Iron and Manganese in Potable Waters by Atomic Absorption Spectrophotometry 1983

Methods for the Examination of Waters and Associated Materials

London Her Majesty's Stationery Office £2.75 net

Iron and Manganese in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1983 Version)

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Contents

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Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturer's catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection, 'Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. 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 reviews 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

About these methods

Although thoroughly tested, the performance characteristics revealed that these methods were not as reliable as expected [1,2,3,4]. However, as they are widely used in the water industry the Working Group agreed that they be published and the Main Committee agree with this recommendation. They are therefore issued with only tentative status to emphasize to users that they must themselves check the reliability of these methods with their own equipment. This booklet does not replace the already published colorimetric methods, it merely supplements them.

Iron and Manganese in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method, (1983 version)

1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series).

Note: Throughout this method iron and manganese are expressed as the elements Fe and Mn respectively.

1.1	Substances determined	Forms of iron and manganese likely to occur in potable waters (see Sections 2 and 8)
1.2	Type of sample	Potable water
1.3	Basis of the method	Direct aspiration of the sample containing 0.1% m/V lanthanum into the flame of an atomic absorption spectrophotometer; for some instruments it may be necessary to pre-concentrate up to four times by evaporation to determine low concentrations of iron and manganese.
1.4	Range of application	Up to 1000 μg Fe/l or 1000 μg Mn/l for direct aspiration of samples and pro rata when concentration by evaporation is used.
1.5	Calibration curve	Linear to 1000 μg Fe/l and 1000 μg Mn/l for direct aspiration of samples and pro rata when concentration by evaporation is used.
1.6	Standard deviation (within batch)	Iron Concentration (μg/l) — Standard deviation (μg/l) 10 — 3.2–10.7 20 — 5.0–14.0 100 — 5.3–12.4 1000 — 4.9–38.6 Manganese Concentration (μg/l) — Standard deviation (μg/l) 10 — 1.1–3.4 20 — 0.9–3.4 100 — 1.7–10.6 1000 — 2.4–39.8 (see Table 1)
1.7	Limit of detection	20.7–51.8 μg/l for iron 6.1–61.3 μg/l for manganese (see Table 1)
1.8	Sensitivity	31–148 μg/l for iron 15–107 μg/l for manganese for 1% absorption (see Table 2)
1.9	Bias	Not known
1.10	Interferences	See Section 3

1.11	Time required for analysis	For direct aspiration the total operator analytical time for 20 samples is approximately 30 minutes. For concentration by evaporation the total analytical time for a batch of 10 samples is approximately 4 hours of which the pretreatment stage occupies approximately 3 hours.

Table 1 Limits of Detection and Standard Deviations (within batch) for Iron and Manganese[1]

Instrument	Limit of Detection µg/l	Standard Deviations (µg/l) at an iron concentration of µg/l							
		10(h)	20(h)	100(h)	200(h)	1000(h)	(i)		(j)
IL 151 (a)	49.3	10.7	14.0	10.0		10.0	16.2	(35.8)	14.9
IL 357 (b)	22.2	4.3	5.0	5.3		4.9	3.1	(35.7)	3.8
IL 951 (c)	41.0	9.2	8.0	8.0	8.9	7.9	7.2	(9.5)	14.4
PE 603 (d)	51.8	9.6	6.6	12.4		62.0	23.0	(230.0)	32.0
V 275 (e)	20.7	3.2	5.9	9.2		38.6	2.6	(28.1)	18.4

Instrument	Limit of Detection µg/l	Standard Deviations (µg/l) at a manganese concentration of µg/l							
		10(h)	20(h)	100(h)	200(h)	1000(h)	(i)		(j)
IL 151 (a)	16.3	3.4	2.3	4.5		3.1	4.5	(<2)	7.0
IL 357 (b)	9.4	1.5	3.3	10.6		2.4	1.5	(19.3)	1.1
IL 951 (c)	6.4	1.1	0.9	1.7	1.8	3.8	1.1	(<2)	1.9
PE 603 (d)	15.6	1.7	3.4	4.5		35.0	3.3	(44.0)	6.8
V 275 (e)	6.1	3.2	3.4	3.9		39.8	1.7	(3.1)	13.0

All these results were obtained by direct aspiration into the flame with background correction and have 9 degrees of freedom. All results obtained are quoted even if the concentration of iron and manganese in the solution tested was less than the limit of detection.

