ABSTRACT

This thesis describes some investigations into the
nature of the transient pink color which develops when a
basic mixture of copper(II) nitrate and dimethylglyoxime
is oxidized by potassium persulfate. This reaction is known
informally as the "red flash".

Experiments were first performed to try to prolong the
reaction by continual addition of some of the reactants.
The success of these experiments indicated that hydroxide,
dimethylglyoxime, and persulfate were consumed by the
reaction, but not copper(II).

Some aspects of the stoichiometry were next
investigated. The stoichiometric ratio of hydroxide
consumed to sulfate produced was measured and found to be
slightly greater than 1.

An attempt was also made to identify some of the
products, using HPLC. It was established that butanedione
monoxime is a product. Butanedione may also be a product but
the HPLC detector could not access the 190 nm region needed.

The feasibility of monitoring both absorbance and pH
during the red flash by interfacing to a computer was then
investigated. Some 19 runs were performed. These indicated
that the reaction goes through several steps, some of which
are pH-dependent. The initial step in which a colored
species is first produced appears to be second order with
respect to copper(II). The rate is also dependent on
persulfate concentration but not enough data could be

collected to establish the order with respect to this

component.

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----------- THE RED FLASH ---------------

A Transitory Copper Complex Of High Oxidation State

A Thesis

presented to

the Division of Physical Sciences

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In Partial Fulfillment

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by

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CONTENTS

INTRODUCTION

The fact that a strong pink color can develop when dilute basic solution of copper(II) salts containing dimethylglyoxime are oxidized by persulfate ion has been known for many years (Welcher 1955). Nevertheless only one quantitative study of this system can be found in the literature. (Mopurgo and Tominson 1977). Most of this paper is concerned with establishing what species are present before the oxidizing agent is added. Very little progress was reported in uncovering the nature of the pink color or even in establishing what the ultimate products of the reaction are.

In 1985 the pink color described above was rediscovered by an undergraduate student at Texas Wesleyan College, (Lavely 1985) while working under the direction of Dr. A. N. Starks. This phenomenen was further investigated by another student at Texas Wesleyan College during the spring semester of 1985 (Croy 1985).She established the conditions under which one could obtain the optimal production of color. Table I gives the composition of the mixture which produces the strongest and longest lasting color.
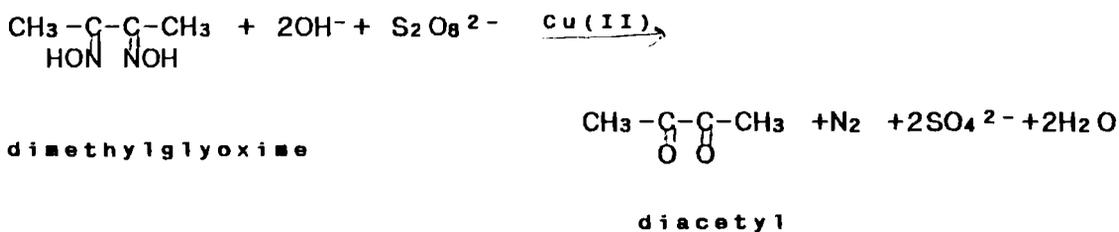
Table I :The Croy formulation

Volume	Solution	Concentration/mol L^{-1}
10 mL	NaOH	4×10^{-3}
10 mL	DMG	2×10^{-3}
10 mL	$Cu(NO_3)_2$	1×10^{-3}
10 mL	$K_2S_2O_8$	1×10^{-2}

Any deviation from these concentrations produced a significantly less intense color, or a much briefer "flash". Large changes in these concentrations quite often resulted in no observable production of red color at all.

In this report, a solution of this composition will be referred to as the Croy formulation . It will be used as a reference standard, when comparing solutions of different composition .

Further research was pursued on this subject at Texas Wesleyan College under the direction of Dr. W. G.Davies as well as Dr. A.N. Starks. As a result of this work, it was discovered that the reaction is accompanied by a decrease in pH (Lavely 1983). Experiments in buffer solutions proved contradictory, the behavior depending on the nature of the buffer. Studies on the variation of the light absorbance with time showed that more than one colored species is produced and that the color is often pH dependent, but the results were too complex to fit to a mathematical model (Welch 1985). It was also noticed that this reaction

produced a characteristic "buttery" odor (Walters 1986). This odor seemed to be identical to that of 2,3 propanedione (diacetyl). In order to explain this result, it was thought that the copper(II) ion acts as a catalyst promoting both the hydrolysis and oxidation of dimethylglyoxime in a reaction similar to:

$$CH_3-\underset{\underset{HON}{\|}}{C}-\underset{\underset{NOH}{\|}}{C}-CH_3 \ + \ 2OH^- + \ S_2O_8{}^{2-} \ \xrightarrow{Cu(II)}$$

dimethylglyoxime

$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \ +N_2 \ +2SO_4{}^{2-} +2H_2O$$

diacetyl

The products could also conceivably include the monoxime of diacetyl rather than the diketone itself. Similarly the oxidation product might be NO or N_2O rather than N_2. Presumably, the red color is a transient complex of copper in an oxidation state great than two.

In the work described in this thesis, it was hoped to build on this earlier preliminary work and to try to confirm (or perhaps disprove) the view of the reaction just described, in particular, it was intended to pursue three lines of investigation as detailed below:

1) <u>Confirmation</u> <u>of</u> <u>the</u> <u>role</u> <u>of</u> <u>the</u> <u>reactants.</u>

If the above view of the reaction were correct, it would be possible to keep the reaction alive by continually adding hydroxide ions, dimethylglyoxime, and persulfate ions. If this were sucessful, then computer control of these additions could be attempted.

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2) Detection of products.

Since it was thought that sulfate ions would be a product, and that these could be easily estimated. It was hoped to be able to measure the stoichiometric ratio of hydroxide ions consumed to sulfate ions produced. It was also hoped to detect some of the breakdown/hydrolysis products of dimethylglyoxime, in particular, to detect and perhaps measure the production of 2,4-butanedione and its monoxime.

3) Spectrophotometic investigation :

Because of the obvious color changes in this reaction it seemed obligatory to investigate changes in light absorbance during the reaction. For this purpose a dipping probe colorimeter seemed to have many advantages. If this detector were used in a reaction vessel, it should be possible to keep the temperature constant. It was hoped that both pH and light absorbance could be measured simultaneously with a computer interface.

SECTION 1 : KEEPING THE REACTION GOING BY ADDING REACTANTS

The original intention in these investigations was to
hold the concentrations of as many of the reactants as
possible constant. In particular, it was hoped that the pH
could be kept constant by adding sodium hydroxide solution
under computer control . It was also hoped that the
intensity of the pink color could be kept constant .The
absorbance of the solution could be measured by a
colorimeter and fed into a computer, dimethylglyoxime could
then be added under computer control to keep the absorbance
constant.

Before a totally computerized set-up was assembled, it
was necessary to investigate the feasibility of this
approach by undertaking some preliminary investigations in
which the pH and color were held constant by manual rather
than computer control.

EXPERIMENTAL:

The set-up used in these preliminary investigations is
shown in Figure 1. The reaction was allowed to occur in a
beaker while being stirred with a magnetic stirrer. No
attempt was made to control the temperature. A glass
electrode was inserted into the reaction solution and was
connected to a digital pH meter. Sodium hydroxide, in a 10
mL buret, was added manually to maintain a constant pH. In

8.05
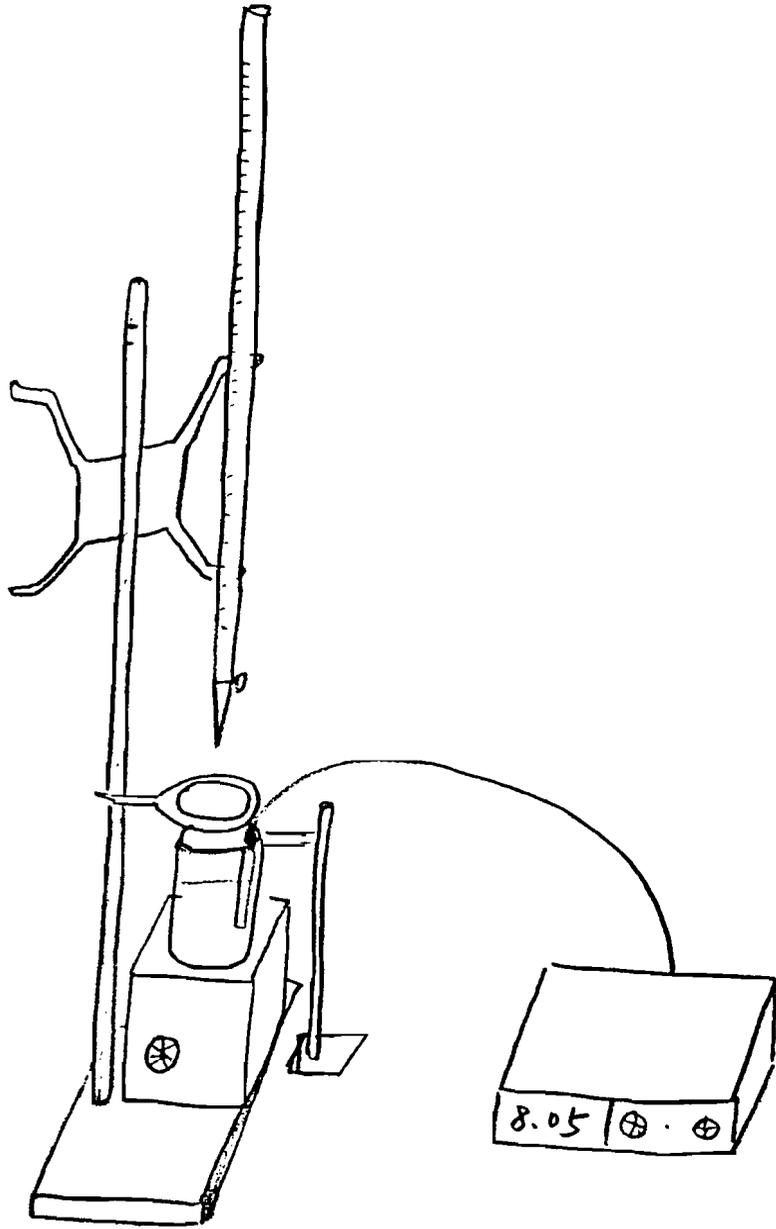
all runs, the initial composition of the beaker was the Croy formulation.

RESULTS:

In the first few runs, $4X10^{-2}$ M NaOH was used in the burette. It quickly became apparent that continual addition of sodium hydroxide alone, although it was able to keep the pH constant, was not able to keep the color reaction alive. The pink color faded after only a few minutes.

The next few runs were performed with the addition of a mixture of NaOH and dimethylglyoxime rather than NaOH alone. The amount of hydroxide ion was twice that of the dimethylglyoxime . The actual concentrations were $4X10^{-2}$ M NaOH and $2X10^{-2}$ M DMG. By adding this mixture to keep the pH at 8, it was possible to maintain a fairly strong color in the solution for as long as 70 minutes .The rate of addition from the burette, however grew progressively slower and the color became gradually, rather than suddenly, less intense with time.

It was felt that one reason for the slowdown in the rate could be a reduction in the concentration of persulfate ion. Accordingly, persulfate was included in the burette solution with a concentration equal to that of the hydroxide ion. The actual concentrations were $4X10^{-2}$ M NaOH, $2X10^{-2}$ M DMG, and $4X10^{-2}$ M persulfate. Using this new solution in the burette, it proved possible to keep the pH

between 8.0 and 8.5 while maintaining a fairy strong color for about 3 hr and 50 minutes. Even though the color was prolonged, it still gradually faded with time.

CONCLUSIONS:

Although these preliminary investigations were only semi-quantitative, they confirmed the role of Cu(II) in the reaction mixture. Replenishment of the hydroxide, persulfate ions, and dimethylglyoxime made it possible to extend the life of the reaction for a very long time. However, this prolongation was achieved without changing the Cu(II) concentration at all. This fact demonstrates that Cu(II) is not permanently consumed by this reaction . Presumably the pink color corresponds to a Cu(III) or Cu(IV) species but this can only be a reactive intermediate. It must return to the Cu(II) state so as to enable the reaction to proceed. In other words, Cu(II) acts as a catalyst in an oxidation reaction which consumes hydroxide ions, persulfate ions, and dimethylglyoxime. It appears also that this catalyst is slowly poisoned. A possible explanation is that the products form a more stable complex with copper(II) than does dimethylglyoxime, thus tying up the copper(II) and preventing it from acting as a catalyst.

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SECTION 2 : SOME STOICHIOMETRIC INVESTIGATIONS

In the second stage of the investigation, it was hoped to detect, and if possibly estimate, some of the products.

When the Croy recipe is used, the amounts involved are only of the order of 20 micromoles, too small to be easily measured. However, if we use the technique just described, in which the reaction is maintained at constant pH by continual addition of reactants, then the amount of products can be increased by an order of magnitude or more. In particular, any sulfate ion produced can be estimated. Under appropriate conditions, SO_4^{-2} combines with Ba^{2+} to form colloidal $BaSO_4$. The colloid scatters light, and its concentration can be determined with a spectrophotometer at 420 nm (Jenkins 1978). Beer's law is usually obeyed up to 40 ppm sulfate. Higher concentrations require dilution. Colored substances absorbing at 420 nm will interfere, as will any turbidity present in the sample before addition of barium. Neither of these factors can be expected to operate. The detection limit is about 1 ppm sulfate in 1-cm cells.

EXPERIMENTAL:

Apparatus: GCA/Mcpherson EU-707-D spectrophotometer

           Stopwatch

           Magnetic stirrer

Reagents: (1) Conditioning reagent: 50 mL glycerol added

to a solution containing 30 mL concentrated
HCL, 300 mL distilled water, 100 mL
isopropyl alcohol, and 75 g sodium chloride.

(2) $BaCl_2.2H_2O$, crystals, 20-30 mesh

.(3) Sulfate standard : prepared by dilution of
0.01 M H_2SO_4 to 50 mL. This solution was
38.4 ppm sulfate.

An aliquot of 25 mL of a solution containing sulfate
was pipeted into a 50-mL volumetric flask, followed by 2.5
mL of conditioning reagent. Distilled water was then added
to the mark. All of this solution was then poured into a
125-mL Erlenmeyer flask and placed on a magnetic stirrer.
Then 0.10 g of solid barium chloride was added .
The mixture was stirred for exactly one minute after which
it was removed from the stirrer. Its absorbance was
measured between 4 and 5 minutes from the initial mixing.

