Truesdale, V.. 1973 *Iron determination in fresh water.* Institute of Hydrology, 24pp. (Subsurface Hydrology Report 59) (Unpublished)

It is often difficult to confirm the validity of a method of analysis directly. Self-consistency in the recovery of known amounts of the reactant can be misleading when the reactant can take on different forms, as is likely to be the case in natural waters. Inter-calibration of different methods of analysis for the same chemical species, together with the systematic investigation of various aspects of the analytical technique can sometimes uncover anomalous behaviour and therefore lead to a more rational choice between alternative methods. Such studies also increase our understanding of the often uncertain details of the chemistry of the reactions involved.

This paper describes the results of a detailed investigation of two methods for the determination of iron in natural fresh water. One method is an automatic spectrophotometric method derived from Henriksen's work. It uses 2,4,6 - tri (2'-pyridyl)-s-triazine as colour forming reagent. The second method is an atomic absorption method recommended by Nix and Goodwin. In the latter method the iron reacts with diethyldithiocarbamate to form a complex which is extracted from the aqueous phase into 4-methyl-pentan-2-one. This combination of methods was chosen because it relies upon two different chemistries. There was some possibility that the methods would respond differently to the various forms of iron purported to be present in natural waters, and therefore, that combination would offer a means of studying the mechanisms that lead to the interconversion of these forms.

If more were known about the stability constants for iron-humic or iron-fulvic acid systems it might be possible to calculate the magnitude of any interference that these organic species exert on analytical methods for iron. Unfortunately, what little information that is available has been gathered under conditions very different to those usually encountered in an analytical method. Thus, for example, whereas determination of stability constants in solution of 0.1 ionic strength are not uncommon, analytical proceedures which involve these same conditions, are. The position has been further complicated in the case of iron since Szilagyi (1971) showed that humic acid can reduce ferric to ferrous iron. Therefore, although a superficial comparison of stability constants is probably worthwhile, an empirical study of the interference offers the most satisfactory answer.

EXPERIMENTAL

APPARATUS AND METHOD -

It was assumed throughout the study that before being presented for analysis each sample would have been filtered through a Millipore membrane filter (0.8μ ADP) and then acidified with sulphuric acid (2 ml of 3.2N to each 100 ml of sample) to prevent loss of dissolved iron by sorption on the vessel walls.

Standard solutions of iron of appropriate strength were prepared from a stock solution of ferrous ammonium sulphate containing 100 mg per litre of iron.

Sulphuric acid solution (6.4×10^{-2}N) was used to dilute the stock solution. De-ionised distilled water prepared using a Manesty still and and Elgastat de-ioniser was used in the preparation of both standard solutions and reagents.

The practical procedure described by Nix and Goodwin, except for the specific modifications made in the light of experience which will be described in detail here was adhered to. During this study a Unicam SP-90 instrument was used in conjuction with a Servoscribe potentiometric recorder.

An automatic spectrophotometric method derived from Henriksen's method was adapted to a Technicon Auto-Analyser. The sample (1.00 ml per minute) is first mixed with a sodium acetate trihydrate buffer (0.32 ml per minute) containing hydroxylamine hydrochloride (100 g per 1 of each compound). After a mixing period of minutes a solution of 2, 4, 6 tri (2'-pyridyl)-s-triazine (280 mg per litre of 1.2×10^{-2}N hydrochloric acid) is added and the final solution, after being mixed for minutes, is passed through 50 mm path length flow cells. The optical density of the mixture at 590 mμ is recorded by the instrument. Sample blanks are determined by repeating the analysis in the absence of the TPTZ reagent. Sample cups were soaked overnight in 20% hydrochloric acid and then washed in distilled water before use. This procedure was necessary because of accumulations of iron on the inside of the cups, presumably formed when a steel mandril was used during their manufacture.

RESULTS OF INVESTIGATIONS

1. NIX AND GOODWIN METHOD

THE BUFFER

Nix and Goodwin obtained the required pH for each mixture using a pH meter together with solutions of acid and alkali; this is time consuming. Where many samples are to be analysed routinely it is preferable to design an analytical procedure which accommodates for any variation of pH between samples whilst at the same time administering the necessary adjustment of pH without recourse to a pH meter in this way. This has been accomplished by substituting a 1M sodium acetate buffer solution in place of the phtallate buffer recommended by Nix and Goodwin. Before addition of the acetate buffer the samples are held at a pH of approximately 2.0 by means of 2 ml of 3.2N sulphuric acid which is added to each 100 ml of sample after collection to prevent sorption of iron on the storage vessels walls. After addition of the buffer the pH of the mixture is approximately 5.0 and after addition of the DDC solution it increases only slightly.

Nix and Goodwin state that whn the pH of the mixture of sample and buffer is greater than 4.0 the amount of iron extracted is greatly reduced. They attribute this to the loss of ferric-iron from solution after its hydrolysis to ferric hydroxide. No evidence of this behaviour was observed during this study. It was found that mixtures of sample (200 μg per litre of ferrous-iron) and acetate buffer could be stored for periods between 10 seconds and 16 minutes without a noticeable deterioration occurring. As the maximum period of storage in the analytical scheme is only approximately 3 minutes, interference from this source seems unlikely to be important at the concentrations encountered in this study (0 -200 μg per litre).

Sandell states that the rate of decomposition of DDC solutions is directly proportional to their hydrogen ion concentration. Further, he records the half life of the DDC ion at room temperature as 4.9 minutes, at a pH of 5.0. There appears, therefore, to be no objection to the use of the acetate buffer and the pH of 5.0 it yeilds, provided that the period of time during which the mixture of sample, buffer and DDC is stored, is kept relatively short. Tests with a sample (100 μg per litre of ferrous-iron) showedthat mixtures containing DDC which were stored from between 30 seconds and 2 hours returned the same result. It is concluded, therefore, that the pH of 5.0, and the reaction time of approximately 3 minutes used here are satisfactory despite the inevitable loss of DDC that must occur.

There is no evidence to suggest that allowing the pH to increase continuously after the DDC has been added is detrimental to the analysis of ferrous-iron in distilled water. However, it seems desirable to fix the pH when natural water samples are analysed because of the lack of information about the form of the iron and its reactivity at different pH's. It is felt, therefore, that the stable pH obtained by the method recommended here is preferable to the continuously increasing value obtained when Nix and Goodwin's instructions are followed.

When the phtallate buffer recommended by Nix and Goodwin was used the atomiser of the SP90 was frequently blocked by a white encrustation. Several different atomisers suffered from the same problem and reproducible results could not be obtained. The white encrustation is presumed to be phtallic acid, or one of its salts. Substituting the sodium acetate for the phthallic buffer overcame the problem.

In the modified procedure the solution of iron complex in ketone is in contact with a small amount of the aqueous phase after it has been centrifuged. It was found that such solutions derived from various amounts of ferrous-iron in acidified de-ionised distilled water (0.500 µg per litre) did not deteriorate when stored for six hours. From this it is concluded that the decomposition of DDC in the aqueous phase, and any subsequent transport of DDC from the ketone phase has only a negligible effect on the stability of the iron complex dissolved in the ketone. The results also show that the solutions of iron complex in ketone are stable for at least six hours under the usual conditions of lighting etc. which prevail in a laboratory. This is particularly useful as it allows a single set of standard solutions to be used for several sets of natural water samples, not prepared simultaneously.