(a) Determined by Thames Water Authority
(b) Determined by Yorkshire Water Authority (Southern Division)
(c) Determined by Laboratory of the Government Chemist; iron and manganese determinations were run simultaneously
(d) Determined by Marine Biological Association
(e) Determined by BDH Chemicals Ltd
(h) Distilled or deionized water spiked with the stated concentration of iron or manganese
(i) Local tap water, the figures in brackets being the mean concentration of iron or manganese in the tap water
(j) Local tap water spiked with 200µg/l iron or manganese; the recoveries ranged between 100 and 103%.

These results are illustrative of the performance achieved with various instruments in routine use in the participating laboratories; different results may be obtained using the same model/make of instrument in different laboratories with different operators. Therefore these results should not be interpreted to mean that any make/model of instrument is superior to another.

Table 2 Sensitivity for 1% Absorption [1]

Instrument	Sensitivity (μg/l)		Nebulization Rate (ml/min)
	Iron	Manganese	
IL 151 (a)	31	15	5.0
IL 357 (b)	36	19	6.0
IL 951 (c)	40	18	6.0
PE 603 (d)	148	107	4.0
V 275 (e)	98	40	
PE 703 (f)	104	47	5.0
V 775 (g)	48	23	5.0

(a) Determined by Thames Water Authority
(b) Determined by Yorkshire Water Authority (Southern Division)
(c) Determined by Laboratory of the Government Chemist
(d) Determined by Marine Biological Association
(e) Determined by BDH Chemicals Ltd
(f) Determined by Manchester University
(g) Determined by Yorkshire Water Authority (South Eastern Division)

All these results were obtained by direct aspiration into the flame. All instruments had impact bead nebulisers except (d) and (f) which had flow spoilers.

These results are illustrative of the performance achieved with various instruments in routine use in the participating laboratories; different results may be obtained using the same model/make of instrument in different laboratories with different operators. Therefore these results should not be interpreted to mean that any make/model is superior to another.

2 Principle

2.1 Iron and manganese in potable waters are determined by atomic absorption spectrophotometry by direct aspiration of the sample in 1% V/V hydrochloric acid and 0.1% m/V lanthanum into the air/acetylene flame. This acidification of the sample should ensure that any iron or manganese in suspended or colloidal forms is converted into soluble forms (see Section 8) and the presence of lanthanum minimizes interelement interference effects.

2.2 With some of atomic absorption spectrophotometers it may not be possible to achieve an adequate limit of detection (approximately 20–40 μg/l for iron and approximately 5–10 μg/l for manganese) by direct aspiration. In these circumstances when low levels of iron and manganese are to be determined, an alternative procedure is described in which the sample in 1% V/V hydrochloric acid is concentrated up to four times by evaporation, made 0.1% m/V in lanthanum and aspirated into the flame of the atomic absorption spectrophotometer. If concentration by evaporation is carried out the performance characteristics quoted in Table 1 no longer apply and if the concentration of other substances in the final solution exceeds those given in Tables 3 and 4 the data on effects of other substances may no longer apply.

2.3 Some laboratories may wish to determine the filtrable iron and manganese content of samples. The method described (for 'total' iron and manganese) may be suitable as the basis for a method for the determination of filtrable iron and manganese if it is combined with a filtration step, for example, using a membrane filter of suitable pore size. If such a procedure were used the performance characteristics quoted in Section 1 would no longer apply. Filtration must be carried out on unacidified samples. Filtration of samples may result in contamination of the filtrable fraction or in loss of iron or manganese by absorption processes. A recent publication [2] gives details of the problems which have been reported and guidance concerning the testing of filtration apparatus.

3 Interferences

The effects of other substances on the determination of iron and manganese vary considerably between atomic absorption spectrophotometers. The effects using direct aspiration of the acidified sample containing 0.1% m/V lanthanum into the flame are given in Tables 3 and 4 respectively [1]. These effects are significantly smaller than the effects observed when the determinations are carried out in the absence of lanthanum [3][4].