A calibration curve was first constructed. Ten
solutions containing sulfate in the range between 0 and 40
ppm were prepared. Each of these solutions was treated as
described above, and their absorbances measured. The results
of this calibration are given in Table II. Figure 2 shows a
plot of these results and the linear least squares "best-
fit" line through the points.

Table II: Sulfate calibration results

	Concentration of standard (ppm)	Absorbance reading
1.	0	0
2.	3.84	0.022
3.	7.68	0.038
4.	11.52	0.053
5.	15.36	0.073
6.	19.2	0.088
7.	23.04	0.115
8.	26.88	0.132
9.	30.72	0.155
10.	34.56	0.180
11.	38.4	0.195

SO4 STD
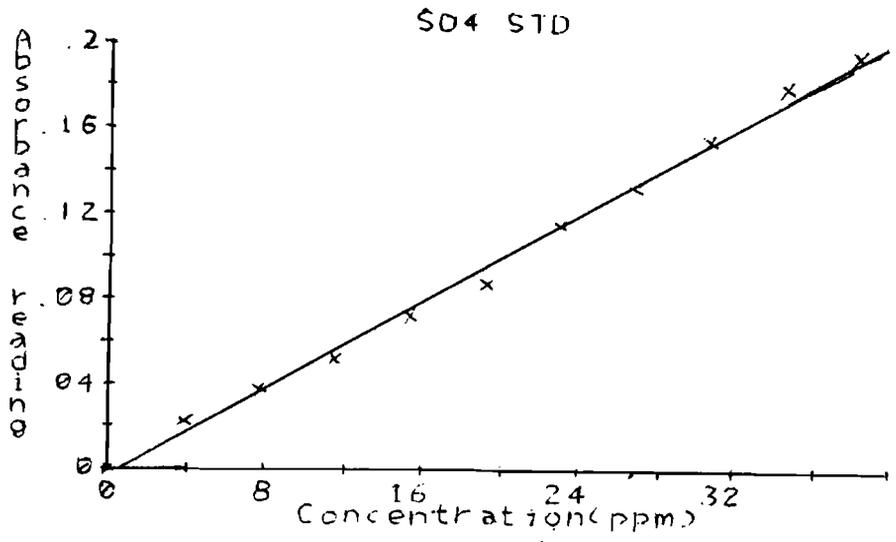
LEAST SQUARES FIT RESULTS

SLOPE = 5.1069015IE-03

INTERCEPT = -2.54545448E-03

UNCERTAINTY IN SLOPE
------------------- = .0248297549
UNCERTAINTY IN Y'S

UNCERTAINTY IN INT.
------------------- = .564076075
UNCERTAINTY IN Y'S

Figure 2: The calibration curve for SO4 2-

This calibration curve in Fig 2 was used to investigate the production of sulfate during the course of the "red flash" reaction. The Croy formulation was used. The reaction was allowed to proceed until the pH had dropped to 8. Once this happened a mixture of hydroxide and dimethylglyoxime (4×10^{-2} M NaOH + 2×10^{-2} M DMG) was added from a microburet to keep the pH at 8. This process was continued until a pre-determined time had elapsed. One or two drops of 1 M HCl was then added to quench the reaction which was then analyzed for sulfate.(see Section 5) The total amount of sulfate produced by the reaction was then compared with the amount of NaOH added from the microburet.   RESULTS:

In a typical run, a 10 mL aliquot of the quenched solution was pipetted into a 50 mL volumetric flask, and treated in exactly the same way as described above . A 10 mL aliquot was used rather than the 25 mL aliquot used previously because the concentrations of sulfate would otherwise have been too high. The absorbance found in such determination was 0.098. From the calibration curve of Fig 2 ,this corresponds to 19.68 ppm SO_4^{2-} in a 25 mL aliquot, or 19.68 ppm X 25 mL/10 mL = 49.20 ppm SO_4^{2-} in a 10 mL aliquot of quenched solution. If we regard 1 ppm as equal to 1 milligram per liter, then the concentration of sulfate in the above solution has a value of

49.20 mg/L X 1/96 mg/mmole = 0.51 mmole/L
$$= 5.1 \times 10^{-4} \text{ mmole/mL}$$

If the total volume of quenched solution was 40 mL, then the total amount of sulfate present in this volume has the value : 5.1×10^{-4} mmole/mL $\times$ 40 mL = 0.020 mmole SO_4^{2-}

The amount of sulfate produced by persulfate alone was also determined. A 10 mL of aliquot 1×10^{-2} M $K_2 S_2 O_8$ was diluted to 40 mL with distilled water, a 25 mL aliquot of this solution was treated in exactly the same way as described above. The amount of sulfate produced in 40 mL of this solution has a value of 9.6×10^{-4} mmole/mL. This value was small enough to be ignored.

Table III shows the results obtained for 9 runs. In each case the Croy formulation was used and a solution containing 4×10^{-2} M NaOH and 2×10^{-2} M dimethylglyoxime was added from a microburette to keep the pH between 8 and 8.5. After the time shown, the reaction was quenched with HCl and analyzed as described above . The amount of SO_4^{2-} determined from this analysis is listed along with the amount of OH^- added from the burette during the reaction to keep the pH constant.

Table III: Determination of stoichiometric ratio
            (no persulfate added)

time hr	volume added mL	total volume mL	nOH, amount of hydroxide added , μmole	nSO4, amount of SO_4^{2-} produced , μmole	$\dfrac{nOH}{nSO4}$
0.5	3.4	43.4	136	107	1.27
1	4.0	44.0	160	116	1.38
1.5	4.6	44.6	184	142	1.30
0.5	3.0	43.0	120	103	1.17
1	3.6	43.6	144	121	1.19
1.5	4.0	44.0	160	143	1.12
0.5	3.0	43.0	120	101	1.19
1	3.6	43.6	144	126	1.14
1.5	4.0	44.0	160	139	1.15

Table IV shows the results obtained for a further 9

runs, in this case the burette solution contained

persulfate in addition to hydroxide and dimethylglyoxime

and had the composition 4×10^{-2} M NaOH + 2×10^{-2} M DMG +

2×10^{-2} M $K_2 S_2 O_8$.

Table IV : Determination of stoichiometric ratio
             (persulfate added)

time hr	volume added mL	total volume mL	nOH, amount of hydroxide added μmole, nOH	nSO4, amount of SO_4^{2-} produced μmole, nSO4	$\dfrac{nOH}{nSO4}$
0.5	3.8	43.8	152	130	1.17
1	4.7	44.7	188	165	1.14
1.5	5.3	45.3	212	190	1.12
0.5	2.6	42.6	104	80	1.30
1	3.2	43.2	128	109	1.17
1.5	3.6	43.6	144	118	1.22
0.5	3.4	43.4	136	140	0.97
1	4.4	44.4	176	189	0.93
1.5	4.9	44.9	196	190	1.03

In both Tables the ratio of amount of OH⁻ added to the amount of SO_4^{2-} produced is also given. Of more interest, though, are the changes in amounts and the ratios of these changes. These are shown in Table V. The difference quoted are the difference between the readings at 0.5 hr and 1.5 hr from Table III and IV. The stoichiometric ratio of hydroxide to sulfate is shown in the last column. The mean of these ratios is 1.12 with a standard deviation of 0.14. The ratios in Table V are to be preferred to these in Table III and IV , because they refer to changes which occur while the pH is constant while those in Table III and IV do not.

Table V: The stoichiometric ratios of changes in amount of
        OH⁻ and SO_4^{2-} at constant pH of 8.0

the difference in volume of OH added, mL	the difference in amount of OH added, nOH	the difference in amount of SO_4^{2-}, nSO4	$\frac{nOH}{nSO4}$
1.2	48	35	1.37
1.0	40	40	1.0
1.0	40	38	1.1
1.5	60	60	1.0
1.0	40	38	1.1
1.5	60	50	1.2
		Mean	1.12+0.14

The fact that this ratio comes out close to one, establishes that one OH⁻ ion is destroyed (or one H⁺ is produced), for every SO_4^{2-} produced. Since the half equation for persulfate is :

        $e + 1/2\ S_2O_8^{2-} \longrightarrow SO_4^{2-}$
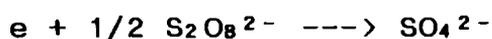
this means that the species oxidized must produce one H⁺

ion per electron donated. The most probable candidates are hydroxylamine or water :

$$2\ NH_2OH \longrightarrow N_2 +\ 2\ H^+ + 2H_2O + 2e$$

$$NH_2OH \longrightarrow NO + 3H^+ + 3e$$

$$2\ NH_2OH \longrightarrow N_2O +\ H_2O + 4\ H^+ + 4e$$

$$2\ H_2O \longrightarrow O_2 + 4\ H^+ + 4e$$
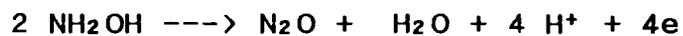
SECTION 3 : SPECTROSCOPIC PROPERTIES OF REACTANTS AND POSSIBLE PRODUCTS.

The spectra of both reactants and possible products in this reaction were investigated for two purposes.

i) It was hoped that some of the products of this reaction could be separated using high performance liquid chromatography (HPLC) and detected using an ultraviolet detector with variable wavelength. Accordingly, it was necessary to know the light-absorbing behavior of all the compounds likely to encountered in the reaction mixture .

ii) It was also hoped to investigate changes in light absorption with time so as to study the kinetics of the reaction. For this purpose also, the spectral behavior of all relevant materials would be useful.

EXPERIMENTAL

The spectrophotometer used was the same GCA/McPherson EU-707-D spectrophotometer used in Section 2. Both wavelength and absorbance are displayed digitally in this machine. An interface designed by Dr. W. G. Davies was used to transfer this digital information to a Commodore 64 computer, allowing a complete spectrum to be stored on disk. Additionally, the data could be displayed on the monitor screen while readings were being taken, as well as plotted on a small digital plotter . Investigations were confined

to the ultraviolet region of the spectrum.

The spectra of a variety of solutions were measured . Plots of these spectra are given in Appendix A . The most important of these results are summarized below .

A) Pure substances

Dimethylglyoxime :   HO-N=C(CH3)-(CH3)-C=N-OH
(see RUN 1)

peak at about 240 nm

2,3-Butanedione monoxime :   O=C(CH3)-(CH3)-C=N-OH
(see RUN 4)

peak at about 230 nm

Diacetyl :   O=C-(CH3)-(CH3)-C=O
(see RUN 5)

peak at about 190 nm

These results showed that both dimethylglyoxime and 2,3-butanedione monoxime can be detected by the UV detector utilized by the available HPLC apparatus . Unfortunately , the diacetyl absorbs at too low a wavelength to be easily detected.

B) Basic solutions of the above

Several solutions of both monoxime and dioxime in base showed large differences from the neutral solution. Presumably , these changes corresponded to the deprotonation of these two oximes .

C) Copper complexes with the above

When copper(II) ions are added to the above basic solutions , there are very large changes in the spectra. Apparently that both dimethylglyoxime and 2,3-Butanedione

monoxime form complexes with copper(II).

D) <u>Croy</u> <u>formulation</u>

The ultraviolet spectrum of the Croy formulation was also measured at various time after mixing . Very obvious spectral changes in the UV during the reaction were observed. Nevertheless, these were judged to be less suitable for observation of this reaction than the visible region when comparisons were made with the results of the Texas Wesleyan group (Keene, 1985).

SECTION 4 : DETECTION OF PRODUCTS BY HIGH-PERFORMANCE
LIQUID CHROMATOGRAPHY

In this section of the research it was hoped to establish the nature of some of the products of this reaction. Particular attention was paid to the possible production of 2,3-Butanedione monoxime, and diacetyl (2,3-butanedione). The reason for this attention was the production of a characteristic "buttery" odor whenever the "red-flash" reaction was allowed to occur. A comparison of this odor with that of diacetyl suggested that both were identical.

EXPERIMENTAL

Apparatus :

HPLC analyses were performed on a Varian 2010 pump/2210 system . The variable-wavelength UV detector, model 2050, was set at 215 nm . The injector was a Rheodyne 7125 with a 10-uL loop. An analog strip chart recorder was operated simultaneously, directly from the detectors. The column was an Alltech C-18 cartridge, 25 cm X 4.6 mm.

Reagents :

Since the pH range of the mixture of the Croy formulation was not the ideal range for this column, it was decided to use acetate buffer and methanol as the solvent. This mildly acidic solution would also have the effect of

quenching the reaction. Hopefully it would also dissociate all copper(II) complexes. Accordingly, a 0.01 M CH_3COOH solution was prepared and mixed with 0.0174 M CH_3COONa, to obtain a buffer solution of pH=5.0. The mobile phase consisted of 60% of this buffer and 40% methanol by volume.

All HPLC analyses were performed at a flow rate of 1.0 mL/min at room temperature. The stock solutions of potassium persulfate , copper(II) nitrate, dimethylglyoxime, and sodium hydroxide were used in these analyses. For possible products, $2X10^{-3}$ M solutions of both diacetyl and 2,3-butanedione monoxime were prepared. A 10 mL aliquot of each of these solutions was diluted to 50 mL with the methanol/acetate buffer. Each of these solutions was filtered through a 0.45 -um membrane before analysis. The 1-mL injection syringe was rinsed twice with sample and filled to 0.2 mL for rinsing and filling the injector loop. Each injection was performed in duplicate. The chart rate was 2 cm/min.

RESULTS:

The strip chart recordings of these runs are shown in Appendix B (Numbers 1,2,3,4,5). The following retention times were found:

     a) persulfate ion   2.2 min

     b) nitrate ion   2.4 min

     c) dimethylglyoxime   4.6 min

d) 2,3-butanedione monoxime   5.4 min

e) diacetyl   not detectable at 215nm

In the next few runs, solutions of the Croy formulation were investigated. The reaction mixture was allowed to react for a predetermined time interval before addition of the quenching buffer, followed by chromatography. The strip charts recording for these runs also can be found in Appendix B (Number 6,7,8,9,10,11, and 12). Figure 3 shows the plot obtained for 0 min. (In practice a few seconds elapsed between mixing and quenching). In this figure clearly shows peaks corresponding to

a)   persulfate ion

b)   nitrate ion

c)   dimethylglyoxime

d)   2,3-butanedione monoxime

are clearly visible. Other peaks were observed also, the negative peaks at 3.0 min (peak e), which occur in all runs, are due to highly polar water. A peak at 3.6 min (peak f), seemed to be an impurity in the dimethylglyoxime since it occurs in all runs in which dimethylglyoxime is present including that for "pure" dimethylglyoxime. At one point there was some uncertainty as to whether peak b) was cause by the nitrate ion or the copper ion. This uncertainty was resolved by performing runs with 0.001 M $CuSO_4$, 0.001 M KNO_3 , and 0.01 M K_2SO_4 (runs 13, 14, and 15, Appendix B), only the KNO_3 showed peak with a retention

-22-

time of 2.4 min.

