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A report on the Development of Methods for:-

(I) the shipboard colorimeteric determination, of iron and manganese

(II) maintaining of soluble ferrous iron and manganese in solution in anoxic porewaters.

(III) extraction of sediment porewaters by use of a centrifuge on board ship

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Introduction

We wish to study the distribution of dissolved trace metals in marine sediments both to understand the processes by which these trace 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 sediments.

Recent work on the solid phase geochemistry of anoxic sediments has highlighted the need for porewater ferrous iron data to accompany the solid phase data[1]. Ferrous iron is difficult to determine accurately in sea water due to its sensitivity to aerobic oxidation. This study was aimed at finding a method of sampling and determining porewater ferrous iron and manganese concentrations on board ship. Previously pore water manganese[2] (along with cadmium, copper and nickel[3]) contents were determined on land by atomic absorption spectroscopy. Shipboard determinations of dissolved oxygen, alkalinity and micro nutrients[4] can and have been performed. A simple shipboard determination of ferrous iron and manganese in these pore waters will provide valuable further information to understanding the nature of sediments being sampled.

This report details methods for shipboard colorimetric determinations of manganese and iron in small samples of pore water. The detection limits for iron and manganese were 0.26μM and 0.23μM respectively with a precision of 2.6% at 5.4μM for iron and 2.4% for a 32.8μM sample of manganese.

There have been various studies made of pore water chemistry amongst the most recent are those by Sawlan and Murray[5] and Klinkhammer[6] which deal with anoxic sediments. Both studies used centrifuge techniques successfully for the extraction of pore water. We decided a similar approach would be less susceptible to oxygen contamination than squeezing techniques when applied to the piston cores to be sampled on Discovery Cruise 149 and so developed the technique described here.

Section 2

Instruments

The spectrophotometer used in these experiments for the determination of soluble iron and manganese was a Pye Unicam SP6-500 single beam visible-U.V. spectrophotometer fitted with a four cm flow cell. Absorbance spectra of iron and manganese complexes were recorded on a Beckman DB-G double beam spectrophotometer in four cm quartz cells with surface sea water as the reference.

Nitrogen for these experiments was supplied from an International Gas Services nitrogen generator coupled with a 200L gas storage cylinder. Oxidation experiments were carried out in the "crystal palace" a 500L perspex box. The centrifuge used for these experiments was an I.E.C. centra-7R refrigerated centrifuge coupled with an I.E.C. 39.6 cm diameter angle head rotor with capacity for fourteen 100ml centrifuge tubes.

Plastic ware

Syringes used were 20ml (B + D Plastipak) 60ml (Brunswick) and 30ml (Gillette). The centrifuge tubes used in these experiments were 50ml and 100 (I.E.C.). Thirteen ml screw top test tubes (Sarstedt) were used for the colorimetric determination of iron and manganese and acid cleaned prior to use[3].

Section 3

Reagents for the determination of dissolved manganese

Hydroxylamine hydrochloride "AnalaR" grade (purity not quoted)

Formaldehyde "AnalaR" grade (37% v/v) (purity not quoted)

Ammonium hydroxide "AnalaR" grade (0.000002% Mn)

Standard Manganese solution "SpetrosoL" grade (1mg/1m)

All of the above reagents were supplied by B.D.H. Chemicals, Ltd., Poole, England.

Sea water used for these experiments was English Channel surface sea water filtered through a Nuclepore filter (0.4 μm). Water used in these experiments was doubly distilled in a quartz still.

The determination of dissolved manganese

In anoxic pore waters manganese is present as dissolved Mn^{2+} at levels up to 100μM[5]. At such elevated levels it is possible to determine manganese by direct injection of sea water into a graphite furnace atomic absorption sectrophotometer. This has been done successfully at I.O.S.[2] However graphite furnace atomic absorption is a shore based technique. If shipboard determination of manganese is required then a colorimetric method is the easiest to employ.

Henriksen reported a colorimetric method for the determination of manganese in 1966[7] which was successfully adapted by Brewer and Spencer (1974)[8] for the determination of manganese in the water column under anoxic conditions. Their method is different to Henricksen's in that sulphide ions (frequently present in anoxic waters) prevented colour formation. To overcome this Brewer and Sencer mixed formaldoxime (the colour reagent) and ammonium hydroxide prior to addition to the sample rather than add them separately as Henriksen had recommended.

We have differed from Brewer and Spencer in only two respects:

(i) 0.5ml of sample is used as opposed to Brewer and Spencer's 35ml.

(ii) We have used a four cm flow cell to observe the absorbance as opposed to Brewer and Spencer's use of a 10cm cell.

Procedure

Prepare a solution of formaldoxime by dissolving 4g of hydroxylamine hydrochloride in 60ml of doubly distilled water, add 2ml of 37% formaldehyde and make up to 100ml. This solution can be stored for several months in a screw top plastic bottle.

Immediately before the determination mix in the ratio 2:1 (by volume) formaldoxime and a 10% ammonia solution. To a 0.5ml sample of pore water (acidified to pH2 previously) add 25µl of the above mixture, shake and almost immediately a red/brown colour of the formaldoxime/manganese complex will be apparent.

The sample is then sucked into the flow cell via 1/16 inch i.d. teflon tubing and its absorbance measured at 450nm where the complex exhibits a maximum in its spectra (fig.1).

Colour stability

Brewer and Spencer observed that the colour was stable for at least 30min,[8] after which time the intensity slowly increased. We investigated this property of the complex and found that the colour was stable for the first 30 minutes but in contrast slowly decreased in intensity after that (a 5% reduction over four and a half hours. Table 1). Two possible causes for this are (i) ultraviolet light is slowly destroying the complex (ii) ammonia is diffusing out of the solution and thus lowering the pH and consequently the intensity of the colour. The slow increase observed by Brewer and Spencer[8] may have been due to slow leaching of manganese from their reaction flasks.

Effect of pH

The colour formation reaction is carried out in an alkaline solution. At high pH precipitation of calcium and magnesium hydroxides can occur from seawater. Precipitation could result in light scattering and consequently non quantitative results. However to achieve colour formation the solution must be basic, addition of reagents as described above results in a solution of pH 9.09. By varying the ratios of reagents to one another in the reaction mixture the pH of the final solution can be altered. The results (fig.2) indicate that when the pH is in the range 8.7-10 (which represents a change in the ratios of the reagent of 2.5:1 to 1:2 formaldoxime:ammonia), quantitative results can be obtained.

Interference studies

As Henriksen reported[7] the principle interference is caused by ferrous iron which may be closely associated with manganese in anoxic pore waters. Ferrous iron forms a pink complex with formaldoxime (fig.3). Henriksen recommended destroying the iron complex by the action of E.D.T.A., however this is an added complication. As the ferrous iron content of these pore waters are to be determined (see later) it would be expected that a simple correction could be made if absorbance (in the presence of manganese) increased linearly with the addition of ferrous iron. Sea water acidified to pH2 was spiked to 200ug/l manganese and varying amounts of ferrous iron. The results (fig.4) indicate that there is a linear increase and so a simple correction can be made.

Comparison with graphite furnace flameless atomic absorption spectroscopy.

R.R.S. Discovery cruise 135 to the eastern equatorial Atlantic retrieved cores which were anoxic and contained elevated manganese levels. To compare the two techniques pore water squeezed from these cores which had been determined previously by atomic absorption[2] were determined colorimetrically. The samples had not been acidified as manganese (unlike iron) is not readily oxidised in sea water when out of contact with the sediment. Colorimetric determination of manganese in one core agreed well. However the other core highlighted one problem with the atomic absorption method. The two sets of data agreed well at low concentrations but diverged at higher levels with the colorimetric method giving higher results. A repeat of the colorimetric determinations gave very similar results.

A repeat of the atomic absorption determination was carried out with a dilution factor of 1:100 as opposed to 1:50 this gave results which were more consistent with the colorimetric determinations but which again significantly diverged at high levels. These samples were rediluted to a factor of 1:200. The results of these determinations did agree with the colorimetric determinations (Table 2).

These results suggest that manganese has only a limited linear range when determined by flameless atomic absorption spectroscopy which means that for accurate work a lot of tedious redilution is required, which is time consuming as standards must be made for each dilution. In this respect colorimetric determination is quicker and easier than atomic absorption.

Accuracy, detection limit blanks and linear range

Sea water spiked with manganese gave good linear results up to 50μM (fig. 5) for manganese concentrations above this we recommend dilution of samples with filtered pH2 surface sea water which is low in manganese.

The blank for this method was determined ten times in acid cleaned tubes the results gave a blank absorbance of 0.0099 which corresponds to a manganese concentration of 0.23μM. The standard deviation of this blank was 0.00367 absorbance units. We have chosen to take our detection limit as the standard deviation of the blank multiplied by three which in this case is approximately 0.011 absorbance units or 0.25μM.

To see where the blank was "coming from" the blank was determined by adding 10,20,30,40,50,60,70,100,150 and 200μl of formaldoxime/ammonia solution to 1ml of surface sea water. The results (fig.6) were corrected for dilution by multiplying the absorbance by the final volume and dividing by the starting volume, and seem to suggest that the reagents are causing the blank but that there is some manganese present in the surface sea water if only in small quantities.

To determine the precision of the method a 32.8μM spiked sea water sample was determined ten times and had a standard deviation of 0.78μM which is a relative standard deviation of 2.4%.

Section 4

The determination of dissolved ferrous iron

As with manganese anoxic conditions in deep sea sediments result in elevated ferrous iron levels. Recent work by Sawlan and Murray[5] found soluble ferrous iron at levels up to 20 μM in their highly reducing sediments.

For shipboard determination of ferrous iron the ferrozine method first reported by Stookey[9] was used. This method has beed well tried for river and boiler water samples[10] and was used by Sawlan and Murray for their iron determinations. Small modifications to Stookey's method have been made and these will be outlined below.

Reagents for the determination of dissolved iron:

Ferrozine (3-(2-pyridyl)-5, 5-di (4-phenyl sulphonate)-,2,4- triazine disodium salt trihydrate) (not assayed for iron).

Ammonium acetate - "AnalaR" grade (maximum 0.002% iron)

Ammonium hydroxide - "AnalaR" grade (maximum 0.00002% iron)

Hydrochloric acid - "AnalaR" grade (maximum 0.00004% iron)

A standard ferrous iron stock solution was prepared from "AnalaR" grade ammonium ferrous sulphate (minimum purity 99%)

All of the above chemicals were obtained from BDH Chemicals Ltd., Poole, England.

Procedure

Acid reagent solution: dissolve 0.514g of ferrozine and 10g of ammonium acetate in a small amount of water, add 50ml of concentrated hydrochloric acid after cooling make up to 100ml with doubly distilled water.

Buffer solution. Dissolve 40g of ammonium acetate in water, add 35ml of ammonium hydroxide (conc.) and dilute to 100ml with doubly distilled water.

