I.O.S.

METHODS FOR THE SHIPBOARD DETERMINATION OF DISSOLVED IRON AND MANGANESE IN SAMPLES OF SEDIMENT INTERSTITIAL WATER

BY

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Methods for the shipboard determination of dissolved iron and manganese in samples of sediment interstitial water

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Report Title: Methods for the shipboard determination of dissolved iron and manganese in samples of sediment interstitial water

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Abstract: Iron is extremely unstable in the presence of oxygen. A working atmosphere containing less than 0.2% oxygen is required if iron losses are not to be significant. Iron can be determined with a single addition of reagent, either manually or by a continuous flow procedure using ferrozine. Using a continuous flow procedure with a 5 cm colorimeter cell the method is linear up to 40 μM Fe and the precision is 2%. Manganese can similarly be determined with a single reagent addition using formaldoxime. For the continuous flow procedure with a 5 cm colorimeter cell the method is linear up to 60 μM Mn and the precision is 1%; however, under these conditions a solution containing 100 μM of iron produces an interference equivalent to 4.7 μM of manganese. A two-reagent procedure was developed using EDTA to suppress the iron interference. Using a 5% EDTA solution interference from a solution containing 100 μM of iron was undetectable.

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This work has been commissioned by the Department of the Environment as part of its radioactive waste management research programme. The results will be used in the formulation of Government policy but, at this stage, they do not necessarily represent Government policy.

CONTENTS

ABSTRACT

This report details some of our experiences over the last three years in the development of methods for the shipboard sampling and determination of iron and manganese dissolved in anoxic sediment pore waters. Iron is extremely unstable in the presence of oxygen. A working atmosphere containing less than 0.2% oxygen is required if iron losses are not to be significant. Iron can be determined with a single addition of reagent, either manually or by a continuous flow procedure using ferrozine. Using a continuous flow procedure with a 5 cm colorimeter cell the method is linear up to 40 μM Fe and the precision is 2%. Manganese can similarly be determined with a single reagent addition using formaldoxime. For the continuous flow procedure with a 5 cm colorimeter cell the method is linear up to 60 μM Mn and the precision is 1%; however, under these conditions a solution containing 100 μM of iron produces an interference equivalent to 4.7μM of manganese. A two-reagent procedure was developed using EDTA to suppress the iron interference. Using a 5% EDTA solution interference from a solution containing 100 μM of iron was undetectable.

1. INTRODUCTION

We wish to study the distribution of dissolved trace metals in marine sediments, both to understand the processes by which these metals are redistributed between different facies as a result of diagenetic reactions and to use what we know of the chemistry of these metals to further our understanding of the active redox state in the sediment.

The two metals mobilised most significantly on the transition from oxic to anoxic conditions in the sediment are iron and manganese. Ferrous iron is difficult to measure accurately in sea water due to its sensitivity to oxidation. Loss of iron from samples also leads to a reduction in concentration of other dissolved components such as silicate and phosphate (Loder, 1978). Because of this sensitivity to oxidation, making it difficult to collect and preserve samples which accurately represent in-situ conditions, it is very useful to have an analytical method available which can be applied on board ship soon after samples have been collected. This allows the quality of the samples to be judged and remedial measures to be taken if perturbations due to oxygen contamination are suspected. This report covers the development of two well-established methods for the determination of iron and manganese into procedures which are suitable for routine application on board ship. We also briefly report some measurements of the likely sensitivity of iron to oxygen contamination.

2. IRON AND MANGANESE OXIDATION EXPERIMENTS

2.1 INTRODUCTION

Iron is well known to precipitate rapidly from solution when oxygen contamination enters a sample of a natural water taken from an anoxic environment. Precipitation of iron gives rise to co-precipitation and adsorption processes which reduce the concentration of other dissolved components such as silicate and phosphate (Loder, 1978). The following experiments were carried out to assess the rate at which iron oxidation might occur in the apparatus used by us to collect interstitial water samples from anoxic sediments.

Iron oxidation reactions have been extensively studied (Hem, 1967; Stumm & Morgan, 1970). Oxidation of iron (II) was reported by Stumm and Morgan to depend on the following rate law at pHs above 5.5:

$$-d\ Fe(II)/dt = K\ Fe(II)\ .\ OH^{-2}\ .\ p\ O_2$$

The rate of oxidation will increase rapidly with increasing pH. Stumm and Morgan reported 90% oxidation of a solution of iron (II) in 30 minutes at a temperature of 20°C and a pH of 7.2, with a partial pressure of oxygen of 0.2 (achieved by constant bubbling of air through the sample). At the higher pH of seawater (7.8 to 8.2), iron, depending on the temperature and partial pressure of oxygen, would be expected to precipitate with similar rapidity.

The process of manganese oxidation, although at least as well studied as that of iron, is less well understood. Stumm and Morgan (1970) suggested that manganese oxidation followed an auto-catalytic rate law at pHs greater than 8.5:

$$-d\ Mn(II)/dt = K_o\ Mn(II) + K\ Mn(II)\ MnO_2\ .\ OH^{-2}\ .\ p\ O_2$$

Marine interstitial water samples usually have pHs below which this rate law applies. However, in accord with this equation, experience in this laboratory indicates that samples of pore water containing several micro-moles of manganese are stable for several years without acidification. These samples have been filtered to remove any solid-phase manganese. At natural pHs, although manganese (II) in solution may be thermodynamically unstable, the oxidation process does need to be "catalysed"; this is thought to be by bacterial activity *in situ* (Diem & Stumm, 1984; Emerson *et al.*, 1982). Although manganese may be stable in filtered solutions which have been exposed to oxygen, manganese may be co-precipitated with iron early in the separation scheme which allows iron oxidation to occur. We report here simple experiments to check if manganese is co-precipitated during iron oxidation.

2.2 IRON OXIDATION RATE

Two sets of simple experiments were carried out to observe the rate of iron oxidation in samples of seawater to which iron had been added as iron (II) in a ferrous ammonium sulphate solution. Firstly, observations were made for solutions of varied pH exposed to the laboratory atmosphere. Secondly, measurements were made inside an isolation box in which the oxygen content of the atmosphere was varied between 5 and 0.15%.

