CATALYTIC-KINETIC DETERMINATION
OF
SOME TRANSITION METALS

By

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OF

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ABSTRACT:

A method has been developed for the determination of iron, copper, cobalt and manganese at levels ranging from a few to several hundred parts per million. A Landolt reaction employing peroxydisulphate, iodide and thiosulphate was used to accomplish this.

All four metals can be determined alone and their binary mixtures, except for mixtures of cobalt and manganese, can be analyzed. These determinations can be carried out by means of simple equipment and procedures.

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INTRODUCTION

Most measurements used for chemical analysis are made after reactions have reached equilibrium. However, the course of reaction before equilibrium is attained can be a source of analytical information. Techniques of analysis which employ measurements of reaction rates are known as kinetic techniques and are applicable to a wide range of problems. Kinetic methods are divided into two main categories: catalytic and non-catalytic. In non-catalytic methods reactions are used in which the analyte substance is consumed during the reaction; this arrangement is particularly useful for resolving mixtures of substances which react at different rates, but it does not offer particularly high sensitivity.

Kinetic methods in which the substance determined acts as a catalyst possess important advantages. High sensitivity can be achieved by means of very modest instrumentation. Indeed, detection limits often approach those of atomic absorption and neutron activation analyses. In favourable instances, high sensitivity is accompanied by excellent specificity. As an example, the reaction between ferric and thiosulphate ions is catalyzed exclusively by copper ions (1). Catalytic-kinetic determinations are thus admirably suited to the trace analyses which are becoming increasingly important.

The advantages of catalytic methods are, however, balanced by a general difficulty in obtaining reproduceable measurements. Uncertainties as much as, though rarely more than, ten percent are not uncommon (2).

Kinetic analyses are carried out by means of "indicator" reactions whose rates are influenced by the materials sought. With a reaction of the general form

$$A + B \rightleftharpoons X + Y \qquad (I)$$

the rate of reaction can be found by monitoring the change in concentration of either a reagent (A or B) or a product (X or Y) as the reaction proceeds. The substance whose concentration is measured is called "the indicator substance": its concentration can be followed by chemical analysis, spectrophotometry, thermometry or any other suitable means. The rate of the reaction is changed by the addition of substances called catalysts which are defined as substances which participate in a reaction, and change its rate, but are not consumed or destroyed by the reaction. A catalyst particle may participate in a reaction many times before equilibrium is reached. This repetitive action produces the amplification effect which is responsible for the high sensitivity of catalytic determinations. If the reaction conditions and the initial reagent concentrations are held constant, the extent of the effect of a catalyst depends upon its concentration; this is the fundamental principle of catalytic analysis.

The concentration-time data collected are usually employed in one of three ways: the initial slope of the concentration versus time plot, the concentration found at a predetermined time after initiation of the reaction, or the time required to produce a fixed change in concentration can be used as a measure of reaction rate. Only the third method will be discussed here as it has been shown (3) to possess advantages over the other two methods when catalysts are determined.

In all three cases, however, calibration curves relating the measured quantity to catalyst concentration are obtained by means of standard catalyst solutions. Data from trials with sample materials are evaluated using these curves.

A general expression for the relationship between measured time and catalyst concentration can be derived for fixed concentration experiments (4). The rate of reaction (I) can be expressed as:

$V(\text{uncatalyzed}) = \frac{dx}{dt}(\text{uncatalyzed}) = k[A]_0([B]o - x)$ (1)

where V is the rate of the uncatalyzed reaction, x is the concentration of a product, k is a constant and [A]o and [B]o are initial reagent concentrations. Reagent A is assumed to be present in large excess and therefore to be at practically constant concentration. This is the usual practice. Similarly, for the catalyzed reaction, $V(\text{catalyzed}) = \frac{dx}{dt}(\text{catalyzed}) = Kf\,[C]\,([B]_0 - x)$ (2) where K is a constant, f is some function of reagent concentrations, [C] is the concentration of the catalyst and [B]o and x are as in equation (1). The overall rate, then, is the sum of these two rates:

$$V = \frac{dx}{dt} = Kf[C]\,([B]o - x) + k[A]o\,([B]o - x) \qquad (3)$$

which, after integration, yields an expression of the form

$$\frac{1}{t} = \frac{1}{\ln\left(\frac{[B]o}{[B]\tau}\right)}\,(Kf\,[C] + k\,[A]o\,) \qquad (4)$$

where t is the time during which [B] changes from [B]o to [B]τ. It is readily apparent that the inverse of the measured time is linearly related to the catalyst concentration. If the indicator reaction scarcely occurs in the absence of a catalyst, equation (4) reduces to

$$\frac{1}{t} = \frac{Kf}{\ln\left(\frac{[B]o}{[B]\tau}\right)}\,[C] \qquad (5)$$

Most catalytic methods employ oxidation-reduction reactions; ones in which an organic reagent is oxidised to a coloured form are particularly popular and useful. Many of these reactions are set out in a book by K.B Yatsimirskii (1). A useful and interesting ligand exchange reaction has been developed by Margerum and Steinhaus (5) for the catalytic determination of metals and of complexing agents. Complexing agents can also be determined by means of their effects upon catalysis by metal ions. (6)

The performance of catalytic determinations is limited in several ways. Reproduceability, and, as a result, detection limits are constrained by the presence of a variable background. This background consists of the uncatalyzed reaction together with catalyzed reactions arising from impurities in reagents, foreign matter and active sites on vessel walls. Further variations are caused by temperature fluctuations since all reaction rates are strongly influenced by changes in temperature.

Specificity may be decreased by the response of reaction rates to changes in the ionic strength of the reaction medium; if the ionic strength of the standard solutions does not approach that of the sample solution, errors will result. In this way, the presence of substances which do not participate in the indicator reaction may, nevertheless, affect its rate.

If the indicator reaction is too fast or too slow, its rate may be either difficult or inconvenient to measure. This consideration limits the range of reactions suitable for use as indicator reactions.

These limitations can be overcome to some extent by proper choice of reaction, clean reagents and working conditions, and careful temperature control.

Sensitivity is governed by the rate of the reaction involving the analyte catalyst. This rate, and consequently the sensitivity, can be increased by increasing the temperature, the ionic strength, and the reagent concentrations. These changes will also increase the rate of the background reactions and thus affect the gain in sensitivity. The addition of substances called activators - usually complexing agents - can, however, increase the rate of the catalysed reaction with only slight effect on the background rate. (7)

A class of reactions collectively known as Landolt reactions has been proposed for analysis by the fixed concentration method. The first application was reported by Svehla and Erdey (8). A summary of examples found in the literature is presented in Appendix A. Landolt reactions are arranged as follows:

$A + C \rightarrow C^* +$ products slow IIa

$C^* + B \rightarrow C +$ products fast IIb

$A + B \rightarrow$ products very slow IIc

If A is added in excess with respect to B, when enough B has been consumed to render the rates of reactions IIa and IIb equal the so-called Landolt effect will occur. That is, C* will appear, having previously been prevented from doing so by fast reaction with B. Reaction IIc is usually much slower than reaction IIa and can be ignored. Note that reagent C acts as a catalyst of reaction IIc.

In what follows, reagent A will be called the substrate, reagent B will be called the retardant - it retards the appearance of C* - and reagent C will be called the indicator catalyst.

The reaction time is the time between mixing of solutions to start the reaction and the appearance of C*. The fixed concentration change is determined by the initial concentration of the retardant. If a second catalyst is added to the reaction mixture, the reaction time will decrease; this decrease can be made to reflect the concentration of the added catalyst. An expression similar to equation (2) can be written to describe this reaction and integrated to give equation (6).

$$\frac{1}{t} = \frac{(Kf[C] + K_I f_I [C_I])}{\ln \frac{[A]o}{[A]\tau}} \qquad (6)$$

$$\text{or, } \frac{1}{t} = \frac{(Kf[C] + K_I f_I [C_I])}{\ln \frac{[A]o}{[A]o - [B]o}} \qquad (7)$$

If $[A]o >> [B]o$, so that [A] can be regarded as a constant, integration gives equation (7a).

$$\frac{1}{t} = \frac{[A]o}{[B]o} (Kf[C] + K_I f_I [C_I]) \qquad (7a)$$

where the subscript I denotes the indicator catalyst. Again, the inverse of the reaction time is linearly related to the analyte catalyst concentration if all other initial concentrations are constant.

Equation (6) holds true only if catalyst C reacts most slowly with the substrate in its cycle. If it reacts in rate-determining fashion with the indicator catalyst a linear relation between $\frac{1}{t}$ and [C] is obtained only if the substrate is in such a large excess that the change in its concentration can be neglected. Under these circumstances, equation (7a) becomes

$$\frac{1}{t} = \frac{k'[C_I]}{[B]_o} [C] + \frac{k'_I [A]o\ [C_I]}{[B]_o} \qquad (8)$$

If the reaction between catalyst C and the retardant is rate-determining, a linear relationship is not obtained.

The requirements for a useful Landolt reaction are now clear. First, the uncatalyzed reaction must be slow. Second, both the indicator and the analyte catalysts must react with the retardant more rapidly than with the substrate. Third, the indicator catalyst must react with the substrate sufficiently rapidly to produce a detectable quantity of its detectable form, C*, soon after the retardant has been exhausted.

The advantage of this type of fixed concentration method is its easy execution. It is not necessary to monitor the concentration of any substance throughout the course of the reaction. It is sufficient to be able to detect the indicator catalyst at the end of the reaction time. If the detected substance is highly coloured, or produces a colour, its appearance can be noted by eye. If it is not coloured, suitable devices must be used to detect it. Polarography (9), thermometry (10) and biamperometric detection (10, 11) have been used. Usually, all that is required is a timing device and some means, such as a thermostatted bath, of controlling temperature.

Although easier to carry out, Landolt procedures are not as sensitive as other catalytic-kinetic methods. The action of the indicator catalyst constitutes a considerable background signal which necessitates a correspondingly large analyte signal. Landolt reactions, as a result, possess less favourable detection limits than do non-Landolt reactions. For example, the Landolt reaction using bromate, iodide and ascorbic acid ions for the determination of vanadium was found by Thompson and Svehla (12) to give a detection limit of 0.33μg of vanadium per millilitre of reaction solution. The non-Landolt reaction between bromate and iodide was found by Yatsimirskii and

Kalinina (13) to detect 10^{-5} μg of vanadium per millilitre of reaction solution.

Most indicator reactions are catalyzed by several substances yet, except in a few cases (5, 14, 15, 16, 17), techniques for analysing mixtures by catalytic-kinetic methods have not been pursued. This study was undertaken to decide whether this could be done by means of a particular reaction which meets the conditions set out for Landolt systems. Pall, Erdey and Svehla (18) proposed the Landolt reaction of peroxydisulphate (hereafter persulphate), iodide and thiosulphate ions for the determination of copper and iron.

The reaction scheme is given as:

$S_2O_8^{=} + 2I^{-} \rightarrow I_2 + 2SO_4^{=}$ slow IIIa

$I_2 + 2S_2O_3^{=} \rightarrow 2I^{-} + S_4O_6^{=}$ fast IIIb

overall $S_2O_8^{=} + 2S_2O_3^{=} \rightarrow 2SO_4^{=} + S_4O_6^{=}$ IIIc

Persulphate acts as the substrate, thiosulphate as the retardant and iodide as the indicator catalyst. Elemental iodine is detected by means of a starch suspension. Table I shows some rate constants collected from the literature which indicate that this reaction fulfills the requirements for a Landolt system. Persulphate is well known for its slow reactions and thiosulphate is known to react rapidly.

Reports by Patat and Prolss (19) and by King and Steinbach (20) indicate that the rate law for this reaction may be expressed as

$$\frac{-d[S_2O_8^{=}]}{dt} = k[S_2O_8^{=}]\,[C] + k\,[S_2O_8^{=}]\,[I^{-}] \qquad (9)$$

which, when integrated, gives

$$\frac{1}{t} = \frac{1}{\ln\left[\dfrac{[S_2O_8^{=}]_o}{[S_2O_8^{=}]_o - \frac{1}{2}[S_2O_3^{=}]_o}\right]}\left(K[C] + k_I[I^-]\right) \qquad (10)$$

If $[S_2O_8^{=}]_0$ is much greater than $[S_2O_3^{=}]_o$

$$\frac{1}{t} = \frac{[S_2O_8^{=}]_o\,(k[C] + k_I[I^-])}{[S_2O_3^{=}]_o} \qquad (11)$$

The similarity of equation (10) to equation (7) demonstrates that this Landolt system belongs to the fixed concentration class of catalytic analysis.

There are several possible approaches to the problem of mixture analysis. If suitable masking agents can be found, it may be possible to isolate the effect of each component of the mixture in turn and so determine its concentration. At the other extreme, if conditions can be changed so that the rates of reaction due to the various catalysts present change to different extents, analysis may be carried out by applying as many different sets of conditions as there are catalysts and using a set of simultaneous equations to calculate individual concentrations.

Changes in reaction rates caused by changes in pH were used by Yatsimirskii and Raizman (15) to analyse mixtures of zirconium and hafnium by means of the reaction between iodide and hydrogen peroxide. The same approach was used by Alekseeva and Nemzer (16) to analyse mixtures of germanium and phosphorus using the molybdic acid-iodide reaction and by Margerum and Steinhaus (5) to analyse mixtures of a variety of metals using a ligand exchange reaction. Worthington and Perdue (17) analysed mixtures of osmium and ruthenium by changing the reactant concentrations for the cerium-arsenic reaction.

A third possibility combines these approaches by isolating one or more catalysts by masking, then using these results to determine other catalysts by their action in the absence of masking agents. Mixtures of iodide and osmium were analyzed in this way by Rodriguez and Perdue (10) who added mercury ions to mask iodide for the determination of osmium, then determined iodide without masking. The cerium-arsenic reaction was used.

The first method is not easy to carry out if similar elements are present since selective masking of oxidation-reduction reactions is not simply done. The third method also suffers from this defect. If the catalysts present interact with each other, the second and third routes may prove difficult to calibrate. The examples quoted above did not suffer from these problems. Where interactions are present a variation of the third arrangement may be possible. Once one element has been determined, the appropriate concentration of that element can be introduced into the solutions used to calibrate for the second element. This avoids the complicated calibrations necessitated by interacting calalysts.

This thesis explores the behaviour of the persulphate-iodide-thiosulphate Landolt reaction and proposes some analytical uses of this system.

TABLE I

Rate Constants of Reactions with Peroxydisulphate and Thiosulphate

Reaction	Rate Constant $mol^{-1}\ min^{-1}$	Reference
$S_2O_8^{=} + 2\ S_2O_3^{=} \quad 2\ SO_4^{=} + S_4O_6^{=}$	0.04	19
$S_2O_8^{=} + 2\ I^{-} \rightarrow 2\ SO_4^{=} + I_2$	0.2	20
$I_2 + 2\ S_2O_3^{=} \rightarrow S_4O_6^{=} + 2\ I^{-}$	9.06×10^{6}	21
$S_2O_8^{=} + 2\ Cu^{+} \rightarrow 2\ SO_4^{=} + 2\ Cu^{2+}$	500^{a}	19
$2\ S_2O_3^{=} + 2\ Cu^{2+} \rightarrow S_4O_6^{=} + 2\ Cu^{+}$	very fast[b]	
$S_2O_8^{=} + 2\ Fe^{2+} \rightarrow 2\ SO_4^{=} + 2\ Fe^{3+}$	8.46×10^{3}	22
$2\ S_2O_3^{=} + 2\ Fe^{3+} \rightarrow S_4O_6^{=} + 2\ Fe^{2+}$	1.44×10^{4}	23

a in the presence of thiosulphate

b this reaction is said to be very fast, (19, 20) but no quantitative data has been found

II EXPERIMENTAL PART

All reagents were used without purification. Water used for persulphate and thiosulphate solutions was doubly distilled; otherwise it was distilled and deionized by means of a Barnstead Still and Sterilizer Co. Bantam Demineralizer. 1,10-Phenanthroline was synthesized by the method of Madeja (24). Metal-ion solutions were standardized by EDTA back-titration with magnesium (copper, cobalt, manganese) (25, 26, 27) or by titration with dichromate (iron) (28). During kinetic experiments, the reaction temperature was held at 26° ± 0.02° C and the following solutions and procedures were used except where otherwise indicated.

Solution I: 7g $K_2S_2O_8$, dissolved and diluted to 500 ml with water

Solution II: 0.4 g $Na_2S_2O_3 \cdot 5H_2O$
1.64 g KI
6.8 g $NaC_2H_3O_2$
5 ml 1M H_2SO_4

dissolved and diluted to 250 ml with water

Solution III: 15 ml 1 M H_2SO_4
5 g starch dissolved and diluted to 250 ml with water.

These solutions yield the following concentrations in the final reaction mixture: 0.0172 M $K_2S_2O_8$, 0.001 M $Na_2S_2O_3 \cdot 5H_2O$. 0.0066 M KI, 0.055 M $NaC_2H_3O_2$, 0.013 M H_2SO_4 and 0.033 g/ml starch.

When appropriate, complexing agents were also included in Solution III.

The following procedure was used: 1 ml of sample solution, 1 ml of distilled deionized water or of another solution being tested, 1 ml of solution III and 1 ml of solution II were pipetted into one arm of a specially built reaction tube (figure 1). Two ml of solution I was pipetted into the other arm. The tube was closed and suspended in a glass water bath thermostatted by a B. Braun Melsungen Thermomix 1420 temperature controller for 30 minutes. The tube was tilted several times to mix its contents and the time was marked. When a blue colour appeared throughout the solution, the time was again marked. Ten tubes were used at once by means of a perspex rack (figure 2). The timer consisted of a battery connected through a hand-held switch to a Bausch and Lomb VOM-5 strip chart recorder. When the switch was thrown, a vertical trace was made on the chart paper. The distances from the mark for the start of the reaction to that for its end in each tube was used as the measure of the reaction time. This simple set-up proved to be reliable and effective. The combination of tubes and rack is particularly suitable for the simultaneous comparison technique elaborated by Bognar (29).