Generally in the presence of lanthanum the effects of the other substances are not significant; however, for some of the other substances and for some of the atomic absorption spectrophotometers the effects were significant. Despite these effects it is considered that the direct aspiration of acidified samples containing 0.1% m/V lanthanum provides the basis of a routine method for determining iron and manganese in potable waters. However, each analyst using this technique must check the interference effects of other substances for his atomic absorption spectrophotometer and decide for himself whether any effects are important considering the particular purpose of his determinations. If concentration by evaporation is used and the concentrations of other substances in the final solution exceed those quoted in Tables 3 and 4 the data on effects of these other substances may no longer apply; analysts may find that they need to use higher lanthanum concentrations to minimize interference effects.

Table 3 Effect of Other Substances on the Determination of Iron[1]

Other Substance	Concentration of other substance (mg/l)	Other substance added as	Effect in μg/l iron of other substances at an iron concentration of (μg/l) (k) 0.0	200.0	1000.0
Calcium (as Ca^{2+})	300	Chloride)		0.0	0.0(a)
Magnesium (as Mg^{2+})	100	Chloride)		−11.7	0.0(b)
Sodium (as Na^{+})	300	Chloride)	+11.9	+1.8	−61.5(c)
Potassium (as K^{+})	20	Chloride)		+5.5	+1.6(d)
				−18.5	+16.9(e)
				+10.0	−20.0(a)
Calcium (as Ca^{2+})	300	Chloride)		−21.5	−14.5(b)
Sulphate (as SO_4^{2-})	300	Acid)	+ 8.2	−13.7	−44.3(c)
				+19.6	−19.2(d)
				−15.7	+28.2(e)
Silicon (as Si)	5	Sodium)		0.0	0.0(a)
		Silicate)		−15.7	−4.8(b)
			+ 8.2	−4.6	+6.3(c)
				−9.5	−23.7(d)
				−14.4	+33.0(e)
Aluminium (as Al^{3+})	5	Chloride)		−10.0	−20.0(a)
				−18.0	−14.5(b)
			− 9.1	+9.1	0.0(c)
				−6.3	−3.1(d)
				−7.2	−10.4(e)
Copper (as Cu^{2+})	5	Chloride)		−10.2	+14.5(b)
Zinc (as Zn^{2+})	5	Chloride)	−10.1	+9.1	0.0(c)
				−9.5	−42.7(d)
				−23.5	+4.6(e)
Phosphate (as P)	10	Acid)		0.0	0.0(a)
Calcium (as Ca^{2+})	100	Chloride)		−7.5	+14.5(b)
			+ 9.1	−6.4	0.0(c)
				−36.8	−36.8(d)
				−19.5	+ 1.5(e)

Key as for Tables 1 and 2

(k) If the other substances did not interfere the effect would be expected (95% confidence) to lie with the ranges:—

0.0± 10.7 and 0.0± 16.8 at 200.0 and 1000.0 μg/l iron respectively (a)
0.0± 11.3 and 0.00± 16.7 at 200.0 and 1000.0 μg/l iron respectively (b)
0.0± 12.7, 0.0± 15.3 and 0.0± 21.9 at 0.0, 200.0 and 1000.0 μg/l iron respectively (c)
0.0± 21.8 and 0.0± 35.1 at 200.0 and 1000.0 μg/l iron respectively (d)
0.0± 12.3 and 0.0± 29.7 at 200.0 and 1000.0 μg/l iron respectively (e)

Table 4 Effect of Other Substances on the Determination of Manganese[1]

Other Substance	Concentration of other substance (mg/l)	Other Substance added as	Effect in μg/l manganese of other substance at a manganese concentration of (μg/l) (l)		
			0.0	200.0	1000.0
Calcium (as Ca^{2+})	300	Chloride)		+10.0	-20.0(a)
Magnesium (as Mg^{2+})	100	Chloride)		-8.2	-27.4(b)
Sodium (as Na^{+})	300	Chloride)	+1.1	-3.8	-47.5(c)
Potassium (as K^{+})	20	Chloride)		-4.7	-8.8(d)
				-0.9	-6.1(e)
Calcium (as Ca^{2+})	300	Chloride)		0.0	30.0(a)
Sulphate (as SO_4^{2-})	300	Acid)		-6.1	-16.9(b)
			-5.9	-4.9	-20.0(c)
				-0.6	-7.5(d)
				-11.0	-25.4(e)
Silicon (as Si)	5	Sodium)		0.0	0.0(a)
		Silicate)		-4.1	-6.3(b)
			-5.1	+12.7	+13.8(c)
				-2.6	-7.7(d)
				-19.1	-26.7(e)
Aluminium (as Al^{3+})	5	Chloride)		0.0	0.0(a)
				-4.1	-4.2(b)
			-4.8	+6.8	+8.8(c)
				+2.7	+1.9(d)
				0.0	0.0(e)
Copper (as Cu^{2+})	5	Chloride)		0.0	0.0(a)
Zinc (as Zn^{2+})	5	Chloride)		+2.0	-8.4(b)
			-2.6	+9.4	+23.1(c)
				-0.1	-4.0(d)
				-0.5	-10.0(e)
Phosphate (as P)	10	Acid)		0.0	0.0(a)
Calcium (as Ca^{2+})	100	Chloride)		0.0	-12.7(b)
			-2.2	+5.7	-4.0(c)
				-1.8	-15.1(d)
				-1.2	-3.1(e)