2.2.1 *Variation of pH*

Procedure: Adjust pH of 90 ml of seawater by addition of sodium carbonate

solution, add iron, start clock, make up to 100 ml mark, mix. Take sample by transferring 20 ml to plastic beaker. Draw into syringe and push the sample through a Swinex filter holder containing a 0.4 μm Nuclepore filter. Collect sample in a test tube containing 10 μl concentrated hydrochloric acid. Record time when half sample collected. Repeat above at different pHs.

Results: Measurements were made at pH 7.78, 8.22 and 8.48. The results are presented in Figure 2.1. The time for 90% oxidation to occur fell from 20 minutes at pH 7.78 to 5 minutes at pH 8.48.

2.2.2 Variation of oxygen in atmosphere

Solutions were manipulated inside a 500 litre rigid Perspex isolation box. The atmosphere for this unit was supplied by a nitrogen generator (0.2-0.1% O_2) and cylinder nitrogen "white spot" (0.0001% O_2). The box was flushed of oxygen by repeated filling of a displacement bag inside the box. By this method a 0.1% oxygen atmosphere could be achieved inside it in about 4 hours. Table 2.1 gives a theoretical listing of the number of displacements required to get to a 0.1% oxygen concentration.

Oxygen-free seawater was produced by degassing with "white spot" nitrogen for at least one hour.

Procedure: Draw 20 ml de-gassed seawater into a syringe, transfer to plastic beaker, de-gas for 30 seconds, add iron (II) and start clock.

Results: Measurements made in atmospheres containing 2.0, 0.5 and 0.15 per cent oxygen are listed in Table 2.2. Even in the 0.5% oxygen atmosphere, 60% oxidation occurred within 10 minutes. As samples may be expected to be subject to contamination for at least an hour while being processed in the isolation box, the degree of oxidation occurring in a 0.5% oxygen atmosphere is not acceptable. Lowering the oxygen atmosphere to 0.15% produces an acceptable result of 10% oxidation after two hours.

2.2.3 Conclusion

The simple experiments outlined above demonstrate just how rapid iron oxidation by atmospheric oxygen is, and indicate the high degree of care that must be taken in order to obtain samples of anoxic waters which represent in-situ conditions.

2.3 MANGANESE OXIDATION

Experiments similar to those outlined in section 2.2.1 were carried out using manganese-spiked solutions. The results listed in Table 2.3 show no indication of manganese being precipitated by atmospheric oxygen, or of its being co-precipitated with iron.

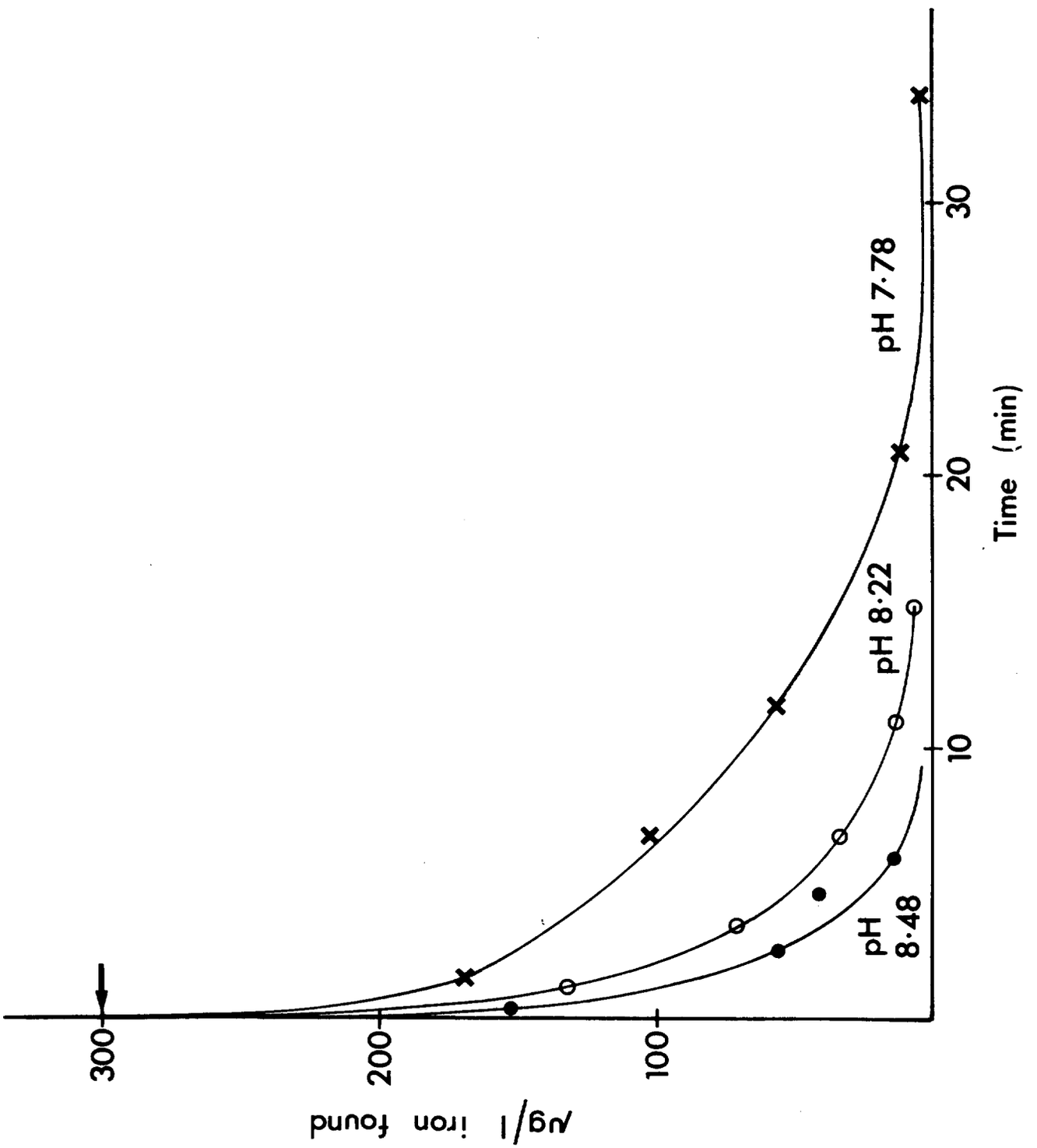

Figure 2.1 Comparison of the rates of iron oxidation at pHs 7.78, 8.22 and 8.48. The initial iron concentration in each case was 300 µg/l.