CLEARING SOLUTIONS

When samples of natural or artificial river water containing appreciable amounts of organic material are analysed the organic material forms a thick suspension with the ketone. This suspension prevents easy separation of the aqueous and ketone phases. The problem is overcome by centrifuging the suspension in a glass tube under approximately 770 g for 2 minutes, followed by gentle stirring of the ketone phase with a fine glass rod. After applying this procedure twice the organic material always packed down to a thin disc at the boundary of the aqueous and ketone phase. The organic material never packed down when only the centrifuge was applied; gentle stirring was essential. All Samples analysed during this study were cleared by this method.

CALIBRATION

The method would be best calibrated by adding known amounts of iron to an iron-free water which otherwise has the same composition as the sample under investigation. If this method were adopted, unforeseen variation in the response of the method to iron in different waters would be avoided. However, as it is difficult, or perhaps impossible, to prepare such iron-free waters a calibration medium which relies upon de-ionised distilled water seems a necessary alternative.

A comparison of the behaviour of the Nix and Goodwin method in some natural waters and in de-ionised distilled water showed, however, that one is not usually justified in using de-ionised water as a calibration medium. The results of some of these analyses are shown in Fig 1. The curves obtained for the natural waters intercepted the ordinate axis at higher positions than the de-ionised water because they contained more iron. It is not possible to compare the behaviour of the method in two waters directly by using a single value of the gradient from each curve because the curves are not linear. However, shifting the axis of the natural water graph along the abscissa, in the manner shown in Fig 1, allows a comparison to be made. A further analysis is made by calculating the proportion of the iron that is removed from each increment added. The amount of iron removed from successive increments is obtained from the difference between the response in de-ionised and natural water. The gradient of the graph of the amount of iron removed versus the amount added can be drawn, and its gradient used as a measure of the complexing ability of the material present in the water under examination. Curves of this kind, Fig 2, have been determined for a variety of natural waters. In most cases a linear relationship was found to exist between the two variables. However, on a few occasions deviations from linearity in either direction were observed at the higher iron concentrations administered (400-700 μg per litre).

The highest and lowest recorded values (of 0.73 and 0.0 respectively) were returned by samples of water from peat bogs. The first was coloured brown whilst the second was apparently colourless. This must no be taken as a suggestion that the colouration of samples is a direct indication of the extent of complexing ability, however, because an apparently colourless sample of mountain stream water returned a value of 0.45. A sample of Thames water taken at Wallingford during a relatively dry period of the year returned a value of 0.14.

These data show, therefore, that the use of de-ionised distilled water as a calibration medium introduces an error of anything between 0 and 73% in the determination of iron in a natural water sample.

Investigations have shown that organic and not inorganic material present in natural water is probably responsible for the behaviour described above. Tests showed that sodium, calcium and potassium (as chlorides) at 2.5 mg per litre, and phosphate-phosphorus and silicate-silicon at concentrations of 100 and 1000 μg per litre, respectively, have no deleterious effects upon the shape of the calibration curves for ferrous-iron in distilled water. Experiments also showed that the apparent loss of iron is not due to any inter-specific interferences in the flame, and therefore, that the suppressed responses are returned because less iron-DDC complex is extracted by the ketone from river waters. This was established when samples of de-ionised water to which iron had been added returned the same result irrespective of whether they were extracted with pure ketone or ketone which had previously been shaken with a mixture of natural water and buffer.

Because interference by organic material present in the samples was suspected, the behaviour of iron toward some compounds which are known to be present in natural waters was studied. Most attention has been given to the role of "humic acid" but some investigations have also been devoted to "fulvic acid".

Fulvic acid was dissolved directly in acidified de-ionised water whereas "humic acid had to be dissoved in sodium hydroxide (2×10^{-2}N) before the pH of the mixture was finally reduced to 2 by means of 3.2N sulphuric acid. In the acidic medium a large proportion of humic material was probably colloidal and particulate, since much of it could be removed from the solution by filtration through a Millipore membrane filter (0.8μ A.P.D.). However, in the experiments described here the humic material was treated as though it were dissolved and no attempt was made to filter the mixture. This does not appear to conflict with the standard proceedure adopted for the analysis of river water samples. This is so because the samples themselves must contain particulate or colloidal humic material after they have been filtered and acidified prior to their analysis.

The results in Fig 3 show that the complexing ability, and therefore the shape of the calibration curve, is relatively constant for solutions containing more than 17 mg per litre of humic acid. Therefore, the shape of the calibration curve is strongly dependent upon the concentration of humic material when its concentration is below this figure. This variation in the position and the form of the calibration in synthetic river waters is therefore in accordance with the results obtained with natural river water where humic acid concentration of this magnitude are to be anticipated.

Tests performed with ferric and ferrous-iron showed that humic acid solution (50 mg per litre) binds ferrous-iron more firmly than ferric-iron. Complexing ratios of 0.38 and 0.27 were returned for ferrous and ferric-iron, respectively. In contrast, tests conducted with the two forms of iron in natural peaty water suggested that ferric-iron can be bound more firmly than ferrous-iron in natural samples. Complexing ratios of 0.35 and 0.30 were returned for ferric and ferrous-iron, respectively. These results are not necessarily contradictory because the natural sample may have contained various types of organic material which behave towards the two forms of iron in the opposite manner to that shown by humic acid. As so little is known about the form of iron in its complexes with humic acid it is not possible to assess the exact implications of these results. However, they do suggest that the errors in iron determination accruing from the application of the Nix and Goodwin method to natural waters arise from several, and not one cause.

The tests using fulvic acid showed that, weight for weight, it does not bind ferrous-iron as strongly as does humic acid. The presence of 10 mg per litre of fulvic acid did not alter the position or the shape of the calibration curve relating to ferrous-iron in de-ionised water, whereas the addition of this same amount of humic acid allowed only one half of the added iron to be extracted. Similarly, the presence of 20 mg per litre of fulvic acid in de-ionised water locked up only onethird of the iron whereas the same amount of humic material bound up twice that amount. It seems, therefore, that unless thevvarious organic components of natural waters are always present in the same proportions the fraction of iron which is extractable will vary from sample to sample even though the total amount of organic material remains the same. Such a situation demands a separate calibration for each individual sample; a procedure which is precluded by the excessive time that would be entailed. The removal of the organic material present in natural water samples seemed to offer a better remedy.

Szilagyi (1971) showed that dissolved ferric-iron is reduced to ferrous-iron by humic acid preparations. The existence of this reaction precludes any clear understanding of the effects of humic material on the analytical method because it removes the clear distinction that usually exists between added ferrous or ferric- iron. It was necessary, therefore, to obtain an estimate of the rate at which this reaction proceeds, to that its importance in the context of the preceeding experiment could be assessed.

The rate of production of ferrous-iron in solutions of 500 μg per litre of ferric iron with either 50 mg per litre of humic acid of 20 mg per litre of fulvic acid was measured. A similar initial rate of ferrous-iron production was observed in each solution. The results showed that about 60% of the ferric iron added to the humic acid solution was reduced within 30 minutes whilst 44% was reduced by the fulvic acid. In the analytical procedure mixtures of humic or fulvic acids with ferric-iron generally stand for no longer than 4 minutes. It appears, therefore, that during this time approximately 20% of any added ferric-iron will be reduced to the ferrous form. Therefore, the real difference between the magnitude of the complexing ratios for ferrous and ferric iron with humic or fulvic acids is probably somewhat larger than that recorded here.

