Iron in Raw and Potable Waters by Spectrophotometry

(using 2,4,6 - tripyridyl - 1,3,5 - triazine)

1977

Methods for the Examination of Waters and Associated Materials

London: Her Majesty's Stationery Office 90p net

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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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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

Iron in Raw and Potable Waters by Spectrophotometry (1977 version)

1 Performance Characteristics of the Method

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

Note: Throughout this method iron is expressed as the element (Fe)

1.1	Substance determined	All forms of iron (see Sections 2 and 8).			
1.2	Type of sample	Raw and potable waters.			
1.3	Basis of method	Reduction of iron to the ferrous state and subsequent reaction with 2, 4, 6-tripyridyl-1, 3, 5-triazine to form a coloured complex whose concentration is measured spectrophotometrically.			
1.4	Range of application (a)	Up to 1 mg/l.			
1.5	Calibration curve (a)	Linear to 2 mg/l at 595 nm.			
1.6	Total standard deviation	Iron concentration (mg/l)	Total standard deviation (mg/l)		Degrees of freedom
	1.6.1 Without pretreatment:	0.150	0.005	(a) (d)	15
		0.250	0.004	(a) (c)	17
		0.400	0.003-0.008	(b) (c)	6-9
		1.000	0.011	(a) (c)	19
	1.6.2 With pretreatment:	0.250	0.013	(a) (c)	13
		0.334	0.019	(a) (d)	8
		1.000	0.013	(a) (c)	13
1.7	Limit of detection				
	1.7.1 Without pretreatment (b)	0.003-0.015 mg/l (with 5 to 10 degrees of freedom)			
	1.7.2 With pretreatment (a)	0.06 mg/l (with 7 degrees of freedom).			
1.8	Sensitivity (a)	1.0 mg/l gives an absorbance of approximately 1.25			
1.9	Bias (a)	No important sources of bias were detected.			
1.10	Interferences (a)	None of the substances tested caused appreciable errors except commercial polyphosphate (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 45 and 60 minutes excluding any pretreatment time.			

(a) These data were obtained by the Water Research Centre (Medmenham Laboratory)[1] using this method and a spectrophotometer with 40-mm cells at 595 nm.

(b) These data were obtained from an interlaboratory calibration exercise in which 5 laboratories took part.[2]

(c) These data were obtained using distilled water spiked with the stated iron concentration.

(d) River Thames water.

2 Principle

2.1 The method is based upon the spectrophotometric measurement of the coloured complex formed by the reaction between ferrous iron and 2, 4, 6-tripyridyl-1, 3, 5-triazine (TPTZ) after reduction of the iron to the ferrous state. It is based on experimental work carried out by the Water Research Centre (Medmenham Laboratory)[1].

2.2 The method specifies the collection of samples into hydrochloric acid and for some waters this can be sufficient to bring into solution all forms of iron. However certain types of water will need a more vigorous pretreatment (see Section 8).

3 Interferences

The effect of other substances on the determination of iron by the TPTZ method is shown in table 1. The data were obtained by the Water Research Centre[2].

Table 1

Other substance	Concentration of other substance (mg/l)	Effect in mg/l Fe of other substances at an iron concentration of (e)	
		0.000 mg/l	1.000 mg/l
Calcium (as Ca^{++})	500		
Magnesium (as Mg^{++})	100		
Potassium (as K^{+})	50		
Sodium (as Na^{+})	190		
Sulphate (as SO_4^{--})	100	0.011	– 0.020
Chloride (as Cl^{-})	100		
Nitrate (as NO_3^{-})	50		
Bicarbonate (as HCO_3^{-})	50		
Silicate (as SiO_3^{--})	50		
Fluoride (as F^{-})	5	0.005	– 0.011
Cyanide (as CN^{-})	1	0.007	0.006
Nitrite (as NO_2^{-})	1	0.003	– 0.004
Citrate	10	0.002	
Humic acids	10	0.024	– 0.020
Fulvic acids	10		
Detergents (f)	5	0.008	– 0.002
Ortho-phosphate (as PO_4^{---})	50	0.002	– 0.004
Pyro-phosphate (as PO_4^{---})	2	0.004	– 0.003
Hexameta-phosphate (as PO_4^{---})	1	0.001	– 0.017
Tripoly-phosphate (as PO_4^{---})	1	0.000	– 0.008
Commercial poly-phosphate (as PO_4^{---}) (g)	20	– 0.011	– 0.532
Alkalinity (as $CaCO_3$)	300	0.000	– 0.004
Copper II (as Cu^{++})	2	0.003	– 0.001
Manganese II (as Mn^{++})	2	– 0.001	– 0.007
Nickel II (as Ni^{++})	2	– 0.002	– 0.041
Cobalt II (as Co^{++})	1	0.002	0.008
Tin II (as Sn^{++})	2	0.007	– 0.005
Zinc II (as Zn^{++})	2	0.000	0.017
Cadmium II (as Cd^{++})	2	0.003	0.009
Lead II (as Pb^{++})	10	– 0.002	– 0.026
Chromium III (as Cr^{+++})	2	0.006	– 0.002