Key as for Tables 1 and 2

(l) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the ranges:—

0.0 ± 4.4 and 0.0 ± 8.2 at 200.0 and 1000.0 μg/l manganese respectively (a)
0.0 ± 4.1 and 0.0 ± 7.7 at 200.0 and 1000.0 μg/l manganese respectively (b)
0.0 ± 3.0 and 0.0 ± 7.3 and 0.0± 20.0 at 0.0, 200.0 and 1000.0 μg/l manganese respectively (c)
0.0 ± 5.9 and 0.0 ± 9.4 at 200.0 and 1000.0 μg/l manganese respectively (d)
0.0 ± 7.4 and 0.0 ± 12.5 at 200.0 and 1000.0 μg/l manganese respectively (e)

4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles (see Section 6.2). Analytical reagent grade chemicals are suitable unless otherwise stated.

5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have an iron or manganese content that is negligible, compared with the smallest concentrations to be determined in the samples (see Section 12.2). Deionized water or water distilled from an all glass apparatus is normally suitable.

5.2 Hydrochloric acid (d_{20} 1.18)

5.2.1 *50% V/V Hydrochloric Acid*

Dilute 500 ± 5 ml hydrochloric acid (d_{20} 1.18) with water to 1 litre in a stoppered measuring cylinder and mix well.

5.2.2 *1% V/V Hydrochloric Acid*

Dilute 20.0 ± 0.2 ml of 50% V/V hydrochloric acid with water to 1 litre in a calibrated flask and mix well.

5.3 Aluminium oxide antibumping granules

The granules should be boiled in 50% V/V hydrochloric acid for one hour and then washed thoroughly with water, dried at 105°C and stored in a clean polyethylene or glass container.

5.4 Standard iron solutions

5.4.1 *Solution A* 1 ml contains 1 mg Fe

Weigh 1.000 ± 0.005 g of iron wire (greater than 99.9% purity) and dissolve it in a mixture of 50 ± 2 ml of hydrochloric acid (d_{20} 1.18) and approximately 50 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. This solution is stable for at least several months. Alternatively use a commercially available standard iron solution in hydrochloric acid.

5.4.2 *Solution B* 1 ml contains 10 μg/ Fe

Dilute 10.00 ml of solution A with 1% V/V hydrochloric acid to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

5.5 Standard manganese solutions

5.5.1 *Solution A* 1 ml contains 1mg Mn

Weigh 1.000 ± 0.005 g manganese turnings (greater than 99.9% purity), and dissolve them in a mixture of 50 ± 2ml of hydrochloric acid (d_{20} 1.18) and approximately 50 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for at least several months. Alternatively use a commercially available standard manganese solution in hydrochloric acid.

5.5.2 *Solution B* 1 ml contains 10 μg Mn

Dilute 10.00 ml of Solution A with 1% V/V hydrochloric acid to 1-litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

5.6 10% m/V Lanthanum solution

Dissolve 58.7 ± 0.1 g of lanthanum oxide in 500 ± 10 ml of hydrochloric acid (d_{20} 1.18) cautiously and with stirring. Dilute with water to 1 litre in a measuring cylinder.

6 Apparatus

6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with iron and manganese hollow cathode lamps. A corrosion resistant nebuliser and burner **must** be used. Background correction must be used: if the instrument is not equipped with facilities to make this correction automatically, a separate measurement for background must be made using a suitable continuum source [5].