REMOVAL OF ORGANIC INTERFERENCE

Henriksen boiled each sample of natural water with mineral acid (0.11N) for 30 minutes before analysis. He claims that this procedure mineralised the organically bound iron which he thought was present in most of his samples. His method, therefore, measures the total concentration of dissolved iron.. Henriksen"s method of overcoming this problem was tested during this study and was found to be suitable for many waters, but inadequate for brown peaty waters. For example, with one sample of brown peaty water the treatment reduced the waters' complexing ability from 0.42 to 0.17. Thus, although the treatment alleviated an appreciable part of the interference it had by no means overcome it. As samples of this type occurred frequently in the field programme which accompanied these investigations it was necessary to seek an alternative procedure which could accomodate them.

The use of Ammonium Persulphate has provided a satisfactory solution to the problem of interference from naturally occurring organic matter. Tests of the efficency of using this compound were conducted using several brown peaty water samples as well as Thames water. Ammonium persulphate (4.4 g per litre) was added to the filtered and acidified samples and each mixture boiled for various periods of up to one hour. In each case a portion of the unheated mixture was analysed immediately. Samples which were boiled for periods of 10 or more minutes appeared to lose all colouration whereas the colouration of the others did not change. Nevertheless, in each case a single calibration curve prepared simultaneously, using de-ionised water containing the same amount of persulphate was found to be appropriate. These results showed therefore, that it is not necessary to oxidise the organic matter completely when mineralising the iron. The action of cold persulphate therefore offers a considerable saving of time.

In many cases where Ammonium Persulphate is recommended as an oxidising agent either silver nitrate or selenium dioxide is used as a catalyst. These compounds were used in some trials here but were not found to offer any improvement to the recommended procedure. In fact, their use is inconvenient because they react with the DDC reagent to produce coloured precipitates. Persulphate, itself, produces a light, white precipitate with DDC reagent. This precipitate disappears when the ketone is added and it does not appear to hamper the analysis.

Spectrophotometric Method

Henriksen accepts the fact that iron occurs mainly in a bound form in natural waters. Further, he states that preliminary treatment of samples is therefore necessary to convert the iron to the ionic state. Whilst the author does not doubt the first statement, and does not deny that there is some merit in using the digestion procedure whilst ingnorance of the forms of iron in natural waters prevails, he has been unable to find any record which shows convincingly that the digestion step is necessary when TPTZ is used. In these preliminary experiments, therefore, there seemed to be some value in operating a method which did not incorporate a digestion step.

Spectrophotometric method

The method described here is very simple. Tests performed manually have shown that the reduction of ferric to ferrous-iron by the hydroxylamine reagent is very rapid and that the time the samples reside in the manifold is adequate for concentrations of iron of between 0 and 1 mg per litre. Similarly, the colour forming reaction is rapid and only the minimum size of coil is needed.

The procedure tolerates relatively large variations in the sample acidity. It returned the same response to a given amount of iron when between 1 and 3 ml of 3.2N sulphuric acid was added to each 100 ml of sample. With 4 ml of acid, however, the reproducibility of the sample peaks was poor and the net response decreased to 83% of its former value.

Reproducibility

Calibration

The change in response corresponding to a given quantity of ferrous-iron was the same in all the water samples tested. Its behaviour with clear as well as densely coloured peaty water samples, and with solutions of humic and fulvic acid preparations (25 mg per litre) was studied. In each case a linear calibration was obtained over a 0-800 μg per litre range. With f. s. d. of the Auto-Analyser corresponding to 1 mg per litre of iron in de-ionised water, a mean gradient of 0.101 units per (μg per litre of iron) was returned with a maximum deviation of 2%. It seems, therefore, that the organic matter in peaty water does not bind iron sufficiently strongly to prevent formation of the TPTZ-iron complex. The complexing ability of the organic matter in a particular sample will obviously depend on the prevailing concentration of the organic compounds capable of complexing iron. But, the fact that samples containing very high concentrations of organic debris were tested lends considerable support to the view that the simple TPTZ method will not suffer from the problems encountered when applying the Nix and Goodwin method to natural waters.

COMPARISON OF METHODS

In order to test the consistency of the results obtained by the two methods, 35 upland water samples containing various amounts of organic material were analysed by both methods. The object of the exercise was to discover any major differences between the results returned by the methods. The iron content of the samples ranged from 0 to 370 μg per litre. The comparison was made by plotting a graph of the atomic absorption results against the colorimetric results. The slope (and its standard error) of the best fitting straight line was 0.9 ± 0.03. The nearness of this value to 1.00 indicates that both methods measure the same variable. The intercept of -6.0 ± 5.0 μg per litre suggests that the results from one of the methods are contaminated by a small systematic error. Such an error might have been introduced during preparation of either set of standard solutions used. However, its magnitude is sufficiently small for it to be neglected within the context of this study.

An examination of the results collected during comparison of the two analytical methods Fig (4) suggested that there might have been discrepencies between the analyses for samples containing appreciable quantities of organic matter. The points for these samples tended to be more scattered. An additional investigation of the behaviour of the colorimetric method in these waters was therefore made to determine whether a discrepancy existed. The test applied consisted of determining the iron content of samples both before and after the organic matter had been decomposed by means of ultra-violet light (Henriksen). Checks showed that the response of the method to a given amount of added ferrous-iron was unaffected by irradiation. The procedure therefore allows one to measure a variable approaching the total iron content. An analysis of ten replicate samples which had been irradiated, and four samples which had not, showed that total and reactive iron analyses were equal. The scatter of the points observed earlier is therefore attributed to errors introduced when the acidified river water was sampled prior to analysis. Under the conditions adopted humic acid is present as a precipitate and care must be exercised if a representative sample of water and particulate matter is to be taken.

FIG. 1. CALIBRATION CURVES FOR DEIONISED DISTILLED WATER & RIVER WATER.