TABLE 2.1 - Theoretical number of repeated fillings of displacement bags of different volumes required to reduce the oxygen concentration inside an isolation box to 0.1%.

VOLUME OF BAG (% of total volume)	NUMBER
50	8
60	6
70	5
80	4
90	3

TABLE 2.2 - The amount of iron remaining in solution after different times starting with a solution containing 5.36 μM Fe at oxygen concentrations of 2%, 0.5% and 0.15%.

OXYGEN CONCENTRATION					
2%		0.5%		0.15%	
Time (min.)	Iron (μM)	Time (min.)	Iron (μM)	Time (min.)	Iron (μM)
2	3.50	2	3.46	2	5.28
5	4.54	6	2.11	4	5.43
10	0.48	8	2.54	14	5.09
21	0.21	18	2.29	49	4.90
52	0.14	30	1.20	139	4.75

TABLE 2.3 - The amount of manganese remaining in a seawater solution at pH 8.5 initially containing 5.45 μM Mn, with and without 5.36 μM Fe, subject to atmospheric oxygen contamination

Time (min.)	Mn (μM)	Mn (with Fe) μM
1	5.55	-
4	-	5.56
6	5.47	-
30	5.62	5.42
60	5.49	5.51
120	5.45	5.60

3. DETERMINATION OF DISSOLVED IRON (II)

3.1 INTRODUCTION

Both the methods described here are based on the ferrozine method reported by Stookey (1970). Iron (II) reacts with ferrozine:

(3-(2-pyridyl)-5, 6-bis(4-phenylsulphonic acid)-1, 1, 4-triazine

to form a stable magenta complex Fe(II) $(ferrozine)_2$ which is very soluble in water and is therefore suitable for the direct determination of iron in water. This method has found its widest application in the determination of iron in boiler feed waters where a determination of total iron present in the sample is required, and so a reduction step is included in the standard procedure to bring particulate iron into solution. Our interest is in dissolved iron. We wish to avoid detecting contamination resulting from any particles which may have passed through the filter during separation of the sample from sediment. The reduction step is therefore omitted from the procedures given below. The manual procedure follows that reported by Stookey, whereas the continuous flow method employs acetic acid to dissolve the ferrozine. Following Stookey's method, the ferrozine forms a stable suspension rather than a true solution which leads to problems with reproducibility. Using acetic rather than hydrochloric acid for the automated method produces a true solution and better reproducibility.

3.2 IRON DETERMINATION - MANUAL PROCEDURE

3.2.1 Equipment

(a) Pye Unicam SP600 Spectrophotometer fitted with a 4 cm flow cell.
(b) 5 ml disposable syringes for drawing solution into spectrophotometer.
(c) Acid-cleaned polypropylene test tubes with caps - for carrying out assay.
(d) Acid-cleaned volumetric flasks for preparation of standard solutions.
(e) 500 µl automatic pipette - for dispensing sample.
(f) 25 µl automatic pipette - for dispensing reagents.
(g) Pipettes for preparation of standards.
(h) Sample and reagent containers.

3.2.2 Reagents

Ferrozine solution: Dissolve 0.5 g of ferrozine and 10 g ammonium acetate in a small amount of water; add 50 ml of concentrated hydrochloric acid. After cooling, make up to 100 ml with distilled water.

Buffer solution: Dissolve 40 g of ammonium acetate in water; add 35 ml of ammonia solution (880) and make up to 100 ml with distilled water.

3.2.3 Standards

Primary - 10 mM. Dissolve 0.392 g ferrous ammonium sulphate 'AnalaR' $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 100 ml distilled water containing 100 µl concentrated hydrochloric acid.

3.2.4 Preservation of Samples

Add hydrochloric acid to a final concentration equivalent to 0.5% concentrated hydrochloric acid (55 mM).

3.2.5 Method

Place 500 µl of sample or standard into an acid-cleaned test tube and add, in immediate succession, 25 µl ferrozine solution and 25 µl of buffer solution. Mix well. Colour development occurs in a few seconds. Measure the extinction of the reacted solution at 562 nm. The absorption spectrum of the ferrozine complex displays a relatively sharp maximum between 550 and 575 nm (Stookey, 1970).

3.2.6 Blanks and Contamination

The reagent blank for this method determined by measuring the iron content of oxic, filtered surface sea water was found to be equivalent to 0.45 µM. The size of the blank varies with the batch of reagent and should be determined each time fresh reagents are prepared.

To avoid contamination, the plastic test tubes were cleaned by successive one-week soakings in 6M nitric acid and 6M hydrochloric acid. Volumetric glassware for the preparation of standards should be cleaned by soaking at least overnight, filled with 1 M hydrochloric acid.

3.2.7 Detection limit, reproducibility and linear range

The detection limit - three times the standard deviation of the blank for ten separate determinations - is 0.26 µM. The precision of nine replicate determinations on a sample containing 5.3 µM was 2.6% (one standard deviation).

Linear results were obtained up to an absorbance of 1.1, equivalent to 8.9 μM.

3.3 IRON DETERMINATION - CONTINUOUS FLOW PROCEDURE

3.3.1 Equipment

(a) Chemlab continuous flow analyser - fitted with the chemistry manifold shown in Figure 3.1 and 5 cm colorimeter cell with 560 nm filter.
(b) Acid-cleaned volumetric flasks for preparation of standards.
(c) Pipettes for preparation of standards, dispensing and acidifying samples.
(d) Reagent and sample containers.

3.3.2 Reagents

Ferrozine solution (stock): Dissolve 0.5 g ferrozine in a mixture of 200 ml distilled water and 62.5 ml acetic acid. Add 33.5 ml concentrated ammonia solution (880) with caution as heat is evolved. Dilute to 500 ml with distilled water. This solution is stable for several months in a clean glass or plastic bottle.

Ferrozine solution (working): Dilute concentrated solution one part with four parts distilled water. Add 0.5 ml Brij 35 solution (25% w/v) per 250 ml.