Standard solutions: Dissolve (0.05g Fe) of ammonium ferrous sulphate in doubly distilled water and make up to 100ml, this solution contains 0.5mg/ml (8.9mM).

To make up acidified iron seawater solutions place a little sea water in a volumetric flask add 100µl of concentrated hydrochloric acid then the desired iron spike and make up to the mark with sea water this solution is now acidified to pH2 which will effectively stop oxidation of ferrous iron to insoluble ferric iron.

To determine iron place 0.5ml of standard or sample into an acid cleaned test tube and add, successively, 25µl of acid reagent solution and 25µl of buffer solution and mix well, colour development (a purple/pink colour) occurs after a few seconds. The complex exhibits a maximum in its spectra at 562nm (fig.7). The sample is then drawn into the flow cell of the spectrometer and its absorbance is measured at 562nm.

Interference studies

Stookey[9] investigated the interference of many metals upon the formation of colour and found that only monovalent copper and divalent cobalt gave feeble complexes. Stookey found that 136µM of divalent cobalt and 78µM monovalent copper when added to 1mg/l ferrous iron only produced deviations from the expected result of 5 and 15% respectively. It is unlikely that there will be any interference from these sources at the low levels of copper and cobalt present in porewaters. The metal which, like iron, is mobilised in anoxic conditions to levels which exceed 1μM is manganese. To see if manganese had any effect on the iron determinations a sample of acidified sea water containing 200μg/l iron was spiked with varying amounts of manganese up to 1.8mg/l manganese, the results (table 3) show that manganese does not interfere to any significant extent.

pH of formation

Stookey observed that the iron-ferrozine complex formed and gave stable colours in a pH range of 3-10. He does not state if the pH quoted is a sample pH or the final pH of the mixture. Stookey formed his complex by boiling the sample with acidified reagent for ten minutes and then adding buffer. We have dropped the boiling stage and found that solutions having a final pH (varied by altering complexant/buffer ratios) of 2-7 (fig.8) gave stable colours.

This difference to Stookey's observation may be a result of the confusion of how he altered his pH and to what pH he is referring to. However the difference (assuming that the pH he quotes is the final solution pH) may be accounted by one of the following (i) the boiling stage Stookey employed may aid complex formation (ii) the seawater matrix (as opposed to Stookeys ground water matrix) is causing an interference or (iii) the changed sample size is making iron oxidation more favourable in alkaline conditions.

Blanks and Contamination

The blank for this method was determined by measuring the iron content of a sample of oxic, filtered, surface sea water and was found to be 0.45μM.

To see what was causing the blank, 1ml aliquots of surface sea water samples were determined using total volumes of 20,40,60,80 and 100μl of acidified reagent and buffer. The results (fig.13) have been corrected for dilution by multiplying the observed absorbance by the total final volume (reagents+sample) and dividing by the sample volume and showed a linear relationship between reactant volume and the absorbance of the blank. Extrapolation of this plot gives surface sea water concentration of 0.045μM. The reagents are clearly contaminated. However careful pipetting can keep variations down to a minimum.

Contamination of the plastic test tubes was avoided by acid cleaning by 6N nitric acid and then 6N hydrochloric acid. When acidified sea water standards of iron were first prepared in volumetric flasks several high results were obtained (equivalent to 1 M Fe) these high results were probably caused by acid leaching of the walls of the volumetric flask so all glass ware was soaked over night in 1M hydrochloric acid prior to use.

Detection limit, reproducibility and linear range

The detection limit of this method as calculated as three times the standard deviation of the blank. The standard deviation of the blank was calculated from ten separate blank determinations. The mean blank was 0.062 absorbance units with a standard deviation of 0.0086 which is equivalent to a detection limit of 0.26μM. Precision was found by nine replicate determinations of a 5.3μM sample which gave a relative standard deviation of 2.6%.

Linear results are obtained to at least 8.9µM (500µg/l) fig.9. To obtain a molar absorptivity figure the results must be corrected for dilution (10%). Multiplication by 1.1 gives a molar absorptivity figure of 28,106[9] which compared favourably with Stookeys figure of 27,900[9] the discrepancy between these two results is only 0.74% and can be accounted for by random errors.

Differences to Stookey's method

This method is different from Stookey's in two ways. Firstly as only small pore water samples can be obtained a hundred scale reduction was made from Stookey's recommended 50ml sample. Secondly no boiling of the sample in between addition of the acidified reagent and addition of the buffer. This second change is because Stookey used it, (primarily) to introduce solid phase iron into solution as the iron in pore water samples is already dissolved this stage was dropped.

Section 5

Iron and manganese oxidation experiments

Iron oxidation reactions have been extensively studied[11,12]. Oxidation of ferrous iron was found by Stumm and Morgan at pH>5.5[13] to depend upon the rate law.

$$-d\,Fe(II)\,/dt = K\,Fe(II)\ \ OH^{-2}pO_2$$

Thus on a 100 fold increase in reaction rate would be expected for one unit increase in pH. Stumm and Morgan reported 90% oxygenation of a pH7.2 sample of ferrous iron in 30 minutes at a temperature of 20°C and a partial pressure of oxygen of 0.2 (achieved by constant bubbling of air through the sample). This would suggest that ferrous iron is highly unstable with respect to aerobic oxidation in sea water (pH 7.8).

Manganese oxidation is more complex Stumm and Morgan suggested that manganese oxidation followed the following auto catylytic rate law at a pH>8.5.

$$-d\,Mn(II)\,/dt = K_o\,Mn(II) + K\,Mn(II)\ \ MnO_2\ \ OH^{-\,2}pO_2$$

Oxidation of manganese in pore waters removed from the sediment was not expected as (i) the pH is not high enough and (ii) no solid phase manganese dioxide is present to "catalyse" the reaction. However it was thought that iron (III) hydroxide produced by the oxygenation of ferrous iron could co-precipitate manganese.

Iron oxidation rate experiments

Initial experiments on the oxidation rate were carried out using the following procedure:

Prepare 90ml of sea water to the required pH (by addition of sodium carbonate), add the spike, start clock, quickly make up to the mark with sea water shake quickly to ensure thorough mixing. Transfer approximately 20ml to a plastic beaker. Draw into a syringe and push the water, through a swinex filter holder containing a nuclepore filter (discarding the first few mls), into a test tube containing 10μl of concentrated hydrochloric acid. Take the time when half the sample is in the test tube. The filters block up very quickly when iron (III) hydroxides have formed leaving a faint yellow colour on the filter, and consequently, in some cases only eight or so mls were obtained.

Though this method is not perfect as we shall see several good results were obtained. The main flaw in this procedure is the changing volume surface area ratio for different samples.

We decided to adjust the pH of sea water (pH 7.78) to two higher pHs by addition of sodium carbonate. As fig 10 shows iron (II) in seawater is oxidised very rapidly with 90% oxidation occurring within twenty minutes. As expected at higher pH's oxidation is much quicker with 90% oxidation occurring within between five and eight minutes for pH's of 8.22 and 8.48 respectively. The rates are much lower than expected possibly because air was not bubbled through the system fully as in Stumm and Morgan's work.

Having observed "the worst conditions we were likely to encounter" we decided to carry out similar experiments in atmospheres containing different amounts of oxygen inside the "crystal palace".

The "crystal palace" is a 500L perspex glove box specially designed for work with deep sea sediments. It is connected to a nitrogen supply by means of a two way gas tap with other gas taps inside for either exit of gases to prevent a pressure build up or to fill an air lock. An oxygen meter is connected to the outlet tap to monitor the quality of air leaving the "crystal palace". Previously the "crystal palace" had been filled with nitrogen (from a nitrogen generator) by passing a flow of nitrogen through the "crystal palace" for a day or so by which time the O_2 level was typically down to 0.5-0.2% (from 21%). This is a very time consuming process and so a new approach was tried whereby we filled two large glove bags inside the crystal palace (taking up 70-80% of the total volume) then deflated the glove bags and then reflated again until the level was approximately 1% O_2 when we changed from generated nitrogen (typically 0.2-0.1% O_2) to "white spot" nitrogen, which was described as oxygen free, until the oxygen level was down to 0.1%. A typical time taken for this to happen is four hours (in total) which compares favourably with the time taken in the old manner. Table 4 gives a theoretical number of bags full of nitrogen required to get the O_2 level down to 0.1%.

In order to make the experiments more realistic anoxic sea water must be used. To produce this we bubbled "white spot" nitrogen through our sea water for at least 1 hour inside the crystal palace. Twenty ml of this degassed water was sucked into a syringe and from there transferred to a plastic beaker where it was again degassed for about 30 seconds, then a spike added and the clock started. Though this is a less accurate method of preparing standards the advantage of a constant volume/surface area ratio for each of the five samples was thought to outweigh this disadvantage.

In a 0.15% O_2 atmosphere iron oxidation was "only" 10% after two hours (table 5a) however when a 2% O_2 atmosphere was used rapid oxidation (90% in 10 minutes), (table 5b) occurred. The 2% O_2 atmosphere was chosen as this was the maximum concentration of oxygen present in the "crystal palace" during squeezing for recent geochemical cruises and this result suggests that a 2% O_2 atmosphere is not pure enough to take "real" porewater samples containing ferrous iron.

Reduction of the O_2 to 0.5% gave approximately 60% oxidation in ten minutes (table 5c), though this was not as fast as oxidation in a 2% O_2 atmosphere this degree of oxidation is still unacceptable. Samples covered in para-film proved susceptable to oxidation to a similar extent to uncovered samples in a 0.5% O_2 atmosphere (table 5d) though the degree of oxidation was variable possibly reflecting the efficiency of covering. To attempt to see if a more efficient covering would result in less oxidation of samples the beakers were covered with cling film rather than para-film. The results (table 5e) show severe contamination (probably from the old cling film used) but little evidence of oxidation.

To see if samples could be stored in working conditions we placed iron samples in syringes in a 0.1% O_2 atmosphere in capped and uncapped syringes. The results (Tables 5F, G) were encouraging the capped syringe samples had suffered only very slight oxidation and open syringes oxidation to a slightly greater extent. The slight oxidation of capped syringe samples probably occurred because (i) degassing was not totally effective and (ii) oxidation could occur when samples were in their beakers rather than in the syringes.

Finally as an operational test spiked sea water was placed in centrifuge tubes four samples just capped and four capped and taped round the top. The tubes were filled in a 0.1% o_2 atmosphere then had the air inside the tube flushed with "white splot" N_2, left in the crystal palace for 1 hour, removed placed in the centrifuge for 1 hour, replaced in the crystal palace and sampled as described above. The results show slight oxidation, as was observed for capped syringes, probably caused by the reasons outlined above. However the level of oxidation was only about 10% with little difference between taped and untaped tubes.