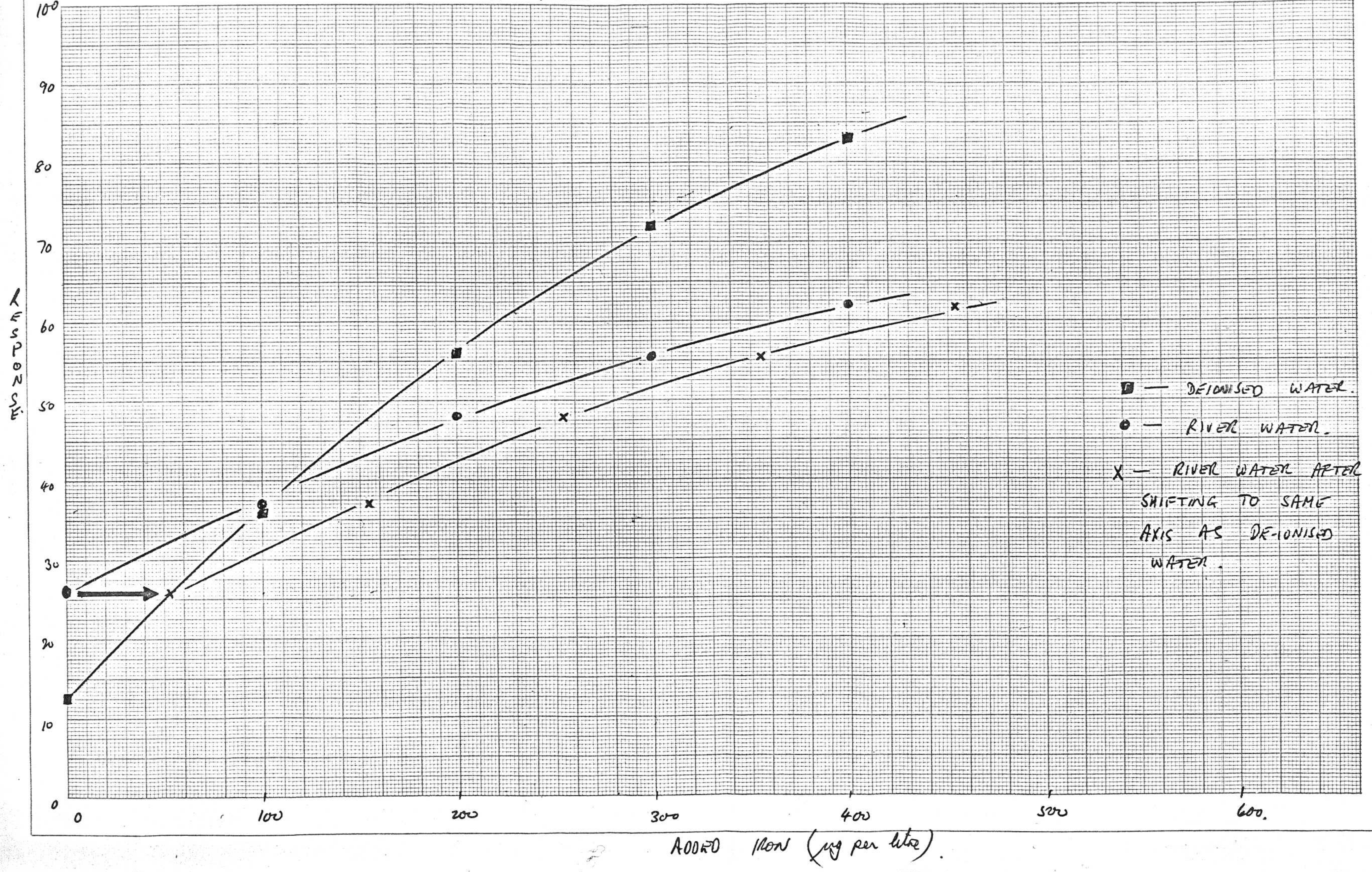


Fig 3. Complexing ability of a humic acid preparation.

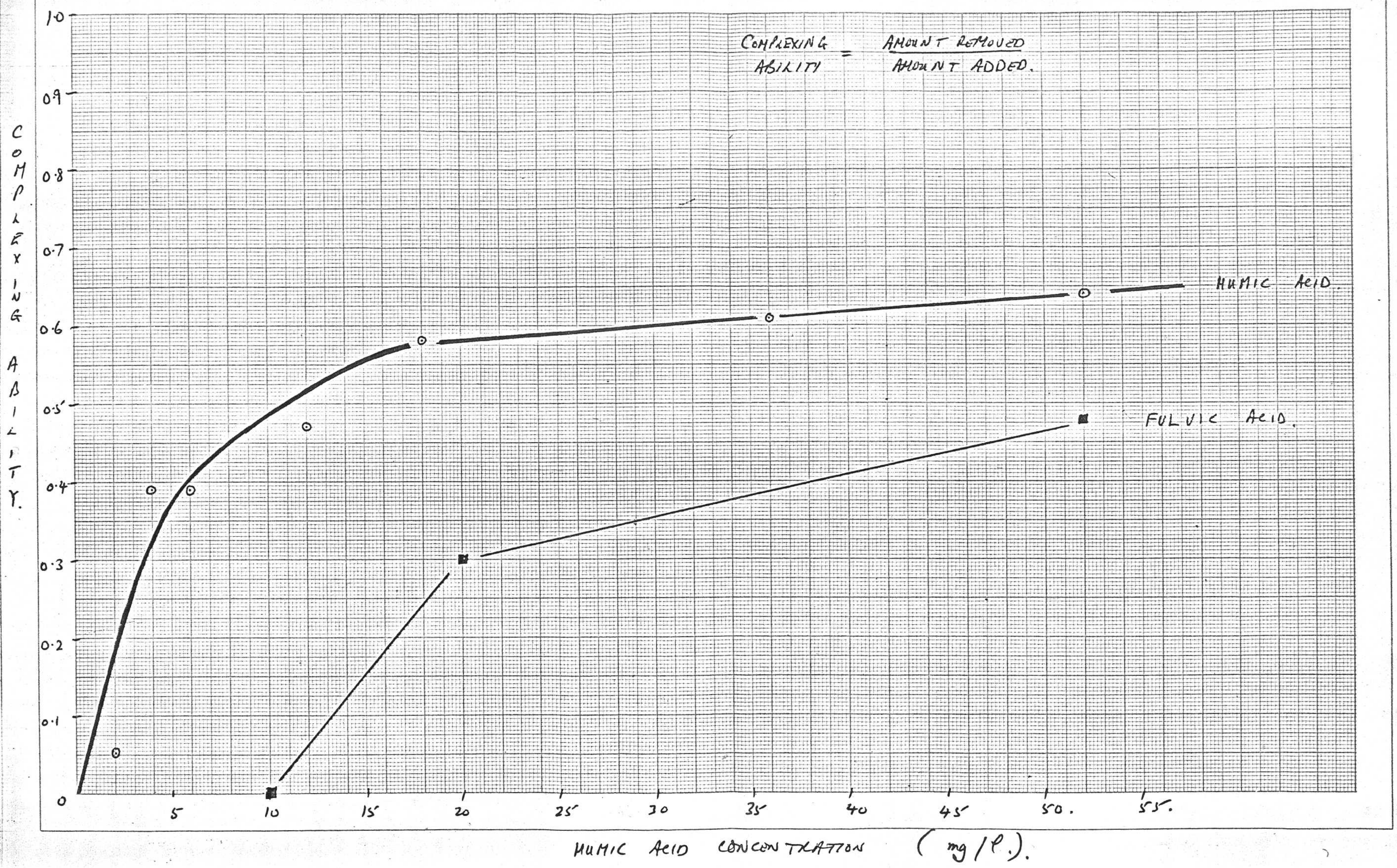
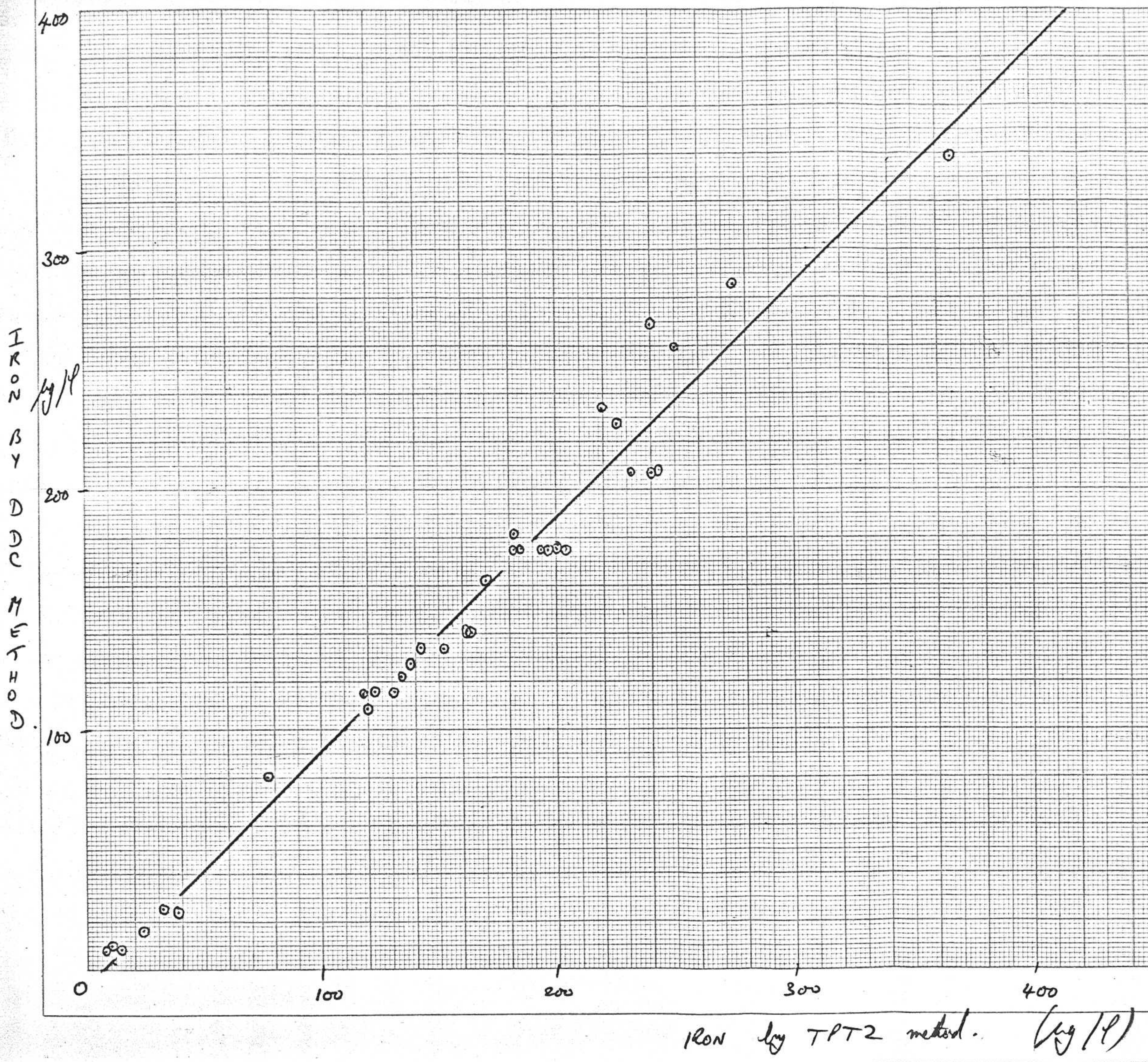