Throughout the rest of this presentation, the metal-ion concentration in the reaction solution is expressed as the number of micrograms of metal added in a one ml volume. It was felt that this convention would be more easily appreciated. One microgram added corresponds to one part per million in the sample solution and to one-sixth part per million in the reaction mixture. Table II gives the molar concentrations corresponding to the addition of one microgram of each of the metals examined. Where graphs are presented, error bars are shown if uncertainties extend beyond the symbols used in plotting.

When the concentration of persulphate or of iodide was

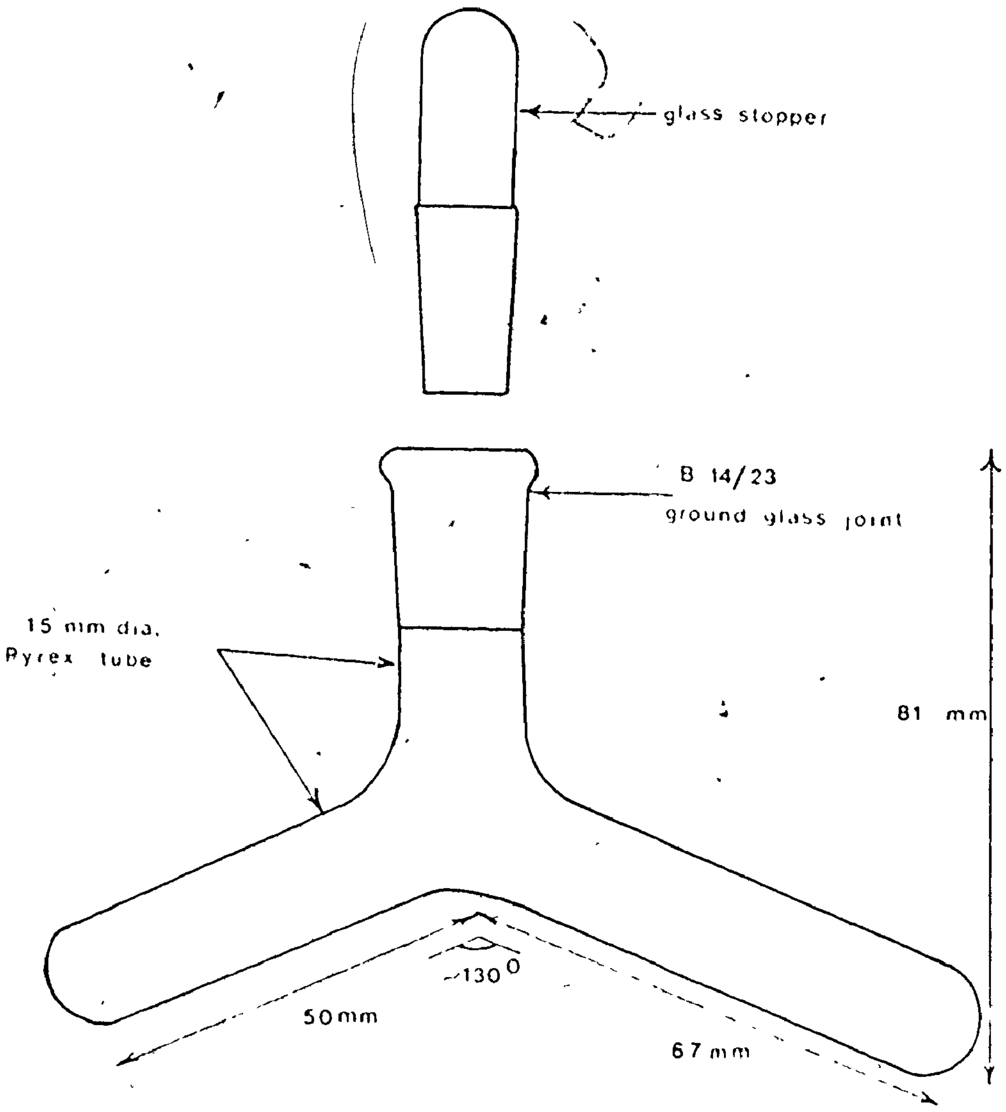

Figure 1

Reaction Tube

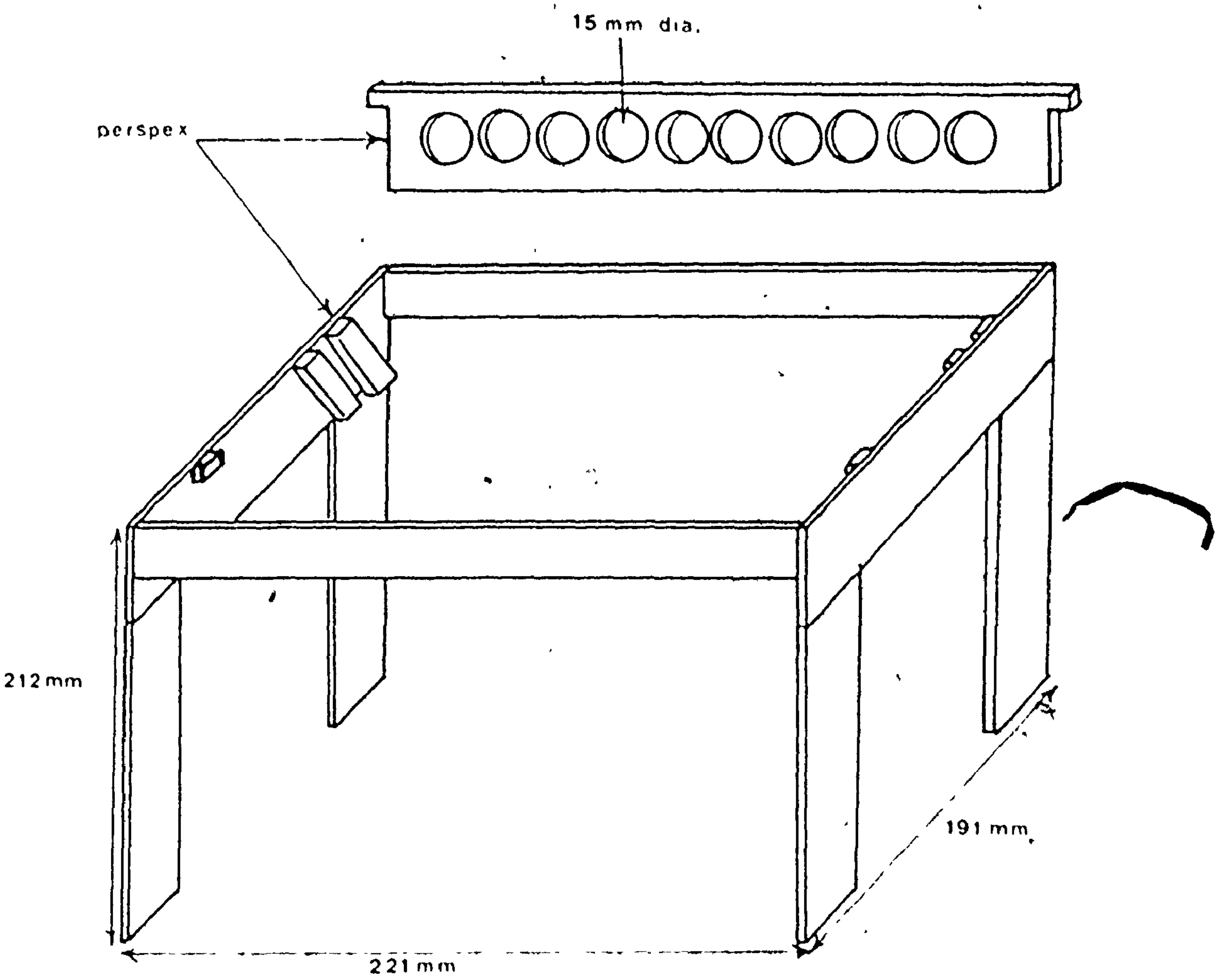

Figure 2

Reaction Tube Rack

of the solution. When the thiosulphate concentration was varied, sodium sulphate was used.

TABLE II

Concentrations Corresponding to Addition of 1μg of Metal

Metal-Ion	Form Used	Concentration (M)
Cu (II)	$Cu\ SO_4 .\ 5H_2O$	2.62×10^{-6}
Fe (II)	$Fe\ (NH_4)_2\ (SO_4)_2 . 6H_2O$	2.98×10^{-6}
Co (II)	$Co\ SO_4 . 7\ H_2O$	2.83×10^{-6}
Mn (II)	metal	3.03×10^{-6}
Zn (II)	$Zn\ SO_4 . 7\ H_2O$	2.55×10^{-6}
Al	Metal	6.18×10^{-6}
Cd (II)	$3\ Cd\ SO_4 . 8\ H_2O$	1.48×10^{-6}
Hg (II)	$HgCl_2$	8.31×10^{-7}
Cr (III)	$Cr_2(SO_4)_3 . 15\ H_2O$	3.20×10^{-6}
As	Metal	2.22×10^{-6}
V (V).	$Na\ VO_3$	3.27×10^{-6}
Ni (II)	NiO	2.84×10^{-6}
W (VI)	$Na_2WO_4 . 2H_2O$	9.06×10^{-7}
Mo (VI)	$(NH_4)_2\ MoO_4$ ·	1.74×10^{-6}
Ag (I)	Ag_2SO_4	1.54×10^{-6}

III RESULTS AND DISCUSSION

1. The Effect of Reagents and Conditions

Iron, copper, manganese and cobalt were found to give useful responses provided that cobalt was examined in the presence of an activating substance. Therefore, the effect of reaction conditions on reaction time was studied for solutions containing either no catalyst or one of these metals. The reaction times used to construct the graphs presented here can be found in Appendix (E).

Figures 3, 4 and 5 show the effects of persulphate, thiosulphate and iodide concentrations. Reaction times are linearly related to thiosulphate concentration; the inverse of the reaction time is linearly related to persulphate and iodide concentrations. This behaviour is consistant with equation (11). The plots for thiosulphate and persulphate show deviations at lower reagent concentrations. The effect of thiosulphate concentration is greatest with weakly catalyzed reactions; the effect of persulphate concentration is greatest with strongly catalyzed reactions.

The plots for the relation of reaction time to iodide concentration are parallel for the blank, iron and manganese. However, the plots for cobalt and copper have different slopes from the other plots. These deviations are considered in Appendix (C) which deals with the reaction mechanism.

Figure 6 shows the effect of temperature on the reaction time. Strongly catalyzed reactions are affected less by changes in temperature