Stumm and Morgan reported that a 10-fold increase in reaction rate was observed for a $15^{o}C$ temperature increase, all of the above experiments were carried out at room temperature, on board ship all sampling and centrifuging will be carried out at $2^{o}C$ which should reduce oxidation significantly. As sediments are more impervious to gases than water samples and as the sediment samples will be fully anoxic, oxygen penetration and oxidation of "real" samples should be much less.

However the only way to tell how effective these measurements are is real sampling which will be carried out on RRS Discovery cruises 147 and 149 in the east North Atlantic where anoxic sediments are expected to be encountered.

Manganese coprecipitation by oxidation of ferrous iron

As already stated manganese oxidation is not expected in sea water however a series of experiments were started and showed that no significant oxidation occurred below pH9 (Table 6).

However ferric iron hydroxides, on precipitation, were thought to be able to coprecipitate manganese. Our results (Table 7) showed that ferric hydroxide precipitation did not coprecipitate manganese.

Section 6

Pore water sampling using a refrigerated centrifuge

At present at I.O.S. pore water samples are obtained by squeezing sediment. This method involves loading pistons with 100-200mls of sediment in the "crystal palace" removing them and squeezing them in a hydraulic jack in a refrigerator. This method is thought to be more susceptable to oxidation than centrifuging would be.

The most recent interstitial water iron data has been obtained by Sawlan and Murray[5] and Klinkhamer[6], both studies utilised refrigerated centrifuges.

The centrifuge used for these experiments was fitted with a 39.6cm diameter angle head rotor to allow greater separation at lower centrifuging speeds. Lower centrifuge speeds are an advantage in that less loading is caused on the central bearings as the ship rolls and pitches.

The main problem found with shipboard centrifuging has been that balancing centrifuge tubes is very difficult on board ship as scales (which would not work very well) would need to be placed inside the "crystal palace".

As the sediments are of similar density down core it was decided to "balance" the centrifuge tubes by volume of sediment. This is achieved by using a syringe with the end cut off, use of which will be discussed later.

Efficiency of centrifuging

Samples of red pelagic clay (from Discovery Cruise 125 Station 10400)[13] fine grained carbonate clays (from Discovery Cruise 129 Station 10554 G.M.E.)[14] and a coarse grained carbonate clay (from Discovery Cruise 135 Station 10702 Kings Trough flank)[15] were used for centrifuging experiments.

The sediments used were stored in large, sealed, plastic boxes in a refrigerator at 2°C. Water loss, due to dewatering and evaporation may have occurred during collection and storage and as such the results obtained may show a lower efficiency than may be obtained with "real" sediments on board ship.

We wished to know (i) how long we need to centrifuge sediments to obtain samples of useable volume and (ii) how centrifuging compares with squeezing in terms of efficiency and contamination.

The water content of the G.M.E. sediment sample was found by drying to constant weight. A water content of 65% was found. On board ship the fine grained G.M.E. sediment was found to be the most difficult to squeeze - due to its fine grain size and so we decided to carry out our efficiency experiments on this "difficult" sediment. 36ml samples were centrifuged for 30,60,90 and 120 minutes the results (Table 8) show efficiency of extraction (water extracted/water content x 100%) vs time. Maximum extraction appeared to be achieved after 90min. However after 30min extraction efficiency was close to maximum. We decided to centrifuge for 30 minutes then shake the sample to remove dried sediment from the inside of the centrifuge tubes which were causing flocs of sediment to appear in the pore water sample. These flocs are removed by filtration but tended to block up the filters making filtration difficult. After this the samples are again placed in the centrifuge and recentrifuged for another ten minutes this gives a total centrifuge time of 40 minutes. This procedure appeared to reduce the problem of flocs.

To compare centrifuging with squeezing all three sediments were squeezed and centrifuged at 2°C and room temperature and the water content of the resultant sediments determined. The results (Table 10) show, as expected, that squeezing is more efficient due to the large pressure applied by this method. Also as a much larger sediment sample can be used volumes of pore water obtained are much larger though more water is discarded during squeezing than centrifuging.

As these sediments were all oxic the iron and manganese contents of the pore waters will be negligable. Extracted water was analysed by continuous flow analysis for silicate and nitrate, silicate because of its temperature dependence and nitrate because previously squeezed samples showed nitrate contamination.

Results (Table 10) showed the expected temperature elevation for silicate with centrifuged samples showing higher levels of silicate at room temperature probably due to the smaller centrifuge samples reacting to temperature differences more quickly.

Nitrate analyses show slight elevation for squeezed samples with respect to centrifuged samples which is probably due to the Whatman 542 paper prefilter which has been shown to produce nitrate contamination though this was thought to have been minimised by sea water washing.

Sediment sampling

Sediment samples are likely to be obtained from 5 different bulk sediment samplers; the Kastenlot (long box corer), IOS box corer, S.M.B.A. multicorer, IOS Driscol or porewater sampler core (IOS PWS MkII).

Use of a "cutoff" syringe for constant volume centrifuge balancing.

Balancing centrifuge tubes on board ship is both difficult and time consuming if weight of sediment methods are used. As the sediments are usually fairly constant in density centrifuge tubes can be balanced by volume. The easiest way to deliver a fixed volume of sediment is to use a syringe with the end cut off.

Kastenlot cores are the easiest to sample, as 5cm diameter subcores collected on deck can be further subcored using a syringe as a piston corer in the oxygen free atmosphere of the crystal palace. Gillette 30ml syringes are the easiest to use as they have a flat rubber plunger and fit inside 100ml centrifuge tubes.

A different loading procedure is needed for piston, box and S.M.B.A. cores. As the sections of these cores are "disk shaped" rather than "tube shaped" the syringes cannot be loaded by driving a syringe into the sediment slice. Instead portions of the slice are placed on the end of a vertical syringe with the piston near the top using a spatula. The plunger is moved down a few ml and more sediment placed on always ensuring that no air pockets are formed. The procedure is similar to putting ice cream on a cornet.

These two procedures have been carried out with success on a centrifuge with a balancing sensitivity of 1g across the centrifuge. Lifting the centrifuge through 45° at the side and front (to simulate pitch and roll) did not cause the centrifuge to stop due to incorrect balancing. However as the pitches and rolls cause great strain on the bearings it is advisable to place the centrifuge in a position where ship movement is at a minimum (on board Discovery this is the Gravimeter room). After centrifuging the centrifuge tubes are placed in a glove bag and pore water samples decanted into a (syringe fitted with a Swinex filter holder fitted with a Nuclepore 0.4μm filter and a paper prefilter), and filtered into a tube containing HCl to lower the pH to 2 to preserve the samples.

Section 7

Field Trials

The above system for sediment pore water extraction was carried out on cores obtained using the S.M.B.A. multicorer on R.R.S. Discovery Cruise 147. 8 cores from 5 stations in the Porcupine Seabight were sectioned at 1.5cm intervals and loaded into centrifuge tubes using the icecream cornet technique. Sediment sample volumes of 30ml were used throughout, and 10 samples could be extracted from one 15cm core. However if 11,9 or any odd number of samples were obtained a "dummy" sample made up of sediment waste can be made to balance the odd centrifuge tube. Pore water samples were routinely obtained on board ship with no balancing problem.

As expected extracted pore water volumes decreased at depth though it is thought that the sediment encountered at 15cm in the Porcupine Seabight was as "stiff" as would be encountered at depth (>5m) using a piston corer in deep sea sediments.

Sample volumes are given in tables 11A to E the 3-5ml of pore water obtained is of sufficient volume to allow determinations of silicate, phosphate, nitrate, manganese and ferrous iron (dilution may be required if sample volumes are less than 3ml, surface sea water being used as the dilutant) though not enough to allow copper, cadmium and nickel to be determined. It is important to note that the pore water samples for iron and manganese must be kept separate from samples for micro nutrients for two reasons, firstly acidification of nutrient samples affects the analysis and secondly the vials for nutrient analysis must not be acid cleaned (nitric acid has a tendency to attach nitrate to the walls of the vials) whereas it is important that the sample vials for trace metals are acid cleaned to remove contamination.

From the 8 cores 72 pore water samples were obtained the results of the determination of micronutrients and trace metals (Fe and Mn) are given in tables 11A to E. Five cores were oxic throughout and showed no sign of manganese or ferrous iron remobilization, however cores 11108#1, 11108#12 and 11112#3 became anoxic at approximately 9cm, 5cm and 5cm respectively. The anoxic (oxic boundary was marked by a colour change buff/grey in the sediment which coincided with the remobilization of iron in all three cores. As can be seen (table 11D) core 11108#12 has a very erratic iron profile. The reason for this was forgetting to flush the centrifuge tubes out with nitrogen before placing sediment inside them. This caused oxidation of the pore water iron giving the observed noisy signal. Cores 11108#1 and 11112#3 were sampled using nitrogen flushed centrifuge tubes and gave reliable low noise iron profiles (apart from the bottom sample of core 11108#1 which may have suffered atmospheric oxidation).

The addition of ferrous iron profiles in pore waters to I.O.S's other pore water data is a very valuable addition, iron is an important redox sensitive element and can be associated with sediment colour changes at anoxic boundaries. This was borne out in cores 11108#1 and #12 and core 11112#3 where the pore water sample below the buff/grey interface contained remobilised iron.

One problem did, however, become apparent. Cores from stations 11108 and 11112 contained dissolved iron and manganese in the top porewater sample. This is highly improbable and the fault was found to be a "memory" effect.

The memory effect is caused by droplets of standard being left in the tubing and cell prior to the introduction of the first sample. This can be minimised by sucking standards and samples very slowly into the cell. This can be difficult as acid, from the samples, attacks the rubber plunger making the syringe stick. The easiest way to overcome this is to lightly grease the plunger frequently.

Following Discovery cruise 147 the methods described in this report were given a more thorough testing on Discovery cruise 149, which was a purely geochemical cruise to the Madeira Abyssal Plain. On this cruise over 700 porewater samples were obtained and had their iron, manganese, silicate, nitrate and phosphate contents determined.

However one problem did present itself in the centrifuging techniques described. When sampling a piston core at least two people are required to fill syringes with sediment. We found that two people tend to fill syringes to differing extents and consequently the centrifuge tubes didn't balance. This lack of consistency in balancing the centrifuge tubes was further increased by the changing density of the sediments over the core length (up to 12m).

The problem was overcome by the use of a electronic pan-balance (University of Cambridge) to identify centrifuge tubes of equal weight. Results from one piston core (station 11143) are presented in table 12.

The above procedures for pore water extraction and subsequent ferrous iron and manganese have been carried out successfully at sea with no need for major alterations of technique. The methods are simple and gave good "low noise" results.

Acknowledgement

We are grateful for the assistance of:- Dr. Sarah Colley for squeezing sediments used in the comparison with centrifuge techniques described in this report, and leading the porewater sampling team from the front on cruise 149. Roger Wilson and John Thomson for their encouraging appreciative reception of the data we achieved using the methods reported here; Richard Lampitt, Dave Billett and Jim Watson for supplying cores on cruise 147; Hilary Kennedy for the loan of the electronic balance on cruise 149.