3.3.3 Standard

Primary - 10 mM. Dissolve 0.392 g ferrous ammonium sulphate 'AnalaR' $(NH_4)_2SO_4.FeSO_4.6H_2O$ in 100 ml distilled water containing 500 μl concentrated hydrochloric acid.

3.3.4 Preservation of Samples

Add hydrochloric acid to give a final concentration equivalent to 0.5% concentrated hydrochloric acid (55 mM). Our normal procedure is to dispense 2 ml of freshly filtered sample into a sample cup containing 100 μl of dilute hydrochloric acid (10% v/v). This should be done in a nitrogen atmosphere to minimise loss of iron due to oxidation.

3.3.5 Blanks and Contamination

The apparent reagent blank comparing a mixture of iron-free surface seawater and distilled water against iron-free seawater plus ferrozine reagent is usually about 0.5 μM Fe.

For the system set up to run at 100 μM Fe full scale, blanks from new 2.5 ml auto analyser cups are negligible (> 0.4 μM Fe).

Volumetric glassware for the preparation of standards should be cleaned by soaking over night, filled with 1 M hydrochloric acid.

3.3.6 Linear range, reproducibility and detection limit

Using the manifold shown in Figure 3.1, with a 5 cm cell in the colorimeter, the method is linear up to 40 µM Fe. Deviation at 100 µM Fe is - 19 µM. This is not reagent limited and doubling reagent concentrations does not shift the calibration line.

Operating with full scale 50 µM Fe (100 mV, 1850 bits) and a colorimeter gain of 1.2, the precision of ten replicate determinations on a sample containing 20 µM Fe was 2.0 %, giving a detection limit (three times the standard deviation) of 1.2 µM.

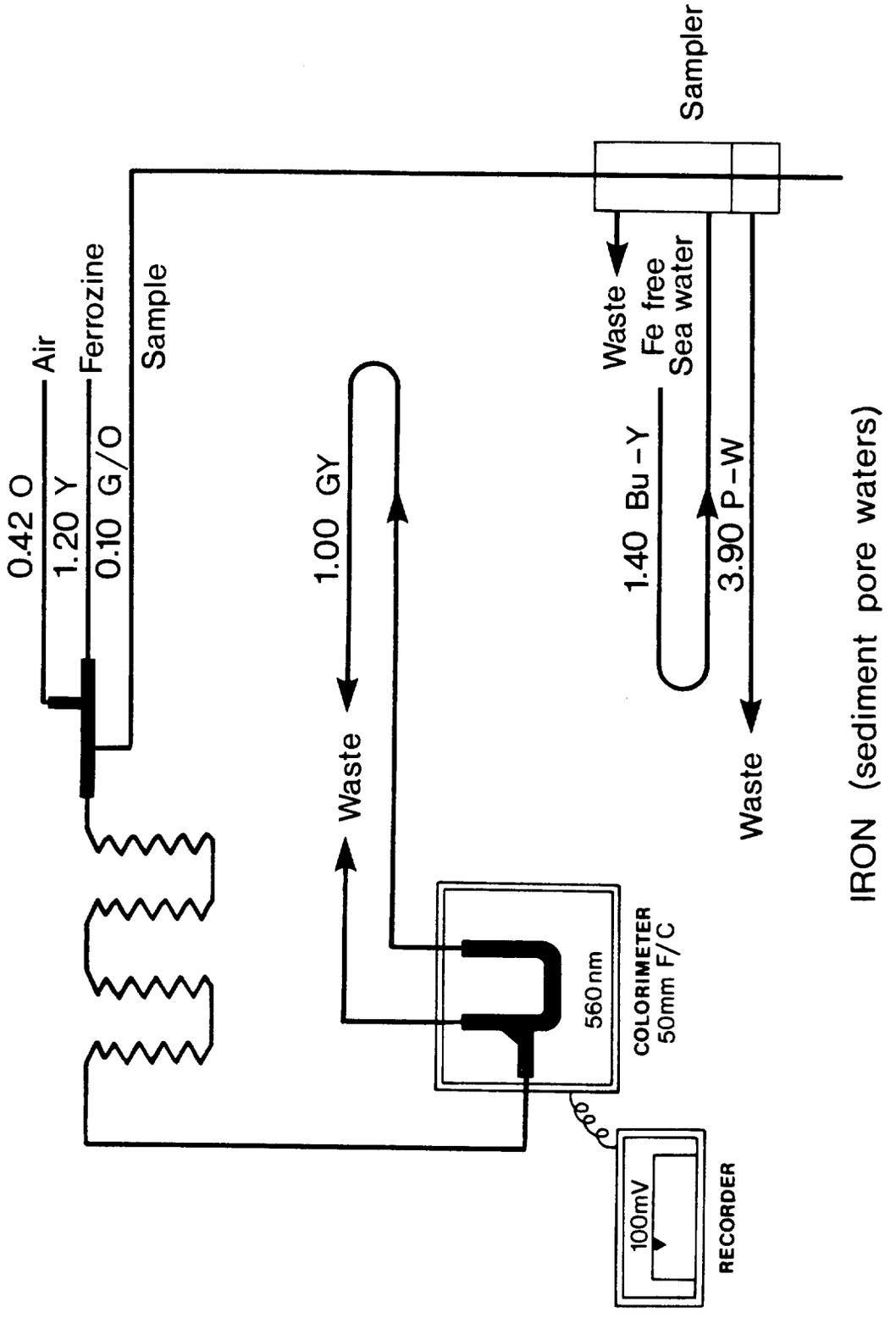

Figure 3.1 Continuous flow manifold for the determination of iron. The same manifold can be used for the determination of manganese using formaldoxime as the reagent and a 450 nM filter.

4. DETERMINATION OF DISSOLVED MANGANESE (II)

4.1 INTRODUCTION

Both the methods described here are based on the formaldoxime method originally reported by Hofman and Ehrhardt (1913). In solutions of pH above 9, manganese reacts rapidly with formaldoxime (prepared from formaldehyde and hydroxyl ammonium chloride) to give an orange-red coloured solution. The advantages of the method are that only simple reagents are required, colour formation is rapid and intense, giving both a simple and sensitive method. The disadvantage of the formaldoxime method is that iron interferes. Iron forms a violet-red coloured complex with formaldoxime with a maximum in its absorbance spectrum at 480 nm close to that of the manganese formaldoxime complex. Previous work on the method (cf. Henriksen, 1966; Goto et al., 1962), although suggesting remedies to remove iron interference, do not appear to have investigated the nature of the iron interference. We have investigated the iron interference and results are presented in Chapter 5 of this report.