CONCLUSIONS:

The relative size of some of these peaks is worth
noting. The size of the monoxime peak increased with time,
while that of the dioxime decreased. After a long period of
time the dimethylglyoxime peak became quite small. These
chromatographic results accord with the general
interpretation of this reaction given at the end of
Section 1. Dimethylglyoxime is consumed by the reaction and
butanedione monoxime is produced by it. Another possible
product is butanedione (diacetyl), but the limitations of
the UV detector available prevented a final decision on
this point.
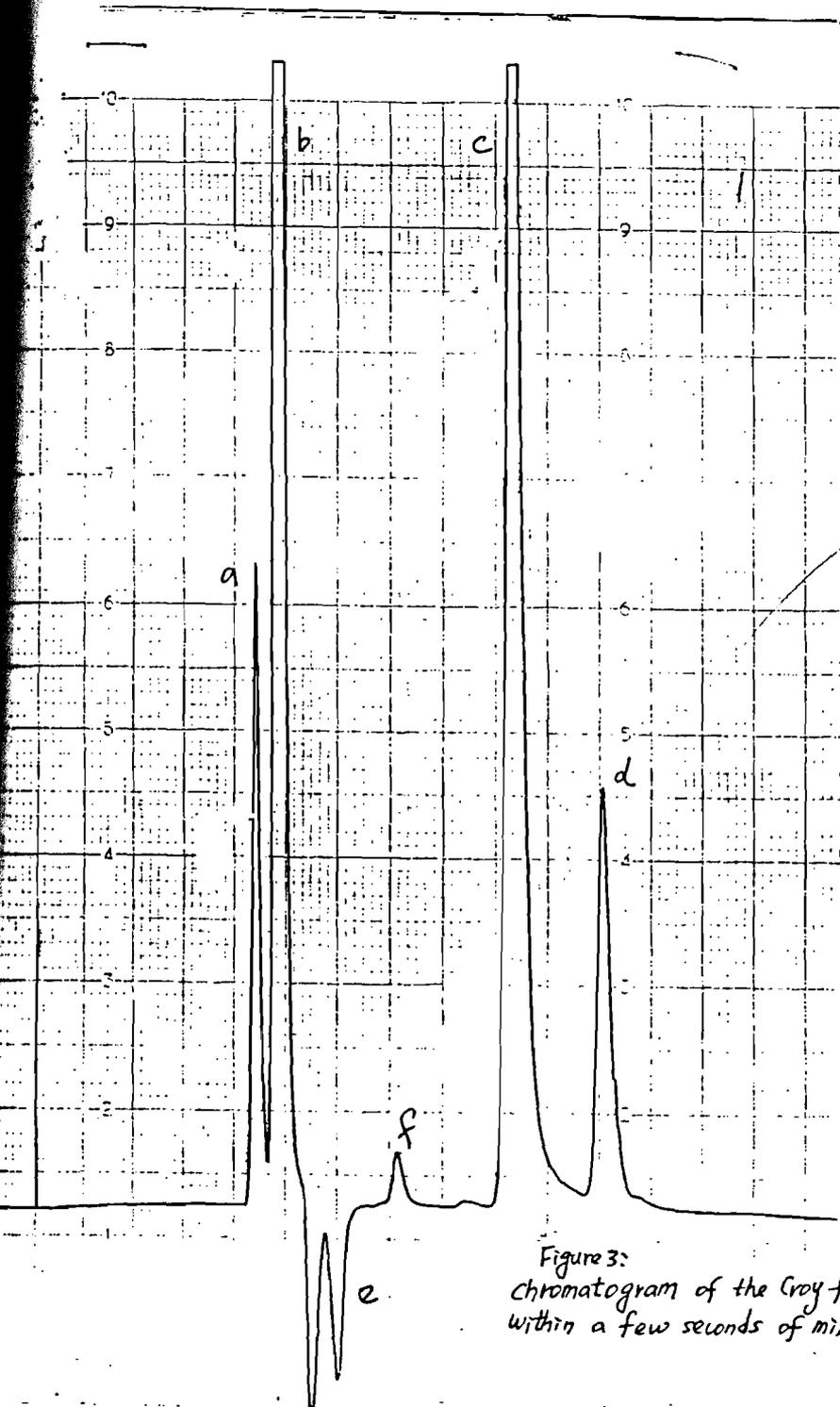
Figure 3:
Chromatogram of the Croy formulations
within a few seconds of mixing.

SECTION 4A : INVESTIGATION OF A POSSIBLE ALTERNATIVE TO DIMETHYL GLYOXIME

In order to see whether the red-flash might also occur with substances similar to dimethylglyoxime, some benzil dioxime (HO-N=C(C_6H_5)-(C_6H_5)C=N-OH) was used in place of dimethylglyoxime, since benzil (O=C(C_6H_5)-(C_6H_5)C=O) absorbs heavily at 215 nm (the wavelength accessible with the available HPLC detector). However, it proved impossible to dissolve sufficient benzil dioxime either in water or in sodium hydroxide solution to produce even a solution as dilute as 2×10^{-3} M .

Even when solid benzil dioxime was left in contact with sodium hydroxide solution for several days, it proved impossible to obtain any reaction similar to the "red flash" when substitued for the dimethylglyoxime.

SECTION 5:SURVEYING THE KINETIC BEHAVIOR OF THE "RED FLASH" REACTION:SIMULTANEOUS PH AND ABSORBANCE MEASUREMENTS

In this stage of the investigation, it was hoped to get some insight into the mechanism of the reaction by simultaneous observation of the variation of both light absorbance and pH with time .

EXPERIMENTAL:

In these experiments, the absorption of light by the solution was measured using a Brinkmann Model PC 700 Dipping Probe Colorimeter. The general appearance of this instrument is shown in Figure 4A, The principle of its operation is shown in Figure 4B. Light from a tungsten lamp in the main housing passes through one side of a flexible fiber-optic guide, enters the solution under investigation, and is then reflected off a mirror which is firmly attached to the end of the fiber optic guide. After reflection the light traverses a further length of solution and passes back into the other side of the fiber-optic guide. On exiting the guide, the light passes first through a filter and then falls on a photodiode where it is detected. The signal from this detector is amplified and fed both to a meter on the front panel, as well as to a recorder output in the back of the instrument.

Fig 4A   PROBE COLORIMETER PC 700

FRONT
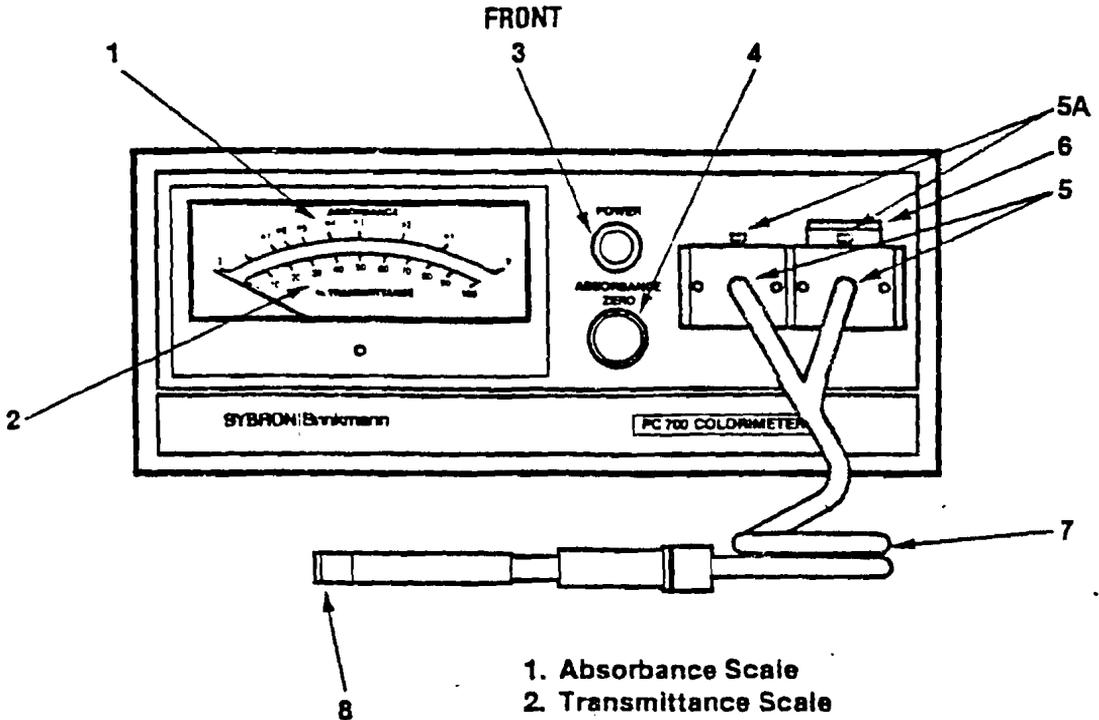
1. Absorbance Scale
2. Transmittance Scale
3. Main Power Button with Power Lamp
4. Absorbance Zero (100%T)
5. Fiber Optic Socket
5A. Knurled Screw
6. Filter
7. Fiber Optics
8. Probe Tip

OPERATIONAL SCHEMATIC FOR PROBE COLORIMETER
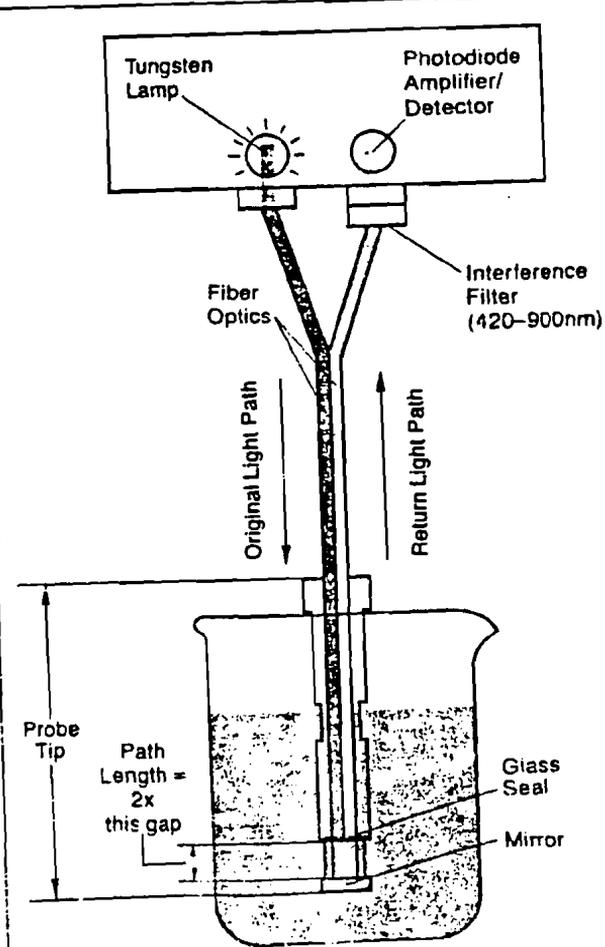
The use of this probe colorimeter in conjuction with a
glass electrode is shown in Figure 5. The reaction was
allowed to occur in a jacketed beaker A. Water from a
constant temperature bath was circulated through the jacket
in order to keep the reaction solution constant at 25⁰C.
Two detectors were placed in the solution in the beaker :
a glass combination electrode B, and the fiber-optic
dipping probe C described above. The jacketed beaker was
placed on top of the magnetic stirrer D, and a stirrer bar
E was placed in the solution in the beaker. It is not easy
to monitor the pH and the absorbance as well as to keep
the solution stirred at a constant temperature. The above
setup is an especially convenient way to achieve all
objectives simultaneously.

Measurements of both the pH and the absorbance were
made and recorded by a computer. The glass electrode was
attached to the "pH box" F. This box contained an
operational amplifier to modify the signal as well as
change its input impedance. The output of the op-amp was
fed to an 8-bit serial analog to digital converter. The
output of the converter in turn was fed to the computer via
its "joystick port" input.

The fiber-optic colorimeter probe was connected to the
colorimeter G. The pen-recorder output of the colorimeter
(at its rear) was then fed to a second 8-bit A/D converter
H(a parallel device). This second A/D converter accessed the

Figure 5
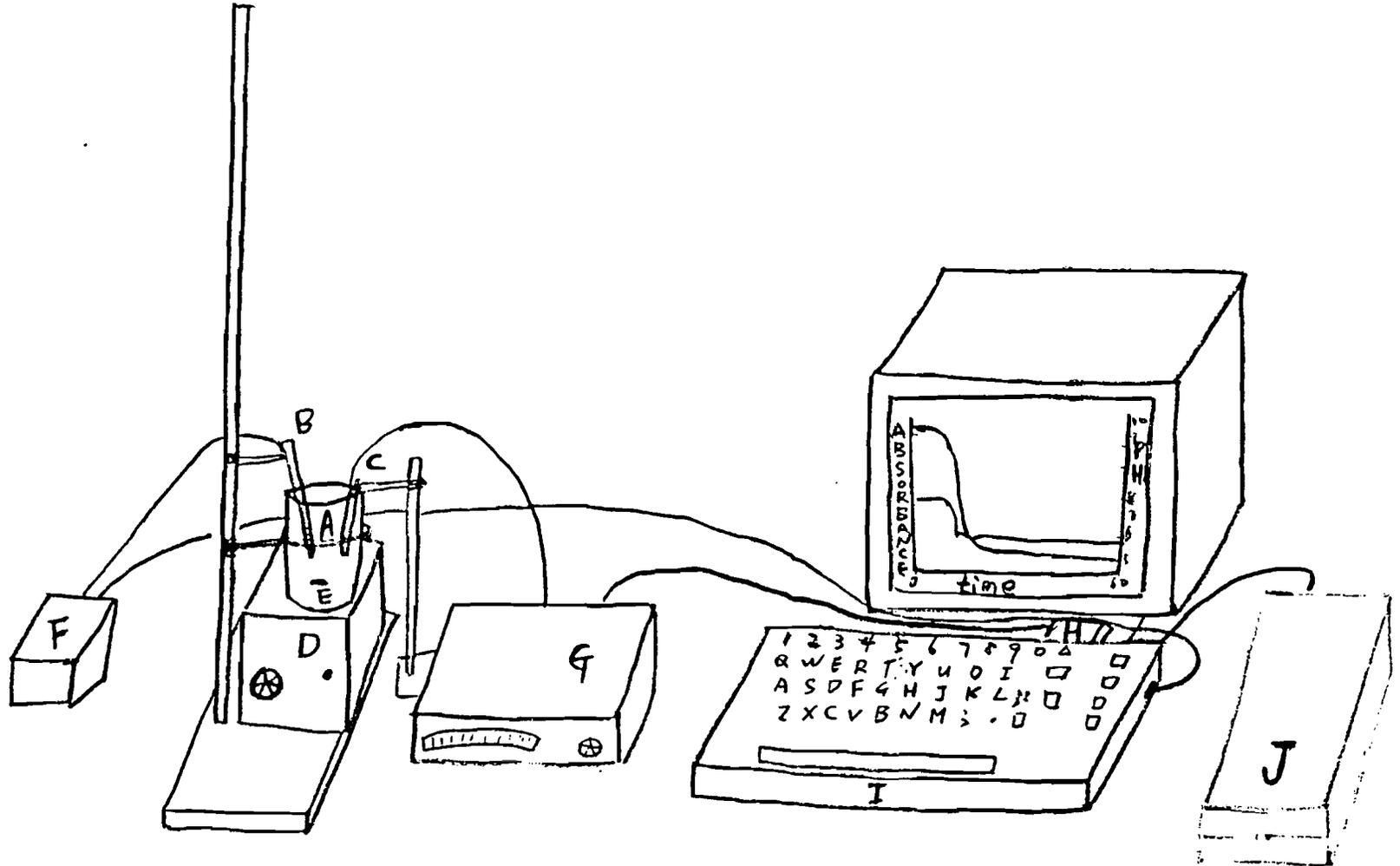
computer through its main expansion slot on the rear. The computer used was a VIC-20. Although this computer has only 3.5 K of memory, it proved quite adequate for data aquisition purposes. In a typical run, measurements were taken every 3 seconds, and immediately transferred to a disk in disk drive J, so that memory requirements were at a minimum.