Fig 4. COMPARISON OF TPT2 & DDC METHODS.



COPIED FROM TECHNICON AUTO ANALYSER METHODOLOGY SHEET 5-68 W.

REAGENTS

THIOGLYCOLIC ACID ($HSCH_2COOH$-98%)	100 ml
Distilled water, q.s.	1 l.

Preparation:

Dilute 100 ml thioglycolic acid to one liter with distilled water. If necessary, the thioglycolic acid can be purified by passage of the acid through a cation resin in the hydrogen form.

NOTE: This reagent should be prepared fresh every three days and refrigerated when not in use.

SODIUM ACETATE - HYDROXYLAMINE HYDROCHLORIDE

Sodium Acetate ($NaC_2H_3O_2.3H_2O$)	mw. 136. 100 g ≃ M
Hydroxylamine hydrochloride ($NH_2OH.HCl$)	100 g
DISTILLED H_2O, q. s.	1 l.

Preparation:

Dissolve 100 g sodium acetate in 500 ml distilled water, add 100 g hydroxylamine hydrochloride, and dilute to one liter.

TPTZ N; C (C_5H_4N) N; C (C_5H_4N) N; C (C_5H_4N)

2, 4, 6-tri (2' - pyridyl) - s - triazine	280 mg
Concentrated HCl	1 ml
Distilled water, q.s.	1 l.

Preparation:

Dissolve 280 mg TPTZ in 50 ml distilled H_2O. Add 1 ml concentrated HCl (sp. gr. - 1.18) and dilute to one liter with distilled H_2O.

STANDARDS

STOCK IRON STANDARD: 100 ppm

Ferrous ammonium sulfate $(NH_4)_2 Fe (SO_4)_2.6H_2O$	0.707g
0.1N Sulfuric acid (2.5 ml conc. (H_2SO_4 (sp. gr. 1.84)/1) q.s.	1 l.

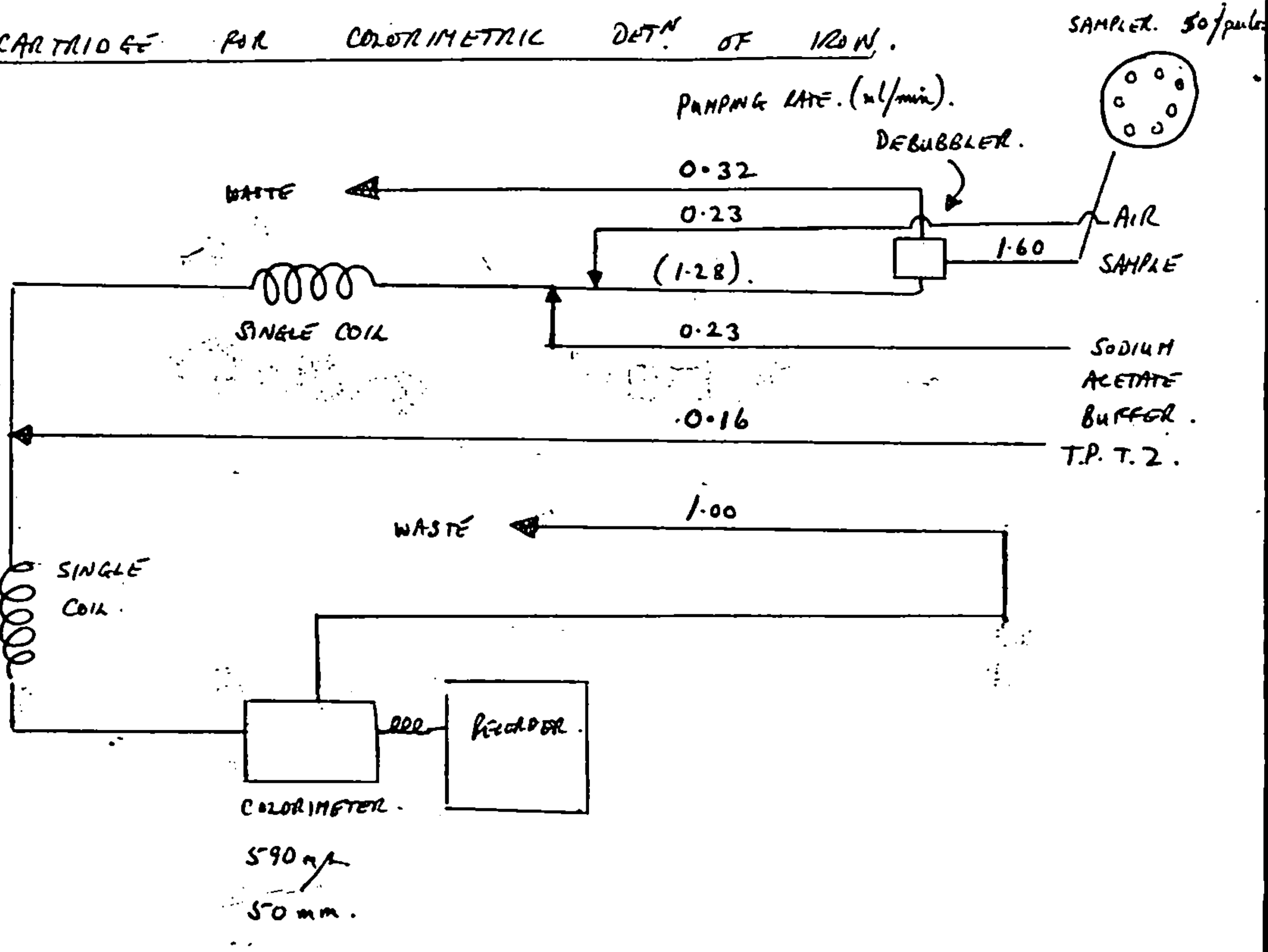
Preparation:

Dissolve 0.707 g of ferrous ammonium sulfate (Mohr's salt) in 0.1N sulfuric acid and dilute to 1 liter with the acid. Prepare standards ranging from 0.01 ppm to 1 ppm in serial dilutions for calibration using 0.1N H_2SO_4 for the dilution.