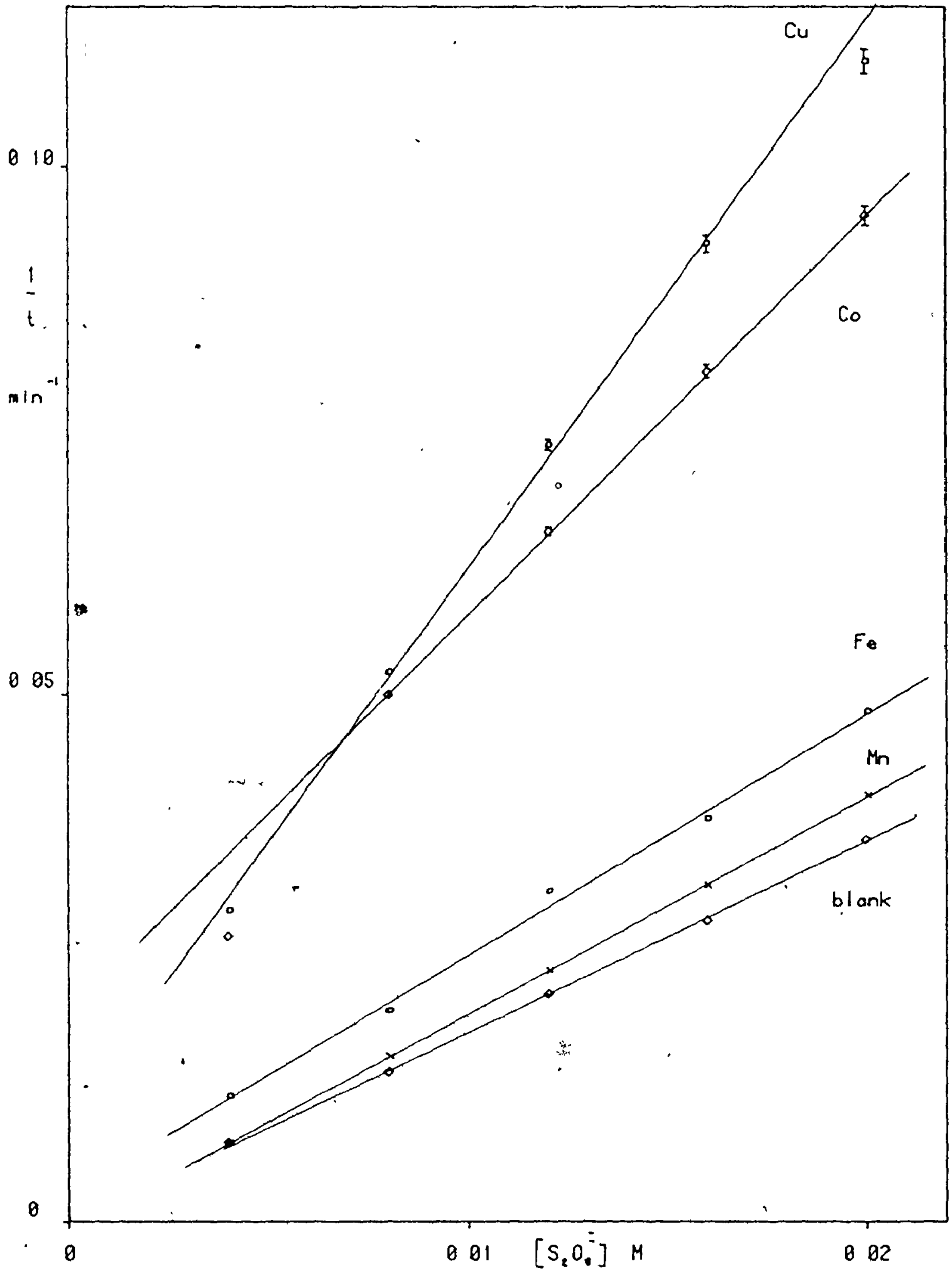

Figure 3

The Effect of Persulphate

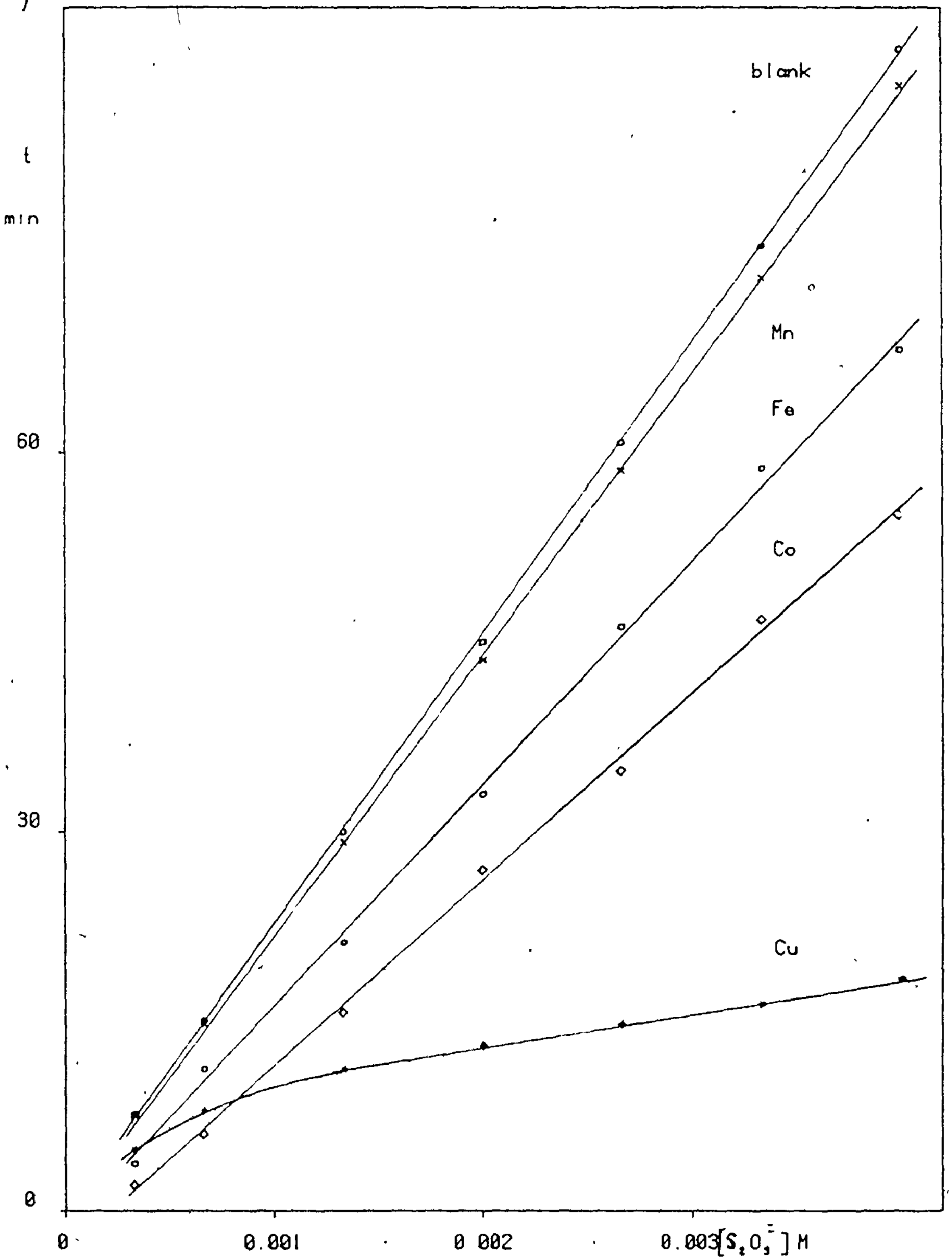

Figure 4

The Effect of Thiosulphate

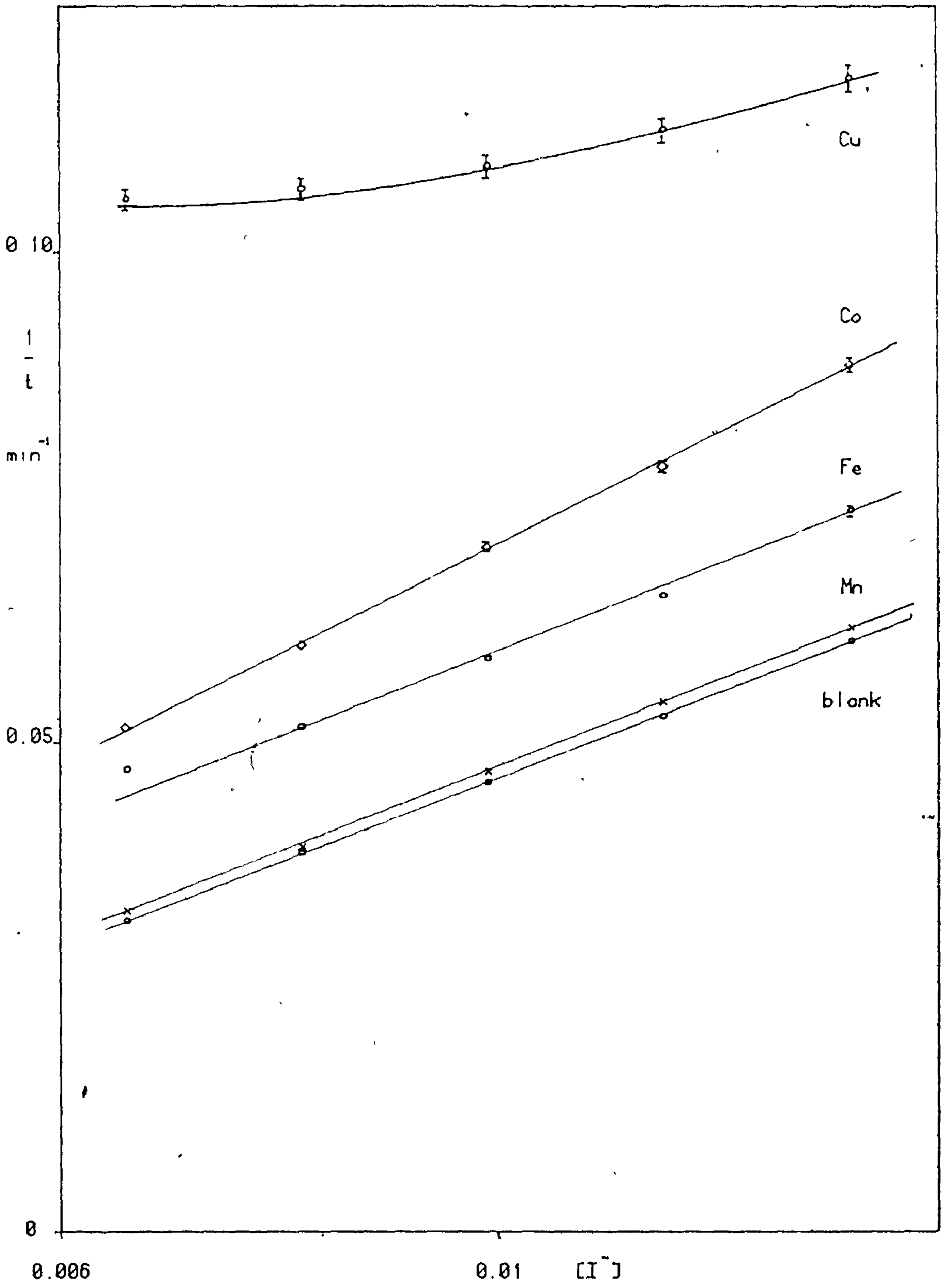

Figure 5

The Effect of Iodide

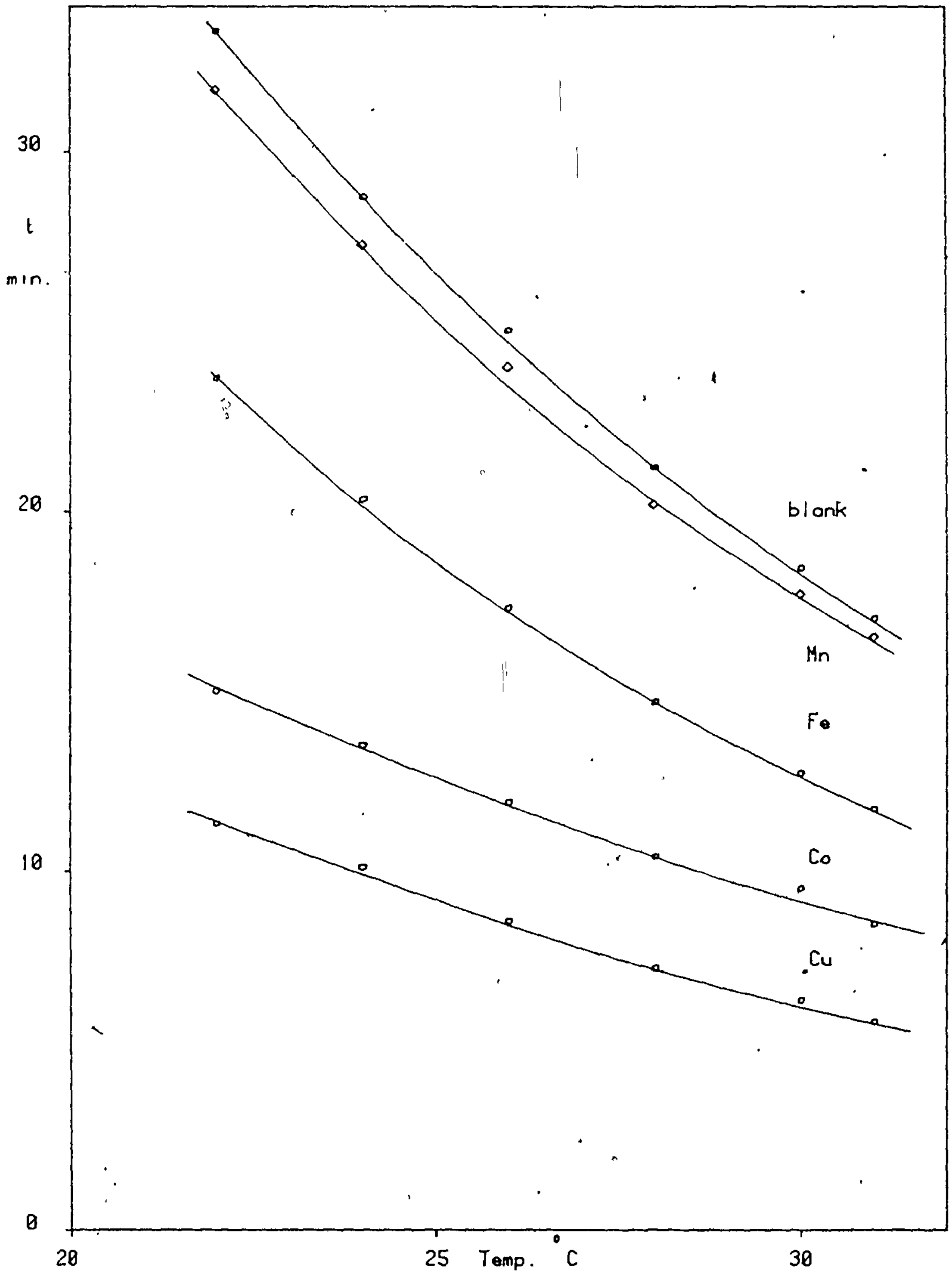

Figure 6

The Effect of Temperature

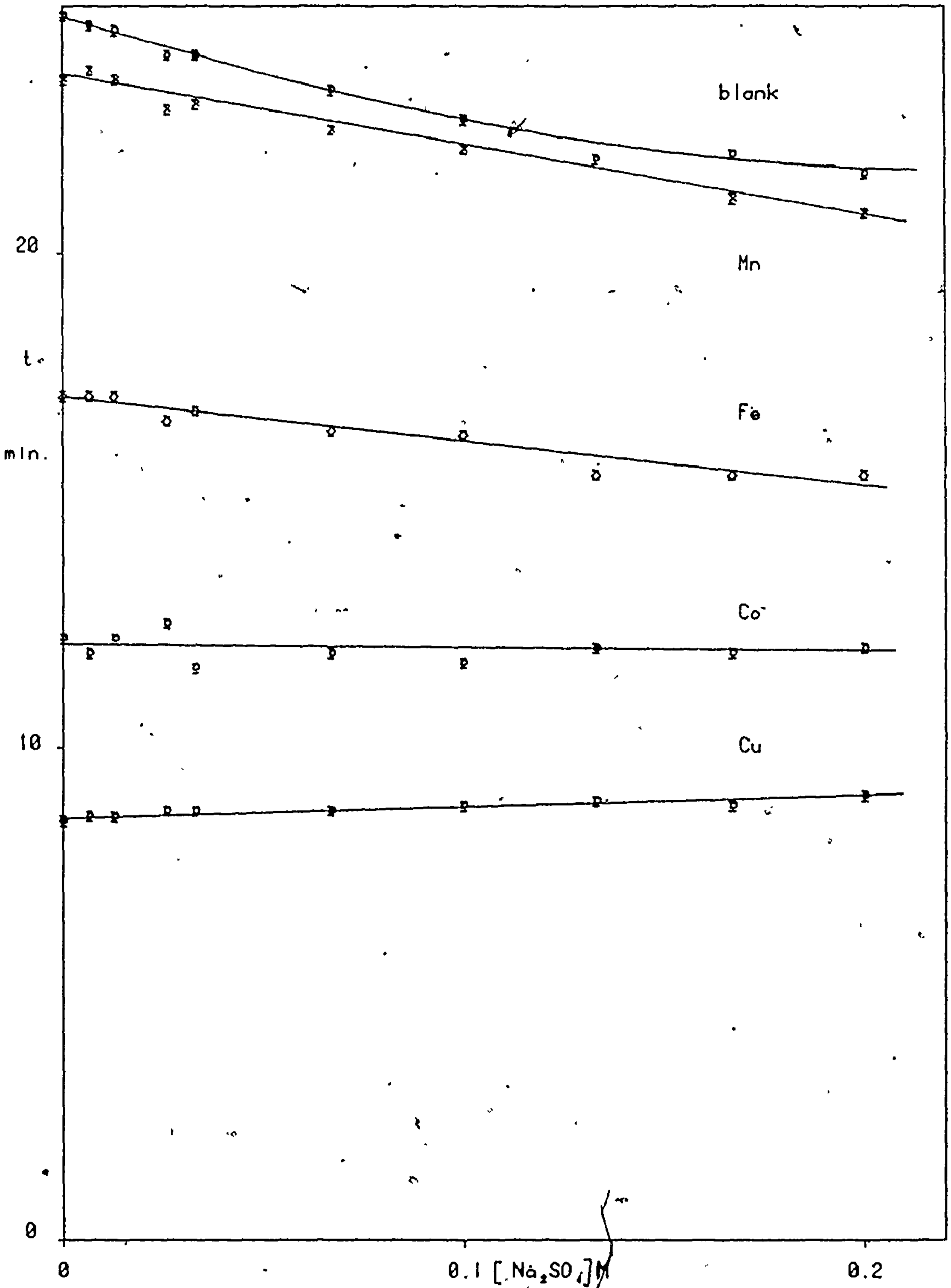

Figure 7

The Effect of Added Salt

than are weakly catalyzed reactions.

Figure 7 shows the effect of additions of the salt sodium sulphate. Such additions change the ionic strength of the reaction medium. The reaction times are not strongly dependent on ionic strength. It is interesting to note that cobalt and copper respond differently from iron, manganese and the blank solution.

Reaction times are not affected by added acid if its concentration in the reaction mixtures is less than about 0.017M. This corresponds to pH in the sample-solution of one. The addition of further acid causes decomposition of thiosulphate.

2. The Effect of Catalysts

Figures 8 and 9 show the relation between reaction time and added catalyst for manganese and iron and for cobalt and copper, respectively. Each plot shows one or more points at which the slope of the curve changes; this behaviour was noted by Patat and Prolss (19) during their study of the persulphate-thiosulphate reaction. If the catalytic action of copper is reduced by adding pyrophosphate, a break is found in its response curve at about forty-five micrograms as well as at three micrograms. Table III gives slopes and intercepts for useful portions of these response curves.

TABLE III

Catalyst Responses

Metal	Lower limit μg	Upper limit μg	Slope $min^{-1} \mu g^{-1}$	Intercept min^{-1}
Cu	3	--	2×10^{-2}	0.0490
Fe	35	150	3.93×10^{-4}	0.0370
Co	60	640	1.09×10^{-4}	0.0440
Mn	50	300	7.16×10^{-6}	0.0407

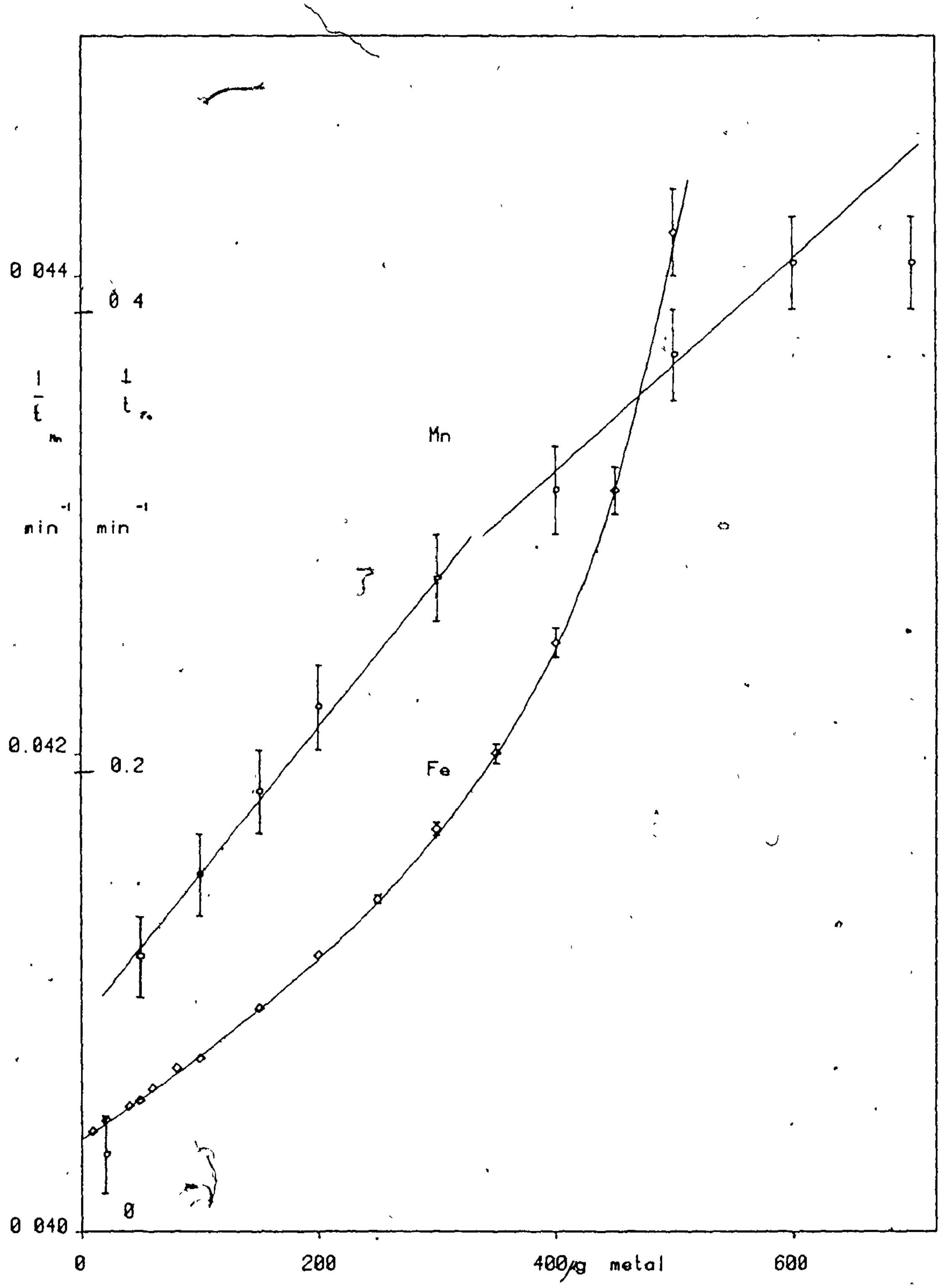

Figure 8

The Responses of Iron and Manganese

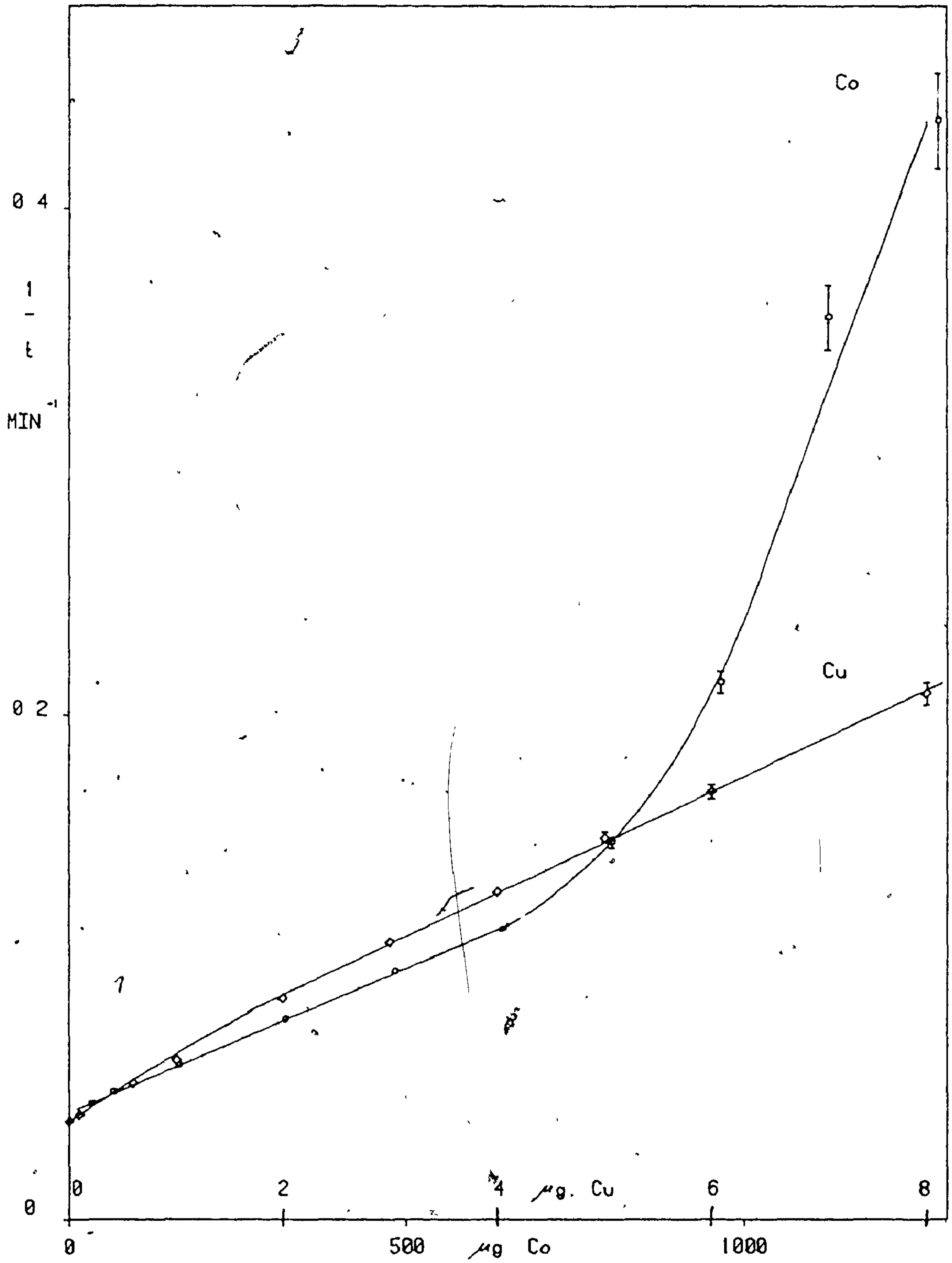

Figure 9

The Responses of Copper and Cobalt

Various metal ions were tested alone and in admixture with iron, copper, manganese or cobalt for catalytic effects. The results are shown in Tables IV to VIII. The figures shown were obtained by subtracting the reaction time found in the presence of the foreign ion from the time found in its absence. If this difference was less than 0.3 min, no entry was made. Mercury was found to increase the reaction time in a regular fashion; possible uses of this effect are considered in Appendix B.