For the methods described in this section, two approaches to the iron interference were taken. For the manual method - to keep it as simple, and therefore as rapid, as possible for processing large numbers of samples - the approach of Brewer and Spencer (1971) was followed. No attempt is made to control the iron interference chemically and, on the basis that in most waters the amount of iron interference is small and that as the interference is proportional to concentration and iron measurements are also being made on the same samples, results can be corrected for iron interference. For the automated method we found the accuracy of the determination could be improved by adding an EDTA solution to the sample stream to limit iron interference without degrading the precision of the analyses.

4.2 MANGANESE DETERMINATION - MANUAL PROCEDURE

4.2.1 Equipment

As for Iron, see section 3.2.1.

4.2.2 Reagents

Formaldoxime solution (stock). Dissolve 4 g of hydroxyl ammonium chloride (AnalaR) in 60 ml of double distilled water; add 2 ml of 37% formaldehyde solution (AnalaR) and make up to 100 ml. This solution can be stored for

several months in a screw-top plastic bottle.

Working reagent. Immediately before the determination mix, in the ratio 1:2, formaldoxime and 10% (v/v) ammonia solution. This solution is not stable - unless tightly enclosed - due to ammonia loss and should be prepared fresh for each batch of determinations.

4.2.3 Standards

(a) Primary - 10 mM. Dissolve 0.233 g manganous sulphate (AnalaR) $MnSO_4 \cdot 4H_2O$ in 100 ml distilled water containing 0.5 ml concentrated hydrochloric acid.

(b) Identical calibration lines were obtained using standards prepared from BDH SpectrosoL solution (1 mg Mn/ml).

4.2.4 Preservation of samples

Add hydrochloric acid to give a final concentration equivalent to 0.5% concentrated hydrochloric acid (55 mM).

4.2.5 Method

Place 500 µl of sample or standard into an acid-cleaned test tube, add 25 µl of the working reagent. Mix well. Colour development occurs in a few seconds. Measure the extinction of the reacted solution at 450 nm.

4.2.6 Colour stability

The colour of the manganese formaldoxime complex was found to be stable for 30 minutes, after which time a slow decrease in absorbance becomes detectable (5% in $4\frac{1}{2}$ hours).

4.2.7 Blanks and contamination

To avoid contamination, all volumetric glassware and test tubes should be acid rinsed before use. The reagent blank measured in a sample of filtered oxic surface seawater was equivalent to 0.23 µM Mn.

4.2.8 Detection limit, reproducibility and linear range

The detection limit - three times the standard deviation of the blank for ten separate determinations - is 0.25 µM. The precision for ten determinations on a spiked sea water sample containing 32.8 µM Mn was 2.4% (one standard deviation). Linear results were obtained up to an absorbance of 1.8 equivalent to 50 µM Mn.

4.3 MANGANESE DETERMINATION - CONTINUOUS FLOW PROCEDURE

4.3.1 Equipment

(a) Chemlab continuous-flow analyser - fitted with the chemistry manifold shown in Figure 4.1 and a 5 cm colorimeter cell with 450 nm filter.

(b) Acid-cleaned volumetric flasks for the preparation of standards.

(c) Pipettes for preparation of standards, dispensing and acidifying samples.

(d) Reagent and sample containers.

4.3.2 Reagents

Formaldoxime solution (Stock): Dissolve 4 g hydroxyl ammonium chloride (AnalaR) in 60 ml of double-distilled water, add 2 ml of 37% formaldoxime solution (AnalaR) and make up to 100 ml. This solution can be stored for several months in a screw-top plastic bottle.

Working reagent: Dilute 4.5 ml concentrated formaldoxime solution in 200 ml double-distilled water, then add 9 ml of 10% (v/v) ammonia solution. Mix well, then add 0.5 ml Brij 35 solution (25% w/v) and make up to 250 ml with double-distilled water. EDTA solution. Prepare a 5% (w/v) solution of ethylenediamine-tetra-acetic acid disodium salt in double-distilled water.

4.3.3 Standard

(a) Primary - 10 mM. Dissolve 0.233 g manganous sulphate (AnalaR) $NSO_4.4H_2O$ in 100 ml distilled water containing 0.5 ml concentrated hydrochloric acid.

(b) Identical calibration lines were obtained using standards prepared from BDH SpectrosoL solution (1 mg Mn/ml).

4.3.4 Preservation of samples

Add hydrochloric acid to give a final concentration equivalent to 0.5% concentrated hydrochloric acid (55 mM).

4.3.5 Blanks and Contamination

The apparent reagent blank comparing a mixture of distilled water against distilled water plus formaldoxime and EDTA solutions is usually equivalent to less than 1 µM Mn. For the system set up to run at 100 µM Mn full-scale, blanks from new 2.5 ml autoanalyser cups are undetectable (> 0.2 µM Mn). Volumetric glassware for the preparation of standards should be cleaned by soaking overnight filled with 1 M hydrochloric acid.

4.3.6 Linear range, reproducibility and detection limit

Using the manifold shown in Figure 4.1, with a 5 cm cell in the colorimeter, the method is linear up to 130 μM Mn. Using the manifold shown in Figure 3.1 (without the addition of EDTA) the method is linear up to 60 μM Mn.

Operating with full-scale 100 μM Mn (100 mV, 2040 bits) and a colorimeter gain of 3.0, the precision of ten replicate determinations on a sample containing 20 μM Mn was 1.0%, giving a detection limit three times the standard deviation of 0.6 μM Mn.