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Table 1 - Stability of the manganese-formaldoxime complex

Time	Absorbance
1 min	0.218
20 min	0.218
120 min	0.214
180 min	0.212
270 min	0.208

Table 2 - A comparison of colourimetric determination of manganese with flameless atomic absorption highlighting the problem of the flameless A.A.'s linear range. Samples from core 8K, station 10702.

Mn Found (µM)

Sample	Colourimetric determination		Flameless AA		
	1	2	Dil 1/50	Dil 1/100	Dil 1/200
145	<0.25	<0.25	0.1	0.2	-
146	<0.25	<0.25	0.07	0.1	-
147	5.0	4.2	3.33	4.0	-
148	11.7	10.5	8.59	10.1	-
149	17.4	16.9	11.23	17.8	-
150	22.5	21.8	14.96	21.0	-
152	33.3	31.6	19.94	28.5	30.1
153	36.2	35.4	24.78	31.5	34.75
154	41.2	43.1	25.2	37.5	43.1

Table 3 - Interference of Manganese on Iron determinations

Iron spike (µM)	Manganese spike (µM)	Absorbance
3.6	0	0.415
3.6	4.7	0.410
3.6	9.5	0.418
3.6	18.0	0.410
3.6	32.7	0.420

Table 4 - Theoretical number of repeated gas bag fills required to reduce the oxygen atmosphere inside the crystal palace to 0.1% (a function of the volume occupied by the bag).

volume of bag (crystal palace - 500 l.)	Number of "bag fills" to reduce O_2 level to 0.1%
50%	8
60%	6
70%	5
80%	4
90%	3

Table 5A - Oxidation of a 6.25μM iron sea water sample in a 0·15% oxygen atmosphere.

Time (min)	Iron found (μM)
2	6.16
4	6.34
14	5.93
49	5.71
135	5.54

Table 5B - Oxidation of a 5.36 μg/l iron sea water sample in a 2% oxygen atmosphere.

Time (min)	Iron found (μM)
2	3.50
5	4.54
10	0.48
21	0.21
52	0.14

Table 5C - Oxidation of a 5.36 μM iron sea water sample in a 0.5% oxygen atmosphere.

Time (min)	Iron found (μM)
2	3.46
6	2.11
8	2.54
18	2.29
30	1.20

Table 5D - Oxidation of a 5.36 μM iron, in sea water, sample covered by parafilm in a 0.5% oxygen atmosphere

Time (min)	Iron found (μM)
2	2.96
8	1.46
15	2.14
27	1.07
50	1.50

Table 5E - Oxidation of a 5.36 μM iron, in sea water, sample covered by cling film in a 0.5% oxygen atmosphere.

Time (min)	Iron found (μM)
1	6.61
9	6.16
13	5.50
22	7.46
34	5.29

Table 5F - Oxidation of a 5.36μM iron, in sea water, sample stored in uncapped syringes in a 0.5% oxygen atmosphere.

Time (min)	Iron found (μM)
2	5.46
10	5.38
23	5.18
42	4.18
55	3.21

Table 5G - Oxidation of a 5.36 μM iron, in sea water, sample stored in capped syringes in a 0.5% oxygen atmosphere

Time (min)	Iron found (μM)
3	5.18
11	5.04
25	5.02
37	5.25
50	5.00

Table 6 - Stability of porewater manganese w.r.t. atmospheric oxidation (5.45 μM Mn sample pH8.9).

Time (min)	Mn found (μM)
1	5.55
6	5.47
30	5.62
60	5.49
120	5.45

Table 7 - 5.45 μM Mn sample pH8.5 + 5.36 μM Ferrous iron.

Time (min)	Mn found (μM)
4	5.56
30	5.42
60	5.51
120	5.60

Table 8 - Efficiency of centrifuging (100% x water removed/total water content of sediment) for a GME clay.

Time (min)	Efficiency (%)
30	27,32,33,34
60	35,37,39,41
90	39,42,43,44
120	41,43

Table 9 - Porewater squeezing and centrifuging - a comparison

	Water content of "spent" sample	
Sample	Squeezed	Centrifuged
10400	40.1%	44.0%
10400	36.4%	42.1%
10554	38.5%	55.1%
10554	46.2%	56.4%
10702	36.4%	43.6%
10701	37.0%	45.5%

Table 10 - Squeezing and centrifuging: A comparison w.r.t. nutrient contamination.

Station	Temp.	Squeezed SiO_4 (µM)	Centrifuged SiO_4 (µM)	Squeezed NO_3 (µM)	Centrifuged NO_3 (µM)
10400	2°C	57.3,55.9	70.8,60.3	14.5,15.1	14.8,15.1
10400	20°C	76.0,73.2	72.6,91.3	17.3,16.2	16.8,15.1
10554	2°C	56.1,57.8	58.1,57.5	1.4,1.1	1.4,0.8
10554	20°C	69.6,68.4	75.7,81.8	3.1,2.8	2.2,3.1
10702	2°C	185.8,194.4	191.9,178.5	2.8,1.1	0.6,0.6
10702	20°C	196.1,200.6	226.8,209.5	2.5,2.5	1.7,1.4

Table 11A - Porewater results from Station 11105 Discovery Cruise 147

Core#3 water depth 4330m

Core description: pale buff clay throughout ∿ 16cm long.

Depth of section	Sediment Volume	Porewater extracted	SiO$_2$ µM	PO$_4$ µM	NO$_3$ µM	Mn µM	Fe µM
0-1.5 cm	30ml	6ml	115	1.1	31.9	<0.25	<0.25
1.5-3 "	"	4.5ml	157	1.2	25.2	"	"
3-4.5 "	"	4ml	188	1.7	28.2	"	"
4.5-6 "	"	2.5ml	208	2.0	25.1	"	"
6-7.5 "	"	2.25ml	-	2.2	25.2	"	"
7.5-9 "	"	2ml	-	2.3	25.2	"	"
9-10.5 "	"	2ml	-	2.6	23.5	"	"
10.5-12 "	"	1.5ml	-	2.9	16.8	"	"
12-13.5 "	"	1.5ml	-	2.9	16.8	"	"
13.5-15 "	"	1.5ml	-	3.2	16.8	"	"

Core#2

Core description: As above

Depth of section	Sediment Volume	Porewater extracted	SiO$_2$ µM	PO$_4$ µM	NO$_3$ µM	Mn µM	Fe µM
0-1.5 cm	30ml	8ml	110	2.1	15.3	<0.25	<0.25
1.5-3 "	"	5ml	150	1.3	25.2	"	"
3-4.5 "	"	4ml	179	1.6	25.1	"	"
4.5-6 "	"	4ml	211	1.8	30.5	"	"
6-7.5 "	"	2ml	224	-	-	"	"
7.5-9 "	"	1.75ml	221	2.1	25.1	"	"
9-10.5 "	"	1.75ml	236	2.3	26.8	"	"
10.5-12 "	"	1.75ml	140	1.4	25.1	"	"
12-13.5 "	"	1.75ml	222	2.8	26.8	"	"
13.5-15 "	"	2ml	249	3.1	28.2	"	"

Table 11B - Porewater results from Station 11106 Discovery Cruise 147

Core #6 water depth

Core description: pale buff clay with black mottling at approximately 5cm, 14cm long.

Depth of section		Sediment Volume	Porewater extracted	SiO_2 μM	PO_4 μM	NO_3 μM	Mn μM	Fe μM
0-1.5	cm	30ml	11ml	165	2.24	25.6	<0.25	<0.25
1.5-3	"	"	8ml	232	2.30	25.0	"	"
3-4.5	"	"	6ml	292	1.74	28.2	"	"
4.5-6	"	"	45ml	329	3.42	29.0	"	"
6-7.5	"	"	3.5ml	345	3.60	27.8	"	"
7.5-9	"	"	2.5ml	344	3.58	26.2	"	"
9-10.5	"	"	2.5ml	371	4.02	24.0	"	"
10.5-12	"	"	2ml	377	4.26	21.6	"	"
12-13	"	24ml	1ml	407	9.48	40.4	"	"
135-14	"	24ml	1ml	398	4.80	22.4	"	"

Core #2

Core description as above

Depth of section		Sediment Volume	Porewater extracted	SiO_2 μM	PO_4 μM	NO_3 μM	Mn μM	Fe μM
0-1.5	"	30ml	10ml	144	1.88	30.0	<0.25	<0.25
1.5-3	"	"	8ml	235.8	2.26	43.0	"	"
3-4.5	"	"	4ml	285.8	1.66	54.8	"	"
4.5-6	"	"	35ml	329.6	3.0	32.6	"	"
6-7.5	"	"	3.5ml	352	3.46	30.8	"	"
7.5-9	"	"	3ml	365	3.84	29.2	"	"

Table 11C - Porewater results from station 11107 Discovery Cruise 147

Core#9 Pale buff core with black mottling at 5cm Core length ∿ 10cm

Depth of section		Sediment Volume	Porewater extracted	SiO_2 μM	PO_4 μM	NO_3 μM	Mn μM	Fe μM
0-1.5	cm	35ml	11ml	145.4	2.22	36.6	<0.25	<0.25
1.5-3	"	"	8ml	181.6	2.36	38.0	"	"
3-45	"	"	5.5ml	229.6	3.20	36.8	"	"
4.5-6	"	"	4ml	247.8	3.50	34.2	"	"
6-7.5	"	"	3.5ml	269.6	3.58	27.4	"	"
7.5-9	"	"	3.5ml	264.4	3.60	24.0	"	"

Table 11D - Porewater results from Station 11108 Discovery Cruise 147

Core#1 buff clay to 10.5cm Grey clay to 18cm.

Depth in section	Sediment Volume	Porewater extracted	SiO_2 µM	PO_4 µM	NO_3 µM	Mn µM	Fe µM
0-1.5 Cm	35ml	16ml	156.8	2.56	47.4	3.8	4.1
1.5-3.5 "	"	11ml	221.2	3.08	44.4	<0.25	<0.25
3.5-5.5 "	"	8.5ml	250.6	3.52	23.4	"	"
5.5-7 "	"	7.5ml	291.2	4.10	15.5	"	"
7-8.75 "	"	5ml	305.4	4.82	7.0	"	"
8.75-10.5cm	"	5ml	342.0	5.58	3.6	1.1	"
10.5-12 "	"	4ml	361.6	7.82	1.0	4.8	6.67
12-13.75 "	"	3.5ml	368.1	6.58	0.6	8.6	0.48
13.75-15.75cm "		3ml	397.4	7.68	0.2	10.6	1.95
15.75-18cm	"	3ml	391.6	7.46	0.0	15.7	1.50

Core#12: buff clay to 6cm grey clay to 15cm

Depth in section	Sediment Volume	Porewater extracted	SiO_2 µM	Po µM^4	NO_3 µM	Mn µM	Fe µM
0-1.5 cm	35ml	14ml	158.0	3.04	71.8	0.69	0.35
1-5.3 "	"	9.5ml	214.6	2.92	32.4	<0.25	<0.25
3-4.5 "	"	8ml	259.0	3.34	13.2	<0.25	"
4.5-6 "	"	7ml	299.4	5.12	4.3	2.02	"
6-7.5 "	"	6.5ml	359.2	6.34	1.6	5.68	1.28
7.5-9 "	"	6.5ml	350.2	7.96	1.2	10.97	5.96
9-10.5 "	"	6ml	366.2	9.12	1.0	13.68	8.00
10.5-12 "	"	5ml	376.2	9.54	1.0	17.24	9.89
12-13.5 "	"	3.5ml	392.8	10.34	0.8	11.61	10.18
13.5-15 "	"	3.5ml	324.4	6.30	1.0	13.82	4.17

Table 11E - Porewater results from Station 11112 Discovery Cruise 147

Core#3: Buff to 7cm then grey to 14cm.