TABLE IV

The Effect of Various Metals Alone

Metal-Ion	Change in Time (min) 1μg	10μg	100μg	1000μg
W(VI)	-	-	-1.0	-0.6
Al(III)	0.4	0.9	0.9	1.5
V(IV)	-	1.7	2.7	3.9
Ni(II)	-	-	0.5	1.9
Ag(I)	-	-	0.6	0.4
Cd(II)	-	-	-	0.4
Zn(II)	-	-	-	1.3
Mo(VI)	-	0.6	1.3	1.3
Cr(III)	-	-	0.6	1.2
Co(II)	-	-	-	0.8
Hg(II)	-	-	-	-13.2
As(III)	-	-	-	- 2.6

TABLE V

The Effect of Various Metal-Ions in the Presence of 2 mg of Cu

	Change in Time (min)			
Metal-Ion	1μg	10μg	100μg	1000μg
W(VI)	-	-	-2.7	-14.4
AI(III)	- -	-	--	-
V(IV)	-	-	0.4	0.4
Ni(II)	-	-	0.3	0.4
Ag(I)	-	-	--	-2.0
Cd(II)	-	-	--	-2.4
Zn(II)	-	-	--	-
Mo(VI)	-	-	--	-0.5
Cr(III)	-	-	--	-
Co(II)	-	-	--	-
Hg(II)	-	-	-1.2	-16.3
As(III)	-	-	--	-0.5
Mn(II)	-	-	--	-

TABLE VI

The Effect of Various Metal-Ions in the Presence of 50 μg of Fe

	Change in Time (min)			
Metal-Ion	1μg	10μg	100μg	1000μg
W(VI)	-	-	-	-3.1
Al(III)	-	0.7	0.4	0.4
V(IV)	-	3.2	4.5	4.2
Ni(II)	-	-	0.4	1.8
Ag(I)	-	-	-	-3.2
Cd(II)	-	-	-0.7	-2.1
Zn(II)	-	-	-	-
Mo(VI)	-	0.4	0.9	-2.1
Cr(III)	-	-	-	-4.3
Co(II)	-	-	-	0.4
Hg(II)	-0.9	-1.1	-1.4	-11.2
As(III)	-	-0.4	-1.3	-2.9

TABLE VII

The Effect of Various Metal-Ions in the Presence of 320μg of Co*

	Change in time (min)			
Metal-Ion	1μg	10μg	100μg	1000μg
W(VI)	-	-	-0.5	-0.4
Al(III)	-	-	-	0.3
V(IV)	-	-1.1	-1.8	-3.0
Ni(II)	-	-	-0.13	-0.7
Ag(I)	-	-	-0.5	-6.5
Cd(II)	-	-	-0.7	-10.9
Zn(II)	-	-	-	1.7
Mo(VI)	-	-	-	-
Cr(III)	-	-	-	-0.3
Mn(II)	-	-	-	-0.94
Hg(II)	-	-	-1.9	-2.6
As(III)	-	-	-	-1.2

* [phen] = 0.01 M

phen = 1.10 phenanthroline

TABLE VIII

The Effect of Various Metal-Ions in the Presence of 200μg of Mn

Change in Time (min)

Metal-Ion	1μg	10μg	100μg	1000μg
W(VI)	-	0.4	0.7	1.1
Al(III)	-	0.4	0.5	1.1
V(IV)	-	0.4	1.8	3.1
Ni(II)	-	-	-	1.2
Ag(I)	-	-	2.0	3.6
Cd(II)	-	-	-	-0.9
Zn(II)	-	-	-	0.4
Mo(VI)	-	-	1.1	1.8
Cr(III)	-	-	0.7	2.7
Co(II)	-	-	-	0.9
Hg(II)	-	-	-	-10.5
As(III)	-	-	-	-0.9

When the catalysts copper, iron, cobalt and manganese are tested in binary mixtures, their effects are not additive. That is, the effect of one is changed by the addition of another. The strongest interaction occurs between copper and iron. Figure 10 illustrates this effect. These data can be described by the expression

$$\frac{1}{t} = k_1 [M_1] + k_2 [M_2] + k_{12} [M_1] [M_2] + I \qquad (12)$$

where k_1, k_2, k_{12} and I are constants and $[M_1]$ and $[M_2]$ are catalyst concentrations. Table IX presents the result of a graphical analysis using this equation. Table IXa gives the values found for the constants of equation (12).

TABLE IX

Interaction of Iron and Copper

μg Fe	μg Cu	$\frac{1}{t}$ found	$\frac{1}{t}$ calc	% difference
70	1.5	0.1640	0.1628	0.7
60	1.5	0.1528	0.1512	1.0
50	1.5	0.1418	0.1397	1.5
40	1.5	0.1297	0.1282	1.2
30	1.5	0.1182	0.1167	1.3
70	2.0	0.1887	0.1835	2.7
60	2.0	0.1744	0.1700	2.5
50	2.0	0.1615	0.1561	3.3
40	2.0	0.1473	0.1433	2.7
30	2.0	0.1338	0.1347	0.7
70	3.0	0.2295	0.2249	2.0
60	3.0	0.2115	0.2076	1.8
50	3.0	0.1944	0.1904	2.1
40	3.0	0.1778	0.1733	2.5
30	3.0	0.1609	0.1610	0.06
70	4.0	0.2738	0.2663	2.7
60	4.0	0.2506	0.2453	2.1
50	4.0	0.2317	0.2243	3.2
40	4.0	0.2090	0.2034	2.7
30	4.0	0.1903	0.1873	1.6

TABLE IXa

Constants for Equation (12)

Constant	Value	
k_1	0.0150	μg^{-1} min^{-1}
k_2	0.000587	μg^{-1} min^{-1}
k_{12}	0.000377	μg^{-2} min^{-1}
I	0.0596	min^{-1}

Unfortunately, since the k_{12} values are from two to three orders of magnitude smaller for the remaining interactions, reliable estimates could not be obtained for them. Figures 11 to 14 show some effects of these interactions; it is interesting to note that k_{12} is apparently negative for the pairs iron-cobalt and manganes-cobalt in the presence of 1,10-phenanthroline. It is clear that the dependence of reaction time on the concentration of a catalyst is changed by the addition of another. Behaviour of this kind was found by Price (30) in the copper and iron catalysis of the persulphate-iodide reaction.

3. The Determination of Isolated Metals

The plots given in figures 8 and 9 can be used as calibration curves for the determination of iron, copper, cobalt and manganese. The properties of the responses will now be examined with regard to their analytical usefulness. Consider the calibration curves to represent a relationship of the form (cf equation (11))

$$\frac{1}{t} = a[C] + b \qquad (13)$$

The sensitivity (S) of a technique can be identified with the slope of its calibration curve (31). However, this slope is not the quantity "a" written above; since the time, t, is measured rather than $\frac{1}{t}$ the quantity $\frac{dt}{(d[C])}$ is the required slope. From equation (13), this