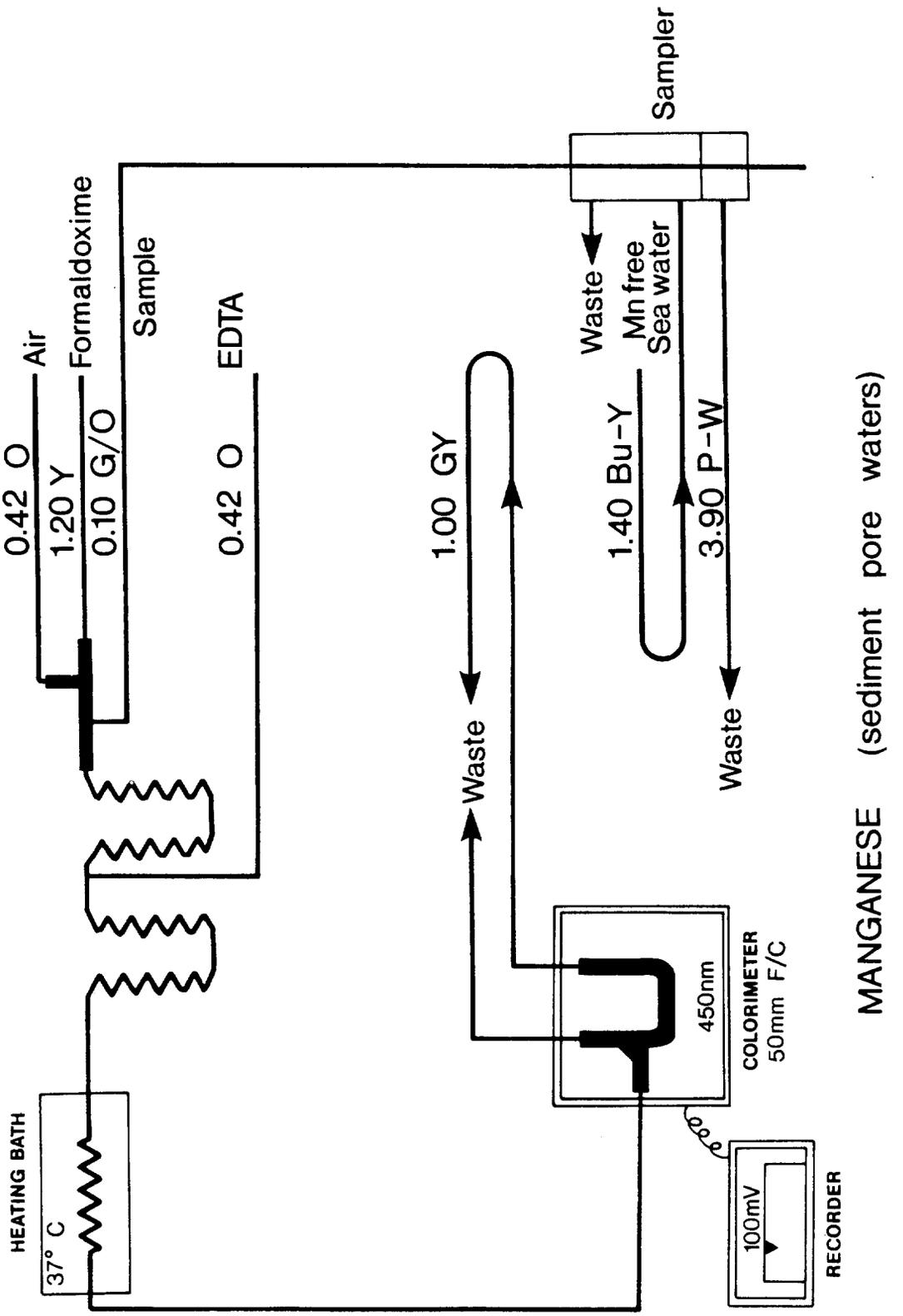

Figure 4.1 Continuous flow manifold for the determination of manganese.

5. DEVELOPMENT OF A CONTINUOUS FLOW METHOD FOR THE DETERMINATION OF MANGANESE USING FORMALDOXIME IN WATERS CONTAINING IRON

5.1 INTRODUCTION

The formaldoxime method is a widely used one for the determination of manganese in natural waters (Henricksen, 1966; Brewer & Spencer, 1971; Sawlan & Murray, 1980). It has advantages in being a very rapid method, based on simple reagents, which has sufficient sensitivity for determinations in natural waters in which dissolved manganese levels have been enhanced by anoxia. The drawback of the method is that iron also forms a complex with formaldoxime with a similar extinction coefficient.

Removal of the iron interference using EDTA was originally suggested by Goto et al. (1962) and then applied to an automated method by Henricksen (1966). Both these papers failed to explain the mechanism by which EDTA was removing the iron interference. In particular, Henricksen suggested that EDTA was ineffective at removing the iron interference at low levels of iron. This chapter reports a reinvestigation of the removal of iron interferences in the formaldoxime method in order to produce a method in which iron interference could be removed reliably.

5.2 EQUIPMENT AND REAGENTS

5.2.1 Analytical

Reagent-grade chemicals were used. A Chemlab continuous-flow analyser was used for the development of the automated method. A Pye SP500 spectrophotometer fitted with a 4 cm path length cuvette was used for measurements of the absorption spectra of the iron and manganese formaldoxime complexes and kinetic measurements of colour development.

5.2.2 Reagents

Formaldoxime solution (Stock): Dissolve 4 g of hydroxyl ammonium chloride (hydroxylamine) in 60 ml distilled water. Add 2 ml of 37% formaldehyde solution and make up to 100 ml. This solution can be stored for several months.

Working reagent: Dilute 4.5 ml stock formaldoxime solution in 200 ml distilled water. Add 9 ml of 10% (v/v) ammonia solution. Mix well, add 0.5 ml Brij 35 solution (25% w/v) and make up to 250 ml with distilled

water. EDTA solution: dissolve 10 g ethylene diamine tetra acetic acid disodium salt in 100 ml distilled water. Hydroxyl ammonium chloride (hydroxylamine) solution: dissolve 20 g in 100 ml distilled water.

5.3 SIMPLE MANIFOLD

Manganese reacts rapidly with formaldoxime to give an orange-red coloured solution. If a single reagent addition method is used following the recommendation of Brewer and Spencer (1971), manganese can be determined using a continuous flow analyser with the simple manifold shown in Figure 3.1. Using such a manifold, the reproducibility of the method was determined and its sensitivity to variations in the pH of the mixed reagent and dissolved iron concentration were determined.