---

1. Henriksen, Arne, Automatic Method for Determination of Iron, "Vattenhygien", 22, May, 1967, pp. 1-8.
2. Collins, P.F., Diehl, H., Smith, D. F., Anal. Chem. 31, 1862 (1959).

LAYOUT OF CARTRIDGE FOR COLORIMETRIC DETN. OF IRON.



THE SIMULTANEOUS EXTRACTION OF IRON, MANGANESE, COPPER COBALT, NICKEL, CHROMIUM LEAD, AND ZINC FROM NATURAL WATER FOR DETERMINATION BY ATOMIC ABSORPTION SPECTROSCOPY

*J. Nix and Tom Goodwin**
Department of Chemistry
Ouachita Baptist University
Arkadelphia, Arkansas

ABSTRACT

A method for the determination of eight heavy metals (iron, manganese, copper, cobalt, nickel, chromium, lead, and zinc) in natural water in the concentration range of a few ppb is presented. The method utilizes a diethyldithiocarbamic acid chelation followed by a methyl isobutyl ketone extraction to preconcentrate all eight of the metals in a single extract. This extract can be used for the determination of the metals by atomic absorption spectroscopy. Using proper field filtration, the method can be adapted for the determination of both the filtered and particulate fraction of these metals in natural waters.

RESUME

Une méthode pour la détermination de métaux lourds (fer, manganèse, cuivre, cobalt, nickel, chromium, plomb et zinc) dahs de l'eau naturelle pour un domaine du concentration de quelques ppb est présentée. La méthode utilise une chélation par acide diethyldithiocarbamique suivie par une extraction dans la méthylisobutylcetone pour préconcentrer en une seule extraction. Cette extraction peut être utilisée ensuite pour la détermination par spectroscopie d'absorption atomique. En utilisant une filtration appropriée, la méthode peut être adaptée à la détermination du filtrat et les fractions métalliques du ces métaux dans les eaux naturelles.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von acht Schwermetallen (Fe, Mn, Cu, Co, Ni, Cr, Pb und Zn) im Konzentrationsbereich von wenigen ppb in natürlichen Wässern beschrieben. Die Methode verwendet eine Komplexierung der acht Metalle durch Diäthyldithiocarbaminsäure sowie anschliessender Extraktion der Chelate mittels Methylisobutylketon. Durch diese Extraktion können alle acht Metalle gleichzeitig und in angereicherter Form vom Wasser getrennt werden. Die extrahierte organische Phase kann zur Bestimmung mittels AAS verwendet werden. Bei Anwendung geeigneter Filter kann die Methode sowohl für filtrierte Wasserproben, wie auch zur Bestimmung der Schwebestoffe in natürlichem Wasser benuzt werden.

INTRODUCTION

The concentration of most heavy metals in unpolluted surface waters is generally below 0.1 ppm (1). Exceptions may occur where there is a sizable influx of heavy mineralized ground water or in streams receiving large silt burdens. Iron and manganese have been reported to exceed this level in organic rich waters (2). It is also well known that iron and manganese exceed this level in the deeper waters of many stratified reservoirs and lakes (3). As the dissolved oxygen level of the deeper water of these bodies of water decreases, the reduced state of both iron and manganese migrate throughout the low oxygen zone (3).

In order to study the distribution of heavy metals in a stratified impoundment in South-Central Arkansas, it was desirable to develop an atomic absorption procedure which could be used to determine a number of heavy metals in the ppb range when relatively large amounts of iron and manganese are often present.

The sensitivity required by the study demanded that some type of preconcentration step be used before determination by atomic absorption. Mulford (4) has described several solvent extraction systems useful in concentrating metals for determination by atomic absorption. Joyner and Finley (5) have used the diethyldithiocarbamate - methyl isobutyl ketone system to concentrate iron and manganese in sea water. Platte and Marcy (6) have used a similar system for the extraction of lead, copper and iron from phosphate compounds. From data reported by these authors, it appeared that the chelation of metals with diethyldithiocarbamic acid followed by extraction with methyl isobutyl ketone would be adptable to the determination of several heavy metals in water from the reservoirs to be studied.

A study was undertaken to determine if several heavy metals could be extracted in one step and the single extract used for the atomic absorption determination of these metals. The metals which were studied were iron, manganese, copper, cobalt, nickel, lead, zinc, and chromium. Since relatively large excesses of iron and manganese could be expected in samples taken from the deeper portion of the reservoir during the summer stratification period, possible interferences by high concentrations of these two metals were also studied.

The results of this study show that a one-step extraction can be used to concentrate the eight trace metals and that these metals could be determined by atomic absorption in this single extract. The procedure was modified so that the concentration of these metals in both the soluble and particulate phases could be determined.

REAGENTS AND INSTRUMENTATION

The reagents used in this study were as follows:

1. Diethyldithiocarbamate (DDC) — 20 g of Eastman diethyldithiocarbamic acid-sodium salt were mixed with 380 ml of deionized water. The resulting solution was filtered through a 0.45-micron Millipore Filter. The filtrate was then extracted two times with 15-ml portions of methyl isobutyl ketone.
2. Methyl isobutyl ketone was Eastman 4-methyl-2-pentanone.
3. Phthalate Buffer — 102 g of Baker Reagent Grade potassium biphthalate were dissolved in deionized water and diluted to 500 ml. Fourteen ml of 1 M HCl were added and the resulting solution diluted to 1.0 liter.
4. Sodium hydroxide and hydrochloric acid used to adjust pH were both reagent grade chemicals.
5. 1,000 ppm stock standards for each of the metals (these standards were acidified with HCl after preparation):
   iron — Baker Reagent Grade powdered iron dissolved in hydrochloric acid

---

*Present address: Department of Chemistry, University of Arkansas, Fayetteville, Arkansas.

manganese — Baker Reagent Grade manganese sulfate
copper — Baker Reagent Grade copper metal dissolved in nitric acid
cobalt — Baker Reagent Grade cobalt carbonate dissolved in hydrochloric acid
nickel — Baker Reagent Grade nickel carbonate dissolved in hydrochloric acid
lead — Baker Reagent Grade lead nitrate
zinc — Baker Reagent Grade zinc metal dissolved in hydrochloric acid
chromium — Baker Reagent Grade sodium chromate

A Perkin-Elmer Model 303 atomic absorption spectrometer was used. During the late stages of the investigation a recorder readout accessory in conjunction with a Sargent Recorder was used. A Beckman pH meter was used for all pH adjustments.