In all runs a filter passing light of wavelength 520 nm was used. These filters are fairly expensive so that only one was available. A wavelength of 520 nm was selected since this seemed to correspond best to the maximum absorbance of the red flash.

Runs were performed solutions of various compositions. Again the Croy formulation was used as a reference, the total volume used in each of the runs was 250 mL. In the jacketed beaker, this volume proved to be the most convenient to allow for stirring while affording ample space for the insertion of both the optical and the electrochemical probes.

The stock solutions for these runs were the same as those used previously, except in the case of persulfate, when two different concentrations were prepared. The solutions were

i) 0.004 M NaOH

ii) 0.002 M DMG

iii) 0.001 M $Cu(NO_3)_2$

iva) 0.010 M $K_2S_2O_8$ ivb) 0,040 M $K_2S_2O_8$

In order to obtain the Croy formulation, 50 mL of each of the first three solutions were added in that order to 50 mL of water making a total volume of 250 mL. Then 50 mL of solution iva) was added quickly as possible to start the red flash reaction.

It quickly became apparent that the Croy formulation gave much too intense a color for measurements to be made in the apparatus used. The maximum absorbance developed at 520 nm was well in excess of 2. Accordingly, the volume of copper(II) solution added in all the mixtures was almost always below 25 mL, as compared to the 50 mL needed for the Croy formulation.

RESULTS

A total of 19 runs were made, each involving a different initial composition. Each run was labelled according to how it differed from the Croy formulation . Thus the run labelled CU12.5A was made up by mixing 50 mL of water and 50 mL of each solution above except for copper(II) solution, 12.5 mL of the copper solution was used plus an additional 37.5 mL of water to make up to 250 mL. Those runs labelled with an A involved the use of 50 mL 0,010 M $K_2S_2O_8$ and were closest to the Croy formulation. Those not labelled with an A were prepared using 50 mL of 0.040 M $K_2S_2O_8$.

All results were stored on disk. The raw data whether for pH or absorbance was always in the form of an integer between 0 and 255 corresponding to the reading of an 8-bit A/D converter. These integers were converted into pH and/or absorbance readings by the VIC-20 program. In order to do this, it was necessary to do a preliminary standardization before each run.

After each run, the disk was transferred to a Commodore 64 computer with a much larger memory. Using a graphics program it was then possible to plot the results of that run directly on a dot matrix printer. Plots for all 19 runs are given in Appendices C and D.

DISCUSSION OF RESULTS

I) Introduction

Figure 6. shows the result for run Cu 21A. The simultaneous values of the pH and absorbance are shown as a function of time . The absorbance curve has been divided into five stages labelled A, B, C, D, and E. These stages correspond to five different features in the behavior of these runs.

Not all features are present in all runs, and their relative importance differs from run to run. A brief description of each stage follows:

Stage A : An initial, fast, production of color.

Stage B : A reduction in intensity, falling off

asymptotically at a rate distinctly slower than in

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Stage A.

Stage C : A second, more gradual increase in intensity.

Note: During Sections A, B, and C , the pH decreases relatively slowly.

Stage D : The intensity again decreases, but more quickly than in Stage B. This decrease is accompanied by a sudden decrease in the pH.

Stage E : As the pH approaches a value of 7.5, the intensity begins to increase again. After a short interval, though, it continues to decrease.
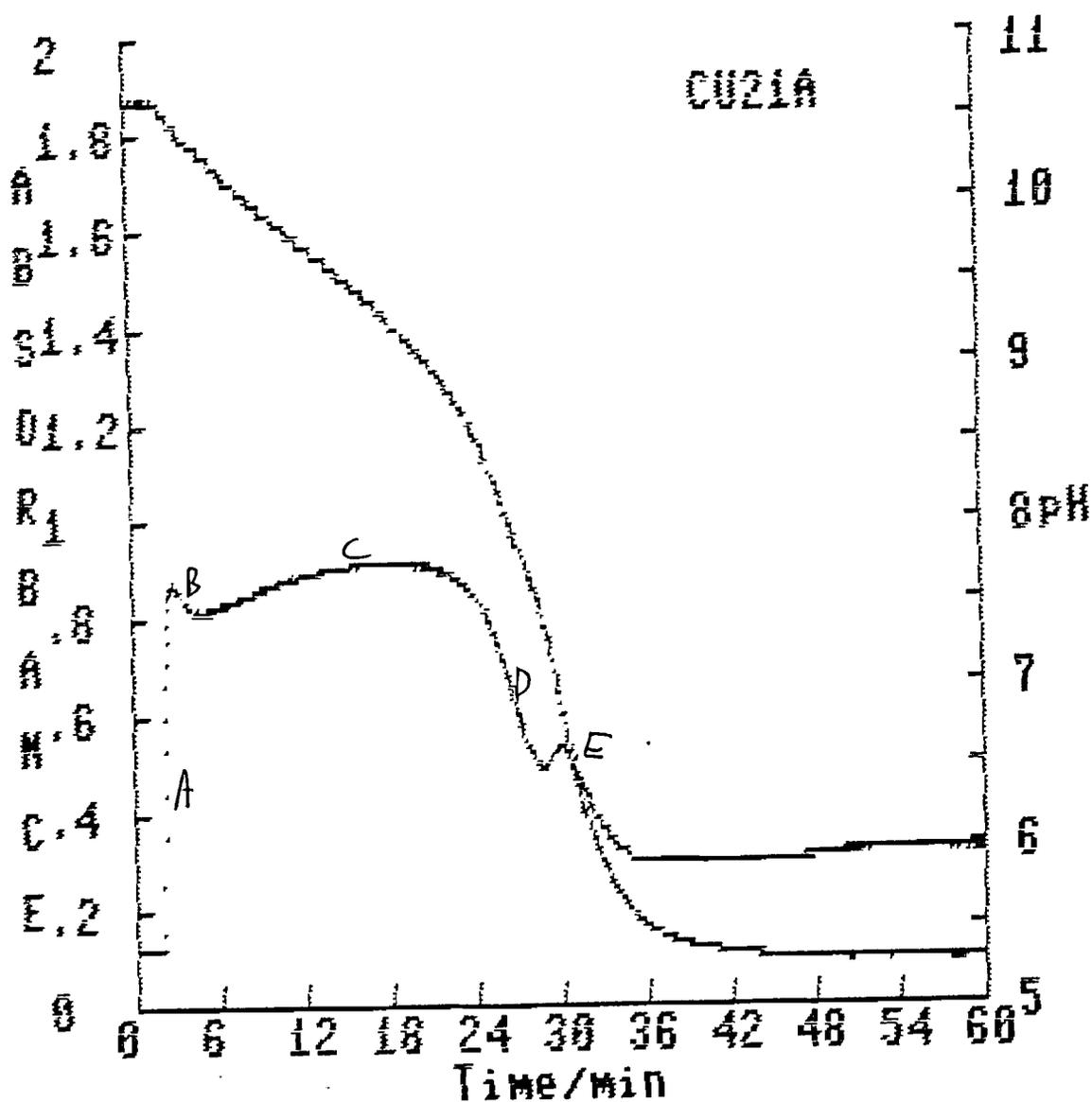
Compositions:

NaOH: 4×10^{-3} M, 50 mL
DMG: 2×10^{-3} M, 50 mL
$Cu(NO_3)_2$: 1×10^{-3} M, 21 mL
$K_2 S_2 O_8$: 1×10^{-2} M, 50 mL
$H_2 O$: 79 mL

Figure 6: pH and absorbance as function of time for run CU21A

II) Variation of concentration of copper(II)

Figure 7 shows the variation of absorption with time for six different runs : Cu17A, Cu18A, Cu20A, Cu21A, Cu22A, and Cu23A. These solutions all had the same initial concentrations of NaOH, DMG, and persulfate, but varied in the concentration of copper(II). The digits 17, 18, etc. refer to the number of mL of 0.001 M $Cu(NO_3)_2$ added when mixing the original solution.

The most obvious feature of these curves is the sensitivity of the reaction to the concentration of copper(II). In run Cu20A , the red flash lasts for over 50 minutes, in run Cu23A, it is essentially over in 12 minutes despite a mere 15% increase in copper(II) concentration.

With the possible exception of runs Cu17A and Cu18A, all these runs exhibit the same five stages enumerated above. Even in the case of the two runs mentioned, where only the first two stages are evident, it is possible that the other three stages would have been observed, if measurements had been taken for a longer time.

It is not at all obvious from these data what is happening, but certain features are clear. Acid is certainly being produced by the reaction. After an initial gradual decrease in pH, there is usually an abrupt downward jump.
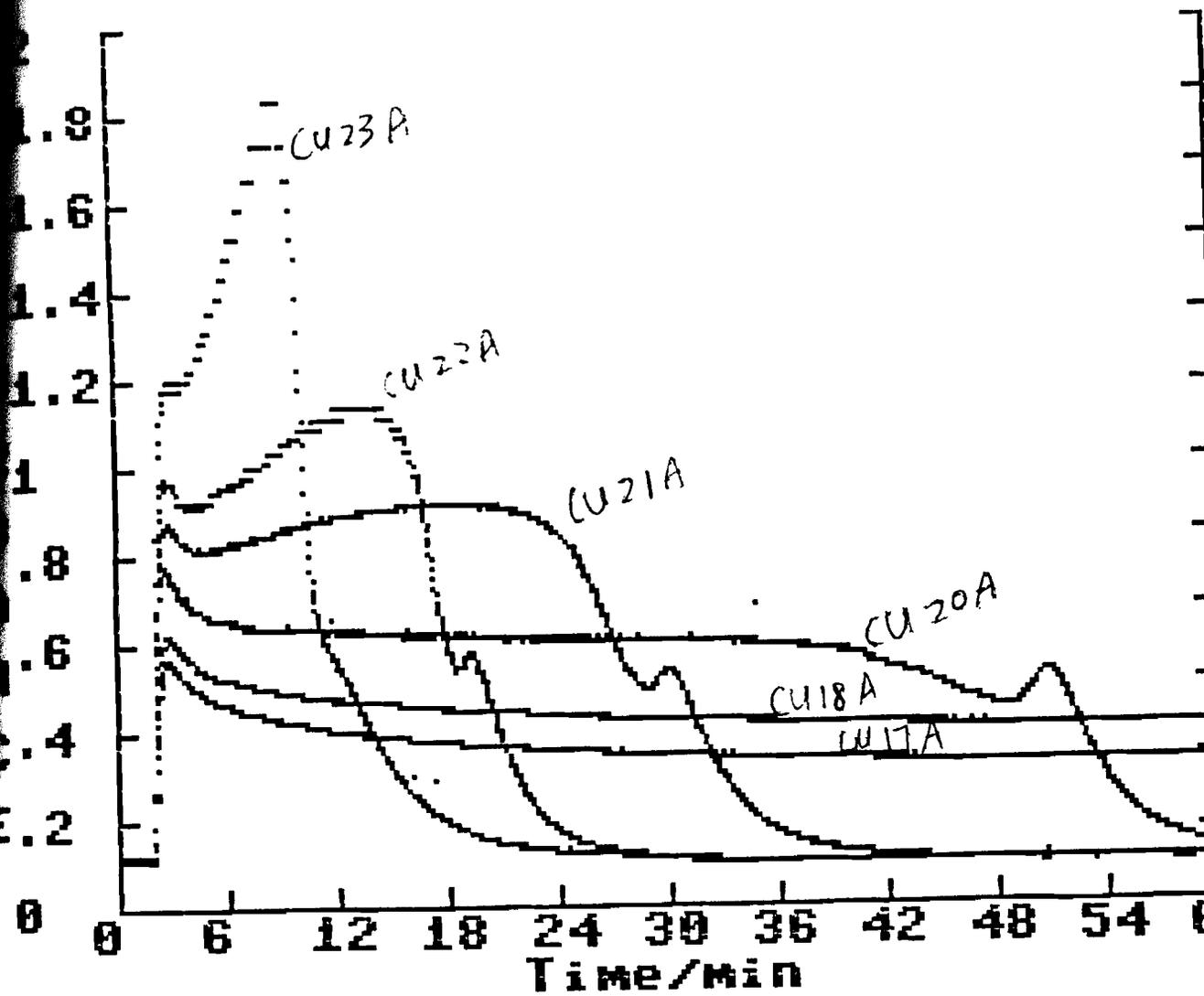
Figure 7: The variation of absoption for various
copper concentrations

This behavior is reminiscent of the end point in a
titration. Presumably the acid formed by the reaction
eventually neutralizes all the base present and the sudden
jump corresponds to a sudden excess of acid.

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At least, three different absorbing species appear to be produced in succession, each corresponding to a maximum in the absorbance vs. time curve. The third species (corresponding to the maximum of Stage E) could possibly be the conjugate acid of the previous species. The fact that this peak consistently occurs at a pH of about 7.5 suggests that the pKa of the acid might be around this value.

Finally, it should be observed that a higher concentration of copper ions not only increases the rate of the reaction, but also produces a higher concentration of colored intermediates. Indeed, the more intense the "flash" the shorter its duration.