5.3.1 Results

Using the manifold in Figure 3.1, the manganese method is linear up to a concentration of 60 μM. The precision for ten determinations on a solution containing 20 μM manganese was 1%, a standard deviation of 0.2 μM. Under the same conditions, a solution containing 100 μM iron produces an interference equivalent 4.7 μM of manganese.

5.4 METHOD DEVELOPMENT

The first step in developing a method for reducing the degree of iron interference was to compare the absorption spectra of the iron and manganese formaldoxime complexes. Our measurements are similar to those of Goto et al. (1962). What these measurements did reveal was that formation of the iron complex is much slower than that of the manganese complex. At pH 9.9, formation of the iron formaldoxime is essentially complete only after two and a half hours, and 100 μM solution of Fe has an absorbance of 0.17. At the same pH, formation of the manganese formaldoxime complex is complete in less than a minute and 100 μM Mn has an absorbance of 0.405.

Measurements were made of the amount of colour formation at different pHs, adjusting the pH of the formaldoxime solution by the addition of hydroxylamine solution. The results shown in Table 5.1 show that formation of the manganese complex is more sensitive to changes in pH than the formation of the iron complex. Simply reducing the pH of a single mixed reagent cannot be used as a means of reducing the amount of iron interference. Addition of 4 ml of 10%

EDTA solution to the working formaldoxime solution (and then adjusting the pH back to 9.3 with ammonia solution) gives a mixture which allows neither the manganese nor the iron formaldoxime complex to form.

5.4.1 Discrete sample measurements

Experiments to distinguish if both hydroxylamine and EDTA were required to bring about the reduction in iron interference as reported by Goto et al. (1962) and Henricksen (1966) were initially carried out on discrete samples. This allowed the measurements to be made at different times after the start of the reaction. Tables 5.2 and 5.3 present the results of observations made by forming the iron and manganese complex from 12 ml of working reagent solution and 1 ml of iron on manganese-spiked acidified sea water, and then after two minutes adding 4 ml of hydroxylamine or EDTA solutions of various dilutions to give the final pH recorded in the tables. Initially, the measurements were made of the effects of adding the hydroxylamine solution after formation of the manganese complex; the results of measurements taken 5 and 100 minutes after addition of the hydroxylamine are shown in Table 5.2. There is obviously considerable hysteresis in the kinetics of the formation and decomposition of the manganese formaldoxime complex. Once formed, it appears to be stable at pHs above 7. Addition of EDTA solutions has at the same pHs a similar effect to the addition of hydroxylamine. This suggests that the decomposition of the manganese formaldoxime complex is principally controlled by the pH of the solution.

For iron (Table 5.3) there is a significant difference in the effects of hydroxylamine and EDTA on the iron formaldoxime complex. The effect of adding hydroxylamine effectively only acts by lowering the pH of the solution so that its influence on the stability of the iron and manganese complexes is similar. However, the chelating ability of EDTA enhances decomposition of the iron complex in the pH region where the manganese formaldoxime complex is still stable.

A number of measurements were made of the rate of decomposition of iron and manganese complexes after the addition of either hydroxylamine or EDTA as a second reagent. Typical results are shown in Figure 5.1. This figure shows that, below pH 8, the change in pH caused by the addition of the second reagent initially causes a rise in the amount of iron formaldoxime complex formed. At a laboratory temperature of 20°C breakdown of the iron formaldoxime complex by EDTA at pH 7.7 is effectively complete after 25 minutes. These measurements indicate that, for the addition of a second reagent to be successful, sufficient

time has to be allowed after its addition for decomposition to occur. This was put into effect in building a continuous-flow manifold by running the reacting solution through a heating bath (37°C) after the addition of the second reagent.

5.5 TWO-REAGENT MANIFOLD

The manifold shown in Figure 4.1 was constructed. A 5% EDTA solution is used and this gives a final pH of 7.7. Using this manifold, interference from 100 μM Fe is undetectable and the interference due to 1 mM Fe is reduced to being equivalent to less than 5 μM Mn. The results of measurements made, with and without EDTA addition and with and without a heating bath, are given in Table 5.4.

Although iron interference is not completely removed using this manifold, this design is adequate for use on natural waters. Levels of iron in excess of 100 μM are very rarely encountered.

5.6 SUMMARY

Henricksen (1966) and Goto et al. (1962) suggested that, for effective breakdown of the iron formaldoxime complex, the addition of both hydroxylamine and EDTA was necessary. We have looked at the process in greater detail than they did. We conclude that they suggested both EDTA and extra hydroxylamine be used because they were unaware of the controlling effect of pH on the stability of the two complexes.

The reaction mechanisms involved in the formation and decomposition of both the manganese and iron formaldoxime complexes are not reversible in terms of the effect of pH nor in terms of competitive complexation of the metals with EDTA.

Manganese

1. Formation of the manganese complex at all pHs where it is formed is rapid and complete within one minute.
2. Destruction of the complex once formed by lowering the pH is slow.
3. Addition of EDTA before the formaldoxime complex is formed prevents formation of the formaldoxime complex.
4. Addition of EDTA after formation of the formaldoxime complex does not appear to enhance the rate of decomposition of the formaldoxime complex above the rate achieved by lowering the pH.
5. The equilibrium constants (K_1) given in Sillen and Martell (1970) for

complexation with EDTA are: Mn(II) 14.04, Fe(II) 14.2, Fe(III) 25.1.

Iron

1. Formation of the iron complex appears to take place by two mechanisms: an initially rapid one followed by a slower one. The initial step is proportional to the amount of iron present and is about 10% of amount of colour formed after $2\frac{1}{2}$ hours.
2. Addition of iron as iron (III) instead of iron (II) decreases the amount of initial colour formation and subsequent colour development is at a slower rate.
3. Destruction of the complex once formed by lowering the pH is slow.
4. Addition of EDTA before the formaldoxime complex is formed prevents formation of the formaldoxime complex.
5. Addition of EDTA after formation of the formaldoxime complex accelerates the decomposition of the iron formaldoxime complex relative to lowering the pH with hydroxylamine. This occurs after a delay period during which the absorbance of the solution continues to increase.