(e) If the other substances did not interfere, the effect would be expected (95% confidence) to lie within the ranges 0.000 ± 0.009 and 0.000 ± 0.024 mg/l Fe at concentrations of 0.000 and 1.000 mg/l Fe respectively.

(f) Six commercial detergent powders[1] (equal proportions by weight were used); the exact composition of these detergents was not investigated.

(g) It has been found that the suppressing effect of 20 mg/l of commercial polyphosphate can be completely eliminated by heating the acidified sample in a water bath at 80°C for 2 hours, cooling and analysing in the usual way[3].

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 and 6.1 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 vapour and to protect the hands, eyes and face. Gloves and goggles must be worn and any suspected contamination washed off immediately.

4.2 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.

4.3 Thioglycollic acid may cause severe toxic effects if it is ingested or inhaled in sufficient amounts (see Sax, 'Dangerous properties of industrial materials', 3rd Ed., London, Reinhold, 1968). Thioglycollic acid and its solutions may produce blisters if they touch the skin. Thioglycollic acid and its solutions should be disposed of by pouring them into a solution of copper sulphate.

5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified.

5.1 Water

Use distilled or de-ionized water for blank determinations and for preparing standard and reagent solutions. This water should preferably have an iron content which is negligible compared with the smallest concentration to be determined in samples. Determine the iron content of the water to be used for blanks as described in steps 9.7 and 9.8.

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 the solution in a polyethylene bottle.

5.3 10% m/V Hydroxyammonium chloride solution

This reagent is hazardous (see Section 4.1). Dissolve 10.0 ± 0.2 ml of hydroxyammonium chloride in water and dilute with water to 100 ml in a measuring cylinder. Store this solution in a borosilicate glass bottle; it is stable for at least 8 weeks.

5.4 0.075% m/V 2, 4, 6-tripyridyl-1, 3, 5-triazine (TPTZ) solution

Dilute 2.0 ± 0.2 ml of 5M hydrochloric acid with water to the mark in a 100-ml calibrated flask. Transfer this solution to a dry 250-ml beaker containing 0.075 ± 0.005 g of TPTZ, and dissolve the TPTZ. Store the solution in a borosilicate glass bottle. Avoid placing the bottle in direct sunlight. This solution is stable for at least 2 weeks.

5.5 Acetate buffer solution

Dissolve 287 ± 1 g of anhydrous sodium acetate in approximately 300 ml of water, warming gently if desired to aid dissolution. Cool, transfer the solution to a 1-litre calibrated flask, add 115.0 ± 0.5 ml of acetic acid (d_{20} 1.05) and dilute with water to the mark. Store the solution in a borosilicate glass bottle; it is stable for at least 8 weeks.

5.6 Nitric acid (d_{20} 1.42)

5.6.1 *10% V/V Nitric acid*

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

5.7 Sulphuric acid (d_{20} 1.84)

5.8 0.02% m/V Meta-cresol purple solution

Dissolve 0.020 ± 0.002 g of m-cresol purple indicator in approximately 80 ml of water containing 2 drops of ammonia solution (d_{20} 0.880). Dilute with water to 100 ml in a measuring cylinder. Store the solution in a borosilicate glass bottle; it is stable for at least 4 weeks.

5.9 50% V/V Ammonia solution

Add 50 ± 1 ml of high purity (less than 0.2 mg/l iron) ammonia solution (d_{20} 0.880) to 50 ± 1 ml of water. Mix well and store in a polyethylene bottle.