In Figure 7, all six runs appear to have the same initial slope. That this is not really the case can be seen from Figure 8 in which the time scale has been expanded by a factor of 12. The results for the initial stages of runs Cu 17A, Cu21A, and Cu23A are shown in this figure (The other three runs are omitted for clarity). It can readily be seen that the initial slope increases with increasing copper(II) concentration.

In these six runs, the dimethylglyoxime, sodium hydroxide, and copper(II) solutions were first mixed. Water was added to bring the volume up to 200 mL, and stirring was commenced. The computer program to take measurements at 3 seconds intervals was then started, and measurements on the

above mixture were taken for two minutes. Only then was 50 mL of persulfate solution quickly added to initiate the reaction. Inevitably, the persulfate was not added exactly on time in each run , thus the first reading in which the absorbance shows an increase is not necessarily exactly three seconds after the addition.
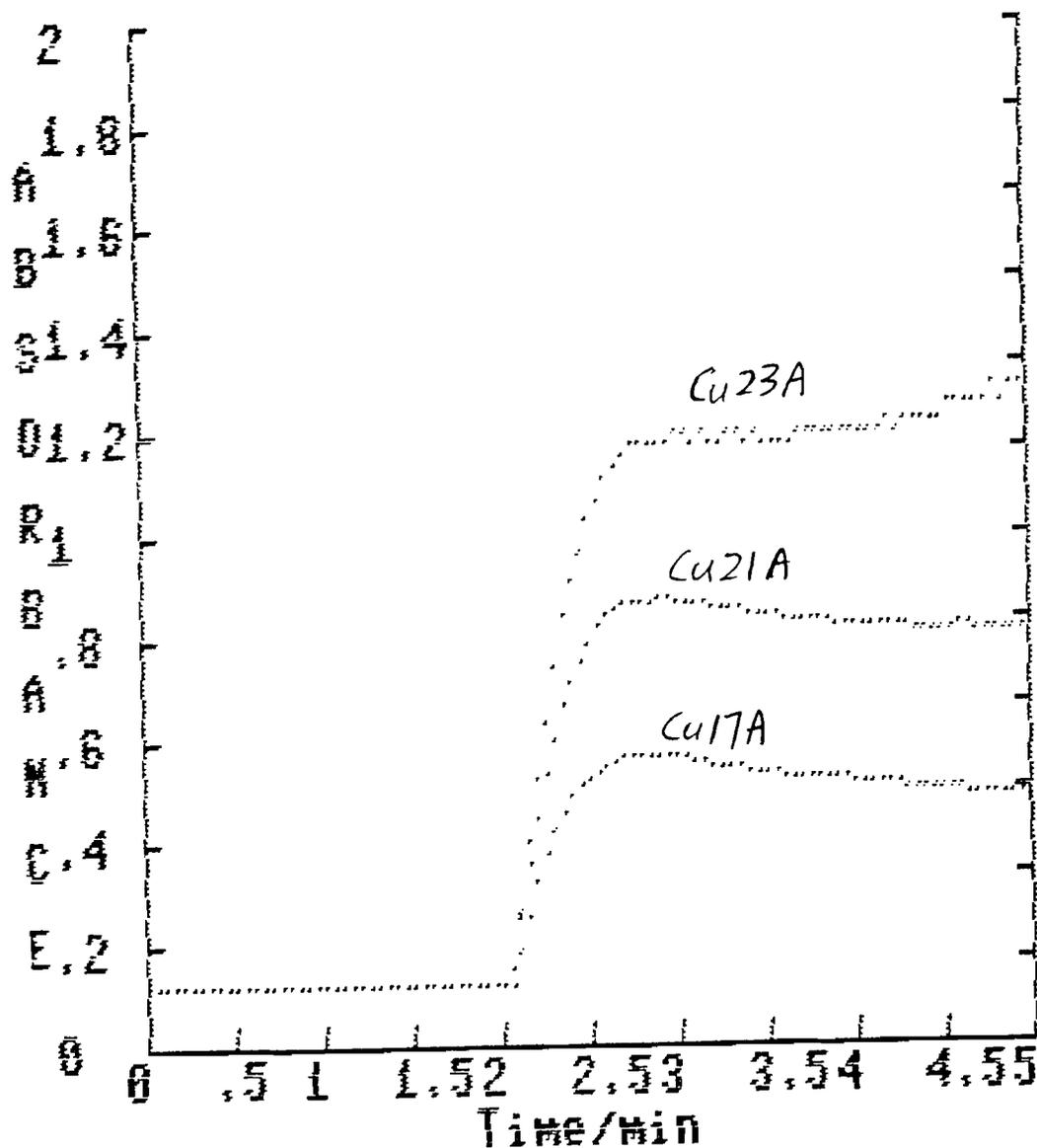
Figure 8: The initial stages of runs CU17A, CU18A, and CU23A.

Nevertheless the second reading is exactly three seconds after the first, so that the change in absorption between first and second readings is a correct measure of the rate of the reaction during that interval which occurs somewhere between zero and three seconds after mixing.

In what follows, the rate of increase in absorption between first and second readings has been regarded as the true initial rate. Though this is not actually the case, these rates are the best estimate we can make of the true initial rate. In Table VI the results for the six runs are given, here N_1 and N_2 , are the actual readings from the A/D converter. Since these values are proportional to the intensity, the term $\log(N_1/N_2)$ is proportional to the change in absorbance $\triangle A$, and hence to the rate of production of the absorbing species. If we now assume that the order of the reaction with respect to the concentration of copper(II) ion, C, is the integer n.

Then: rate = $k\ C^n$

   or $\triangle A = K\ C^n$, where K is another, different constant

Taking logs: $\log \triangle A = \log K + n \log C$

volume Cu2+ added/ml	N_1	N_2	$\log(N_1/N_2)$ $= \triangle A$	log vol Cu^{2+} added	$\log \triangle A$ (obs)	$\log \triangle A$ (calc)
17	173	148	0.068	1.23	−1.17	−1.17
18	173	147	0.071	1.26	−1.15	−1.11
20	193	147	0.118	1.30	−0.93	−1.01
21	188	149	0.101	1.32	−1.00	−0.97
22	193	148	0.115	1.34	−0.94	−0.92
23	146	108	0.131	1.36	−0.88	−0.88

Regression output:
constant	−3.87626
Std Err of Y Est	0.049006
R Squared	0.866873
No. of Observations	6
Degree of Freedom	4

X Coefficient(s)	2.20
Std Err of Coef.	0.43

Figure 9 shows a plot of log absorbance against log
volume of added Cu(II) solution using the data of Table VI.
Five of the six points lie very close to a straight line.
Including all six points in a linear regression analysis,
yields a slope of 2.20 with a standard deviation of 0.43.
Considering that these runs were intended as a survey rather
than designed to measure the initial rate, this is very
satisfactory agreement. There is now strong evidence to
suggest that the order of this reaction with respect to
copper is two.

log rate

log concentration

1	
2	

-1.21
-1.14
-1.07
-1.01
-0.937
-0.869
-0.8

1.20
1.30
1.40
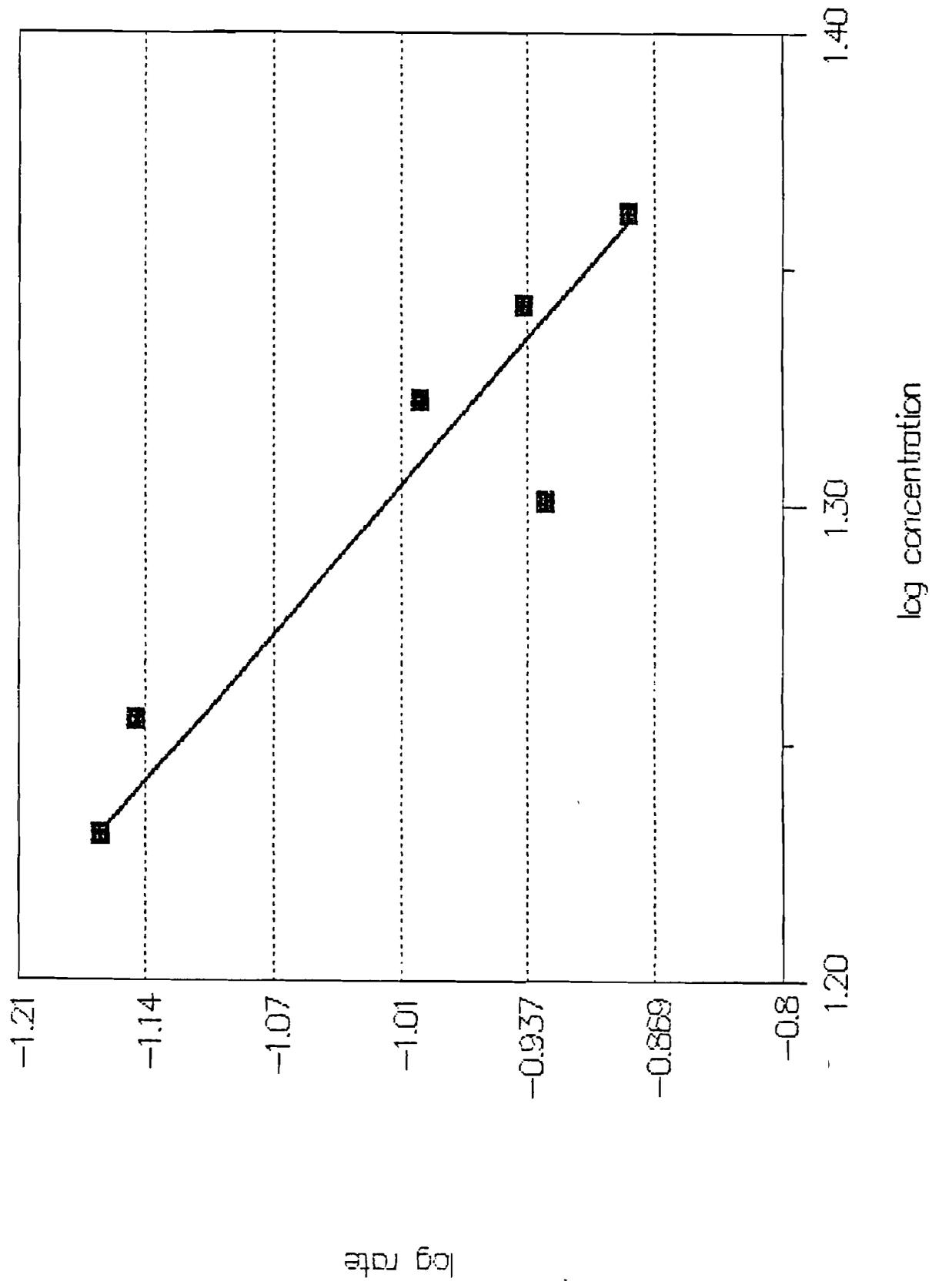
DEPENDENCE ON PERSULFATE CONCENTRATION

Some of the runs described above were designed to see whether varying the persulfate concentration has any effect on the behavior of the " red flash". Figure 10 shows the variation of absorption with time for eight different runs using 4×10^{-2} M persulfate, rather than the 1×10^{-2} M concentration used above. These eight runs are CU12.5, CU16, CU17, CU18, CU18.75, CU19, CU20, and CU25. These solutions all had the same initial concentrations of NaOH, DMG, and persulfate, but varied in the concentration of copper(II) used.

Since solutions were prepared using graduated cylinders, none of these can be guaranteed to better than about 10%. These runs were not as uniform in their behavior as the A series of solutions discussed above. For instance runs CU16 and CU17 exhibit some features in the reverse order to that expected from the behavior shown in the other runs. This is probably because not all these runs were done in sequence. Some were done before the A series and some after. In the process, the stock solutions from which these runs were prepared became exhausted and new solutions had to be prepared. Nevertheless, these runs exhibited the same overall behavior as the runs labeled with an A, that is, increasing the concentration of copper(II) gave a quicker and more intense color reaction. Also, at the lowest copper concentrations the behavior was less complex.
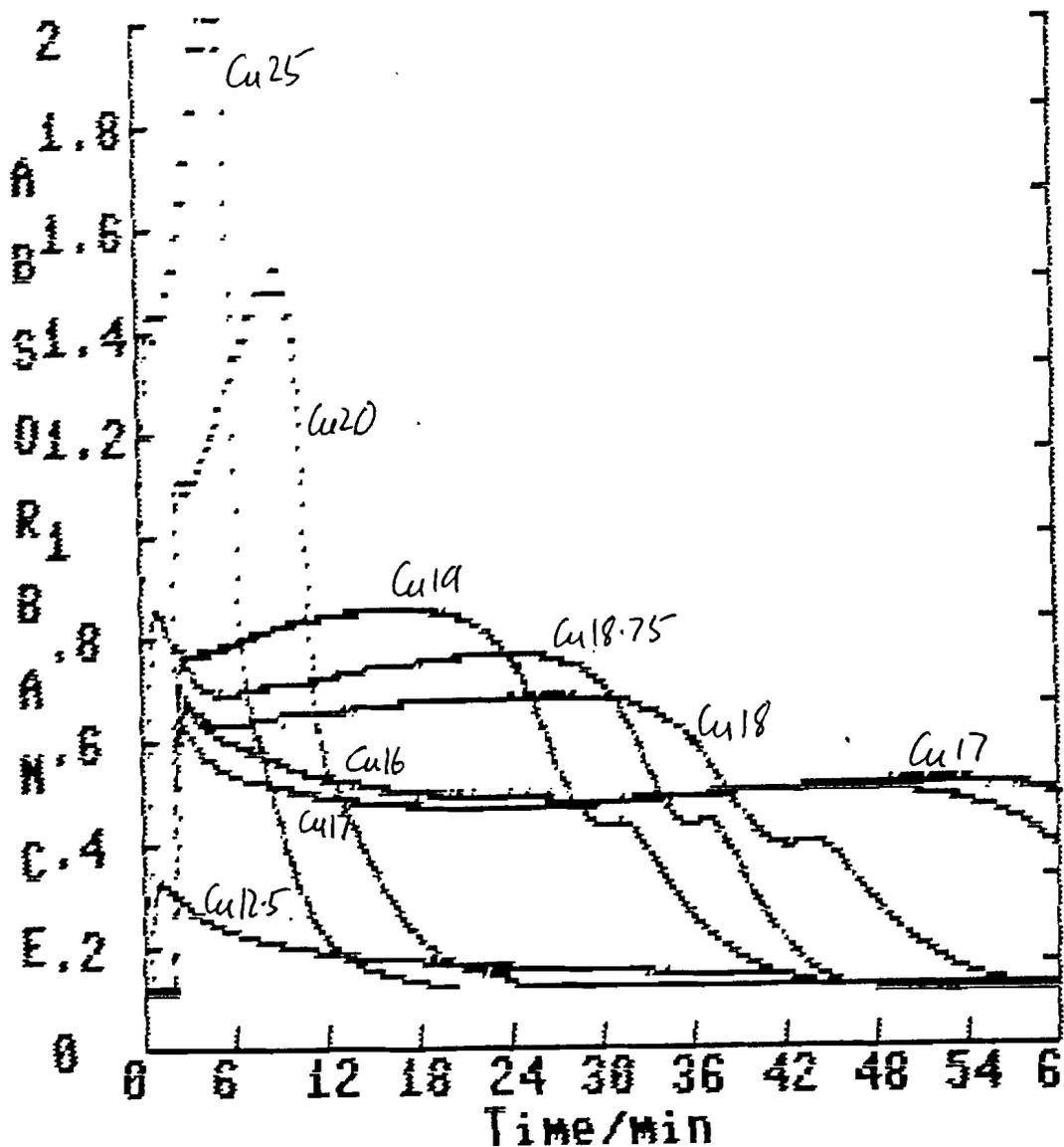
Figure 10 : The variation of absorption with time for various copper concentrations. The concentration of stock $K_2 S_2 O_8$ is 4×10^{-2} M

If we compare the runs in Fig 10 to those shown in Fig 7, we see that they obviously occur more quickly at the same copper concentration. In other words, the rate of the overall reaction increases with increasing persulfate concentration. However, only runs 17, 18, and 19 have the

-43-

same copper concentrations in the two series, not enough to be able to come to any firm conclusion on the order of the initial reaction with respect to persulfate.