Depth in section	Sediment Volume	Porewater extracted	SiO_2 µM	PO_4 µM	NO_3 µM	Mn µM	Fe µM
0-1.5 "	35ml	12ml	139.4	2.4	36.2	<0.25	0.51
1.5-3 "	"	8ml	202.0	2.76	28.6	"	<0.25
3-4.5 "	"	7ml	248.8	2.42	20.6	"	"
4.5-6 "	"	6ml	276.0	2.54	11.0	0.41	"
6-7.5 "	"	4.5ml	295.6	3.58	3.0	0.62	"
7.5-9 "	"	4.5ml	306.8	5.04	1.0	3.96	0.46
9-10.5 "	"	4ml	323.0	6.42	1.4	5.81	1.71
10.5-12 "	"	3.5ml	246.6	8.44	1.6	8.68	1.84
12-15.5 "	"	3.5ml	252.4	9.26	1.0	12.72	1.67

Table - 12 Pore water data from Discovery cruise 149 11143#3P (top section was not sampled sections are 1.5M in length).

Section (cm)	Depth (cm)	SiO$_2$ (μM)	PO$_4$ (μM)	No$_3$ (μM)	Mn (μM)	Fe (μM)
2	3-7	251	2.7	2.3	31.6	2.1
	18-23	195	3.2	2.8	37.2	0.4
	43-48	202	2.6	1.3	13.9	<0.3
	80-85	202	3.6	1.7	1.2	"
	114-118	215	4.3	2.6	<0.3	"
3	12-16	234	5.2	2.4	1.9	"
	51-57	236	5.5	2.3	<0.3	"
	90-94	243	5.8	4.4	<0.3	"
	129-133	222	6.3	2.0	<0.3	"
4	6-10	231	6.8	2.7	2.4	"
	22-28	229	6.1	4.0	4.4	"
	73-77	248	4.7	4.4	9.9	0.9
	119-123	271	3.7	2.6	15.9	0.6
5	10-19	252	4.8	3.6	25.3	5.2
	44-49	248	4.8	3.2	31.2	4.2
	80-84	256	4.9	2.9	35.1	5.1
	107-112	253	4.9	1.8	38.8	4.8
	127-130	251	4.1	3.2	30.4	0.6
	133-137	252	5.6	3.9	41.2	6.9
	143-146	230	5.1	2.4	31.8	0.8
6	10-14				41.9	2.4
	42-46	220	6.8	2.4	34.8	<0.3
	63-55	240	5.8	5.6	38.9	0.6
	116-120	238	4.3	20.1	31.1	<0.3
7	31-36	327	5.8	2.8	34.5	9.3
	53-58	316	4.7	2.1	30.2	5.6
	68-73	335	5.2	2.0	30.3	5.3
	85-89	355	5.8	1.9	28.2	5.9
	119-123	392	6.4	1.9	28.6	7.3
8	8-13	380	5.7	2.5	21.0	3.0
	47-52	387	5.2	1.9	19.1	1.0
	87-92	434	6.7	2.2	22.5	2.7
	119-123	436	6.5	1.6	19.0	2.2

Figures

(1) Absorption spectrum of the manganese-formaldoxine complex in seawater.

(2) Effect on the absorbance of the manganese-formaldoxime complex of pH. High absorbance at pH probably due to light scattering by MgOH precipitate.

(3) Absorbance spectrum of the iron-formaldoxime complex in seawater.

(4) Effect of increasing iron concentrations on the apparent absorbance of manganese-formaldoxime in seawater.

(5) Calibration line for manganese-formaldoxime in seawater.

(6) Effect of increased reagent volume on the absorbance of "blank" manganese-formaldoxime solutions.

(7) Absorption spectrum of the iron-ferrozine complex in seawater.

(8) Effect on the absorbance of the iron-ferrozine complex of changes in pH of final solution.

(9) Calibration line for iron-ferrozine in seawater.

(10) Oxidation of iron (II) at pH 7.78 (x), pH 8.22 (a) and pH 8.48 (°) in seawater.