Note: Extreme caution must be taken to avoid contamination of glassware and reagents. Rinsing of all glassware with 1:1 nitric acid containing a small amount of hydrofluoric acid followed by rinsing with distilled water, acetone, then deionized water proved to be successful.

THE EFFECT OF pH ON EXTRACTION OF HEAVY METALS

Lakanen (7) has discussed the effect of pH on the extraction of metals chelated with pyrrolidine dithiocarbamic acid. Chelation of several metals with this compound as well as with diethyldithiocarbamic acid is usually carried out in acidic solution. The manganese chelate formed by these reagents has been reported to have a low extraction efficiency in solutions with a pH lower than 3 (7).

A solution containing 0.50 ppm of each of the trace metals studied was prepared by diluting the stock standards. The pH of the resulting solution was 3.0. A 10.0-ml portion of the DDC solution was added to six 100-ml aliquots of the solution and allowed to stand for 10 minutes. Dilute sodium hydroxide and dilute hydrochloric acid were used to adjust the pH of these solutions in the range from pH 2 to pH 7. After pH adjustment, each solution was extracted with a 10.0-ml portion of MIBK. The organic extract was removed from the separatory funnel and was aspirated into the flame of the atomic absorption spectrometer. The absorbance was determined for each of the metals at the recommended settings for the instrument (8). The results of this determination are shown in Figure 1. It is clear that with the exception of manganese, all of the metals studied can be extracted with equal efficiency over the pH range from 2 to 7.

Further experiments indicated that, in addition to the pH of the media which is extracted, the pH at which the chelation takes place is also important. For example, if the pH of the initial solution was in excess of 4.0 (before addition of the DDC), the amount of iron which can be extracted is greatly reduced. Since the hydrolysis of the iron (III) ion can be expected as the pH is increased, it is highly likely that precipitation of iron prior to chelation may cause this decrease in extractibility. Since some of the samples were expected to contain relatively large amounts of iron, the possibility of coprecipitation of other ions with large amounts of hydrated iron (III) could serve as a potential source of error.

To eliminate this problem, samples, standards, and test solutions were maintained at pH 1-2 until the beginning of the procedure. The pH of the solution to be extracted was adjusted to 3.6 immediately prior to the addition of the DDC. A phthalate buffer was used to facilitate this pH adjustment. No loss of the extractibility of iron was found at this pH.

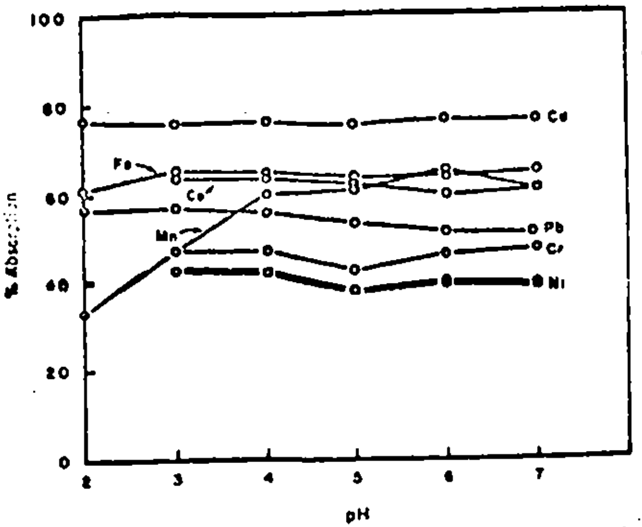


Fig. 1. pH dependence of extraction of heavy metals from diethyldithiocarbamic acid–methyl isobutyl ketone system.

A 7.0-ml aliquot of the DDC solution was determined to provide an adequate excess of the chelating agent. The addition of the DDC solution to the sample at pH 3.6 resulted in a solution with a pH of 7.0. Extraction at pH 7.0 provided a reasonable recovery of the eight metals which were studied.

STABILITY OF EXTRACT

Five 100-ml aliquots of a solution containing 0.50 ppm of the metals which were being studied were measured and the pH adjusted (after addition of 2.0 ml of phthalate buffer) to 3.6. After the addition of 7.0 ml of DDC, the solutions were extracted with 10.0 ml of MIBK. These solutions were aspirated into the flame of the atomic absorption spectrometer and the absorbance of each metal was determined at varying times after the extraction. The results of this study for copper, iron and manganese are shown in Figure 2. The results obtained for the other metals gave

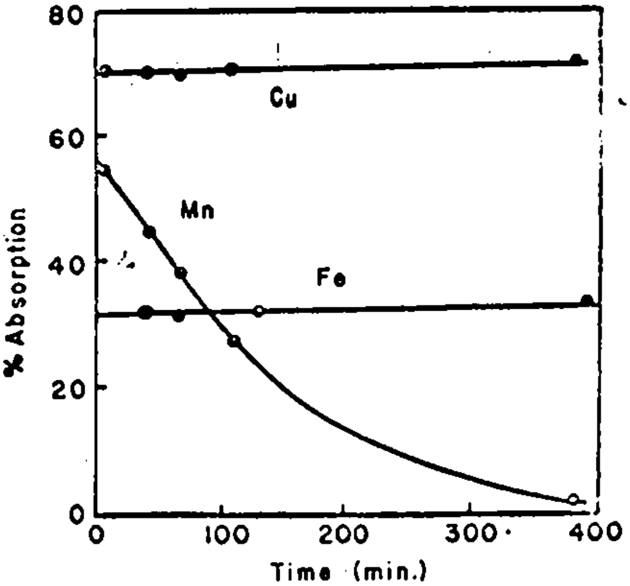


Fig. 2. Stability of extracted heavy metals (data for cobalt, nickel, chromium, lead, and zinc show no time dependence over the 400 minute period).

TABLE I
Instrument Settings for Determination of Heavy Metals

Element	Wavelength Setting (mμ)	Lamp Current (ma)	Slit Width (A)	Meter Response	Scale Expansion
Fe	248	30	2	3	5
Mn	279	20	7	2	2
Cu	325	40	7	2	2
Co	241	30	2	3	5
Ni	232	25	2	3	5
Cr	358	25	2	3	5
Pb	217	30	7	3	5
Zn	214	15	20	3	5

lines essentially parallel to those shown for copper and iron. It is clear that the atomic absorption determination of manganese must be carried out very soon after extraction. A delay of one hour can cause a 60 percent reduction in sensitivity for this metal. In all cases, care should be taken to insure that the time period between extraction and aspiration of standards and unknowns is the same.

STANDARDIZATION AND SENSITIVITY

Solutions containing 10, 25, 50, 75, and 100 ppb of each of the eight metals were prepared by appropriate dilution of the stock standards. The pH of these solutions was adjusted to 3.6 after the addition of 2.0 ml of the phthalate buffer. Seven ml of the DDC solution were added and the solutions were extracted with 15.0-ml portions of MIBK. The resulting extract was aspirated into the flame of the atomic absorption spectrometer and the absorption determined for each metal. The instrument settings for each of the determinations are shown in Table I. All elements used an air flow of 9 and a fuel flow of 5. The sample uptake rate was 5.4 ml/min except for lead and zinc where it was 5.0 and 4.0 ml/min respectively. A set of typical standard curves for the eight metals studied is shown in Fig. 3.