6.2 Cleanliness

Cleanliness is essential for these determinations. If possible, apparatus should be reserved solely for iron and manganese determinations; all residual iron and manganese from previous determinations must be removed. Clean all new glass and polyethylene ware by filling with, or soaking in, 50% V/V hydrochloric acid (or alternatively 10% V/V nitric acid) for several hours. Rinse thoroughly with water. Thereafter, a thorough rinse in 50% V/V hydrochloric acid, followed by a thorough rinse with water after each determination should suffice.

7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section 6.2, add 20.0 ± 0.2 ml of 50% V/V hydrochloric acid per litre of sample to be collected, and then collect the sample. This acidification minimizes the absorption of iron and manganese onto the walls of the bottle and precipitation of iron and manganese compounds. If filtrable iron or manganese is to be determined see Section 2.3.

8 Sample Pretreatment

The method described specifies collection of the sample into hydrochloric acid so that the sample contains 1% V/V hydrochloric acid. If direct aspiration of the acidified sample is used then the acidified sample should be allowed to stand for at least 24 hours to convert any iron and manganese in suspended or colloidal forms to soluble forms. This should ensure conversion for most samples. If the analyst suspects that conversion is not complete this can be checked by taking a second 200 ml aliquot and evaporating as in step 9.2.1, diluting with water back to 200ml, carrying out the determination and comparing the result with that obtained by following the procedure given in Section 9.1. If concentration by evaporation is to be used, the concentration procedure converts any suspended or colloidal iron and manganese into soluble forms.

9 Analytical Procedure

Read Section 4 on Hazards before Starting This Procedure

Two procedures are described. The choice of which procedure to use depends on the limit of detection of the atomic absorption spectrophotometer. If possible, direct aspiration of the acidified sample should be used; for those instruments with inadequate limits of detection concentration by evaporation should be used for samples containing low levels of iron and manganese. Each analyst should determine for his own instrument which procedure is the most appropriate after considering the instrument sensitivity, the limit of detection achievable and the possible interference effects from substances present in typical samples.

Step	Procedure	Notes
	9.1 Direct aspiration of the acidified sample	
	Pretreatment stage	
9.1.1	Allow the acidified sample (1% V/V with respect to hydrochloric acid) to stand for at least 24 hours. To 100 ± 1ml of sample add 1.00 ± 0.05 of 10.0% m/V lanthanum solution	
	Blank determination	
9.1.2	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for samples. 1% V/V hydrochloric acid solution is used as the blank. Add 1.00 ± 0.05 ml of 10.0% m/V lanthanum solution to each 100 ml of blank	

Step	Procedure	Notes
	Calibration Standards	
9.1.3	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations. Pipette 10.0 ml of standard iron or manganese solution B into a 100 – ml calibrated flask and dilute with 1% V/V hydrochloric acid to the mark. Add 1.00 ± 0.05 ml of 10.0% m/V lanthanum solution	
	Atomic absorption stage	
9.1.4	Set up the instrument according to the manufacturers instructions for determining iron or manganese in an air/acetylene flame with background correction. The burner and the spray chamber should be washed out to remove any iron or manganese from previous samples (note a). For iron use either a stoichiometric or a slightly fuel lean flame; for manganese use a stoichiometric flame. The wavelengths required are: iron 248.3 nm manganese 279.5 nm	(a) Cleaning of the burner in an ultrasonic bath containing a solution of a proprietory laboratory detergent has been found to be satisfactory.
9.1.5	Aspirate acidified water (1% V/V hydrochloric acid) until equilibrium conditions are established. Aspirate one of the calibration standards and adjust the instrument to give a suitable response. Aspirate acidified water and readjust the zero.	
9.1.6	Aspirate the calibration standards with an aspiration of acidified water between each. Let the instrument responses of the calibration standards be C_1 and C_2. Aspirate the blank followed by acidified water. Let the instrument response of the blank be B_1.	
9.1.7	Aspirate the samples with an aspiration of acidified water between each. Record the instrument response of the sample. Correct for background (note b) and let the corrected response be S.	(b) Background correction must be carried out on all samples, blanks and standards.
9.1.8	After each batch of 10 samples re-aspirate the blank and both calibration standards with an aspiration of acidified water in between each. Note the instrument responses of the blank (B_2) and the calibration standards (C_3 and C_4).	
	Calculation of result	
9.1.9	Iron or manganese concentration $= 1.02 \frac{(S - \bar{B})}{\bar{C} - \bar{B}} \times 1000$ µg/l (note c) where $\bar{B} = \frac{B_1 + B_2}{2}$ and $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$ This calculation assumes a linear calibration curve. This must be checked (see Section 10).	(c) The factor 1.02 allows for the dilution of the sample by the acid into which it was collected.