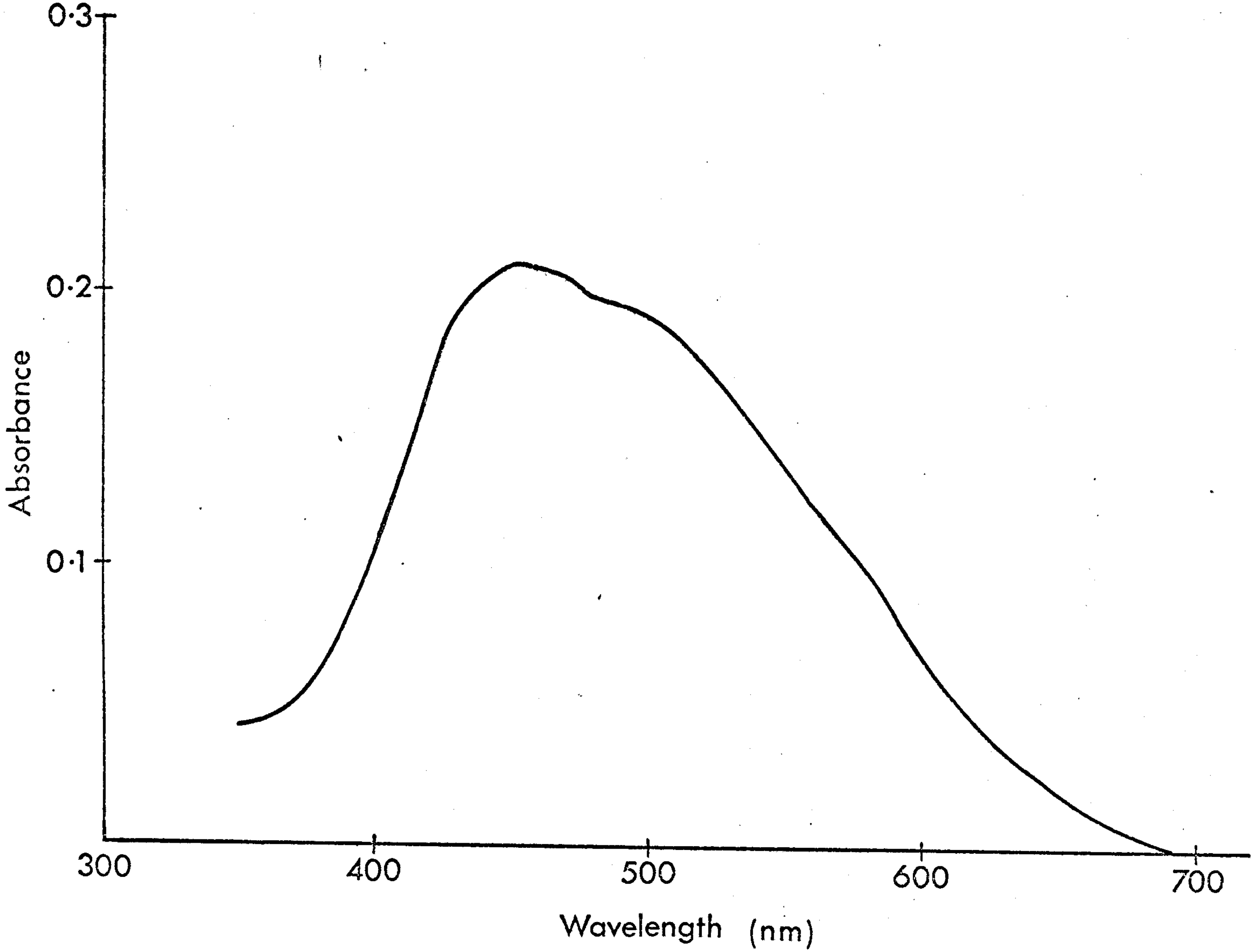

Fig 1

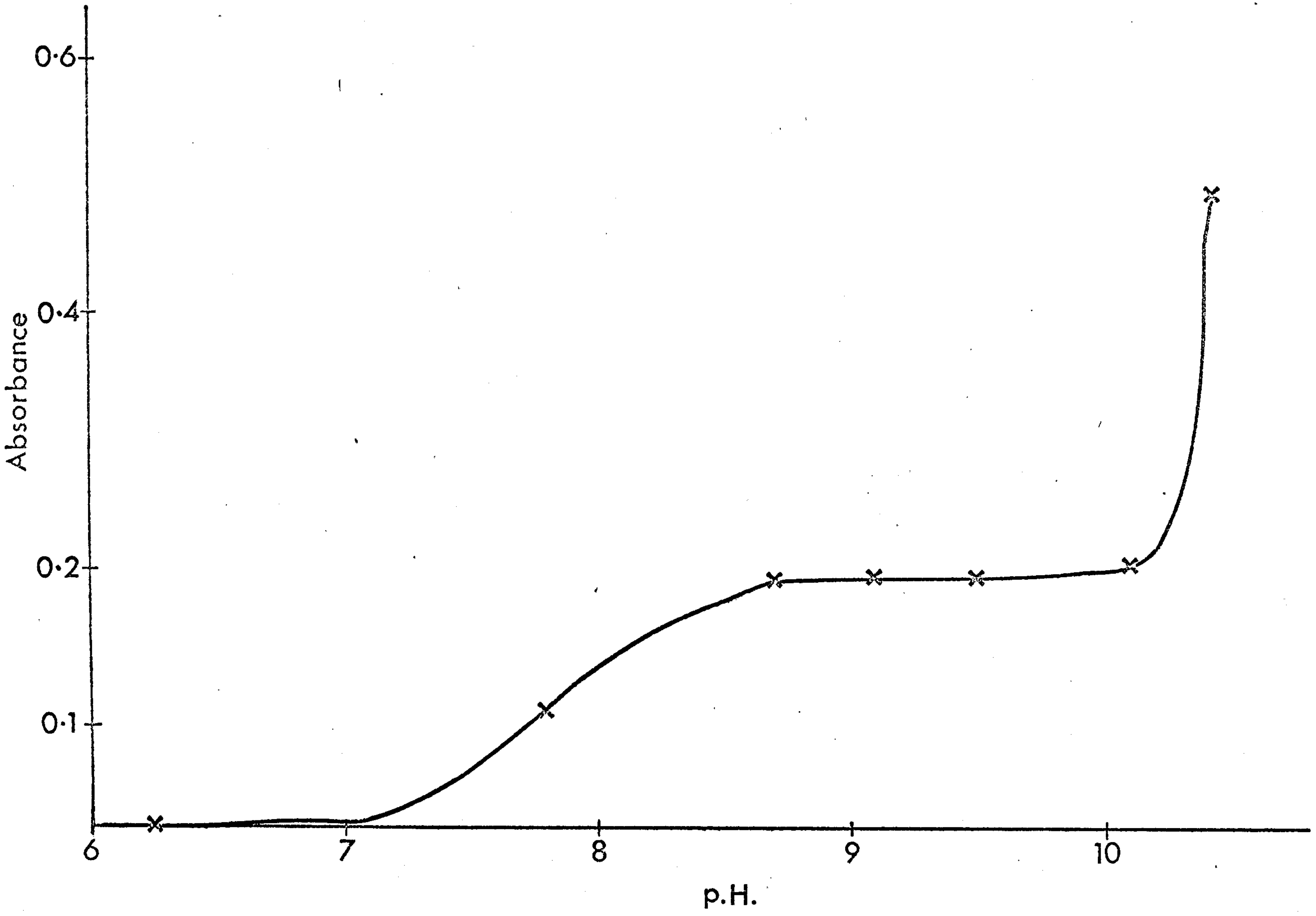

Fig 2

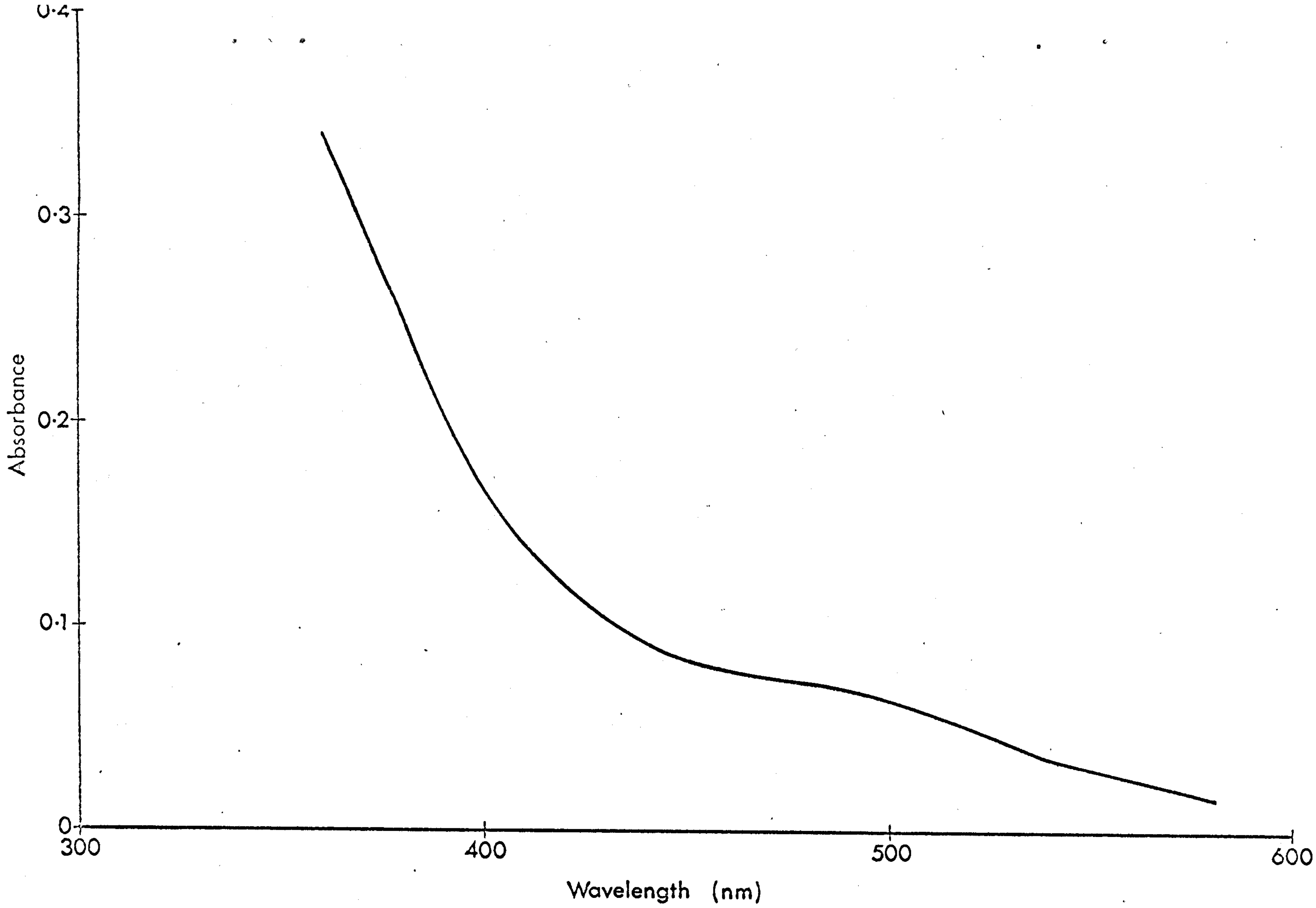

Fig 3