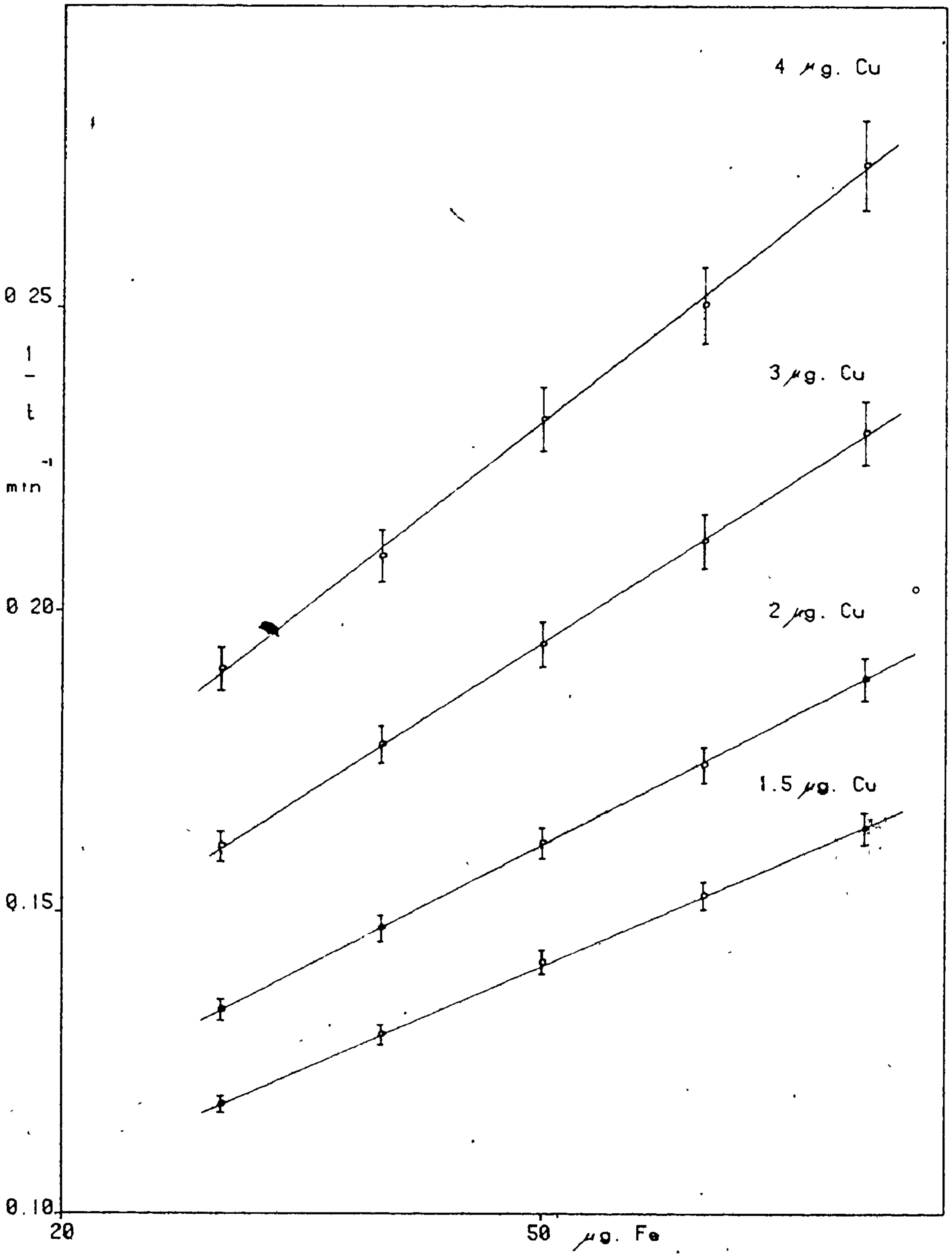

Figure 10

The Interaction of Iron and Copper

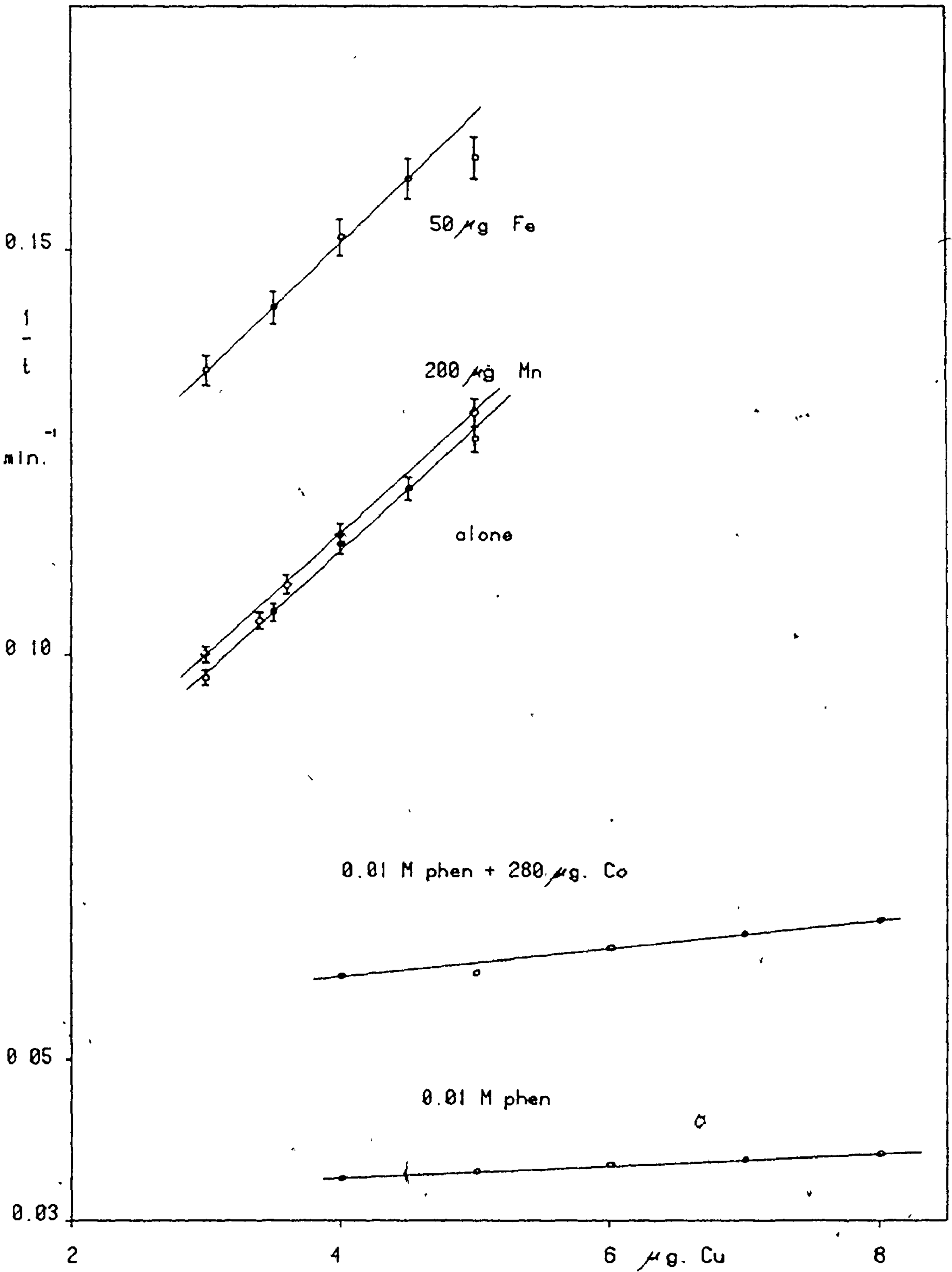

Figure 11

Interactions With Copper

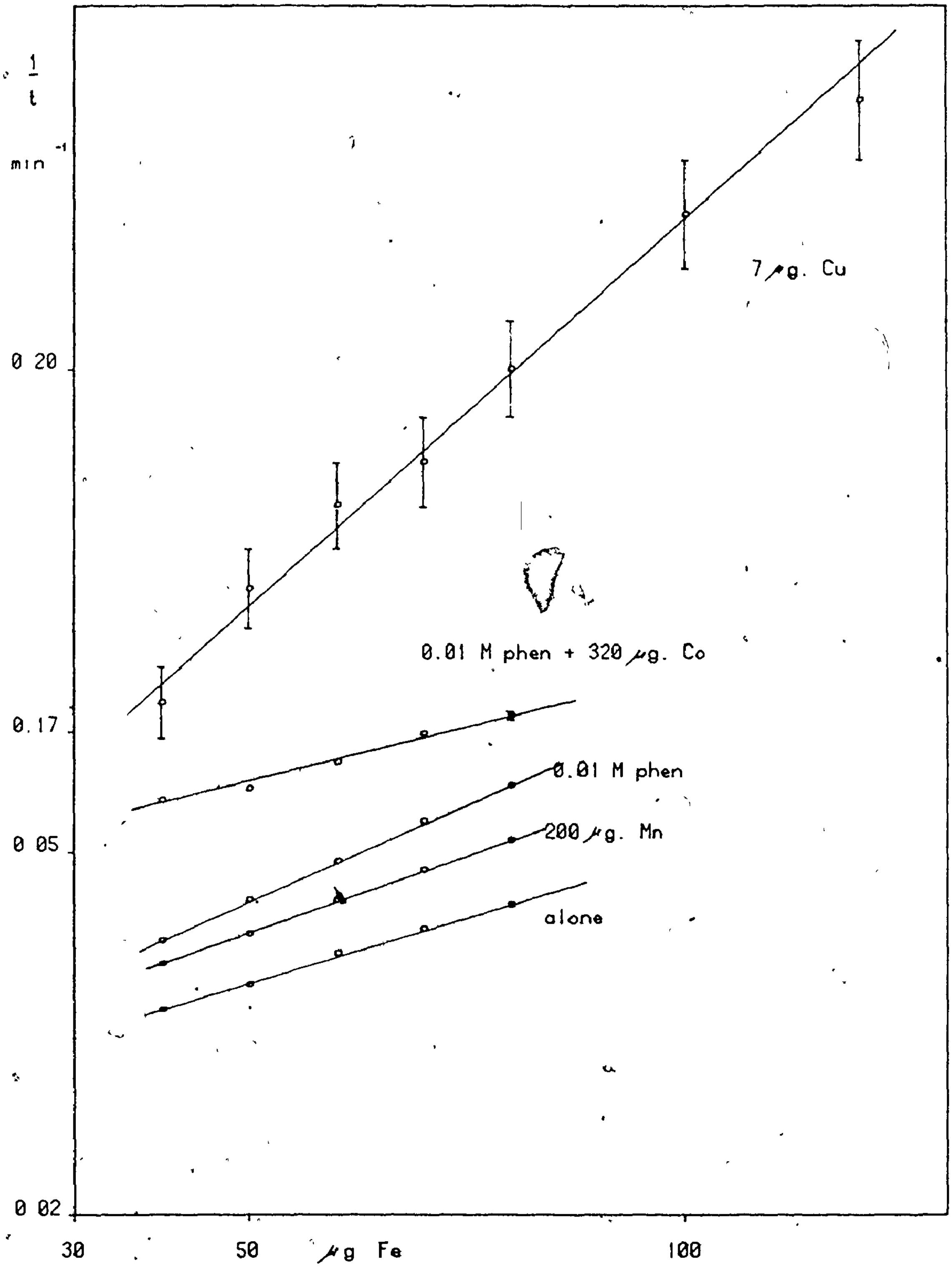

Figure 12

Interactions With Iron

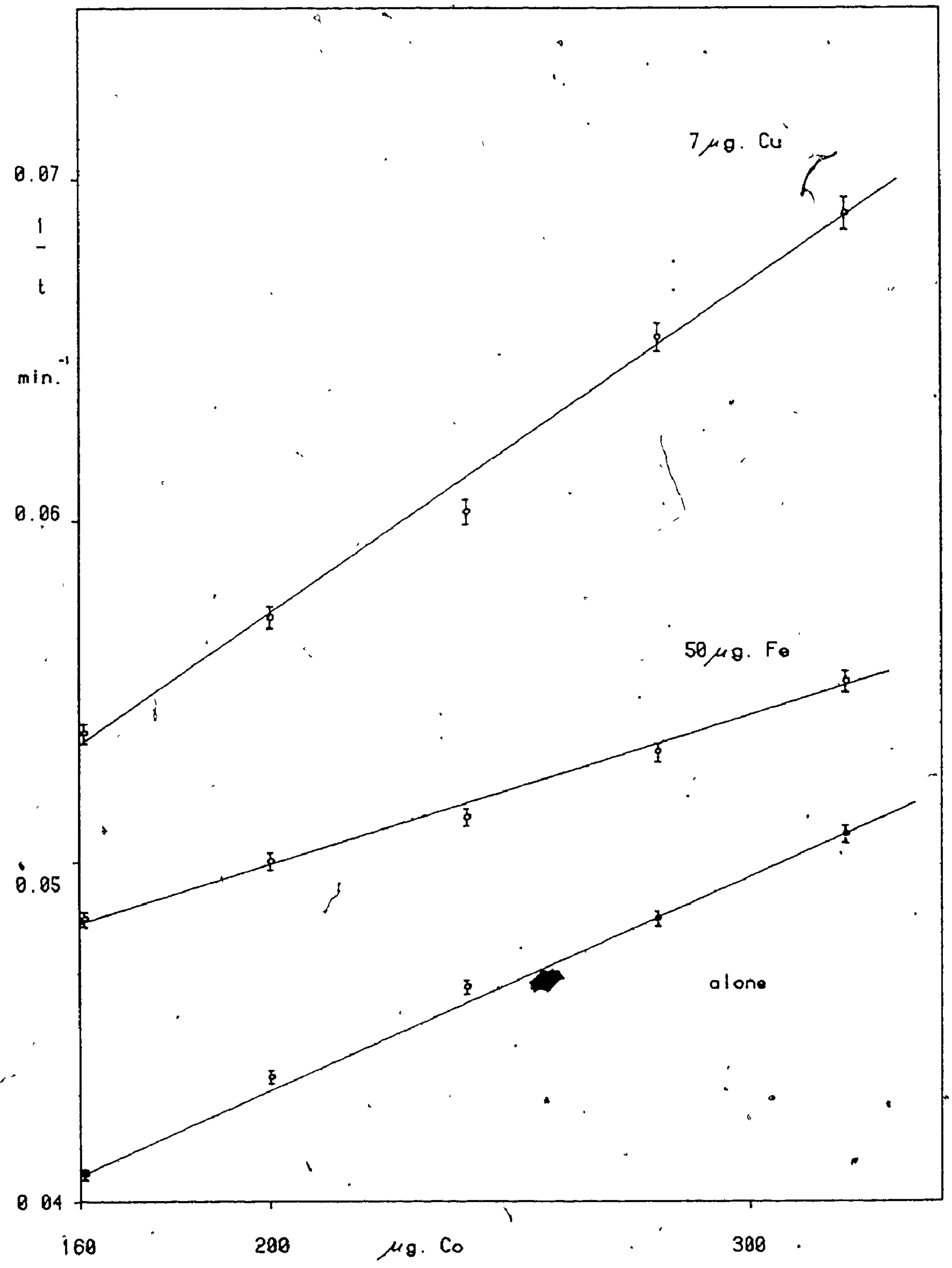

Figure 13

Interactions With Cobalt

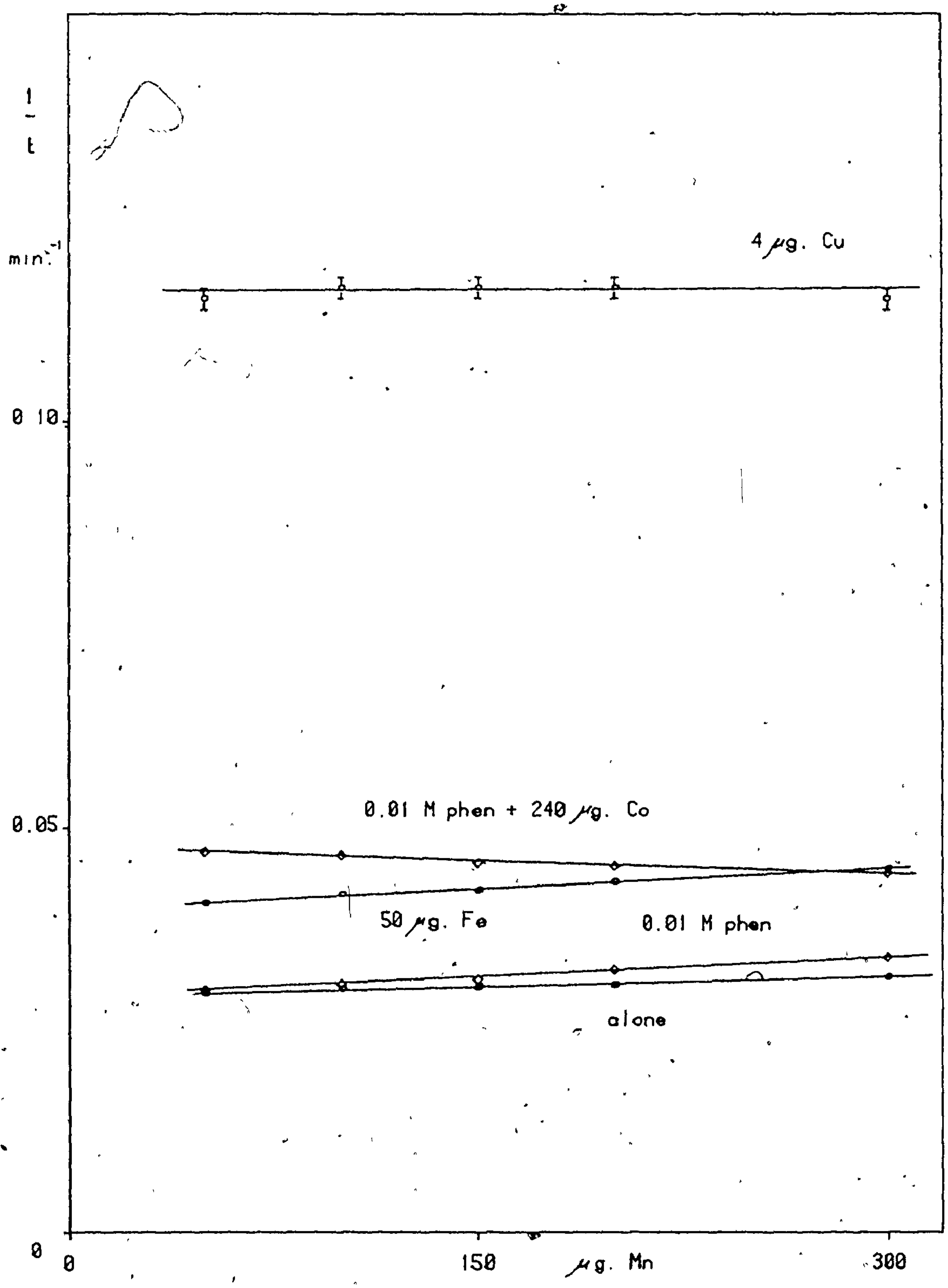

Figure 14

Interactions With Manganese

slope is found to be:

$$S = \frac{dt}{d[C]} = at^2 \qquad (14)$$

The limit of detection - the smallest quantity of analyte which can be measured with confidence - can be expressed as (31)

$$C_L = \frac{K\, s_{bl}}{S} \qquad (15)$$

where C_L is the minimum detectable additon of catalyst, s_{bl} is the standard deviation of the reaction time without added catalyst and K is a constant. A value of three has been recommended for K(31). This gives, for the detection limit,

$$C_L = \frac{3\, s_{bl}}{at_{bl}^2} \qquad (16)$$

where t_{bl} is the reaction time without added catalyst.

Equations (14) and (16) show that large values of "a" and of t or t_{bl} improve the sensitivity and the detection limit. The magnitude of "a" depends on the reagent concentrations and on the rate constant of the reaction catalyzed by the analyte catalyst. The magnitude of t_{bl} depends on the rate of the reaction catalyzed by the indicator catalyst and on the position of the low-concentration limit of the useful portion of the analytical calibration curve.

The data presented in Table (X) indicate that an appropriate value for s_{bl} is about 0.1 min. Experience has shown that this value is appropriate. The sensitivities and detection limits corresponding to the lower limits of the useful portion of the calibration curves for iron, copper, cobalt and manganese are shown in Table (XI).

TABLE X

Reproduceability of Reaction Time (min)

	Cu (2μg)	Fe (40μg)	blank	
	10.80	17.62	25.38	24.95
	10.90	17.91	25.07	25.23
	10.69	17.71	25.23	25.24
	10.70	17.78	25.22	25.25
	10.76	17.79	25.13	25.07
	10.66	17.74	25.28	25.13
	10.74	17.85	25.12	25.14
	10.76	17.78	25.17	25.26
	10.74	17.81	25.23	25.25
	10.78		25.35	25.01
			25.19	25.43
average	10.75	17.78	25.20	
S (min)	0.07	0.08	0.11	
S%	0.6	0.4	0.4	

TABLE XI

Sensitivities and Detection Limits

Metal	Amount μg	Sensitivity min μg^{-1}	Detection Limit μg
Cu	3	1.68	0.2
Fe	35	0.15	2
Co$_{\text{0.01 M phen}}$	60	0.04	7
Mn	50	0.004	71

Since manganese possesses only a very weak catalytic activity, the effects of a variety of complexing agents were examined in the hope of finding an activator for manganese. Table (XII) shows the results of this study. Slopes are in units of min^{-1} μg^{-1}; intercepts are in units of min^{-1}; and sensitivities describe the behaviour found in the presence of the amount of catalyst given in brackets and are in units of min μg^{-1}. The behaviour of copper was opposite to that of the other catalysts; the catalytic action of copper was decreased while the action of iron, manganese and cobalt was increased. 1,10-phenanthroline and 2,2'-bipyridine were the most effective activators tried. Ethylenediaminetetraacetic acid destroyed the catalytic effect of all four metals.

As shown before, the effect of one catalyst can be increased by the addition of another. If the increase in the blank value is not too great, both sensitivity and detection limit can be improved in this way.

The addition of both 1,10-phenanthroline and another catalyst yielded the best results in the determination of manganese. It is recommended that manganese be determined only under these conditions as, otherwise, low sensitivity renders the analysis very difficult. If 1,10-phenanthroline is used, a yellow precipitate forms at the end of the reaction time which is probably $Mn(phen)_3(I_3)_2$ and which can be used instead of starch to detect iodine. If 2,2'-bipyridine is used, no precipitate forms.

Equations (14) and (11) indicate that sensitivity should be increased by: (a) increasing the persulphate concentration or decreasing the thiosulphate concentration to increase the slope of the calibration curve; (b) decreasing the iodide concentration to increase $t_{b,1}$. However, the limited solubility of potassium persulphate prevents much

Table XII

The Effect of Various Complexing Agents

	$[S_2O_3^=]_0$	alone	en	pyp	trien	2-ap	2-amp	bipy	phen
				Copper					
slope	0.0015	1.4×10^{-2}	6.0×10^{-3}	5.1×10^{-4}	1.6×10^{-3}	1.3×10^{-2}	5.7×10^{-4}	8.4×10^{-4}	8.9×10^{-4}
intercept		0.0520	0.0440	0.0305	0.0390	0.0570	0.0520	0.0338	0.0297
S (3μg)		1.58	1.56	0.50	0.83	1.41	0.22	0.64	0.85
				Iron					
slope	0.0015	2.7×10^{-4}	1.8×10^{-4}	--	3.6×10^{-4}	1.8×10^{-4}	3.1×10^{-4}	4.5×10^{-4}	5.4×10^{-4}
intercept		0.0265	0.0382	--	0.0540	0.0295	0.0382	0.0305	0.0419
S (50μg)		0.17	0.08	--	0.07	0.12	0.11	0.16	0.11
				Manganese					
slope	0.0010	7.7×10^{-6}	5.0×10^{-6}	--	2.2×10^{-5}	6.2×10^{-6}	1.1×10^{-5}	1.5×10^{-5}	1.6×10^{-5}
intercept		0.0407	0.0578	--	0.0814	0.0430	0.484	0.0489	0.0407
S (100μg)		0.004	0.001	--	0.003	0.003	0.004	0.006	0.009
				Cobalt					
slope	0.0015	--	1.2×10^{-5}	--	1.1×10^{-5}	--	4.7×10^{-5}	3.8×10^{-5}	6.0×10^{-5}
intercept		--	0.0455	--	0.0590	--	0.0325	0.0300	0.0310
S (100μg)		--	0.005	--	0.003	--	0.03	0.03	0.04

[ligand] = 0.01M

en	ethylenediamine
pyp	pyrophosphate
trien	triethylenetatramine
2-ap	2-aminopyridine
2-amp	2-aminomethylpyridine
bipy	2,2′-bipyridine
phen	1,10-phenanthroline

increase in its concentration; the gain in sensitivity obtained by decreasing the thiosulphate concentration is offset by the resulting decrease in reaction time and if the iodide concentration is lowered, the onset of the starch-iodine colour becomes slow and difficult to detect. These considerations preclude much improvement in sensitivity if the reagent concentrations are changed.

The reduction of the action of copper when ligands are added is useful if a large amount of copper is present.

When an activating ligand is used, it must be present in sufficient excess over the metal ions present. Each complex species possesses its own degree of catalytic action. Figure 15 shows, as a cautionary example, the behaviour of cobalt in the presence of two micrograms of copper and varying concentrations of phenanthroline.

The useful ranges of these determinations must be considered as well as their sensitivities and detection limits. The response curve for copper shows a linear region between 3μg and 45μg and another above 45μg. Below 3μg the plot is curved. If no complexing agent is added, the useful range is reduced by the rapid decrease in reaction time as copper is added. At about 14μg, the time is reduced to 3 min. If a complexing agent is used, its concentration will determine the upper limit of the range.

Iron gives a linear response between about 1μg and 35μg and between 35μg and 150μg.

Cobalt responds linearly between 60μg and 640μg in the presence of 0.01M phenanthroline. At other levels of cobalt, the graph is curved. The upper limit depends on the activator concentration.