Step	Procedure	Notes

Concentration by Evaporation

9.2 This procedure is for the less sensitive atomic absorption spectrophotometers when it is required to determine low concentrations of iron and manganese (see Section 2.1). The procedure given is for concentration four times by evaporation; other concentration factors less than 4 may be used. If interference effects are expected to be significant higher concentrations of lanthanum may be used.

Pretreatment stage

(Carry out this stage in a Fume Cupboard)

9.2.1 Add 200 ± 1ml of the acidified sample (1% V/V acid) to a 400-ml tall form borosilicate glass beaker. Add 4 or 5 acid washed aluminium oxide antibumping granules. Cover the beaker with a watch glass and simmer on a hot plate (note d) until the solution volume is reduced to between 20 and 30 ml (note e) and allow to cool.

(d) The hot plate surface temperature should not exceed 160°C. This may be measured by a thermometer standing in a drilled metal block placed on the surface of the hotplate

(e) The 20 to 30 ml volume may be judged by premarking the beaker. It is important to ensure that the liquid does not evaporate to less than 10 ml

9.2.2 Quantitatively transfer the contents of the beaker to a 50-ml calibrated flask. Add 0.50 ± 0.03 ml of 10.0% m/V lanthanum solution. Dilute with water to the mark, stopper and mix thoroughly.

Blank determination

9.2.3 A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for samples. Carry out steps 9.2.1 and 9.2.2 using 200 ± 1ml of 1% V/V hydrochloric acid.

Calibration Standards

9.2.4 Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations. Pipette 12.5 ml of standard iron or manganese solution B into a 500 ml calibrated flask and dilute with 1% V/V hydrochloric acid to the mark and mix well. Take two 200 ± 1 ml aliquots and carry out steps 9.2.1 and 9.2.2.

Atomic absorption stage

9.2.5 Set up the instrument according to the manufacturers instructions for the determination of iron or manganese in an air/acetylene flame with background correction. The burner and the spray chamber should be washed out to remove any iron or manganese from previous samples (note f). Use either a stoichiometric or a fuel lean flame. The wavelengths required are:

iron	248.3 nm
manganese	279.5 nm

(f) Cleaning of the burner in an ultrasonic bath containing a solution of proprietory laboratory detergent has been found to be satisfactory.

Step	Procedure	Notes
9.2.6	Aspirate acidified water until equilibrium conditions are established. Aspirate one of the calibration standards and adjust the instrument to give a suitable response. Aspirate acidified water and readjust the zero.	
9.2.7	Aspirate the calibration standards with an aspiration of acidified water between each. Let the instrument responses of the calibration standards be C_1 and C_2. Aspirate the blank followed by acidified water. Let the instrument response of the blank be B_1.	
9.2.8	Aspirate the samples with an aspiration of acidified water between each. Record the instrument response of the sample. Correct for background (note g) and let the corrected response be S.	(g) Background correction must be used.
9.2.9	After each batch of 10 samples re-aspirate the blank and both calibration standards with an aspiration of acidified water in between each. Note the instrument responses of the blank (B_2) and the calibration standards (C_3 and C_4).	
	Calculation of the result	
9.2.10	Iron or manganese concentration $= 1.02 \frac{(\bar{S} - \bar{B})}{\bar{C} - \bar{B}} \times 1000\ \mu g/l$ (note h) where $\bar{B} = \frac{B_1 + B_2}{2}$ and $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$ This calculation assumes a linear calibration curve. This must be checked (see Section 10).	(h) The factor 1.02 allows for the dilution of the sample by the acid into which it was collected.