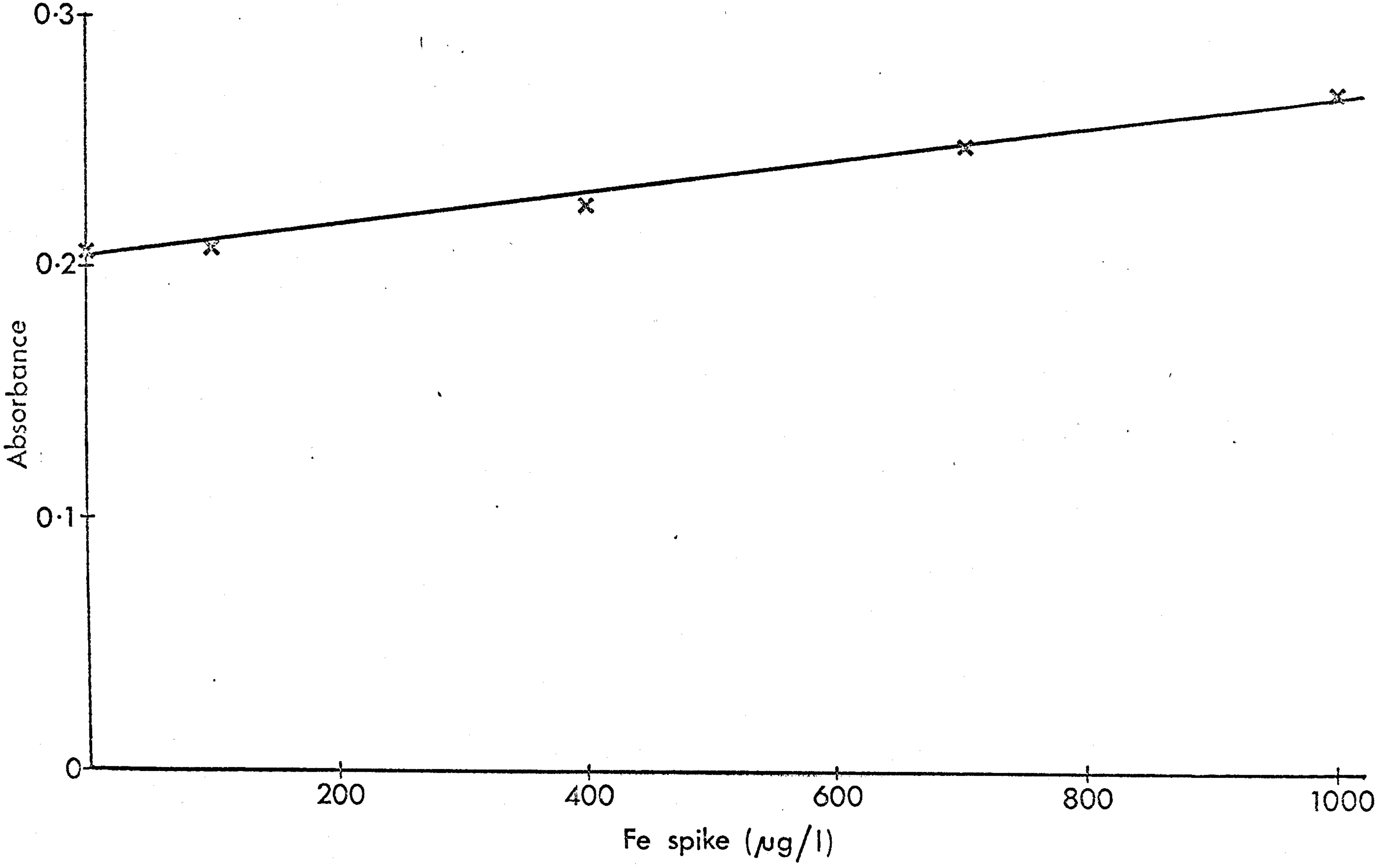

Fig 4

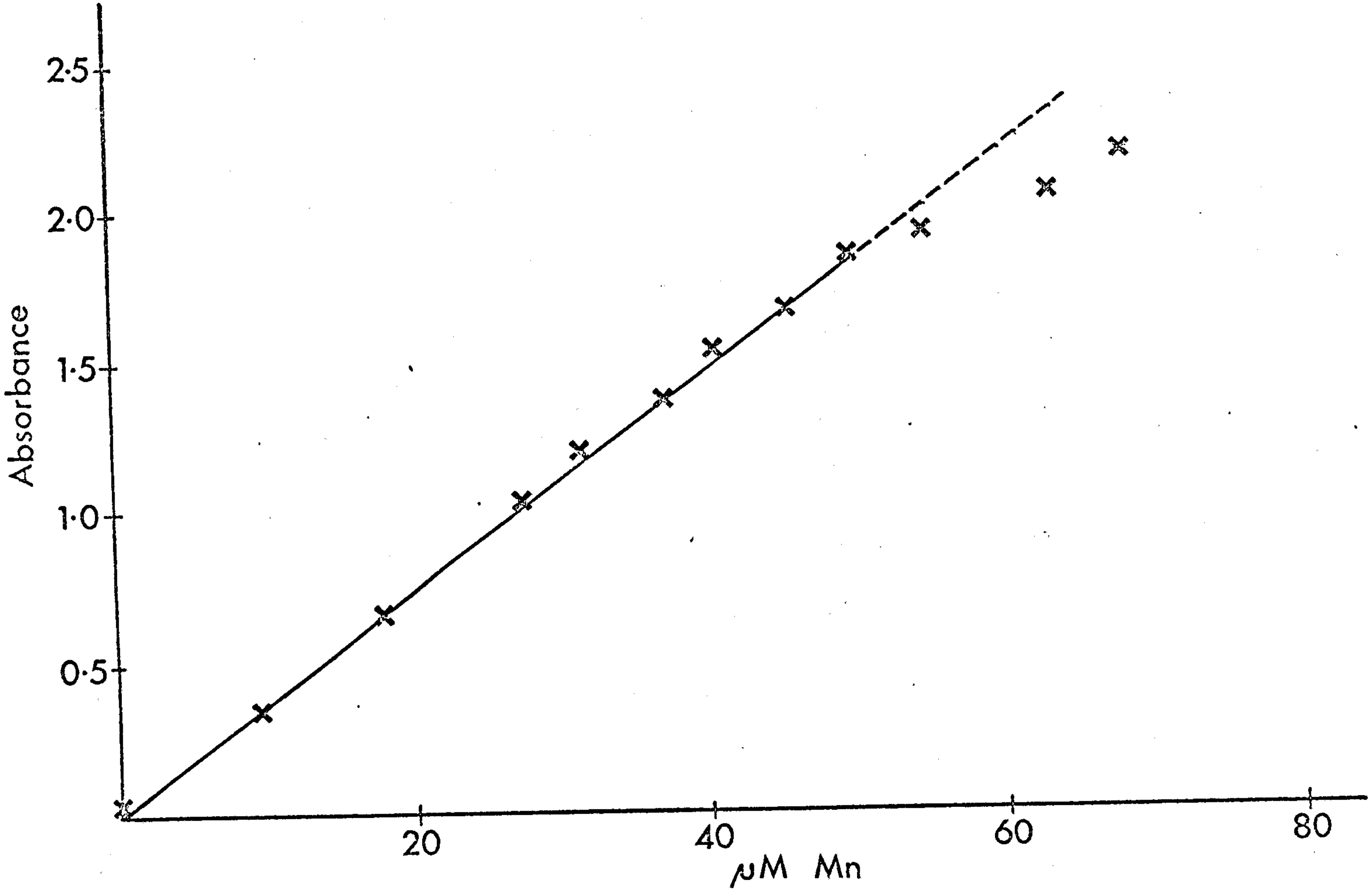

Fig 5

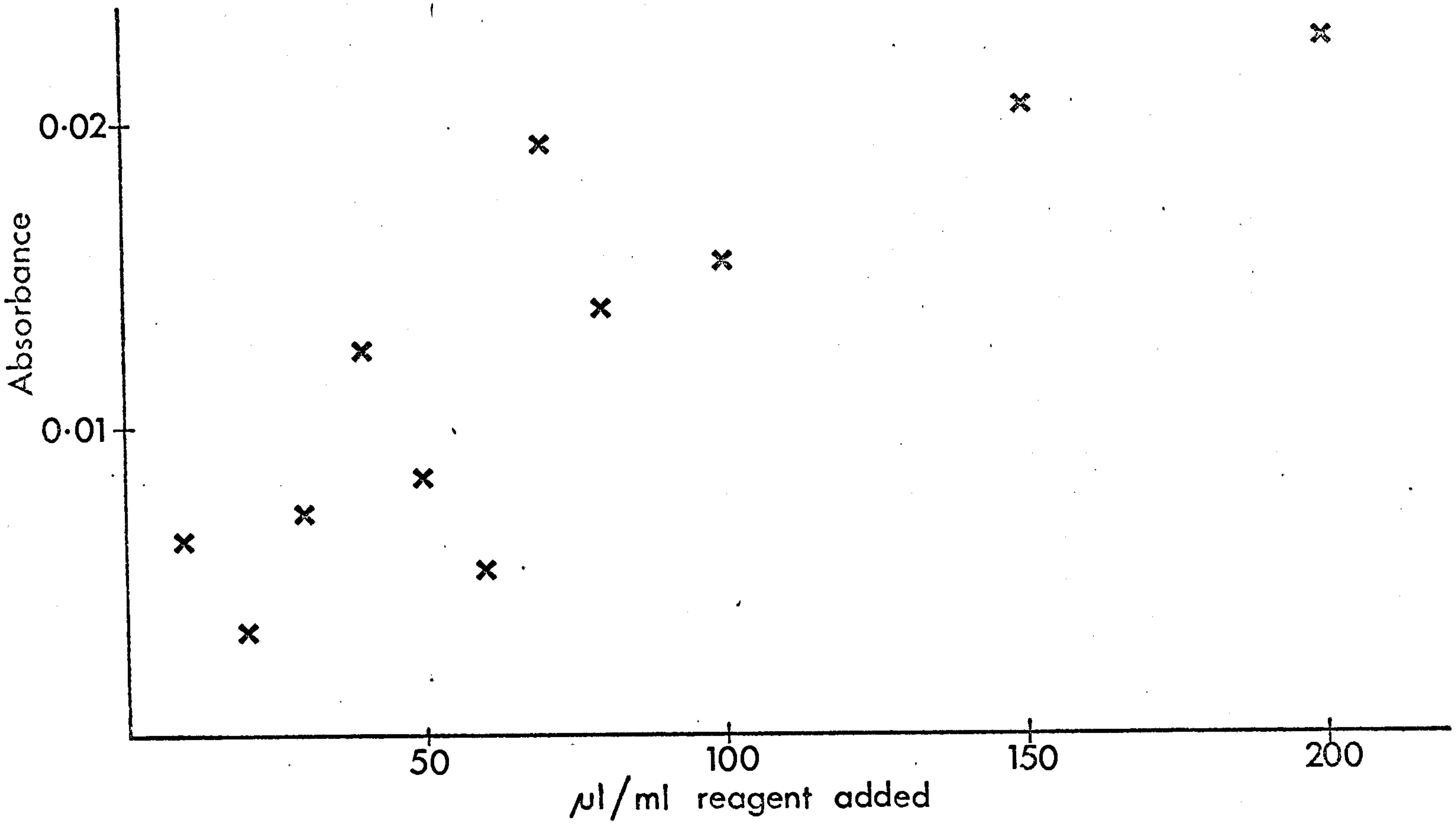

Fig 6

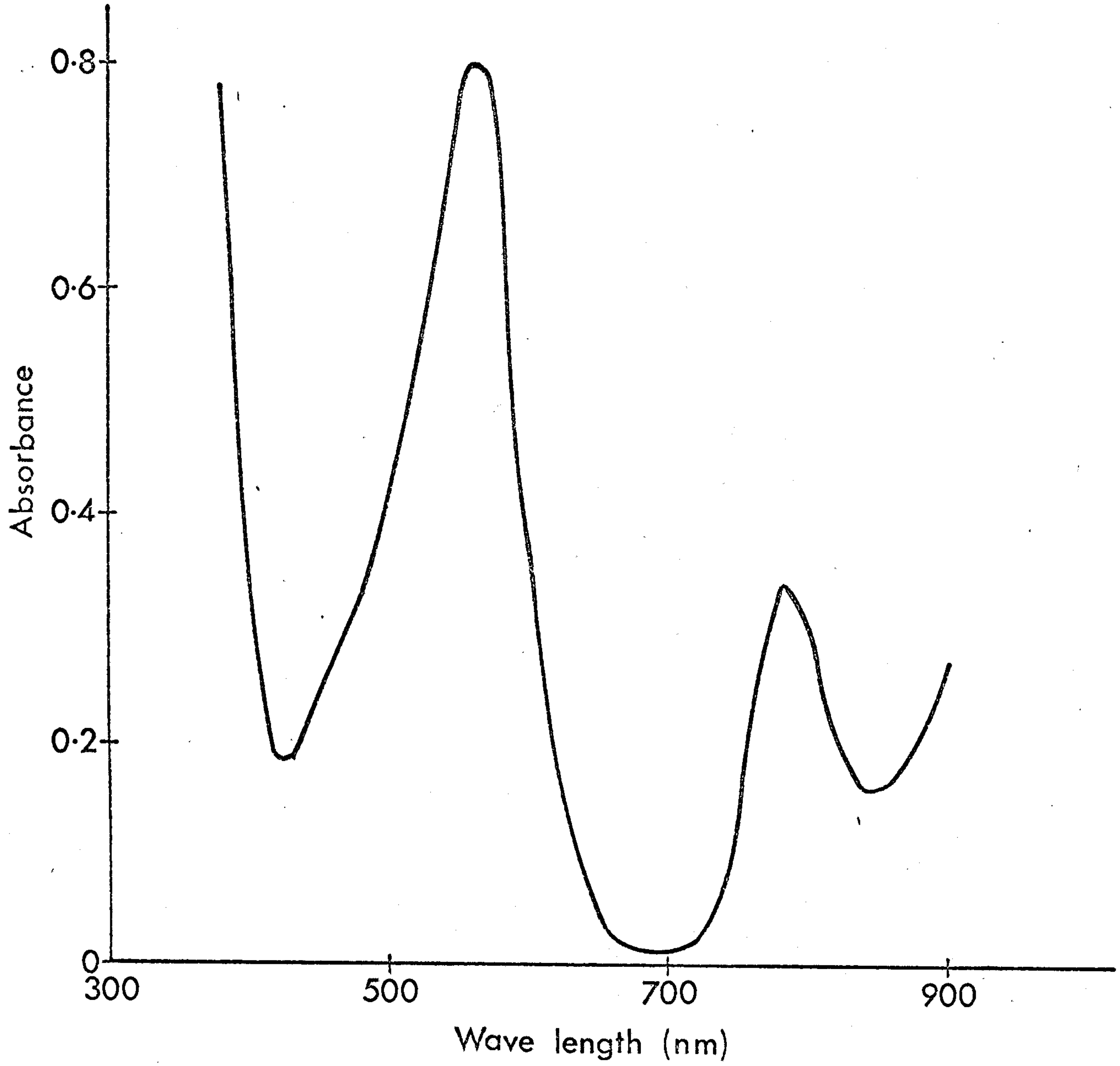