Figure 11 shows the variation of absorption for six different runs with various compositions:CU22DM25NA50, CU22DM40NA50, CU22DM50NA50, CU22DM50NA40, CU22DM50NA25, and CU22DM25NA25. These solutions all had the same initial concentrations of copper and persulfate, but varied in the concentration of DMG, and NaOH. The figures 25, 40, 50 refer to the number of mL of stock solution added.

i) Variation with DMG

Only three runs of varying DMG concentration were investigated, not enough for quantitative conclusions to be made. Qualitatively, though, one can conclude that the lower the DMG concentration the quicker the reaction is concluded. The reaction time seems to be very DMG sensitive. Halving the volume of DMG added from 50 to 25 mL reduces the reaction time from about 18 minutes to less than a minute.

ii) Variation with NaOH

Three runs of varying in NaOH concentrations, CU22DM25NA50, CU22DM50NA25, and CU22DM50NA40 were investigated. Two of these runs appear to show that less NaOH results in a quicker reaction, but it is difficult to make conclusions about the third run which may have been prepared incorrectly. Unfortunately time did not permit a repeat of this run.

CU22DM50NA25   CU22DM50NA40   CU22DM50NA50
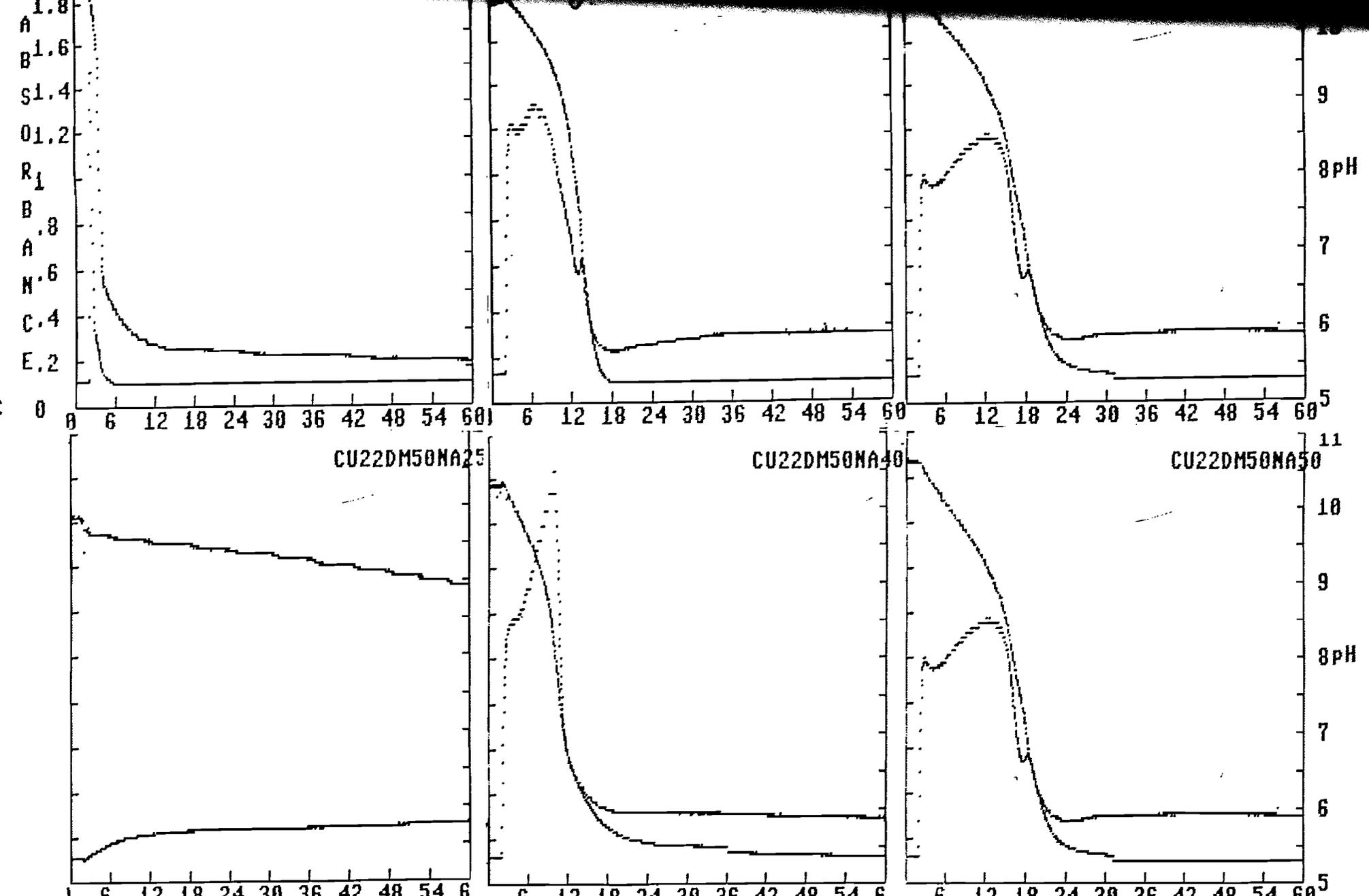
CONCLUSIONS:

The investigations described in this thesis have made some progress in elucidating the nature of the "red flash" reaction which occurs where basic solution containing dimethylglyoxime and copper(II) are mixed with persulfate. In particular, the following points have been established :

i) Dimethylglyoxime, hydroxide ion and persulfate are consumed by the "red flash" reaction, but copper(II) is not.

ii) Within the limits of experimental error, one sulfate ion is produced for each hydroxide ion consumed by the reaction.

iii) Butanedione monoxime is definitely a product of the reaction. There is some evidence that butanedione is also produced.

iv) The reaction occurs in several stages. At least three species absorbing strongly at 510 nm are involved.

v) There is strong evidence that the initial color reaction is second order with respect to copper(II) and hence must involve two copper atoms in the activated complex.

vi) The initial rate also depends on the persulfate ion concentration, but evidence was insufficient to establish the order with respect to this component.

SUGGESTIONS FOR FUTURE RESEARCH:

The red flash is clearly a very complex reaction and much work remains to be done before it can be said to be well understood. A serious deficiency in our knowledge of the reaction is the exact nature of the products. Although some of the hydrolysis products have been identified, none of the oxidation products are known. These are probably oxides of nitrogen or perhaps nitrogen itself. A serious effort should be made to look for these possible products. Unfortunately, low concentrations of these gases in water could be very difficult to detect and measure.

An aspect of the reaction which seems particularly promising for continued investigation is the rate of the initial color reaction. More work, using carefully prepared solutions, should be done to confirm the order of the reaction with respect to copper(II) and to establish its order with respect to persulfate.

More work should also be done to follow the variation of absorbance with time for different initial compositions. In particular, an attempt should be made to keep the pH constant during this reaction. Since buffer mixtures appear to interfere with the reaction, the pH should be kept constant by other means such as the addition of base under computer control. Wavelengths other than 510 nm used in this work should also be used.

An aspect not yet investigated is the possibility of

side reactions. Is there any appreciable reaction when persulfate is added to an aqueous solution of Cu(II)? Likewise, if persulfate and dimethylglyoxime are mixed, is there any change, say, in the pH? These are questions which could easily be answered experimentally.

APPENDICES

APPENDIX A

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DMG-1

Absorbance

5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
.50
.00

150   200   250   300   350   4

Wavelength/nm
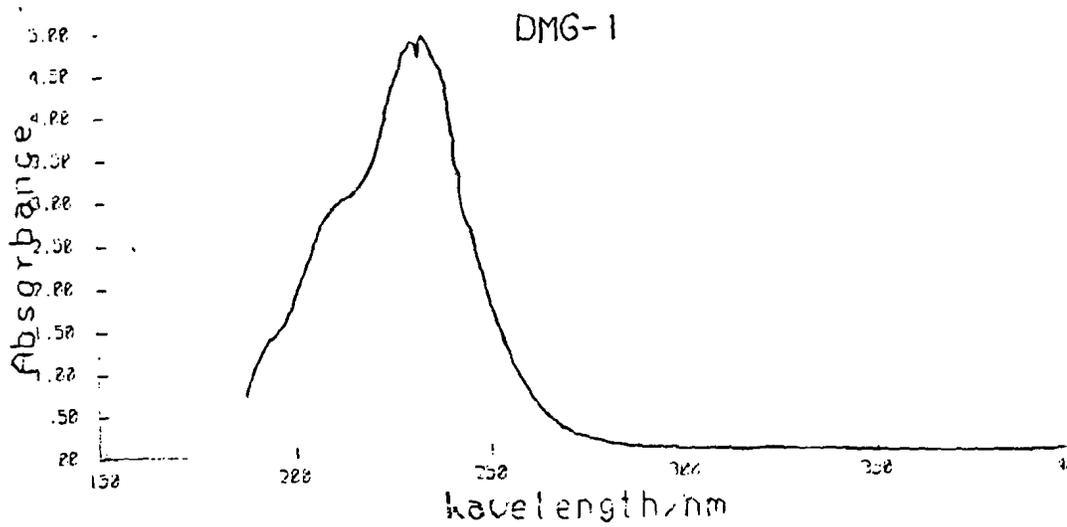
RUN 1

DMG : 2X10⁻⁵ M, 10 mL
Distilled H₂O : 30 mL
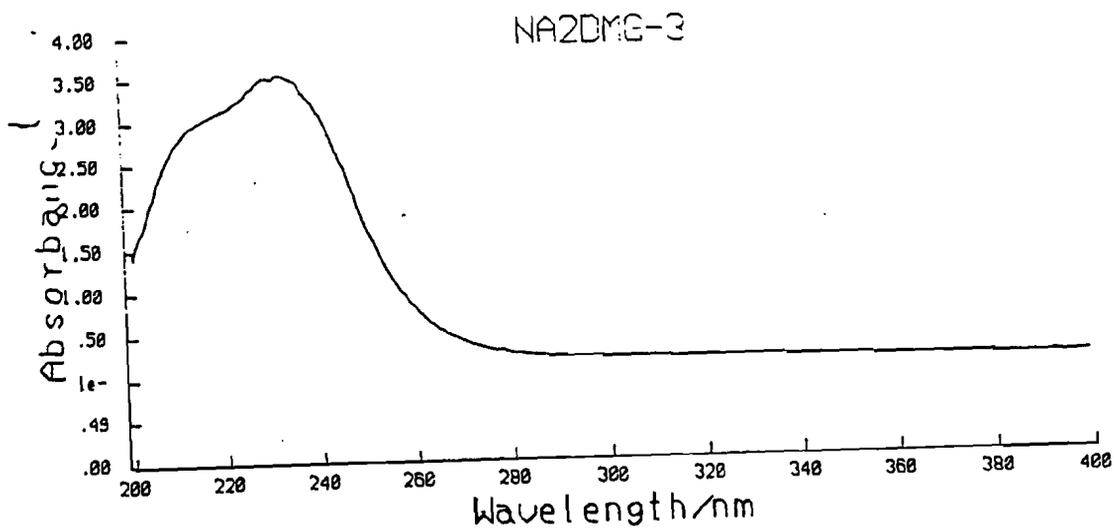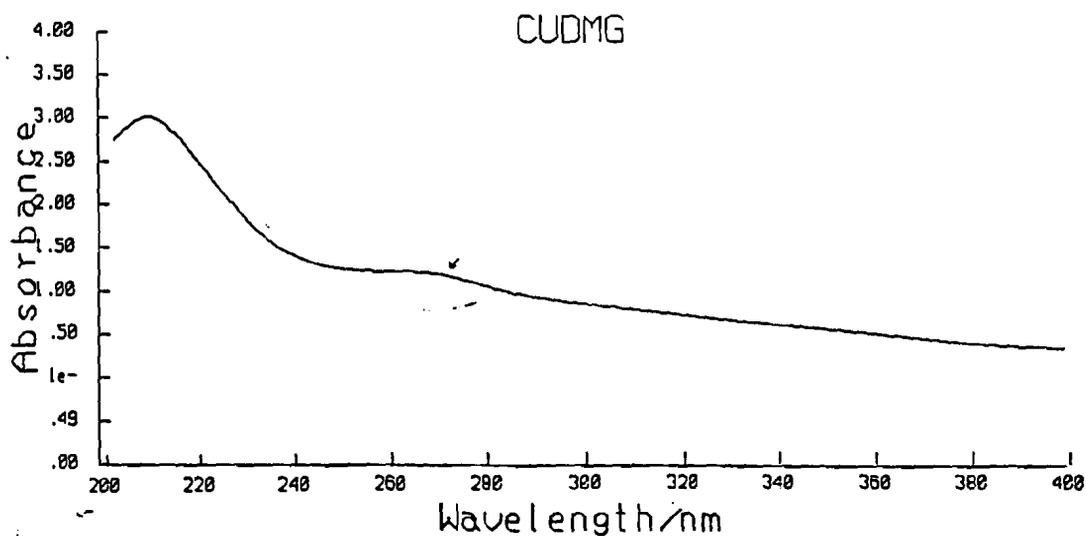
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NA2DMG-3