10 Checking the Linearity of the Calibration Curve

This procedure must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

10.1 Direct aspiration of samples

Pipette respectively into a series of 100-ml calibrated flaks 0.0, 2.0, 4.0, 6.0, 8.0 and 10.0 ml of standard iron or manganese solution B, dilute with 1% V/V hydrochloric acid to the mark mark and mix thoroughly. These flasks contain respectively, 0,200, 400,600, 800 and 1000 μg/l Fe or Mn. Carry out the procedure given in Section 9.1 treating these solutions as if they were samples. Plot the instrument response of each solution against μg/l iron or manganese. The calibration curve is normally linear; however, the linearity should be checked. If the calibration curve departs from linearity, the calibration standard in step 9.1.3 may not be appropriate, nor the range given in Section 1.4. In such a case, the calibration standard chosen for step 9.1.3 should be the highest concentration on the linear portion of the calibration curve, and the concentration range of the method should be amended accordingly.

10.2 Concentration by evaporation

Pipette respectively into a series of 200-ml calibrated flasks 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of standard iron or manganese solution B, dilute with 1% V/V hydrochloric acid to the mark and mix thoroughly. These flasks contain respectively 0, 50, 100, 150, 200 and 250 μg/l iron or manganese (ie 0, 200, 400, 600, 800 and 1000 μg/l when concentrated four times).

Carry out the procedure given in Section 9.2 treating these solutions as if they were samples. Plot the instrument response of each solution against $\mu g/l$ iron or manganese. The calibration curve is normally linear; however, the linearity should be checked. If the calibration curve departs from linearity, the calibration standard in step 9.2.4 may not be appropriate, nor the range given in Section 1.4. In such a case, the calibration standard chosen for step 9.2.4 should be the highest concentration on the linear portion of the calibration curve, and the concentration range of the method should be amended accordingly.

11 Change of concentration range of the method

11.1 Direct aspiration of samples

If the iron or manganese concentration of the sample is likely to exceed 1000 $\mu g/l$, an appropriate aliquot (V_1 ml) of the sample must be taken for analysis, diluted with 1% V/V hydrochloric acid to V_2 ml and the procedure described in Section 9.1 carried out. The calculation of the result (step 9.1.9) must then be multiplied by $\frac{V_2}{V_1}$

Alternatively if the calibration curve is linear beyond 1000 $\mu g/l$ for a particular spectrophotometer the range of the method may be extended up to the extent of linearity of the calibration curve.

11.2 Concentration by evaporation

If the iron or manganese concentration of the sample is likely to exceed 250 $\mu g/l$ use direct aspiration.

12 Sources of error

The attention which it is necessary to pay sources of error depends on the accuracy required of the analytical results. The following sub-sections summarize the main sources of error.

12.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of iron or manganese or their compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular, it is desirable to reserve the glass apparatus used for the iron and manganese determinations solely for this purpose, and to carry out a preliminary series of blank determinations, to ensure low blank values before analysing any samples. Also the burner and the spray chamber of the atomic absorption spectrophotometer should be washed out before each set of determinations.

12.2 Iron or manganese content of the water used for preparing the blank.

The iron or manganese content of the water used should be negligible if prepared according to Section 5.1. If the blank levels are unacceptably high then fresh water and hydrochloric acid should be used.

12.3 Interfering substances

See Section 3. The effect of possible interfering substances may be determined by analysing water spiked with iron or manganese and various concentrations of the potential interfering substance.

12.4 Calibration standards

The calibration curve for this method has been found to be linear, though its slope may vary from one set of determinations to another. Therefore, a calibration standard must be run for each batch of analyses, and steps 9.1.3 or 9.2.4 onwards give the necessary procedure. This procedure assumes a linear calibration curve and linearity must be checked (see Section 10).

13 Checking the Accuracy of Analytical Results

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 tests are possible[6] and they should be used as appropriate. As a minimum, however, it is suggested that a control standard solution of iron or manganese of suitable concentration, a typical sample and the same sample spiked with a suitable concentration of iron or manganese, be analysed at the same time, and in exactly the same way as normal samples (see step 9.1.3 or step 9.2.4). The results for the standard solution, and the recoveries obtained from the spiking, should be plotted on separate quality control charts, which will facilitate detection of inadequate accuracy and will, also, allow the standard deviation of routine analytical results to be estimated.

14 References

(1) Department of the Environment, File WS/646/50, paper SCA/4.2/6

(2) Hunt DTE, *Filtration of Water Samples for Trace Metal Determinations,* Water Research Centre Technical Report RT 104, 1979

(3) Department of the Environment, File WS/646/50, paper SCA/4.2/3

(4) Hydes O D and Thompson K C, *Analytical Newsletter No 2,* Water Research Centre, 1982.