Fig 7

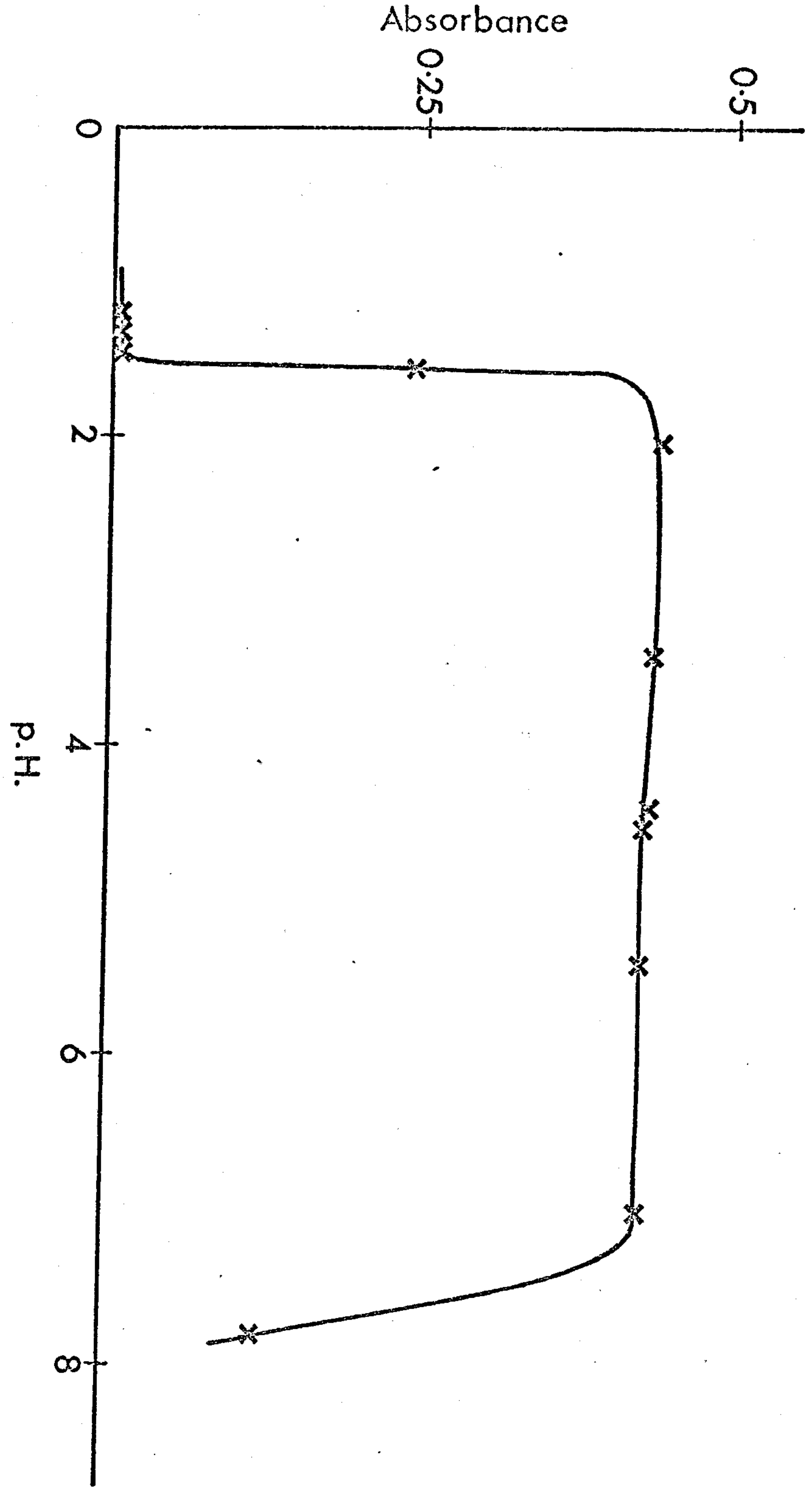

Fig 8

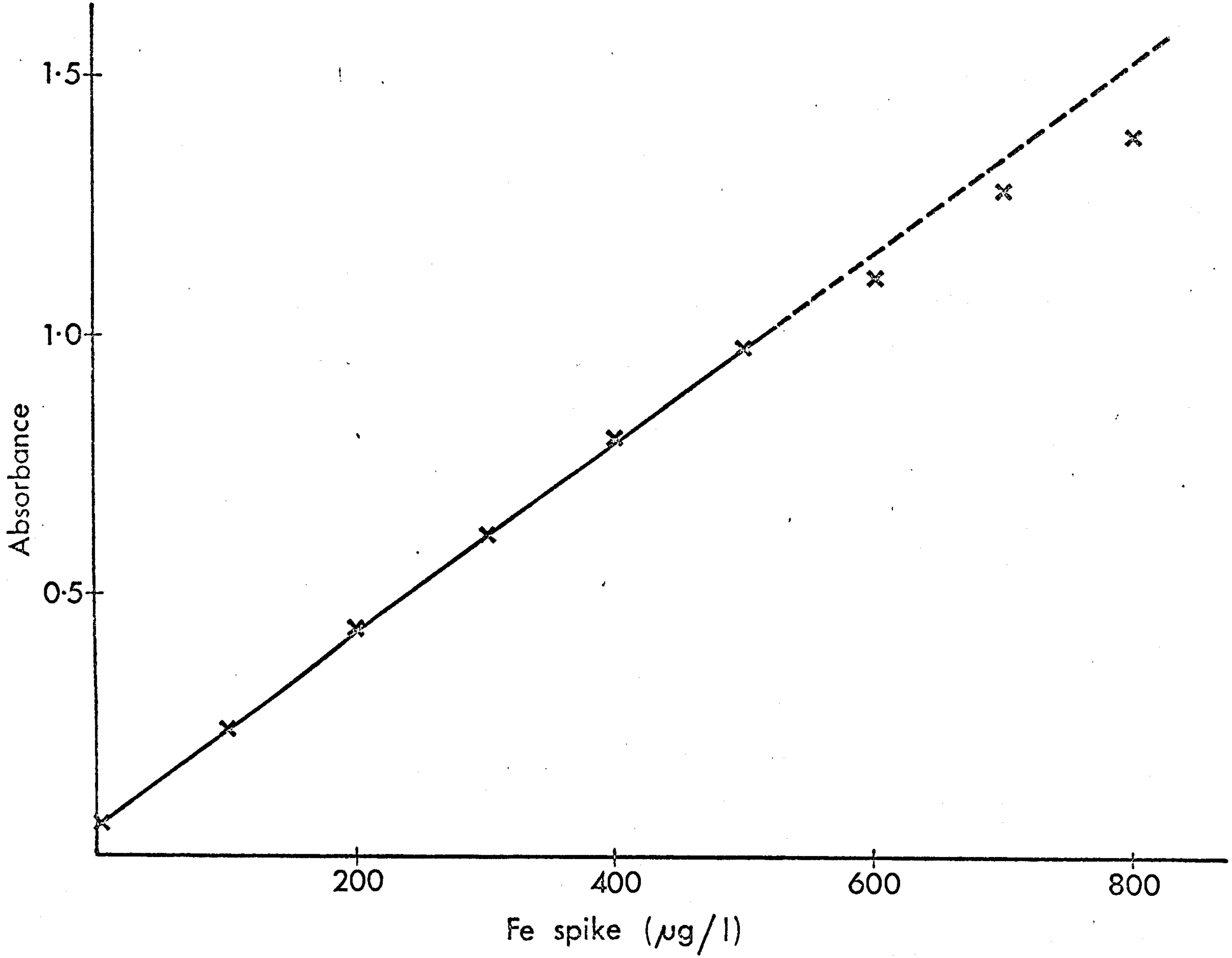

Fig 9

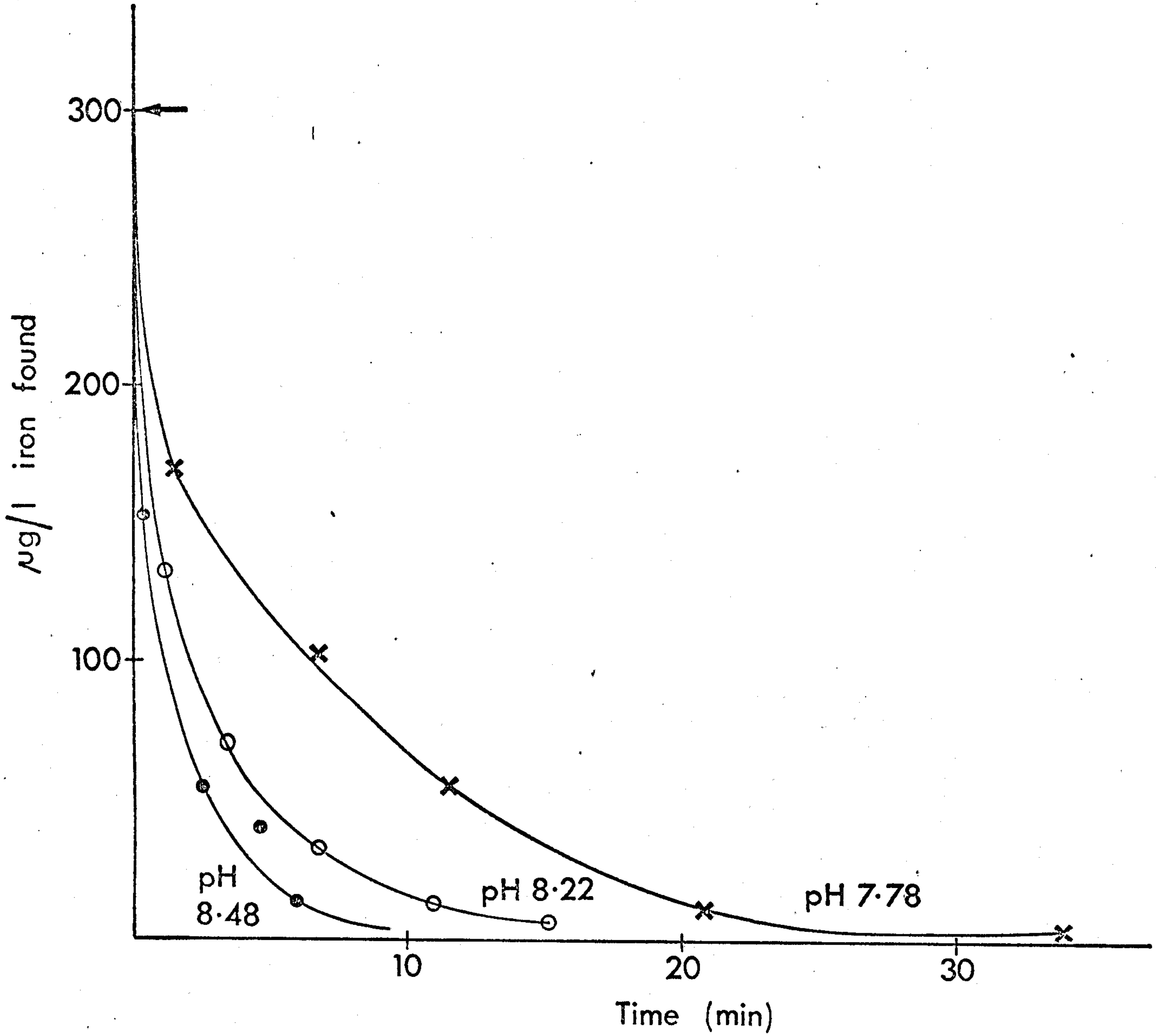

Fig 10