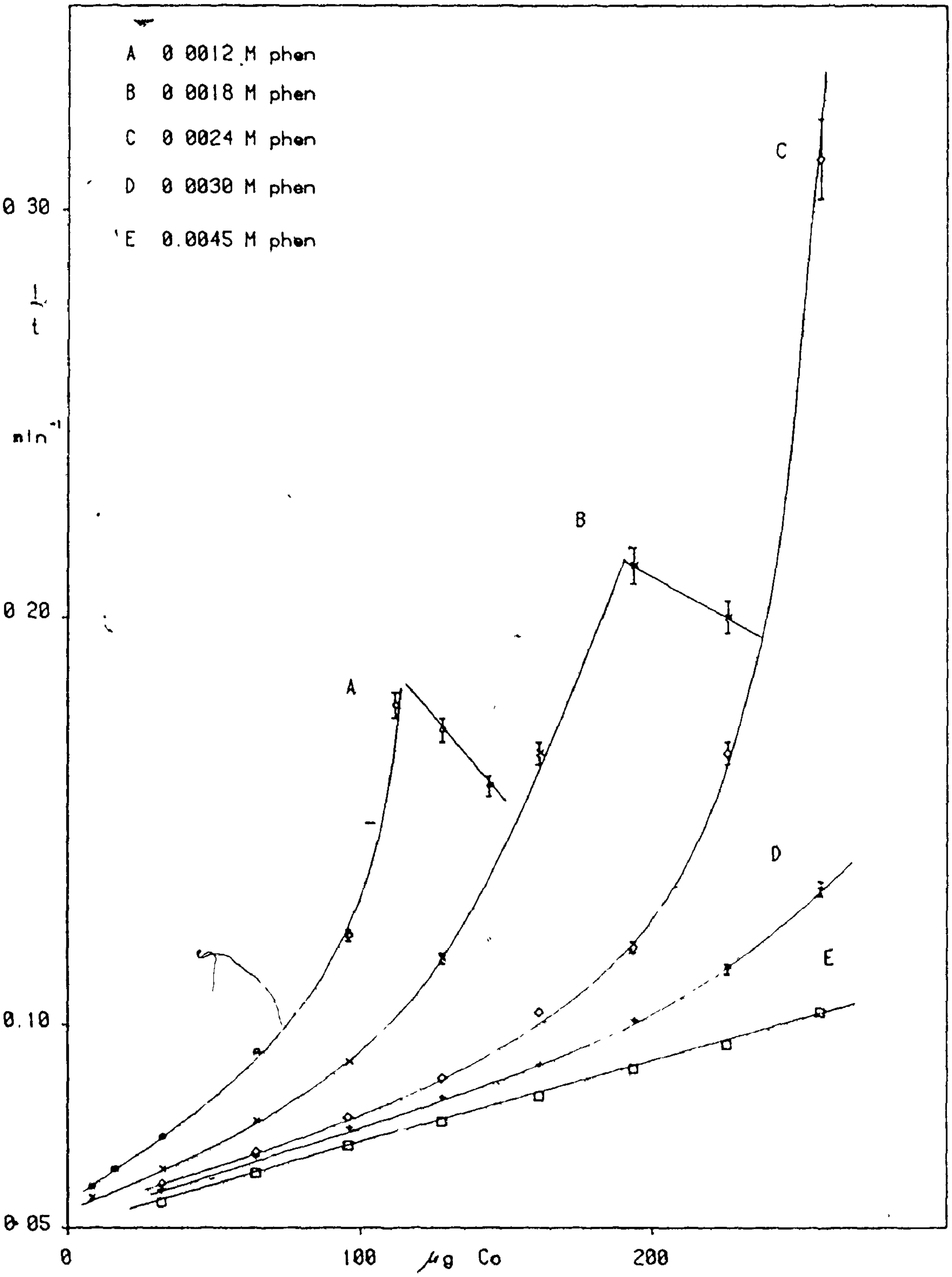

Figure 15

The Effect of Activator Concentration on Cobalt Response

Manganese gives two linear regions: one from 50μg to 300μg and another above 300μg. The upper limit is restricted by the activator concentration.

In all cases, the regions close to the inflections should be avoided as the calibrations become ambiguous near these points.

Another point of interest is the degree of uncertainty attached to the result of an analysis. General arguments will now be given to indicate the uncertainty due to the uncertainties of individual time measurements. Thompson and Svehla (32) have used a formula derived by Hald (33) for this purpose:

$$c' = \frac{\frac{1}{t'} - a}{b} \pm \frac{\tau(95,n-2)}{b} S_y \left[\frac{1}{N} + \frac{1}{n} + \frac{(c'-\bar{c})^2}{\sum_{i=1}^{n} (c_i-\bar{c})^2} \right]^{1/2} \tag{17}$$

where c' is the analytical result (a concentration);

$\bar{c}$ is the average of the concentrations used for calibration;

c_i is an individual concentration used for calibration;

t' is the reaction time measured to find c';

$S_{y/c}$ is the standard deviation of the calibration points about the line;

a and b are the intercept and slope, respectively, which describe the calibration plot;

N is the number replicate measurements used to obtain t';

n is the number of points used to construct the calibration curve

and τ is the value of the student distribution for 95% confidence and n-2 degrees of freedom.

Let the uncertainty in equation (17) be $\pm U$ and examine the lowest value of ±U. This occurs when the calibration plot is fit well by a straight line ($\chi_\nu^2 = 1$) and $c' = \bar{c}$.

$\chi_\nu^2 = \dfrac{S_{y/c}^2}{\bar{S}_i^2}$ where $\bar{S}_i^2$ is the weighted average of individual variances and is given (34) by

$$\bar{S}_i^2 = \frac{1}{\frac{1}{n}\sum_{i=1}^{n}\frac{1}{S_i^2}} \tag{18}$$

S_1 are the values $S_{\frac{1}{t}}$ of the calibration curve. The uncertainty in a given time measurement (S_t) has been shown to be about 0.1 minutes and has been found to be approximately constant with regard to t. S_i can be shown to be equal to $\dfrac{S_t}{t_i^2}$.

Therefore;

$$\bar{S}_i^2 = \frac{1}{\frac{1}{n}\sum_{i=1}^{n}\frac{t_i^4}{S_t^2}} \tag{19}$$

If χ_ν^2 is assumed to be equal to one, $S_{y/c}$ is given by

$$S_{y/c} = \bar{S}_i = \frac{S_t}{\left[\frac{1}{n}\sum_{i=1}^{n} t_i^4\right]^{1/2}} \tag{20}$$

The lowest value of ±U is then

$$\pm U_{min} = \pm\frac{\tau(95,n-2)}{b}\,\frac{S_t}{\left[\frac{1}{n}\sum_{i=1}^{n} t_i^4\right]^{1/2}}\left[\frac{1}{N}+\frac{1}{n}\right]^{1/2} \tag{21}$$

Table XIII has been constructed from the values given in Table III except that the slope and intercept for Mn were taken from a run using 40μg of copper and 0.01 M phenanthroline (slope 4×10^{-5} min^{-1} μg^{-1}, intercept 0.0505 min^{-1}). Five equally spaced values of c have been used which span the ranges given in Table III. An upper limit of 14μg has been used for copper and N has been set equal to one. The uncertainties, $\pm U$ min, therefore represent the minimum uncertainties in the analytical result if one time measurement is used for the analysis and five calibration points are used.

The uncertainty $\pm U$ min can, of course, be reduced if the number of replicate measurements performed on the sample (N) is increased. (vide equation (21)) Increasing the number of concentrations used for calibration (n) also reduces the uncertainty of the analytical result.

TABLE XIII

Minimum Analytical Uncertainties

Metal	$\bar{c}$ μg	$\pm U$ min ($\pm$μg)	$\pm U$ min %
Cu	8.5	0.4	5
Fe	92.5	3.7	4
Co	350	14.5	4
Mn	175	28.2	16

4. The Analysis of Mixtures

It is clear that all catalysts of a reaction used for analysis will interfere with the determination of an individual catalyst. This problem can be approached in two ways when mixtures of catalysts are encountered; interferences may be eliminated by appropriate manipulation of the reaction medium, or calibration of the combined catalysis may be carried out. A combination of these approaches was found to be suitable for the system studied here.

Earlier it was established that the catalysts of this reaction do not show additive effects but rather interact; it was also found that a quantitative description of this interaction is difficult to obtain. Therefore, in order to analyse a mixture of these catalysts it is necessary to first isolate the response of one and determine its concentration, then calibrate for another catalyst in the presence of the proper concentration of the first and so determine the second. Methods of doing this for binary mixtures of iron, copper, cobalt and manganese will now be examined.

Copper and Iron

Table XII shows that pyrophosphate ions mask the effects of iron but not of copper although the magnitude of the action of copper is reduced. It is possible, therefore, to determine copper in the presence of iron by adding sodium pyrophosphate to the reaction mixture. Pall, Svehla and Erdey (18) have stated that sodium fluoride can be used for this purpose, but trials have not confirmed this statement. Iron can be determined subsequently by calibration in the presence of the amount of copper found. If much copper is present, the iron determination may be carried out in the presence of an organic activator. Table XIV shows the results of analyses of synthetic mixtures of iron and copper.

TABLE XIV

Analysis of Iron-Copper Mixtures

Metal Sought	Addition to sample	Addition to Standard	Taken µg	Found µg	% Error
Cu	0.01 M pyrophosphate	0.01 M pyrophosphate	4	4.35	+8.7
				4.35	+8.7
				3.91	-2.2
				av4.20	+5.0
Fe		4.2µg Cu	100	96.8	-3.2
				96.8	-3.2
				96.8	-3.2
				av96.8	-3.2
Cu	0.01 M pyrophosphate	0.01 M pyrophosphate	40	41.1	+2.7
				41.1	+2.7
				41.1	+2.7
				av41.1	+2.7
Fe	0.01 M phenanthroline	0.01 M phenanthroline 41.1µg Cu	40	42.5	+6.2
				41.8	+4.5
				40.2	+0.5
				av41.5	+3.7

Copper and Manganese

Copper, in the absence of an added complexing agent, has such an intense action in its useful range that manganese does not interfere with the determination of copper. However, in the presence of 1,10-phenanthroline, the action of manganese becomes detectable in the presence of copper. These facts permit the analysis of mixtures of copper and manganese.

Table XV shows the results of analysis of synthetic mixtures of copper and manganese.

TABLE XV

Analysis of Copper-Manganese Mixtures

Metal Sought	Addition to sample	Addition to standards	Taken µg	Found µg	% Error
Cu			3	2.97	-0.8
				2.97	-0.8
				2.97	-0.8
				av 2.97	-0.8
Mn	0.01 M phenanthroline	0.01 M phenanthroline 2.97 µg Cu	250	253	+1.2
				252	+0.8
				250	0
				av 252	+0.8
Cu*			45	44.9	-0.2
				44.5	-1
				44.3	-1
				av 44.6	-0.9
Mn	0.01 phenanthroline	0.01 phenenthroline 44.6 µg Cu	50	59	+18
				53	+6
				46	-8
				av 53	+6

* diluted to $\frac{1}{10}$ concentration

Copper and Cobalt

Mixtures of copper and cobalt can be analyzed in the same way as mixtures of copper and manganese. Table XVI displays analyses of synthetic mixtures of copper and cobalt.

TABLE XVI

Analysis of Copper-Cobalt Mixtures

Metal Sought	Addition to Sample	Addition to Standards	Taken µg	Found µg	% Error
Cu			3	3.08	+3
				3.04	+1
				3.02	+0.8
				av3.05	+2
Co	0.01 M phenanthroline	0.01 M phenanthroline 3.05 µg Cu	321	353	+10
				353	+10
				321	0
				av342	+6
Cu	0.01 M pyrophosphate	0.01 M pyrophosphate	30	29.3	-2.2
				29.6	-1.5
				28.9	-3.6
				av29.3	-2.4
Co	0.01 M phenanthroline	0.01 M phenanthroline 29.3 µg Cu	128	127	-0.9
				124	-3.1
				124	-3.1
				av125	-2.4

Iron and Manganese

If a few micrograms of copper are present, manganese does not interfere in the determination of iron. Once iron has been found in the presence of copper, manganese can be found by calibration with added iron but without added copper. Table XVII gives examples of this process.

TABLE XVII

Analysis of Iron-Manganese Mixtures

Metal Sought	Addition to Sample	Addition to Standards	Taken μg	Found μg	% Error
Fe	3 μg Cu	3 μg Cu	40	38.2	-4.5
				37.8	-5.5
				37.8	-5.5
				av37.9	-5.2
Mn	0.01	0.01 M	250	226	-9.6
	bipyridine	bipyridine		224	-10.4
		37.9μg Fe		235	-6.0
				av228	-8.8
Fe	3μg Cu	3 μg Cu	100	99.2	-0.8
				101.0	+1.0
				98.0	-2.0
				av99.4	-0.6
Mn	0.01 M	0.01 M	50	62	+24
	bipyridine	bipyridine		58	+16
		99.4 μg Fe		46	-8
				av55	+10

Iron and Cobalt

If no activator is added, cobalt does not interfere with the determination of iron; if an activator is present cobalt does interfere. Therefore, iron can be determined without an activator and cobalt can be determined subsequently in mixtures with iron using an activator. Table XVIII demonstrates this point.

TABLE XVIII

Analysis of Iron-Cobalt Mixtures

Metal Sought	Addition to Sample	Addition to Standards	Taken- µg	Found µg	% Error
Fe			40	43.0	+7.5
				43.0	+7.5
				42.5	+6.2
				av42.8	+7.0
Co	0.01 M phenanthroline	0.01 M phenanthroline 42.8 µg Fe	321	319	-0.5
				313	-2.5
				310	-3.5
				av315	-2.0
Fe			100	95.5	-4.5
				94.8	-5.2
				94.5	-5.5
				av94.9	-5.1
Co	0.01 M phenanthroline	0.01 M phenanthroline	128	149	+16
				149	+16
				144	+13
				av147	+15

Manganese and Cobalt

It is, in principle, possible to determine manganese in the presence of cobalt. However, as pointed out before, unless an activator is used, the determination of manganese is difficult, and, if an activator is added, cobalt interferes. The analysis of mixtures of manganese and cobalt, therefore, is not recommended. These metals are easily separated by ion exchange chromatography and can be more effectively determined after such separation.

Attempts were made to analyze three component mixtures but in every case the third component produced an interference even where Table XII indicates that this should not occur.

The useful ranges for mixture analyses are not easy to specify. The ranges are, of course, limited by the curve-shape considerations described earlier, but the decrease in sensitivity caused by the reaction-time shortening due to the presence of one catalyst can raise the detection limit of another catalyst determined in the presence of the first. Also, the sensitivity of the determination of one catalyst depends on the concentration of other catalysts present in the reaction mixture. In any case, tests should be made with standard solutions to ensure that the range of concentrations expected can be handled satisfactorily.

5. Interferences

Tables IV to VIII indicate the interferences due to twelve foreign metals. Iron is particularly susceptible to disturbance while copper is affected much less.

Aluminium (III) and vanadium (IV) cause the worst interference and must be removed prior to analysis. Cadmium (II), chromium (III), silver (I) and nickel (II) are permissable in quantities at least as great as several tens of micrograms. If no activating ligand which can be complexed by zinc is used up to a milligram of zinc is permissable. Zinc can, therefore, be used in small amounts to reduce iron (III) prior to analysis in order to prevent premature consumption of thiosulphate. In the presence of iron, arsenic (III) and mercury (II) cause unusually large perturbations, but are otherwise usually acceptable in amounts as great as a few hundreds of micrograms.

Of the other ions tested, sodium, potassium, sulphate, nitrate, bromide and chloride did not produce interference apart from ionic strenth effects. Fluoride, phosphate, pyrophosphate, iodide and ammonia interfere and should be removed before analysis. Persulphate and thiosulphate ions should also be avoided.

Foreign complexing, oxidising and reducing agents must not be introduced with the sample solution as they may change the reaction time. Highly coloured materials interfere with the observation of the starch-iodine colour and so should also be absent.

The combination of separations by means of anion exchange in hydrochloric acid and determination by the present method reduces difficulties arising from both operations. Aluminium, nickel, vanadium and chromium ions can be made to pass through an exchange column while the analyte ions remain on the column. Zinc, silver and mercury ions can be made to remain on the column while the analyte ions are eluted. The separation of copper and cobalt has been found to be inconvenient (35) but is unnecessary if the analysis of their mixtures described in this work is used. Manganese and iron can be eluted separately and determined alone.

6. Analysis of Standard Material

N.B.S. standard reference material 85B, an aluminium alloy, was analysed for iron, copper and manganese to test the proposed method. The procedure used was as follows: a 0.5 - gram sample was dissolved in dilute hydrochloric acid with the help of a few millilitres of 30% hydrogen peroxide solution. The resulting solution was evaporated to about 10 ml. cooled in ice and saturated with hydrochloric acid gas. The aluminium chloride precipitate was filtered off and the filtrate was evaporated nearly to dryness. Concentrated hydrochloric acid was added and the solution was then applied to a column (11 mm dia. x 480mm) of Dowex 1 anion exchange resin conditioned with concentrated hydrochloric acid. The column was then washed with 10 M HCl to remove nickel II, chromium III, vanadium IV, and the remaining aluminium III. Manganese was eluted with 6 M HCl and iron and copper were eluted together with 0.5 M HCl. Both sample solutions were evaporated carefully to dryness.

The manganese salts were dissolved in distilled, deionized water and diluted to 25 ml. One millilitre samples were taken for analysis in triplicate in the presence of 40 micrograms of copper and 0.01 M 1,10-phenanthroline.

The iron and copper salts were dissolved in distilled deionized water and diluted to 100 ml. An aliquot of 10 ml. was diluted to 50 ml. and 1 ml. samples were taken for analysis in triplicate. Copper was determined in the presence of 0.01 M sodium pyrophosphate; iron was determined in the presence of 0.01 M 1,10-phenanthroline with 37.8 μg of copper added to the calibration mixtures. The small quantity of iron present did not necessitate pre-reduction.

Table XIX displays the results of the analysis. Copper and iron were both determined satisfactorily even though the ratio of copper to iron was about seventeen. The results for manganese were less impressive although the high values may have been due to the formation of small amounts of chromate ion rather than to defects in the method of determination.

The deviations from the certified values were in all cases compatible with the uncertainties predicted in Table XIII and are acceptable if the concentrations measured during analysis are considered.

The combination of ion exchange separation and kinetic determination has, therefore, proven effective. The separation was simplified by eluting iron and copper together, and interfering materials were removed.