5.10 2% V/V Thioglycollic acid solution

This reagent is hazardous - see Section 4.2. Dilute 20 ± 1 ml of thioglycollic acid (d_{20} 1.32) with water to 1 litre in a measuring cylinder. Store in a borosilicate glass bottle.

5.11 Standard iron solutions

5.11.1 *Solution A* 1 ml contains 1 mg of iron.

Weigh 1.000 ± 0.001 g of iron metal (rod, wire or foil but not powder or sponge; purity at least 99.9%) and transfer to a 250-ml borosilicate glass beaker. Add 20.0 ± 0.5 ml of 5M hydrochloric acid and cover with a watch glass. Warm gently to aid dissolution of the iron and when all the iron has dissolved, cool the solution, and add 1.0 ± 0.2 ml of nitric acid (d_{20} 1.42) cautiously in small portions down the side of the beaker. Cover with a watch glass, and warm gently until the dark brown colour in the solution has been dispelled. Quantitatively transfer the solution to a 1-litre calibrated flask containing 100 ± 5 ml of hydrochloric acid (d_{20} 1.18), dilute the solution with water nearly to the mark, cool to room temperature, and dilute with water to the mark. Store the solution in a polyethylene bottle; it is stable for at least 1 year.

5.11.2 *Solution B* 1 ml contains 100 µg of iron.

Pipette 100.0 ml of *solution A* into a 1-litre calibrated flask, and dilute with water to the mark. Store the solution in a polyethylene bottle; it is stable for at least 6 months.

5.11.3 *Solution C* 1 ml contains 1.6 µg of iron.

Pipette 4.0 ml of *solution B* into a 250-ml calibrated flask, and dilute with water to the mark. Prepare this solution freshly each time just before it is required and when the solution has been used, empty the flask and wash it several times with water.

6 Apparatus

6.1 Glass and polyethylene ware

Cleanliness of glass and polyethylene ware is essential for this determination. To achieve the precision stated in the performance characteristics it is desirable that apparatus should be reserved solely for iron determinations; all residual iron from previous determinations must be removed. Cleaning of all glass and polyethylene ware by filling with or soaking in 10% V/V nitric acid should normally suffice. However, before using the apparatus to analyse any samples, its cleanliness should be checked by carrying out a series of blank determinations (see Section 9.7).

6.1.1 If a more rigorous cleaning procedure is required for polyethylene ware (eg the sample collection bottle) proceed as follows. Wash the bottles thoroughly with water and fill them with 2% V/V thioglycollic acid solution. (This reagent is hazardous - see Section 4.2). Heat in a water bath at 80°C for at least 8 hours, then wash thoroughly with water and drain.

6.1.2 If a more rigorous cleaning procedure is required for glassware proceed as follows. Fill with or soak the glassware in nitric acid (d_{20} 1.42) overnight, wash thoroughly with water, fill with or soak in 2% V/V thioglycollic acid, (this reagent is hazardous - see Section 4.2) at least overnight and then wash 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 approximately 595 nm and 40-mm cells.

6.3 100-ml graduated borosilicate glass beakers together with suitable watch glasses to cover them. Clean this glassware by the procedure given in Section 6.1 and when it is not in use store it in 10% V/V nitric acid and wash thoroughly with water before use.

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 prevents the precipitation of iron, minimizes the adsorption of iron on the walls of the bottle and assists in the dissolution of colloidal and particulate forms of iron. The dilution of the sample by the acid must be allowed for when calculating the final result (see step 9.11).

8 Sample Pretreatment

8.1 Samples containing suspended colloidal, or organic material may require pretreatment to convert iron to a form capable of reduction to the ferrous state. Pretreatment should be carried out unless it has been shown to be unnecessary by analysts for their particular water samples by comparing the results obtained by carrying out the procedure in Section 9 alone with those obtained using the procedures in both Section 8.2 and Section 9. The sulphuric acid added during the pretreatment procedure must be neutralised so that the solution after the addition of the acetate buffer solution in step 9.2 has a pH of 4.6 ± 0.1.