RUN 2

NaOH : 4X10⁻⁵ M, 10 mL
DMG : 2X10⁻⁵ M, 10 mL
Dis. H₂O : 30 mL

CUDMG

RUN 3

NaOH : 4X10⁻⁵ M, 10 mL
DMG : 2X10⁻⁵ M, 10 mL
Cu(NO₃)₂ : 1X10⁻⁵ M, 10 mL
Dis. H₂O : 20 mL

MONOXIME
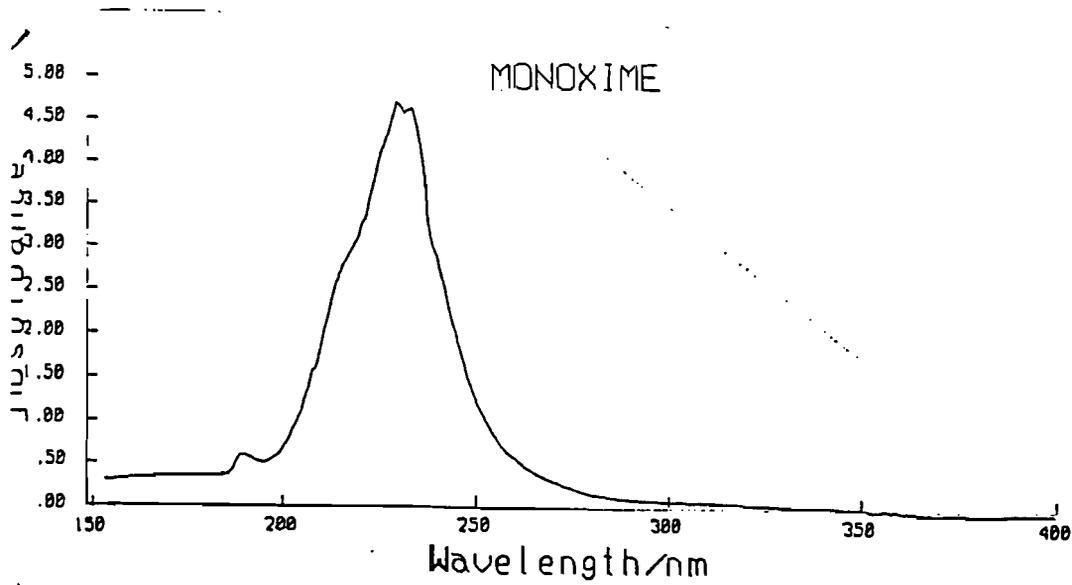
RUN 4

2,3-Butanedione monoxime: 2x10⁻⁵ M
                                    10 mL
Dis. H₂O : 30 mL
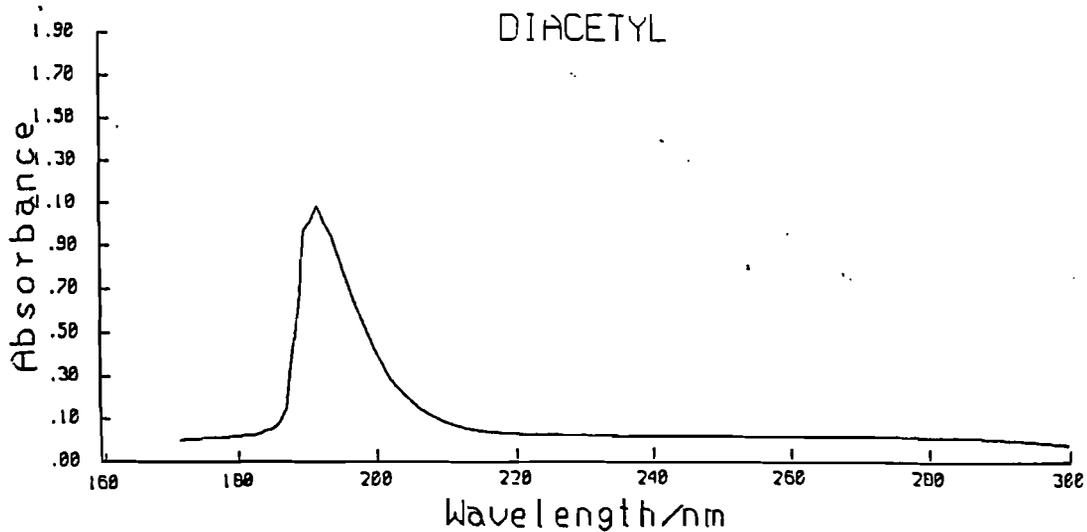
DIACETYL

RUN 5

Diacetyl : 2X10⁻⁵ M, 10 mL
Dis. H₂O : 30 mL

RUN 6

NaOH : 4X10⁻⁵ M, 10 mL

2,3-Butanedione monoxime : 2X10⁻³ M,
10 mL

Dis. H₂O : 30 mL

RUN 7

NaOH: 4X10⁻⁵ M, 10 mL

2,3-Butanedion monoxime : 2X10⁻³ M,
10 mL

Cu(NO₃)₂: 1X10⁻³ M, 10 mL

Dis. H₂O: 30 mL

DILUTED NAOH-MONOXIME

RUN 8

NaOH : 4X10⁻ M, 10 mL
2,3-Butanedione monoxime : 2X10⁻ M
10 mL

Dis. H₂O : 60 mL

DILUTED NA MONO-CU

RUN 9

NaOH: 4X10⁻ M, 10 mL
2,3-Butanedion monoxime: 2X10⁻ M
10 mL
Cu(NO₃)₂: 1X10⁻ M, 10 mL
Dis H₂O: 60 mL

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NA-DMG-CU-S2O8 1MIN

(Absorbance vs Wavelength/nm plot)

RUN 10

NaOH : 4X10⁻ M, 10 mL
 DMG : 2X10⁻ M, 10 mL
Cu(NO₃) : 1X10 M, 10 mL
K₂S₂O₈ : 1X10⁻ M, 10 mL

NA-DMG-CU-S2O8 10MIN

(Absorbance vs Wavelength/nm plot)

RUN 11

NaOH : 4X10⁻ M, 10 mL
 DMG : 2X10 M, 10 mL
Cu(NO₃) : 1X10 M, 10 mL
K₂S₂O₈ : 1X10⁻ M, 10 mL

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APPENDIX B

CONDITIONS:

Varian 2010 pump/2210 system
UV detector, model 2050
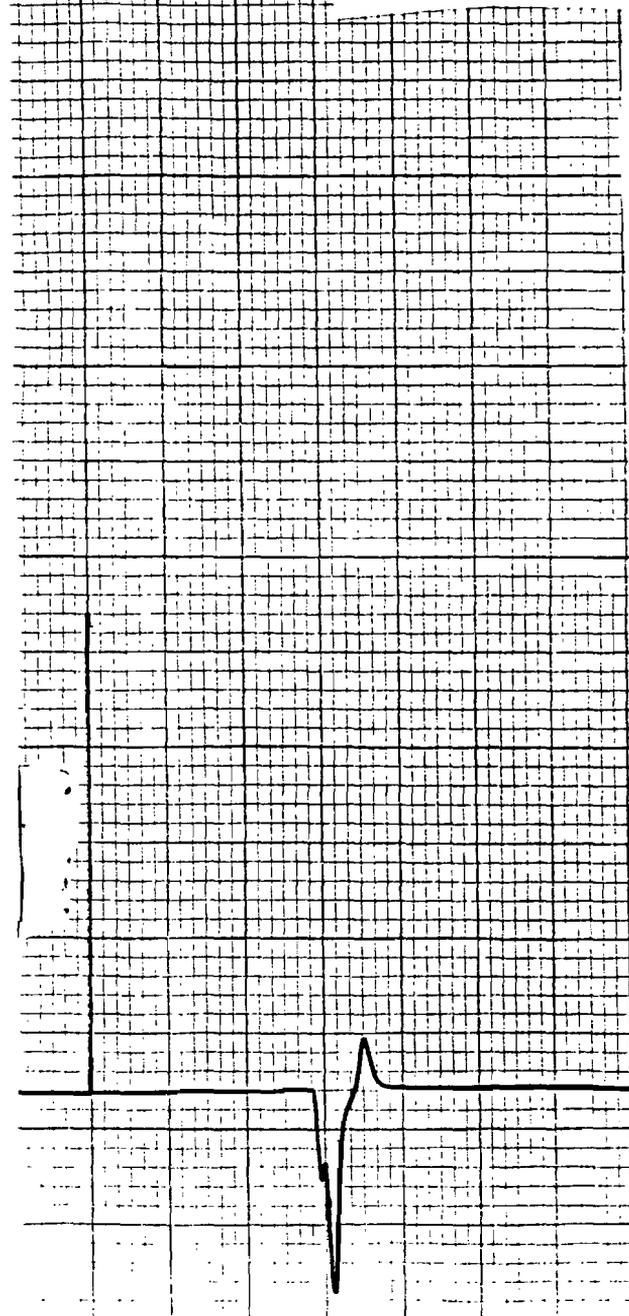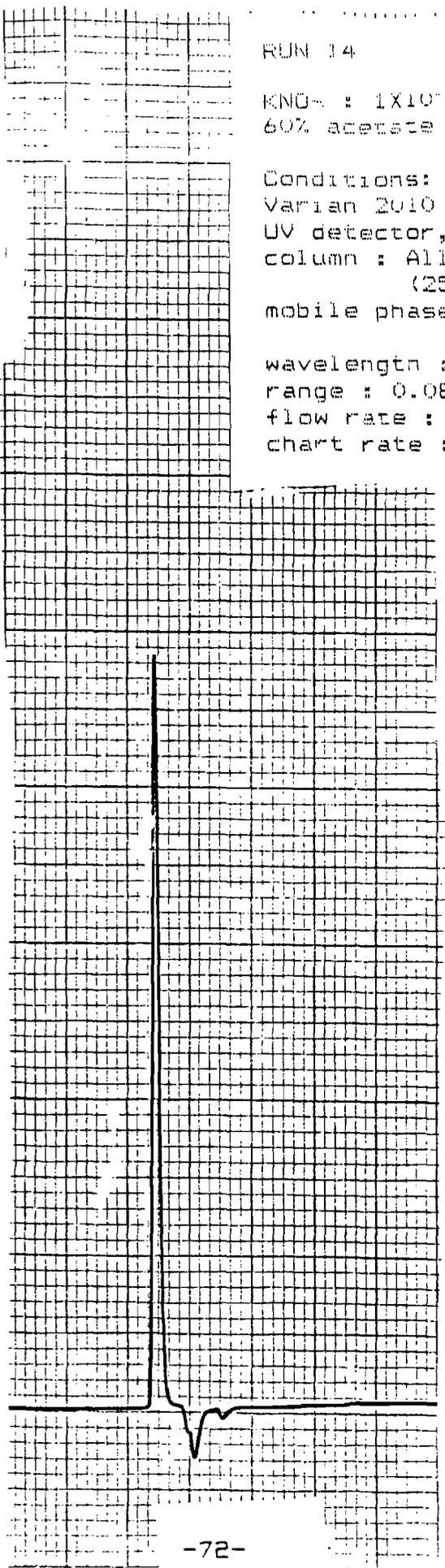column : Alltech C-18 cartridge
         (25 cm X 4.6 mm)
mobile phase : 60% of acetate buffer
                 and 40% methanol
wavelength : 215 nm
flow rate : 1.0 mL/min
chart rate : 2.0 cm/min

RUN 2

Cu(NO₃)₂: 1X10⁻⁵ M, 10 mL
60% acetate buffer/40% methanol, 40 mL
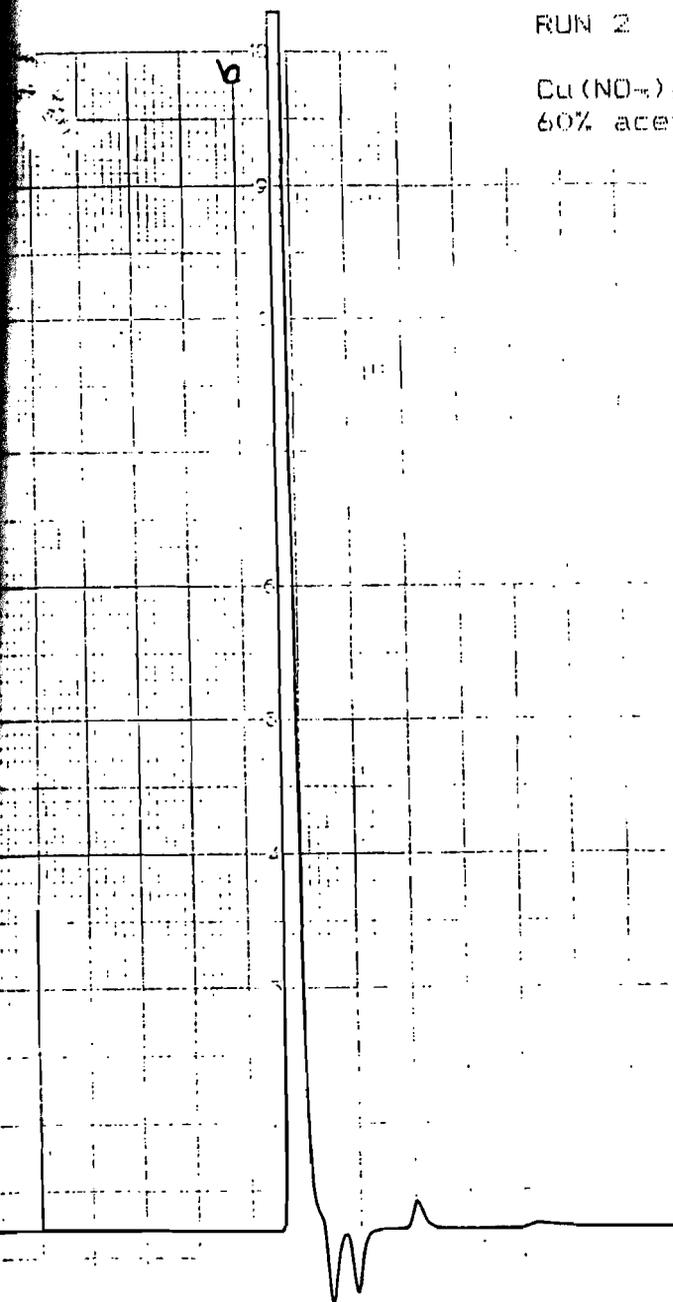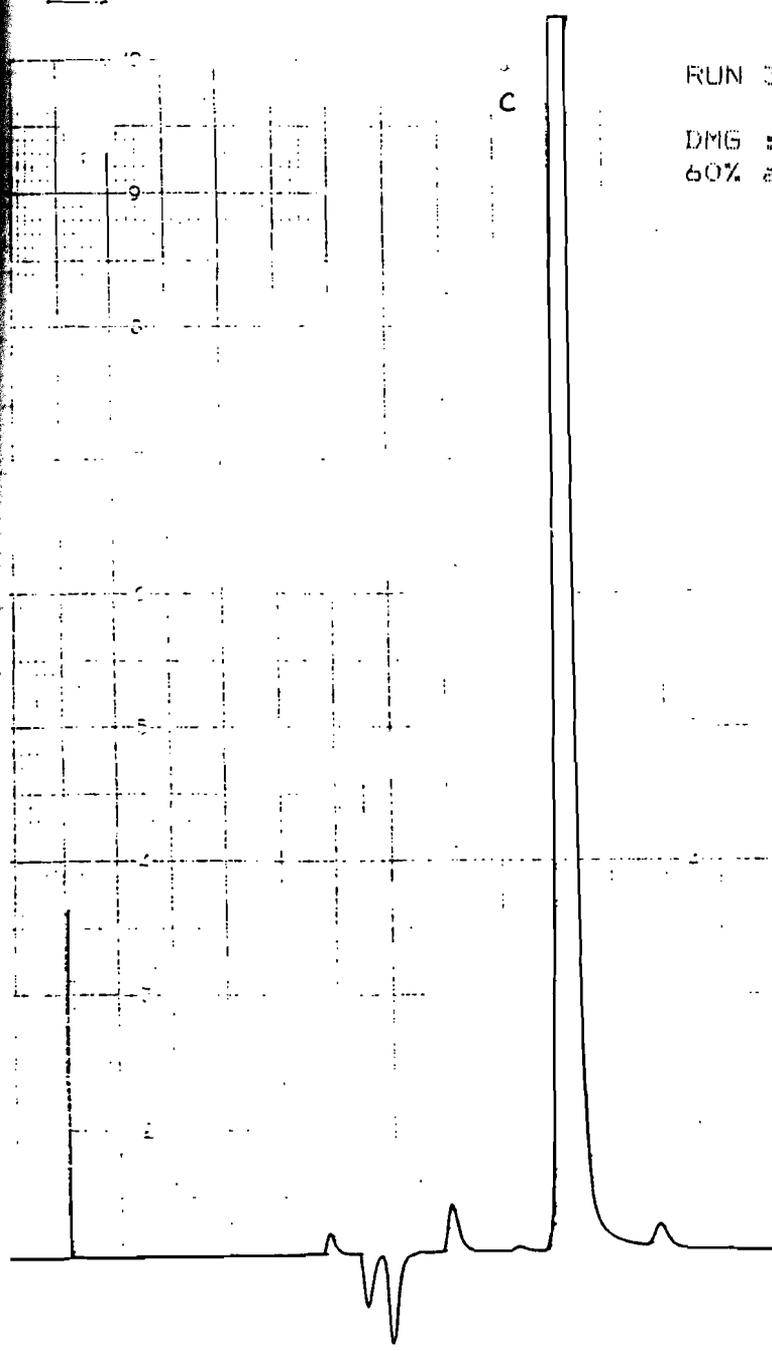
RUN 3