TABLE XIX

Analysis of Standard Material

Element	Certified Content %	Found %	% Error
Mg	1.49	-	-
Si	0.18	-	-
Cr	0.211	-	-
Ni	0.084	-	-
Zn	0.030	-	-
Ti	0.022	-	-
Pb	0.021	-	-
Ga	0.019	-	-
V	0.006	-	-
Cu	3.99	3.83	-4
		3.79	-5
		3.71	-7
		av 3.78	-5
Fe	0.24	0.243	-1
		0.239	-0.4
		0.237	+1
		av 0.239	-0.4
Mn	0.61	0.72	+18
		0.69	+13
		0.75	+23
		av 0.72	+18

7. Simultaneous Comparison

Bognar (29) has proposed an ingenious variation of the usual kinetic analysis technique. A series of test solutions is made up consisting of solutions some of which contain known amounts of analyte and others unknown amounts. The indicator reaction is initiated in all of the solutions at the same time and the solutions are examined (for colour intensity, for example) to find which standard tests most closely match each of the unknown tests. The quantity of analyte in each unknown test is deduced from the result of this examination. This procedure carries the following advantages: time need not be measured; as long as the temperatures of all the reaction vessels are the same, temperature need not be controlled (a well mixed water bath can be used to maintain uniformity of temperature); the form of the response of the reaction rate to the catalyst concentration need not be linear or even accurately known.

The conditions for successful analysis are a range of standard analyte concentrations wide enough to encompass the range of unknown analyte concentrations, and an interval between standard analyte concontrations sufficiently narrow to yield the desired accuracy. If the expected range of analyte concentration is very wide, several experiments with decreasing intervals between standard concentrations may be required.

Landolt reactions are particularly suited to this technique; only the order in which the reaction tubes show colour need be noted. The apparatus suggested by Bognar (29) for simultaneously starting several reactions consisted of a series of pipettes suspended from a system of stopcocks which was opened to drain the pipettes together.

The reaction-tube-and-rack system used in this work is much simpler to construct and to use; furthermore, it guarantees that the solutions mixed are all at the same temperature.

The simultaneous comparison method is particularly useful with the present reaction since the non-linear portions of the responses can be used for analysis. Regions close to changes in shapes of responses should still be avoided, however, because reversals in order may occur among the standard solutions.

IV CONCLUSIONS

This study has demonstrated that it is possible to determine iron, copper, cobalt and manganese by means of the persulphate-iodide-thiosulphate Landolt reaction. Further, binary mixtures of these metals can be analyzed except for mixtures of manganese and cobalt. Determination of cobalt and manganese and analysis of mixtures by this reaction have not been reported before.

When this method is used in conjunction with simple ion exchange separations, most interferences can be removed and even interfering matrices can be analyzed.

The equipment required for this technique is simple, and, except for the reaction tubes used for this study, is found in most analytical laboratories. When the simultaneous comparison variation is used, no electronic devices are required.

These determinations are amenable to a considerable degree of automation. The basic requirements are a means of measuring time and a means of detecting the Landolt effect. This detection can be accomplished by a variety of instruments as described in the introductory discussion. Timing and data handling can be performed excellently by the small computers which are becoming increasingly available and inexpensive or by specially built electronic circuits.

It is desirable to carry out automatic measurements on many samples at once; two different approaches immediately present themselves. A series of solutions can be rapidly and repetitively examined by a single detector. The device known as a centrifugal fast analyzer achieves this by passing sample curvettes mounted at the edge of a spinning disk through the beam of a photometer. Alternatively, each sample can be provided with its own detector. This arrangement is perhaps easier to construct. An attempt to use photometric detection in this way is described in Appendix D.

A major drawback of this method of analysis is the tedium associated with the large number of pipettings required and with waiting for colour changes. Suitable automation could, of course, overcome these disadvantages. As with most wet chemical analyses, sample preparation is likely to consume most of the total analysis time.

The determination described in this thesis should be suitable for routine analysis where the composition of the sample is approximately known and, especially in the simultaneous comparison version, for educational use. It may also be useful for work in remote locations.

V SUGGESTIONS FOR FUTURE INVESTIGATIONS

The results of the study reported in this thesis suggest several interesting topics for further work. Landolt systems other than the one studied in this report could be examined in order to find families of ions which can be determined without interaction between ions present in mixtures. The mechanism of catalyst interaction proposed in this work could be tested and, if correct, used to aid in the search mentioned above.

More efficient activating and masking ligands could be sought for; the design and synthesis of such compounds would provide a useful and stimulating area of inquiry.

The catalytic-kinetic determination of trace metal ions in mixtures, whether by Landolt reaction or not, will be useful for analysis of such samples as natural waters and could be profitably pursued with that end in mind.

Finally, the possibility of determining mercury using the peroxydisulphate-iodide-thiosulphate reaction should be explored as mercury is of great environmental interest and may prove easy to measure using this reaction.

APPENDIX A

Summary of Examples of Landolt Reactions Used in Analysis

Table XX gives a variety of Landolt reactions found in the literature. These examples are typical if not exhaustive.

TABLE XX

Substrate	Indicator Catalyst	Retardand	Catalysts Determined	Ref.
H_2O_2	I^-	ascorbic acid	Mo	8
H_2O_2	Br^-	"	Mo,Cu,Fe,W,V	36
H_2O_2	I^-	$S_2O_3^=$	Mo	11
$B\ O_3^-$	I^-	ascorbic acid	V	12
$B\ O_3$	Br^-	"	V,Fe,Cu,Ti	37
$B\ O_3$	Br^-	hydrazine	Se	37
ClO_3^-	I^-	ascorbic acid	V	38
ClO^-	I^-	Zn II	V	38
ClO_3^-	Cl^-	hydrazine	Se	39
ClO_3^-	Cl^-	ascorbic acid	V,Os,Fe,Cu,Mo,Se	40
ClO_3^-	Cl^-	Zn II	V	41
ClO_3^-	Br^-	ascorbic acid	V,Fe,Os	42
$S_2O_8^{2-}$	I^-	$S_2O_3^=$	Cu,Fe	18
$S_2O_8^{2-}$	I^-	ascorbic acid	Cu,Fe	43
BO_3^-	I^-	ascorbic acid	Fe,Mo	44

APPENDIX B

Determination of Mercury

Figure 16 shows a calibration curve for mercury II in the presence of 100μg of iron. Tables IV to VIII show that mercury exerts a greater effect with iron than under the other conditions examined. The reaction time is linearly related to the concentration of mercury with a slope of 0.01 min μg^{-1} and an intercept of 15.5 min. This indicates a sensitivity of 0.01 minμg^{-1} and a detection limit of 30μg.

The determination of mercury using this reaction is certainly possible, but is subject to many interferences.

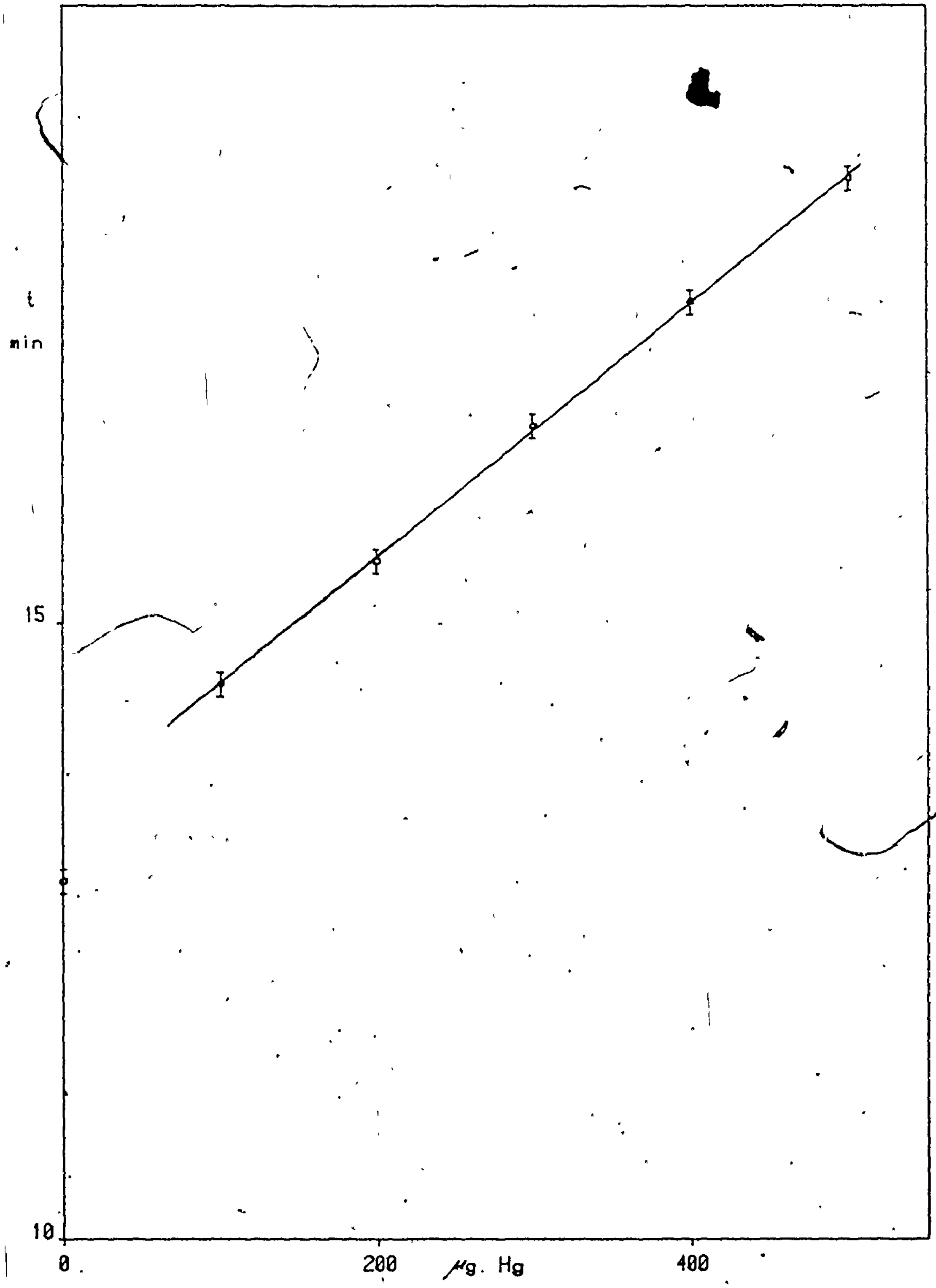

Figure 16

Mercury Calibration Curve

APPENDIX C

Reaction Mechanisms

Catalysis of the persulphate-thiosulphate reaction by iodine, copper and iron has been investigated by several researchers (30, 19, 20). In all cases, the mechanism proposed consists of a cycle in which the catalyst is alternately oxidised by persulphate and reduced by thiosulphate and in which the oxidation step is rate determining.

The general reaction scheme can be written as follows (19) where L represents a ligand

$$M^{n+}L_x + S_2O_8^{2-} \rightarrow M^{(n+1)+} + xL + SO_4^{2-} + \cdot SO_4^{-} \qquad \text{slow} \quad 1$$

$$2M^{(n+1)+} + 2S_2O_3^{2-} \rightarrow 2M^{n+} + S_4O_6^{2-} \qquad \text{fast} \quad 2$$

$$2\cdot SO_4^{2-} + 2S_2O_3^{2-} \rightarrow 2SO_4^{-} + S_4O_6^{2-} \qquad \text{fast} \quad 3$$

Step 3 has also been described as proceeding by a hydroxyl radical (19) intermediate.

The rate of step one is influenced by the nature of the ligand, L. (In iodine catalysis, of course, no such ligand is involved). The effects of added ligands outlined in Table 12 demonstrate this influence. When no complexing agent is added, the ligand is the thiosulphate ion. The curved portions of the calibration plots for iron and cobalt at higher catalyst concentrations are the result of ligand concentrations insufficient to maintain the catalyst in one complexed form.

Copper is known (45) to form mixed complexes with thiosulphate and iodide ions. Its anomalous response to changes in iodide concentration presumably reflect this; the catalytic activity of pure and mixed complexes can be expected to differ, with the thiosulphate-iodide complex being the less active form.

The behaviour of the cobalt-catalyzed reaction when the iodide concentration is changed follows equation (8). However, the slope of the plot for cobalt when the persulphate concentration is changed is not the same as the slope for the blank as equation (8) predicts. Cobalt presumably does not react in rate-determining fashion with iodide but forms a quickly-reacting complex containing iodide.

It is possible to speculate about the mechanism responsible for the interactions between catalysts. The reaction scheme which follows would behave in the manner observed experimentally.

$$M_1^{n+} + S_2O_8^{2-} \rightleftarrows M_1^{n+}S_2O_8^{2-} \qquad 1$$

$$M_2^{m+} + S_2O_8^{2-} \rightleftarrows M_2^{m+}S_2O_8^{2-} \qquad 2$$

$$M_1^{n+}S_2O_8^{2-} + M_2^{m+} \rightleftarrows M_2^{m+}S_2O_8^{2-} + M_1^{n+} \qquad 3$$

$$M_1^{n+}S_2O_8^{2-} \rightarrow M_1^{(n+1)+} + SO_4^{2-} + \cdot SO_4^{-} \qquad \text{slow} \quad 4$$

$$M_2^{m+}S_2O_8^{2-} \rightarrow M_2^{(m+1)+} + SO_4^{2-} + \cdot SO_4^{-} \qquad \text{slow} \quad 5$$

$$2\,(M_1^{(n+1)+}, M_2^{(m+1)+}, \cdot SO_4^{-}) + S_2O_3^{2-} \rightarrow 2(M_1^{n+}, M_2^{m+}, SO_4^{2-}) + S_4O_6^{2-} \qquad \text{fast} \quad 6$$

where M stands for a metal ion.

Reactions 1 to 3 tend to increase the concentration of one of the persulphate complexes. This leads to two possible results.

I. If the complex whose concentration is increased decomposes faster than the other (steps 4 and 5), the increase in the overall reaction rate due to additions of either ion will be augmented.

II. If the concentration of the slower-decomposing complex is increased, the increase in the overall reaction rate due to additions of either ion will be reduced. Indeed, if the slower decomposition is very much slower than the faster one, additions of the slower-reacting metal ion will reduce the overall reaction rate.

The interaction between copper and iron catalysts behaves according to case I; the behaviour of the iron-cobalt pair follows the mild version of case II and the manganese-cobalt pair follows the extreme version of case II.

Catalyst-persulphate complexes have often been proposed as intermediates in persulphate oxidations (19, 46, 47). This possibility is supported by the brown colour which has been observed during the present investigation when persulphate solutions are mixed with solutions containing iron.

If the interaction mechanism proposed is correct, it may be that only those oxidising agents which cannot form complexes with catalysts are suitable for analysis of mixtures of catalysts by means of simultaneous equations. That is, interactions may be expected when oxidant-catalyst complexes form.

APPENDIX D

Automatic Reaction Timer

A device was constructed which passed a light beam through ten reaction tubes and, when colour appeared in a given tube, passed a signal of a corresponding, preset voltage to a strip chart recorder. A set of push-buttons was also provided for manual operation. The sensing light emitting diodes (LED) and photo-transistors were housed in a solid block bored to place the reaction tubes between them. This block was immersed in the water bath and connected to the rest of the instrument by a cable. The circuitry used is given in figures 17 to 20 and its operation is described in the following paragraphs.

With a colourless sample between the sensor LED and photo-transistor - for example LED and Q1 - VREF is adjusted by means of a potentiometer so that the output of the LM339 comparator (see figure 17) is in a logical 0 state (low) and the voltage at P1 is high. When colour appears in sample 1, light is absorbed and the base-emitter current of Q1 decreases. This causes the voltage of the non-inverting input of the comparator to increase; when this voltage exceeds VREF1, the comparator output switches to a logical 1 state (high) which briefly sets the voltage at P1 to a low state. That is, when a colour intensity set by the potentiometer is reached, the voltage at P1 drops but quickly rises again due to the action of the astable multivibrator 74121.