8.2 **Pretreatment Procedure**

Step	Experimental Procedure	Notes
	Pretreatment Procedure (Notes a and b)	
8.2.1	Add 40.0 ± 0.5 ml of 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). 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 run through this pretreatment procedure (see Section 11.1). (b) This pretreatment procedure is prone to contamination and precautions should be taken to minimize errors from this source.
8.2.2	Without removing the watch glass add 0.50 ± 0.05 ml of nitric acid (d_{20} 1.42) dropwise. Heat until *all* brown fumes cease to be evolved.	
8.2.3	Repeat step 8.2.2 a further three times. When no more brown fumes are evolved and white fumes are apparent, remove the beaker from the hot plate and cool.	
8.2.4	Cautiously wash down the watch glass, glass saddle and sides of the beaker with water until a volume of 25 ± 1 ml is in the beaker. Replace the watch glass and cool.	
8.2.5	Add 2 to 3 drops of 0.02% m/V m-cresol purple indicator solution, and add slowly with stirring 50% V/V ammonia solution until the colour changes from faint pink to incipient yellow (pH 2.7 ± 0.2).	
8.2.6	Transfer the solution quantitatively to a 50-ml calibrated flask, dilute to 35 ± 5 ml with water (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	
8.2.7	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 39 ± 1 ml of water to a 100-ml graduated borosilicate glass beaker. Carry out steps 8.2.1 to 8.2.6 inclusive beginning with the addition of the sulphuric acid. Transfer to a 50-ml calibrated flask and proceed as in step 9.5.	

Step	Experimental Procedure	Notes
	Compensation for colour and turbidity in the sample (note)	
8.2.8	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 8.2.1 to 8.2.6 inclusive then proceed as in step 9.2 but omit the addition of TPTZ in step 9.2.	(d) This step may be omitted if the analyst, due to his experience, judges it to be unnecessary.

9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
9.1	Add 40.0 ± 0.5 ml of the well mixed sample to a 50-ml calibrated flask. Adjust the temperature of the sample, if necessary, to between 15 and 30 °C (notes e and f).	(e) If the sample contains polyphosphate, see Section 3 note (g). (f) See Section 12 for concentration range.
9.2	Add to the flask, swirling after each addition, 2.0 ± 0.1 ml of 10% m/V hydroxylammonium chloride solution, 2.0 ± 0.1 ml of 0.075% m/V TPTZ solution, and 5.0 ± 0.2 ml of acetate buffer solution. Dilute with water to the mark, stopper the flask, and mix the contents well (notes g and h). Allow to stand between 5 minutes and 2 hours.	(g) If a batch of samples is to be analysed, each reagent can be added to all samples before adding the next reagent. (h) If pretreatment has been used see Section 8.1.
9.3	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 595 nm using 40-mm cells (note i). Recheck the instrument zero. Let the absorbance of the sample be S.	(i) Other sizes of cells may be used but the performance characteristics quoted in Section 1 would no longer apply.
	Blank determination (if pretreatment not required)	
9.4	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 0.80 ± 0.05 ml of 5M hydrochloric acid and 39 ± 1 ml of water to a 50-ml calibrated flask and adjust the temperature to between 15 and 30 °C.	
9.5	Carry out steps 9.2 and 9.3, let the absorbance of the blank be B.	

Step	Experimental Procedure	Notes
	Compensation for colour and turbidity in the sample (note d)	
9.6	A sample compensation solution must be included with each sample for which a colour/turbidity correction is necessary using the same batch of reagents as for samples. Carry out steps 9.1 to 9.3 but omitting addition of the TPTZ reagent. Let the absorbance of the sample compensation solution be S_1.	
	Determination of iron in the water used for the blank (notes j and k)	
9.7	Add 1.60 ± 0.05 ml of 5M hydrochloric acid and 29 ± 1 ml of water to a 50-ml calibrated flask and adjust the temperature to between 15 and 30 °C. Add to the flask, swirling after each addition, 4.0 ± 0.1 ml of 10% m/V hydroxyammonium chloride solution, 4.0 ± 0.1 ml of 0.075% m/V TPTZ solution and 10.0 ± 0.2 ml of acetate buffer solution. Dilute with water to the mark, stopper the flask, mix the contents well and carry out step 9.3. Let the absorbance be D.	(j) This determination is not needed if the iron content of the water used for the blank is known or is negligible (Section 13.3). (k) All reagents must be from the same batch as for the samples.
9.8	The absorbance due to iron in 50 ml of water W is given by: $W = 2B - D - C$ where C = absorbance of sample cell when it and the reference cell are filled with water. Calculate the iron concentration in the water C_w from 0.8 W (note l) and the calibration curve. (See Section 11).	(l) The factor 0.8 allows for the fact that the calibration curve is for 40 ml samples whereas W was obtained for an effective 50 ml sample.
	Calculation of results	
9.9	Calculate the apparent absorbance due to iron in the sample, R, from $R = S - B$ or, when a correction for colour/turbidity is made $R = S - B - S_1 + C$	
9.10	Determine the apparent iron concentration, C_a, in the sample from R and the calibration curve. (See Section 11).	
9.11	Calculate the iron concentration in the original sample, C_f, from $C_f = 1.02 (C_a + C_w)$ mg/l (note m)	(m) 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 for 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