5.7 CONCLUSION

Based on the above observations, we would suggest that EDTA is able to remove iron interference by complexing with iron as Fe(III).

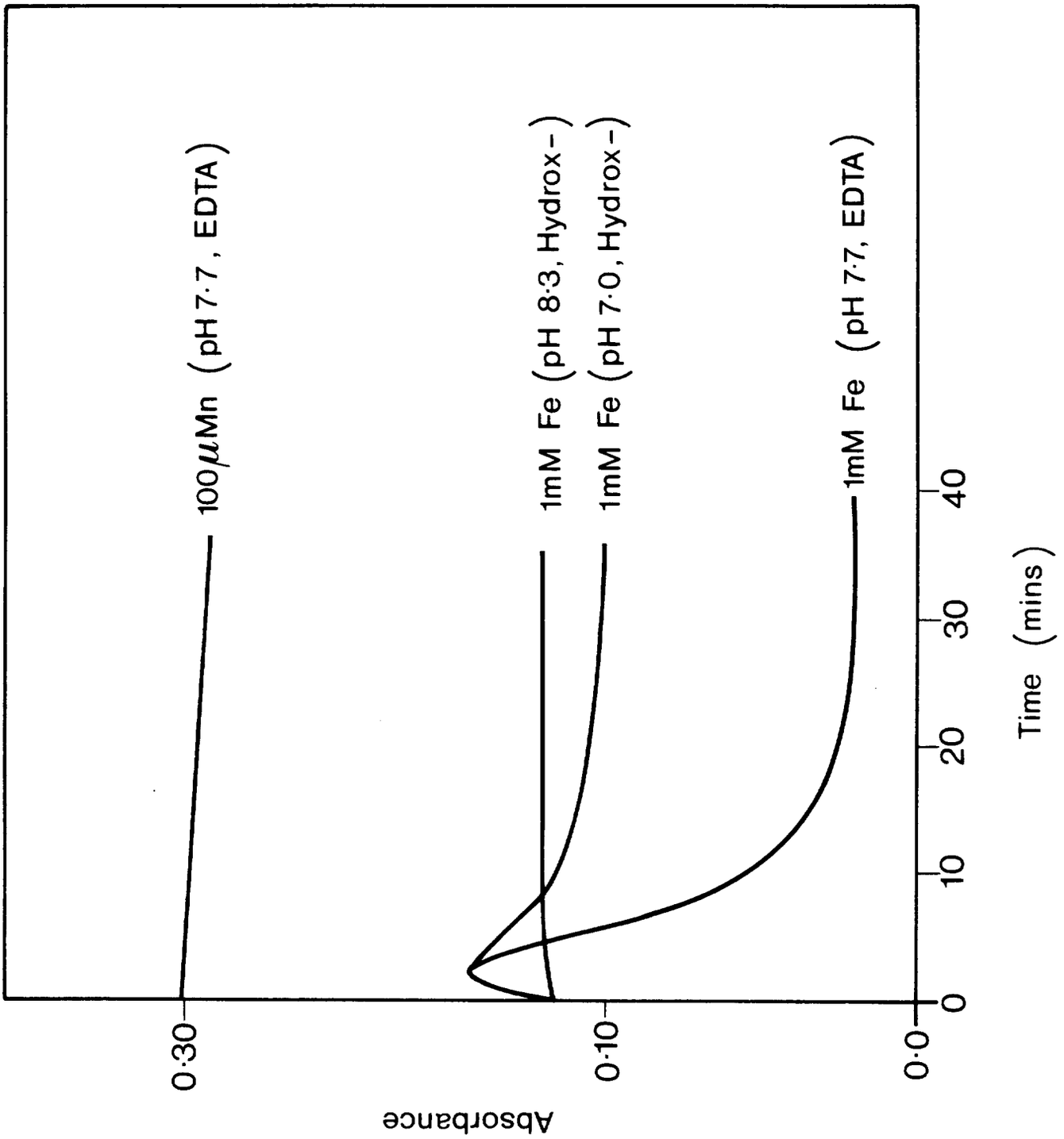

Figure 5.1 Variation in the absorbance of solutions containing the iron or manganese formaldoxime complex initially formed at pH 9.9, and then perturbed by the addition of hydroxylamine or EDTA solution.

TABLE 5.1 - Peak heights produced by solutions containing 80 μM Mn, or 1 mM Fe reacting with formaldoxime solutions of different pH, using manifold shown in Figure 3.1

Peak Height (cm)		pH
Mn	Fe	
Not detectable	1.9	4.7
Not detectable	2.2	5.8
Not detectable	3.0	7.03
9.2	4.8	8.69
11.5	5.6	9.37
11.8	6.0	9.93

TABLE 5.2 - Effect of reducing the pH of the reaction mixture after formation of the manganese formaldoxime complex at pH 9.9. pHs listed below are after addition of hydroxylamine

pH	Absorbance	
	After 5 minutes	After 100 minutes
9.86	0.318	0.332
9.42	0.318	0.332
8.96	0.321	0.323
7.67	0.289	0.286
6.72	0.260	0.223
6.47	0.242	0.136
6.30	0.227	0.050

TABLE 5.3 - Effect of EDTA on the absorbances of the Fe and Mn formaldoxime complexes, added after complex formation at pH 9.9

pH	Mn Absorbance		Fe Absorbance	
	5 minutes	60 minutes	5 minutes	60 minutes
9.9	0.342	0.341	0.166	0.309
7.4	0.278	0.249	0.065	0.007
7.2	0.267	0.196	0.032	0.005
6.6	0.215	0.189	0.011	0.007
6.3	0.213	0.189	0.014	0.007

TABLE 5.4 - Comparison of the peak heights measured for formation manganese and iron formaldoxime complexes on the manifold shown in Figure 4.1, with and without the addition of EDTA and with and without heating

Metal concentration -->	100 μM Mn	100 μM Fe peak heights (cm)	1 mM Fe
No heating			
No EDTA	14.6	0.9	6.3
EDTA	10.1	0.2	1.8
Heating bath 37°C			
No EDTA	15.2	1.5	8.4
EDTA	8.6	Not detectable	0.4

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