The 7430, 7404 and 7420 combination (see figure 18) performs the

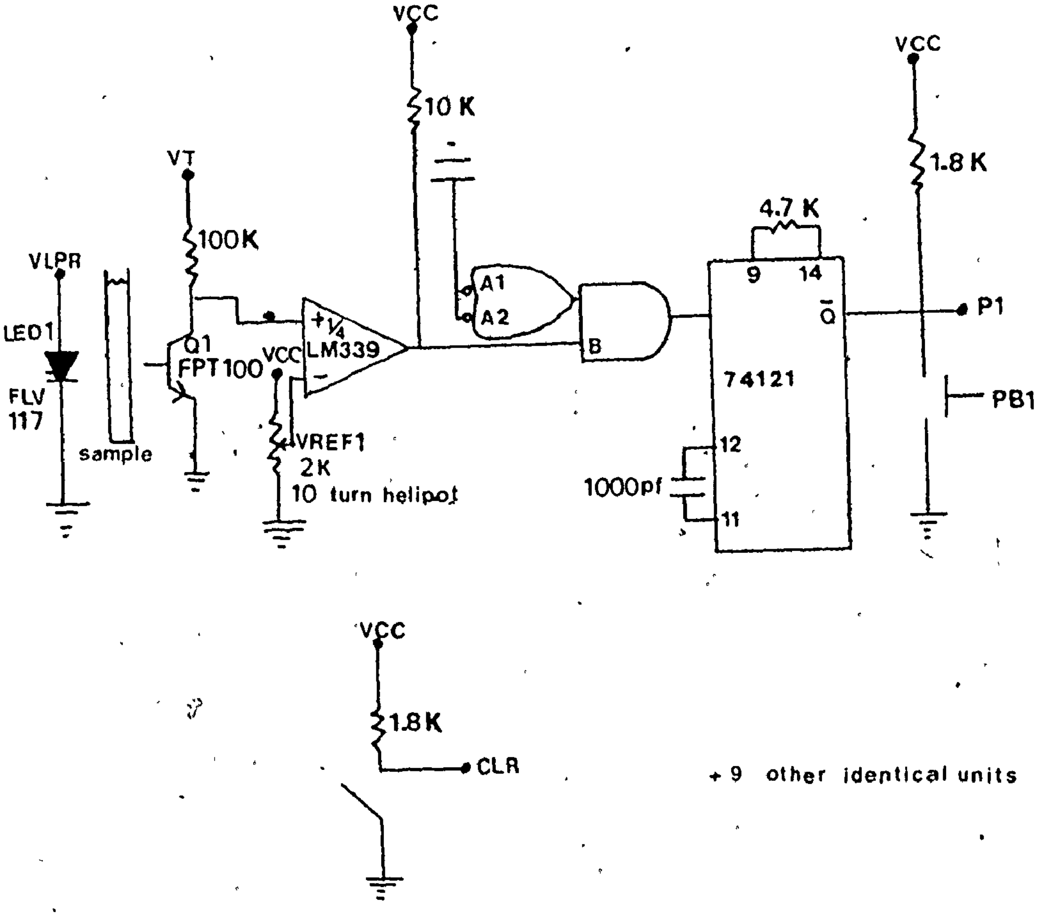

Figure 17

Inputs and Signal Conditioning

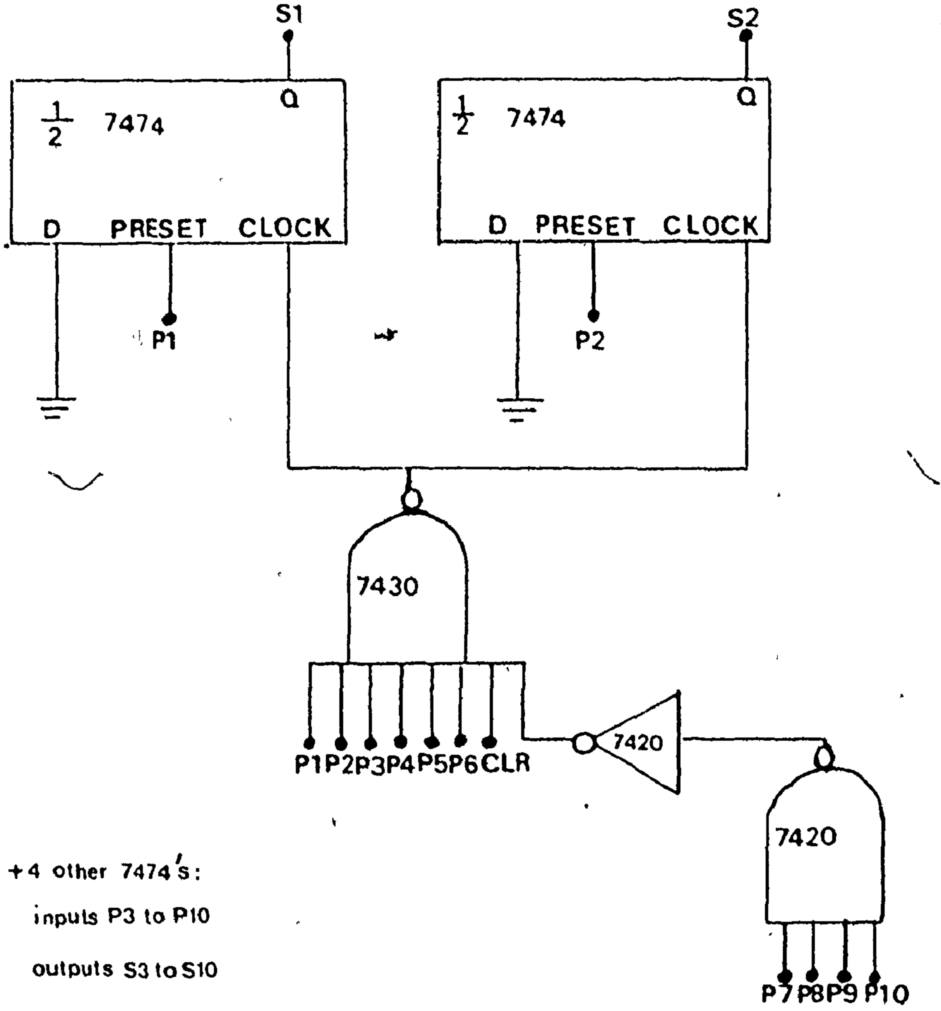

Figure 18

Input Selection

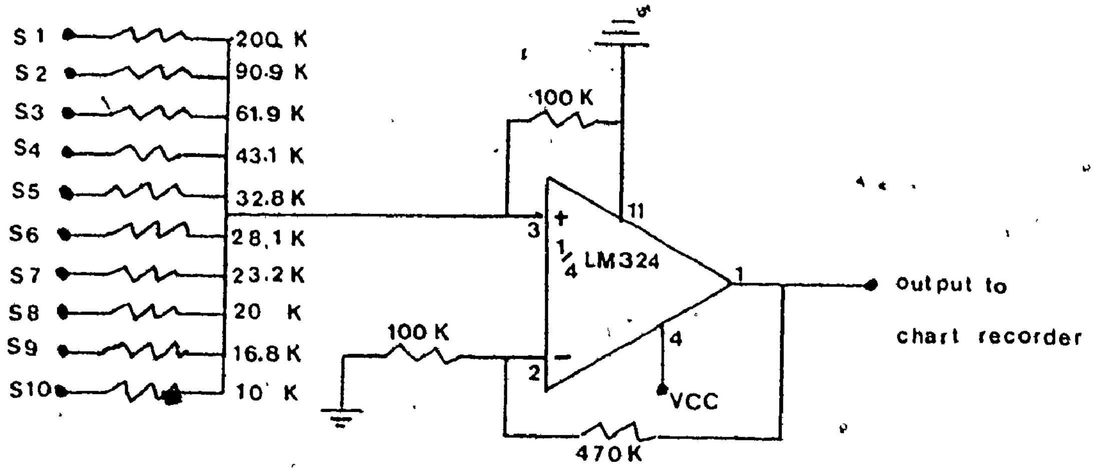

Figure 19

Digital-to-Analogue Conversion

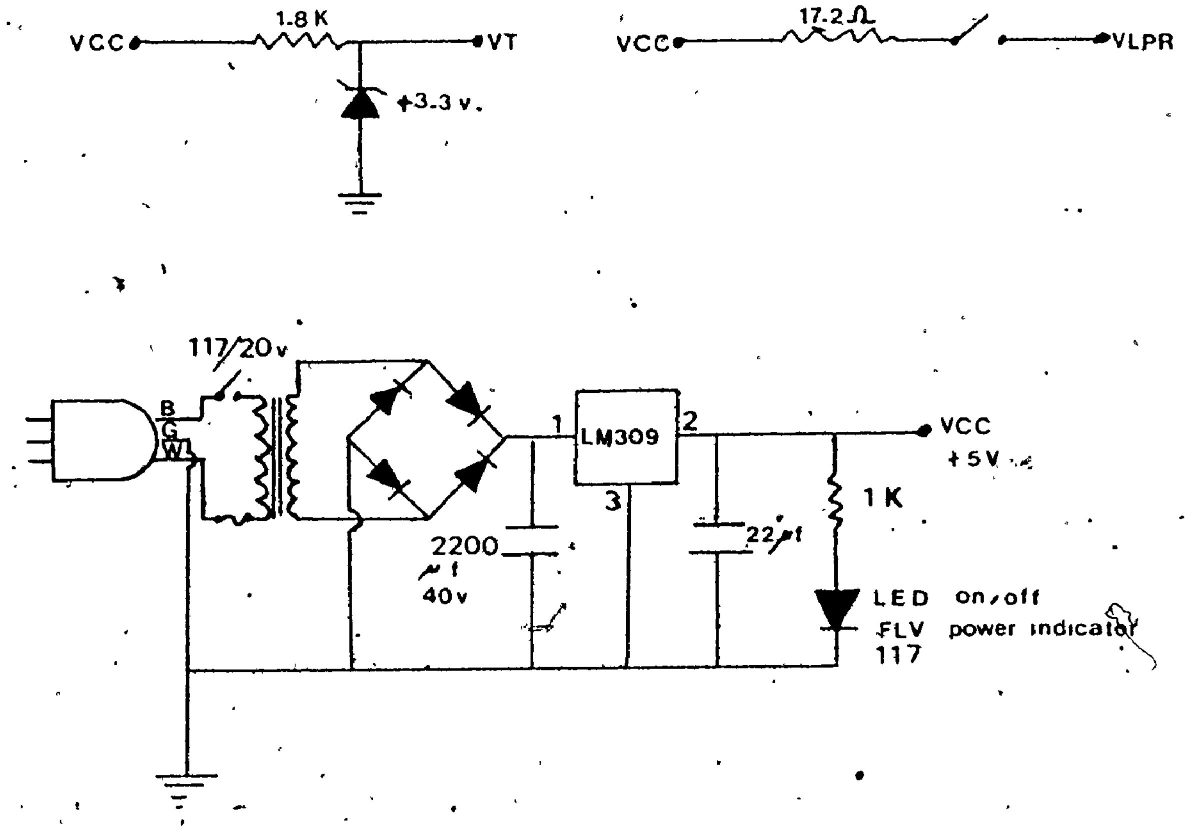

Figure 20

Power Supply and Reference Voltages

function $\overline{P1}$, + $\overline{P2}$ +...$\overline{P10}$ + $\overline{CLR}$ so that if any of the inputs P1, P2,... P10, CLR are low, the clock line of all 7474 D flip-flops becomes high. The clock pulse strobes the data line D, which is set at logical zero (low). The preset line is high for inputs P2, P3,...P10, CLR so that the outputs S2 to S10 are forced to the low condition. The preset line for input P1 is low so the clock pulse and the data line are ignored and output S1 is set high. That is, as colour appears in each of the ten samples, the corresponding output S is set high and the rest are set low. The push-buttons PB1, PB2,..., PB10 accomplish the same result. The CLR switch clears all ten flip-flops since it is not connected to any preset.

The LM324 operational amplifier (see figure 19) is used as a sum amplifier with a gain of approximately four. The resistors in the summing network have been chosen to yield voltage increments of about one half volt. Output is to a high impedance chart recorder which yields an edge at the time of each colour change and a level corresponding to the last sample to change colour. The horizontal location of an edge in the chart trace defines the reaction time and the level after an edge identifies the sample which produced it. Time resolution is dictated by the chart recorder.

This device performed as described but with several drawbacks. It proved difficult to find phototransistors all having the same sensitivity; each potentiometer had to be set at a different level to give switching at the same colour intensity in each sample. This was difficult to arrange since another set of tubes containing coloured solutions could not be used to set the threshold intensity because the tubes themselves absorb varying amounts of light. The sensor array was sensitive to ambient light and so produced occasional spurious traces. Finally, this arrangement cannot handle simultaneous events in several tubes; only one trace is produced.

In spite of these drawbacks, this circuit provides a valuable starting point for the construction of automatic detection systems. The substitution of, for example, biamperometric detection for the optical arrangement tried here and of independent registration of events should prove more successful.

I wish to express sincere thanks to Mr J.E. McFee for his generous help in designing and constructing the instrument described here.

APPENDIX E

Numerical Data

The experimental results used to plot the graphs given in the text are recorded in the following series of tables. Each table is identified by the number of the figure to which it corresponds.

TABLE XXI

Data for Figure 3

$[S_2O_8^=]_0$ M	$[SO_4^=]$ added M	t min				
		Cu (2μg)	Fe (45μg)	Mn (500μg)	Co (320μg)	blank
0.0200	0	9.1	20.7	24.8	10.5	27.6
0.0160	0.0040	10.8	26.2	31.4	12.4	35.0
0.0120	0.0080	13.6	31.9	41.9	15.3	46.2
0.0080	0.0120	19.2	50.0	63.7	20.0	69.9
0.0040	0.0160	33.9	84.1	131.5	36.9	131.5

$[S_2O_3^=]_0$ 0.0015 M

TABLE XXII

Data for Figure 4

$[S_2O_3^=]_0$ M	$[SO_4^=]$ added M	t min				
		Cu (2μg)	Fe (45μg)	Mn (100μg)	Co (320μg)	blank
0.00399	0	18.3	68.0	88.8	55.0	91.7
0.00333	0.00067	16.3	58.6	73.6	46.7	76.1
0.00266	0.00134	14.7	46.1	58.4	34.8	60.6
0.00200	0.00200	13.1	32.9	43.5	27.0	44.9
0.00133	0.00267	11.2	21.2	29.1	15.7	29.9
0.00066	0.00334	7.9	11.2	14.7	6.1	15.0
0.00033	0.00367	4.8	3.7	7.5	2.1	7.6

$[S_2O_8^=]_o$ 0.0172 M

TABLE XXIII

Data for Figure 5

$[I^-]$ M	$[SO_4^=]$ added M	t min Cu (3μg)	Fe (50μg)	Mn (200μg)	Co(320μg)*	blank	blank*
0.0066	0.0033	9.5	21.2	30.5	19.4	31.5	33.1
0.0082	0.0025	9.4	19.4	25.5	16.7	25.9	-
0.0099	0.0016	9.2	17.1	21.3	14.3	21.8	22.2
0.0115	0.0008	8.9	15.4	18.5	12.8	19.0	-
0.0132	0	8.5	13.6	16.25	11.3	16.6	17.1

* 0.06 M phenanthroline

$[S_2O_3^=]_o$ 0.0015 M $[S_2O_8^=]_o$ 0.0172 M

TABLE XXIV

Data for Figure 6

temperature °C	t min				
	Cu (3μg)	Fe (50μg)	Mn (200μg)	Co (320μg)	blank
22	11.3	23.7	31.7	15.0	33.3
24	10.1	20.3	27.4	13.5	28.7
26	8.6	17.3	24.0	11.9	25.0
28	7.3	14.7	20.2	10.4	21.2
30	6.4	12.7	17.7	9.5	18.4
31	5.8	11.7	16.5	8.5	17.0

TABLE XXV

Data for Figure 7

$[Na_2SO_4]$ added M	t min				
	Cu (3μg)	Fe (50μg)	Co (320μg)	Mn (200μg)	blank
0	8.5	17.1	12.2	23.5	24.8
0.0066	8.6	17.1	11.9	23.7	24.6
0.0130	8.6	17.1	12.2	23.5	24.5
0.0260	8.7	16.6	12.5	22.9	24.0
0.0330	8.7	16.8	11.6	23.0	24.0
0.0670	8.7	16.4	11.9	22.5	23.3
0.1000	8.8	16.3	11.7	22.1	22.7
0.133	8.9	15.5	12.0	lost	21.9
0.167	8.8	15.5	11.9	21.1	22.0
0.200	9.0	15.5	12.0	20.8	21.6

TABLE XXVI

Data for Figure 8

µg Mn	t min	µg Fe	t min
20	24.8	10	22.8
50	24.3	20	20.6
100	24.1	40	18.2
150	23.9	50	17.5
200	23.7	60	16.0
300	23.4	80	14.0
400	23.2	100	13.2
500	22.9	150	10.3
600	22.7	200	8.3
700	22.7	250	6.9
		300	5.7
		350	4.8
		400	3.9
		450	3.1
		500	2.3

TABLE XXVII

Data for Figure 9

μg Co	t min	μg Cu	t min
32	21.7	0.1	23.9
64	19.7	0.6	18.4
161	16.3	1.0	15.7
320	12.6	2.0	11.4
482	10.2	3.0	9.1
642	8.7	4.0	7.7
803	6.7	5.0	6.6
964	4.7	6.0	5.9
1124	2.8	8.0	4.8
1285	2.3	0	25.5

TABLE XXVIII

Data for Figure 10

see Table IX

TABLE XXIX

Data for Figure 11

μg Cu	t min additions none	50μg Fe	200μg Mn	0.01 M phen	280μg Co
3.0	10.3	7.4	10.0	--	--
3.4	--	--	9.6	--	--
3.5	9.5	7.0	--	--	--
3.6	--	--	9.2	--	--
4.0	8.8	6.6	8.7	28.4	16.6
4.5	8.3	6.3	--	--	--
5.0	7.9	6.2	7.7	27.7	16.5
6.0	--	--	--	27.1	15.7
7.0	--	--	--	26.7	15.3
8.0	--	--	--	26.2	14.9

$[S_2O_3^{=}]_o$ 0.0015 M

TABLE XXX

Data for Figure 12

μg Fe	t min additions				
	none	7μg Cu	200μg Mn	0.01 M phen	320μg Co
40	27.0	5.8	24.5	23.4	18.4
50	25.6	5.5	23.1	21.7	18.1
60	24.0	5.3	21.7	20.3	17.4
70	22.9	5.2	20.6	19.0	16.7
80	21.9	5.0	19.6	18.0	16.3
100	--	4.7	--	--	--
120	--	4.5	--	--	--

$[S_2O_3^{=}]_o$ 0.0015 M

TABLE XXXI

Data for Figure 13

µg Co	t min		
	additions		
	none*	50µg Fe	7µg Cu
161	24.5	20.7	18.6
200	22.9	20.0	17.5
241	21.6	19.5	16.6
281	20.7	18.8	15.3
320	19.7	18.1	14.5

* 0.01 M phen in all cases

$[S_2O_3^{=}]_o$ 0.0015 M

TABLE XXXII

Data for Figure 14

μg Mn	t min				
	additions				
	none	50μg Fe.	4μg Cu	0.01 M phen	240μg Co
50	33.9	24.6	8.7	33.3	21.3
100	33.3	24.0	8.6	32.6	21.5
150	33.0	23.7	8.6	32.0	21.9
200	32.7	23.1	8.6	30.8	22.1
300	31.8	22.3	8.7	29.4	22.6

$[S_2O_3^=]_o$ 0.0015 M

TABLE XXXIII

Data for Figure 15

µg Co	t min				
	[phenanthroline] M				
	0.0012	0.0018	0.0024	0.0030	0.0045
8	16.6	17.4	--	--	--
16	15.5	--	--	--	--
32	13.8	15.5	16.4	16.8	17.7
64	10.7	13.1	14.5	14.8	15.7
96	8.2	11.0	12.9	13.4	14.2
112	5.6	--	--	--	--
128	5.8	8.6	11.5	12.2	13.1
144	6.3	--	--	--	--
161	--	6.0	9.7	11.1	12.1
193	--	4.7	8.4	9.9	11.2
225	--	5.0	6.0	8.8	10.5
257	--	--	3.2	7.5	9.7

TABLE XXXIV

Data for Figure 16

μg Hg	t min
100	14.5
200	15.5
300	16.6
400	17.6
500	18.6
0	12.9

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