To a series of 100-ml graduated borosilicate glass beakers add 0.80 ± 0.05 ml of 5M hydrochloric acid, then pipette into these beakers 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml respectively of standard iron *solution C* and finally add sufficient water to each beaker to make up the volume to 40.0 ± 0.5 ml. Carry out steps 8.2.1 to 8.2.6 inclusive beginning with the addition of the sulphuric acid. These determinations should be repeated at least once on another day and then again as required until the calibration curve is defined with the accuracy required for the particular application. Normally two batches of determinations will suffice. Subtract the average absorbance of the blank from the average absorbances for the other solutions and plot the corrected results against concentration of iron. The above solutions are equivalent to 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/l Fe respectively.

11.2 When pretreatment is not carried out

To a series of 50-ml calibrated flasks, add 0.80 ± 0.05 ml of 5M hydrochloric acid, then pipette into these flasks 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml respectively of standard iron *solution C* and finally add sufficient water to each flask to make up the volume to 40.0 ± 0.5 ml. Carry out steps 9.2 and 9.3 on each solution. These determinations should be repeated at least once on another day and then again as required until the calibration curve is defined with the required accuracy. Normally two batches of determinations will suffice. Subtract the average absorbance of the blank from the average absorbances for the other solutions, and plot the corrected results against the concentration of iron. The above solutions are equivalent to 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0 mg/l Fe respectively.

11.3 When measurements are made at 595 nm, the calibration curve is linear to at least 2 mg/l Fe. When absorptiometers are used, the linearity of the calibration curve should be checked. For measurements at 595 nm, the slope of the calibration curve decreases by approximately 0.4% for an increase in temperature of 1 °C.

12 Change in Concentration Range of the Method

The method has been thoroughly tested in the concentration range 0 to 1 mg/l. Therefore, although the calibration curve is linear to greater concentrations, it is recommended that, when samples are likely to contain more than 1 mg/l an appropriately smaller aliquot should be taken. Place this volume, V ml, of sample 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. Dilute with water to 40 ± 1 ml and proceed as in Section 9. The concentration of iron in the original sample is then given by

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

13 Sources of Error

The analytical method can be applied to a wide range of samples and the attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections describe the main sources of error and how they can be minimized and each analyst must decide which precautions are appropriate to his particular requirements.

13.1 Contamination

Iron is a commonly occurring element and its determination is often prone to contamination, both airborne and otherwise. The technique, working conditions, apparatus and reagents should therefore be critically examined and any sources of contamination eliminated or minimized.

13.2 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 procedure in step 9.6 allows a correction to be made when required.

13.3 Effect of iron in the water used for blank determinations

If the water used for the blank determination contains iron, the blank correction will be falsely large and results for samples falsely low. Again, whether or not a correction is required for the effect depends on the magnitude of the error that can be tolerated and the concentration of iron in the blank water. The procedure in steps 9.7 and 9.8 allows a correction to be made when required.

When a correction is required, 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 C_w may then be used for all subsequent batches of analyses for which the same water is used for the blank.

13.4 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 the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of test are possible and should be used as appropriate. As a minimum, however, it is suggested that a standard solution of iron of suitable concentration should be analysed at 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) Dougan WK and Wilson AL, Water Research Association, June 1972, *Technical Paper 83.*

(2) Department of the Environment, file WS/646/50, Paper SCA/4.2/3, February 1976.

(3) Dougan WK and Wilson AL, Water Treatment and Examination, Vol *22*, 1973, p100-113.

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
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