1.0, 2.0, 4.0, 6.0, and 8.0 ml respectively of standard manganese *solution B*. Add 0.8 ± 0.1 ml of 5M hydrochloric acid into each beaker, dilute with water to the 40 ml mark, mix by swirling, and carry out steps 8.4.1 to 8.4.5 inclusive beginning with the addition of the sulphuric acid. Subtract the average absorbance of the blank from the average absorbances for the other solutions, and plot the corrected results against the concentration of manganese. The above solutions are equivalent to 0.000, 0.125, 0.250, 0.500, 0.750, and 1.000 mg/l Mn respectively. This calibration curve should be checked at frequent intervals.

11.2 When pretreatment is not carried out

Make a mark on a series of 50-ml calibrated flasks corresponding to a volume of 40 ml. Pipette into these flasks 0.0, 1.0, 2.0, 4.0, 6.0, and 8.0 ml, respectively, of standard manganese *solution B*. Add 0.8 ± 0.1 ml of 5M hydrochloric acid to each flask, dilute with water to the 40 ml mark, mix by swirling and carry out step 9.6. Subtract the average absorbance of the blank from the average absorbances for the other solutions, and plot the corrected results against the concentration of manganese. The above solutions are equivalent to 0.000, 0.125, 0.250, 0.500, 0.750 and 1.000 mg/l Mn respectively. The calibration curve should be checked at frequent intervals.

11.3 The calibration curve is linear to at least 1.0 mg/l Mn when measurements are made at 450 nm using a spectrophotometer or to at least 0.5 mg/l Mn using an absorptiometer fitted with a filter. The sensitivity with the latter is less than that obtained by measuring with a spectrophotometer at 450 nm. For measurements with a spectrophotometer at 450 nm, the slope of the calibration curve decreases by approximately 0.2% for an increase in temperature of 1 °C.

12 Change in Concentration Range of the Method

For samples containing manganese concentrations greater than 1.0 mg/l an appropriately smaller volume of sample should be taken. Dilute this volume V ml to 40 ml with water in a 50-ml calibrated flask and add sufficient 5M hydrochloric acid so that there is the same total volume of 5M hydrochloric acid present as there would be in 40 ml of sample. The manganese concentration in the original sample is given by:

$$C = 1.02\left(\frac{40}{V} C_a + C_w\right)$$

13 Sources of Error

The analytical procedure can be applied to a wide range of raw and potable waters and the attention which it is necessary to pay to sources of error depends upon the accuracy required. The total manganese concentration should be verified, if in doubt, by the use of the pretreatment procedure (see Section 8). The following sub-sections describe the main sources of error and how they can be minimized, but each analyst must decide what precautions are appropriate to his particular requirements.

13.1 Correction for colour and turbidity in samples

In spectrophotometric methods of analysis, the presence of coloured and/or suspended materials in samples will cause falsely high results to be obtained. Whether or not a correction is required for this effect depends on the error that can be tolerated and the nature of samples. The procedures in steps 8.4.7, 8.4.8 and 9.7. to 9.10 allow a correction to be made if required.

13.2 Effect of manganese in the water used for blank determinations

If the water used for the blank determination contains manganese, the blank correction will be falsely large and results for samples falsely low. Again, whether or not a correction is required for this effect depends on the error that can be tolerated and the concentration of manganese in the blank water. The procedure in steps 9.11 to 9.13 allows a correction to be made when required.

When it is necessary to make a correction, to avoid the need for determining C_w in every case it is convenient to estimate C_w for one large batch of water. This value of C_w may then be used for all subsequent batches of analyses for which the same water is used for the blank.

13.3 Interfering substances

See Section 3.

14 Checking the Accuracy of Analytical Results

(For further information see another publication in this series).

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. However, as a minimum, it is suggested that a solution of known manganese concentration should be analysed at exactly the same time and in exactly the same way as normal samples. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy and will also allow the standard deviation of routine analytical results to be estimated.

15 References

(1) Department of the Environment file WS/646/50, Paper SCA/4.2/15, September 1976.

(2) Department of the Environment file WS/646/50, Paper SCA/4.2/19, February 1977.

(3) Cheeseman R V and Wilson A L, Water Research Association, Medmenham, *Technical Paper* 85, September 1972.

(4) Department of the Environment file WS/646/50, Paper SCA/4.2/17, December 1976.

Appendix

Estimation of the Accuracy of Analytical Results using the Manganese Method

1 Introduction

Quantitative investigation of the accuracy achievable when the manganese method is used appears to be limited to work at the Yorkshire Water Authority and at the Water Research Centre using their own similar method. Before firmly recommending the method for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the Metals and Metalloids Working Group of the Department of the Environment's Standing Committee of Analysts*.

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Any information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible, more complex designs are possible and would give more information.

2 Basis of Suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the concentration of manganese in the sample analysed and on the type of sample, eg, worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following solutions on each of n days, where n is at least 5 and preferably greater up to 10.

Solution No	Description
1	Blank
2	Another blank
3	Standard solution 0.05 mg/l Mn
4	Standard solution 1.00 mg/l Mn
5	Typical sample
6	Same sample spiked with 1.00 mg/l Mn

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section 9 (and Section 8.4 if necessary) of the method be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should contain the same amount of hydrochloric acid as is present in the samples. The same batch of water should be used on each day to prepare all four solutions. For solutions 5 and 6 a total of 2 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows; add with a bulb pipette 2.00 ml of an intermediate standard manganese solution to 100 ml of solution 5. (The intermediate standard manganese solution is prepared by diluting 10.00 ± 0.02 ml of standard manganese *solution A* with water to 50 ml in a calibrated flask). When analysing solution 6 it will be necessary to take into account Section 12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the manganese concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked manganese from 100% may give an indication of the presence of interfering substances.

3 Evaluation of Results

The raw experimental results should be sent direct to the Department of the Environment* for evaluation together with the results obtained from the standards used to establish the calibration curve in each batch of analysis. However, for those laboratories wishing to make the calculations themselves the details are given below.

3.1 Convert all results to concentrations as described in the method. Deduct the first of the two blank values (*solution* 1) from each of the other solution values.

3.2 Calculate the mean concentration of the n results for each solution.

3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{\Sigma\ (x_i - \bar{x})^2}{n-1}}$$

where x_i = the result from the ith batch

$\bar{x}$ = the mean value of x_i.

3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

$$s_w = \sqrt{\frac{\Sigma\ (x_{1i} - x_{2i})^2}{2n}}$$

where x_{1i} = the 1st blank result (*solution* 1) from the ith batch

x_{2i} = the 2nd blank result (*solution* 2) from the ith batch.

3.5 Calculate the mean percentage recovery, R, of the spiked manganese (*solution* 6) from:

$$R = (1.02\,\bar{x}_6 - \bar{x}_5) \times 100$$

where $\bar{x}_5$ = the mean value of the results for *solution* 5

$\bar{x}_6$ = the mean value of the results for *solution* 6.

3.6 Summarize the results as in the following table:

Solution	No of results n	Mean manganese concentration mg/l	Standard deviation mg/l	Mean recovery %
2 Blank				—
3 Standard, 0.05 mg/l				—
4 Standard, 1.00 mg/l				—
5 Sample.....				—
6 Solution 5 + 1.00 mg/l				

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the blank solution 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6. If the pretreatment procedure (Section 8.4) was carried out this should also be stated.

* *Results to be sent to the following:*

The Technical Secretary
The Metals and Metalloids Working Group
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
England

Address for Correspondence

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

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

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