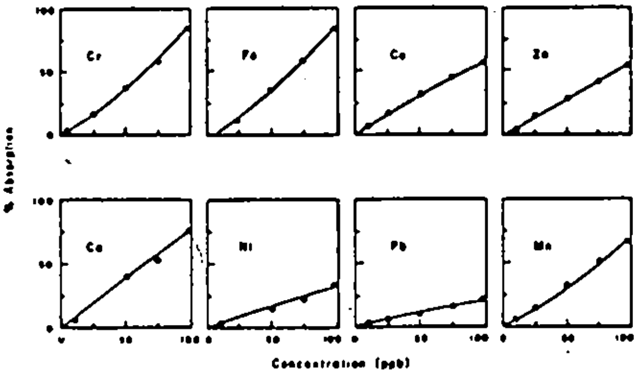


Fig. 3. Typical calibration curves for the eight heavy metals.

The approximate concentration of each of the metals which gives 1.0 percent absorption was as follows: chromium — 1 ppb, iron — 1 ppb, copper — 2 ppb, zinc — 2 ppb, cobalt — 1.5 ppb, nickel — 3 ppb, lead — 4 ppb, and manganese — 1.5 ppb. Sensitivity was improved by determining the amount of absorption using a recorder readout accessory with scale expansion.

INTERFERENCES

No spectral interferences are reported in the procedure manual for the spectrometer (8). Since relatively large excesses of iron and manganese could be expected in some of the samples, the contribution of large excesses of both of these metals was investigated. A standard curve was prepared for each of the metals as described above and the contribution (in ppb) from a solution extracted similarly containing 5.0 ppm of iron and another containing 5.0 ppm manganese was determined. The contribution by 1.0 ppm iron and 1.0 ppm manganese was computed for each of the metals. These contributions in ppb are given in Table II. Using the information given in this table, it was possible to correct for the contribution from large concentrations of iron and manganese. It is clear that for most of the metals, the concentration of iron and manganese would have to exceed 100 ppb before the correction would become significant. For other metals, clearly no correction is needed until iron or manganese exceeds 1.0 ppm.

TABLE II
Contribution (ppb) Caused by 1.0 ppm of Fe and 1.0 ppm of Mn

	Metal Being Determined							
	Fe	Mn	Cu	Co	Ni	Pb	Cr	Zn
1.0 ppm Fe		9.0	0.6	0.0	0.0	4.6	0.0	0.0
1.0 ppm Mn	1.2		0.8	0.4	0.6	0.0	0.0	9.2

SAMPLING AND PRESERVATION OF SAMPLES

Water samples were taken from the reservoirs using a Van Dorn type sampler. Immediately [illegible] collection of the sample, a 200-ml aliquot was filtered through a 0.45-micron Millipore Filter. The filter was washed with 100 ml of deionized water immediately prior to filtration. The filtrate was acidified with 16 drops of concentrated hydrochloric acid and transported to the laboratory for analysis. The filters were reserved for analysis of the particulate fraction.

SUMMARY OF PROCEDURE

A 100-ml aliquot of the acidified water sample was measured into a 250-ml Erlenmeyer flask. Two ml of the phthalate buffer were added and the pH adjusted to 3.6 ± 0.1. After adjustment of the pH, 7.0 ml of the DDC solution were added. The solution was transferred into a 500-ml separatory funnel (Teflon stopcock) and a 15.0-ml portion of MIBK was pipetted directly into the funnel. The mixture was shaken vigorously for 30 seconds, then allowed to separate. The MIBK layer was drawn off into a glass stoppered test tube.

A set of standards (10, 25, 50, 75 and 100 ppb) and a blank (deionized water) were prepared for each set of determinations. Between 20 and 30 water samples can be handled by this procedure at one time. Manganese must be determined immediately upon completion of the set of extractions in order to prevent loss of sensitivity. The other metals are generally determined within the following two to three hours.

REPRODUCIBILITY

A set of ten test samples containing 50 ppb of each of the metals was subjected to the analysis procedure described above. The results of these analyses are shown in Table III.

TABLE III
Recovery of 50 ppb of Each Metal Added

Determination Number	ppb Found							
	Mn	Cu	Zn	Fe	Pb	Co	Ni	Cr
1	52	46	48	48	44	46	51	47
2	52	48	44	47		52	48	47
3	52	46	44	47		53	53	50
4	49	48	44	46		51	48	50
5	47	44	48	45	42	51	52	46
6	48	50	49	50	46	50	50	49
7	53	46	46	46	45	50	50	49
8	52	47	47	45	44	50	51	52
9	58	46	46	45	56	50	47	50
10	52	47	47	47	52	49	47	49
Mean Value	51	47	46	47	47	50	50	49

DETERMINATION OF METALS IN PARTICULATE FRACTION

One half of the Millipore Filter which had been reserved from the initial field filtering was treated with 3 ml of 1:1 hydrochloric acid and warmed for approximately 30 minutes. The acid and washings were quantitatively transferred to a 100-ml volumetric flask and diluted to the mark with deionized water. The diluted samples were subjected to the same procedure described above.

SAMPLE RESULTS

Table IV shows the results for the analysis of the eight heavy metals in both the filtered and particulate fractions in samples taken from Lake Hamilton (reservoir on the Ouachita River near Hot Springs, Arkansas).

CONCLUSION

The determination of eight heavy metals — iron, manganese, copper, cobalt, nickel, chromium, lead, and zinc — in surface water can be determined at concentrations of a few ppb using a single step chelation-extraction system. It is possible to correct for the interferences from relatively large concentrations of iron and manganese. Using proper field sampling and filtration procedures, the concentration of the metals in the filtered and particulate fraction (greater than 0.45 microns) can be determined.

Preliminary results indicate that silver and cadmium may be included in this one step extraction procedure and measured with a relatively high degree of sensitivity.

TABLE IV
Trace Metal Concentration
Lake Hamilton, Arkansas, July 16, 1968

Filtered Fraction	Concentration (ppb)							
Depth (M)	Fe	Mn	Cu	Co	Ni	Cr	Pb	Zn
0	14	5	15	4	1	0	4	0
8	1	3	12	2	0	0	8	10
15	9	47	13	5	3	0	0	4
20	7	50	18	4	0	0	0	3
26	35	225	17	5	1	0	4	13
Particulate Fraction (greater than 0.45 microns)								
0	2	4	4	2	0	0	1	3
8	13	6	6	2	0	0	0	14
15	47	13	5	4	0	0	3	1
20	107	30	4	2	0	0	2	2 3
26	157	38	6	4	0	0	14	5

ACKNOWLEDGMENT

The work upon which this report is based was supported in part with funds provided by the Office of Water Resources Research, U. S. Department of the Interior, under Contract No. B-002-ARK, as authorized under the Water Resources Research Act of 1964, P.L. 88-379 as amended by P.L. 89-404.

Received August 20, 1970

REFERENCES

1. John D. Hem, *Study and Interpretation of the Chemical Characteristics of Natural Water*, U. S. Geological Survey Water-Supply Paper 1473, U. S. Government Printing Office, Washington, D. C. (1959).
2. J. Shapiro, Journal Am. Water Works Assoc. 56, 1062 (1964).
3. G. E. Hutchinson, *A Treatise on Limnology*, Volume I, pp. 691, 801, John Wiley and Sons, Inc., New York, N. Y. (1957).
4. C. E. Mulford, Atomic Absorption Newsletter 5, 89 (1966).
5. T. Joyner and J. Finley, Atomic Absorption Newsletter 5, 4 (1966).
6. J. A. Platte and V. M. Marcy, Atomic Absorption Newsletter 5, 289 (1965).
7. E. Lakanen, Atomic Absorption Newsletter 5, 17 (1966).
8. *Analytical Methods for Atomic Absorption Spectroscopy*, Perkin-Elmer Corp., Norwalk, Connecticut (1967).