(5) Standing Committee of Analysts, *Atomic Absorption Spectrophotometry – an Essay Review,* 1980, K C Thompson, HMSO, London

(6) Wilson A L and Cheeseman R V, *Technical Report,* Water Research Centre, TR 66, 1978.

Appendix

Estimation of the Accuracy of Analytical Results Using the Iron and Manganese Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the iron and manganese methods are used appears to be limited to within batch standard deviation estimations in several laboratories. 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 Secretary of the Metals and Metalloids Working Group of the DOE/NWC 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 results at zero determinand concentration. The precision of analytical results may depend on the concentration of iron and manganese in the samples 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 up to 10.

Solution No.	Description	Iron (μg/l)	Manganese (μg/l)
1	Blank*		
2	Another Blank*		
3	Standard solution containing	50	20
4	Standard solution containing	1000	1000
5	Typical sample		
6	Same sample spiked with	500	500

*To be regarded as samples having zero determinand concentration and NOT as true blanks.

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section 9 be rigidly followed except that a second true blank should be run with that prescribed in exactly the same manner (ie each of the two true blanks should be analysed in the batch of samples). The six solutions described above should be analysed in random order in with 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. On any one day the same batch of water should be used to prepare those four solutions. For solutions 5 and 6 a total of at least 2 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows: add with a pipette 5 ml of an intermediate iron or manganese standard solution (prepared by diluting 10 ml of standard iron solution A (see section 5.4.1) or standard manganese solution A (see section 5.5.2) to 100 ml with 1% V/V hydrochloric acid) to 1 litre of solution 5. When analysing solution 6 it may be necessary to take into account Section 11 and to take an appropriately smaller aliquot. The total period of the test may be any convenient time so long as the iron or 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 iron or manganese from 100% may give an indication of the presence of interfering substances.

3 Evaluation of Results

The raw experimental results should be sent directly 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 calculation themselves the details are given below.

3.1 Convert all results to concentrations as described in the method. Deduct the mean response of the first blank when performing the conversions for solutions 1, 3, 4, 5 and 6 and deduct the mean responses for the second true blank when performing the conversion for solution 2.

3.2 For solutions 3, 4, 5 and 6 calculate the standard deviation, S, of the n results for each solution from:

$$S = \sqrt{\frac{(X_i - \overline{X})^2}{n - 1}}$$

where X_i = the results from the ith batch

$\overline{X}$ = the mean value of X_i.

3.4 Calculate the within-batch standard deviation S_{wr}, of the results of zero concentration from:

$$S_{wr} = \sqrt{\frac{(X_{1i} - X_{2i})^2}{2n}}$$

where X_{1i} = the result for solution 1 for the ith batch (see 3.1)

X_{2i} = the result for solution 2 from the ith batch (see 3.1)

Note: S_{wr} is not to be confused with the within-batch standard deviation of blank determinations, S_w, from which the limit of detection is often calculated.

3.5 Calculate the mean percentage recovery, R, of the spiked iron or manganese in solution 6 from:

$$R = \frac{(1.005\,\overline{X}_6 - \overline{X}_5) \times 100}{500}$$

Where $\overline{X}_5$ = the mean value of the results for solution 5.

Where $\overline{X}_6$ = the mean value of the results for solution 6.

3.6 Summarize the results as in the following tables:

Solution	No. of results	Mean iron concentration (μg/l)	Standard deviation (μg/l)	Mean Recovery (%)
1 and 2 blanks	2n =			—
3 standard 50 μg Fe/l	n =			—
4 Standard 1000 μg Fe/l	n =			—
5 sample ...	n =			—
6 Solution 5 + 500 μg Fe/l	n =			

Solution	No. of results	Mean manganese concentration (μg/l)	Standard deviation (μg/l)	Mean Recovery (%)
1 and 2 Blanks	2n =			—
3 standard 20 μg Mn/l	n =			—
4 standard 1000 μg Mn/l	n =			—
5 sample ...	n =			—
6 solution 5 + 500 μg Mn/l	n =			

It should be stated whether the direct aspiration or concentration by evaporation procedure was used.

† *Results to be sent to the following:*

The Secretary
The Metals and Metalloids Working Group
The Standing Committee of Analysts
The Department of the Environment
43 Marsham Street
London SW1P 3PY

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 booklet are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
43 Marsham Street
London SW1P 3PY
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Department of the Environment

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