DMG : 2X10⁻⁵ M, 10 mL
60% acetate buffer/40% methanol, 4
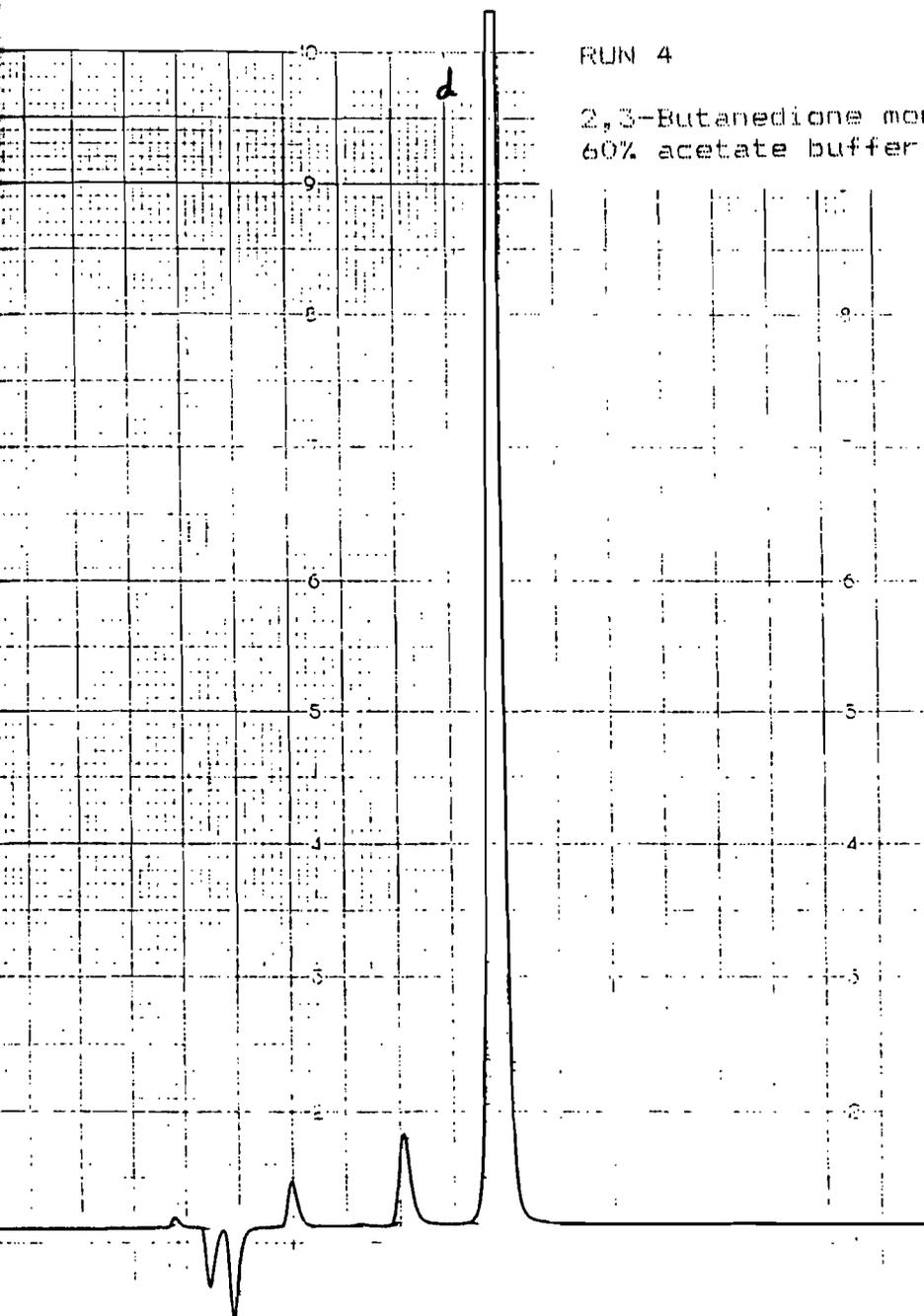
RUN 4

2,3-Butanedione monoxime: 2×10^{-3} M, 10
60% acetate buffer/40% methanol, 40 mL.

RUN 5

Diacetyl : 2X10^{-5} M, 10 mL
60% acetate buffer/40% methanol, 40 mL
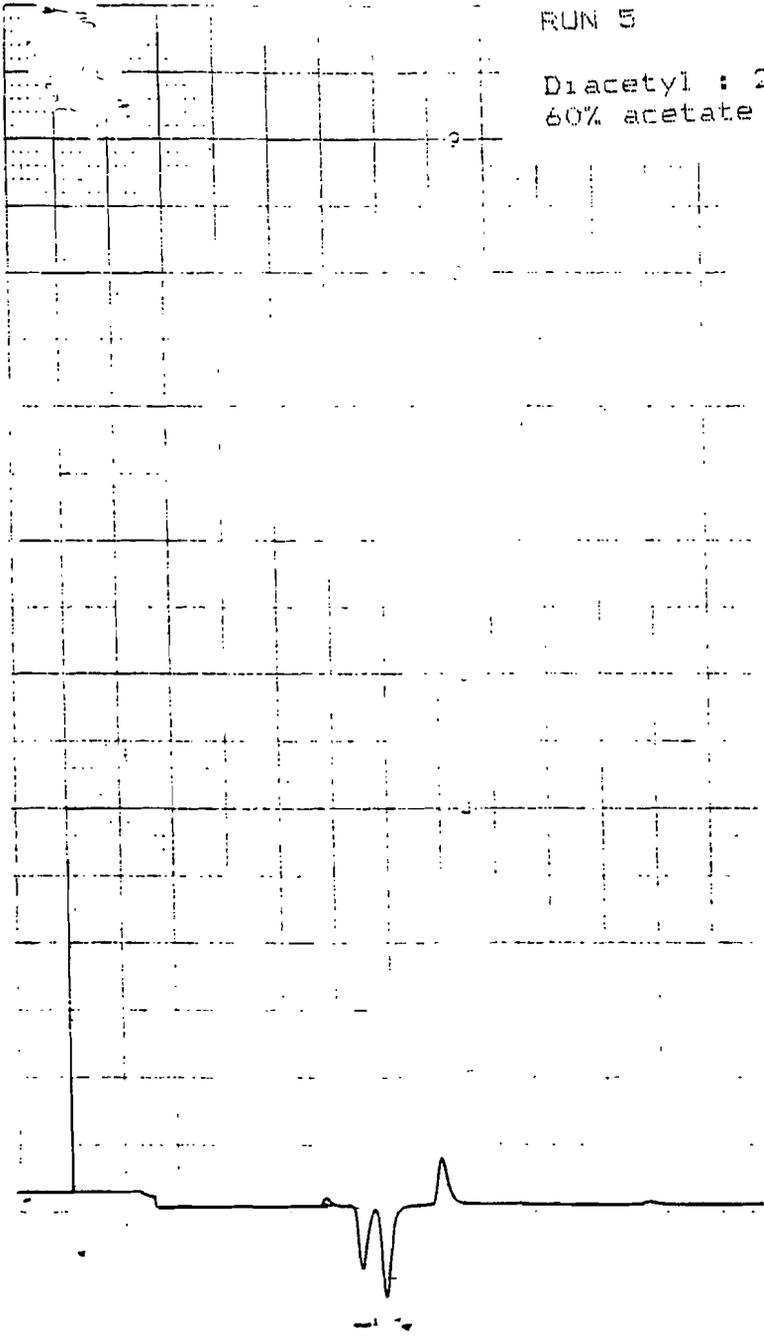
RUN 6

NaOH: 4X10⁻⁵ M, 10 mL
DMG: 2X10⁻⁴ M, 10 mL
Cu(NO₃)₂: 1X10⁻⁴ M, 10 mL
K₂S₂O₈: 1X10⁻⁵ M, 10 mL
60% acetate buffer/40% methanol, 10 mL
10 min after mixing

Chart Paper   Fisher Scientific Co. Pittsburgh, PA 15219   Catalog No 13-639-40
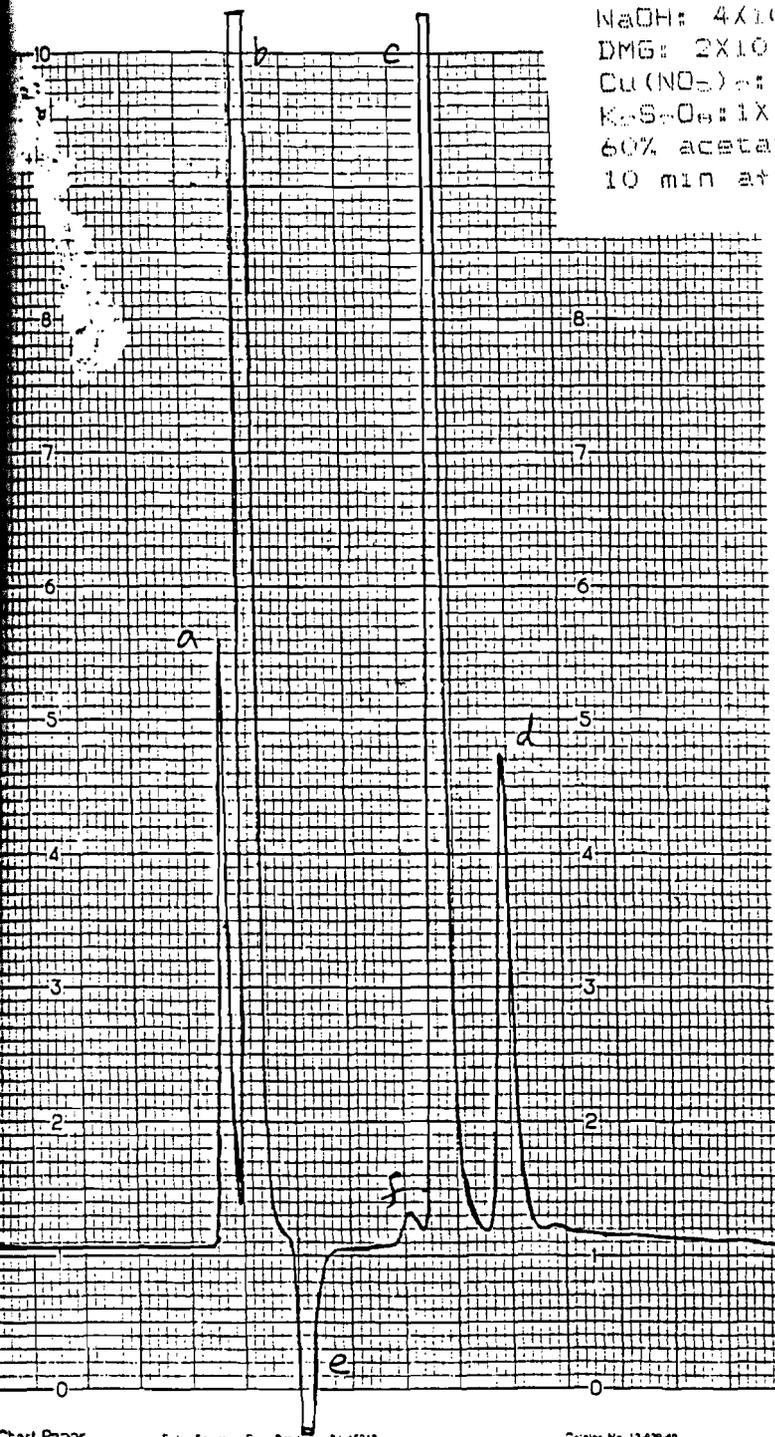
RUN 7

NaOH: 4×10^{-2} M, 10 mL
DMG: 2×10^{-2} M, 10 mL
Cu(NO$_3$)$_2$: 1×10^{-3} M, 10 mL
K$_2$S$_2$O$_8$: 1×10^{-2} M, 10 mL
60% acetate buffer/40% methanol, 10 mL
20 min after mixing
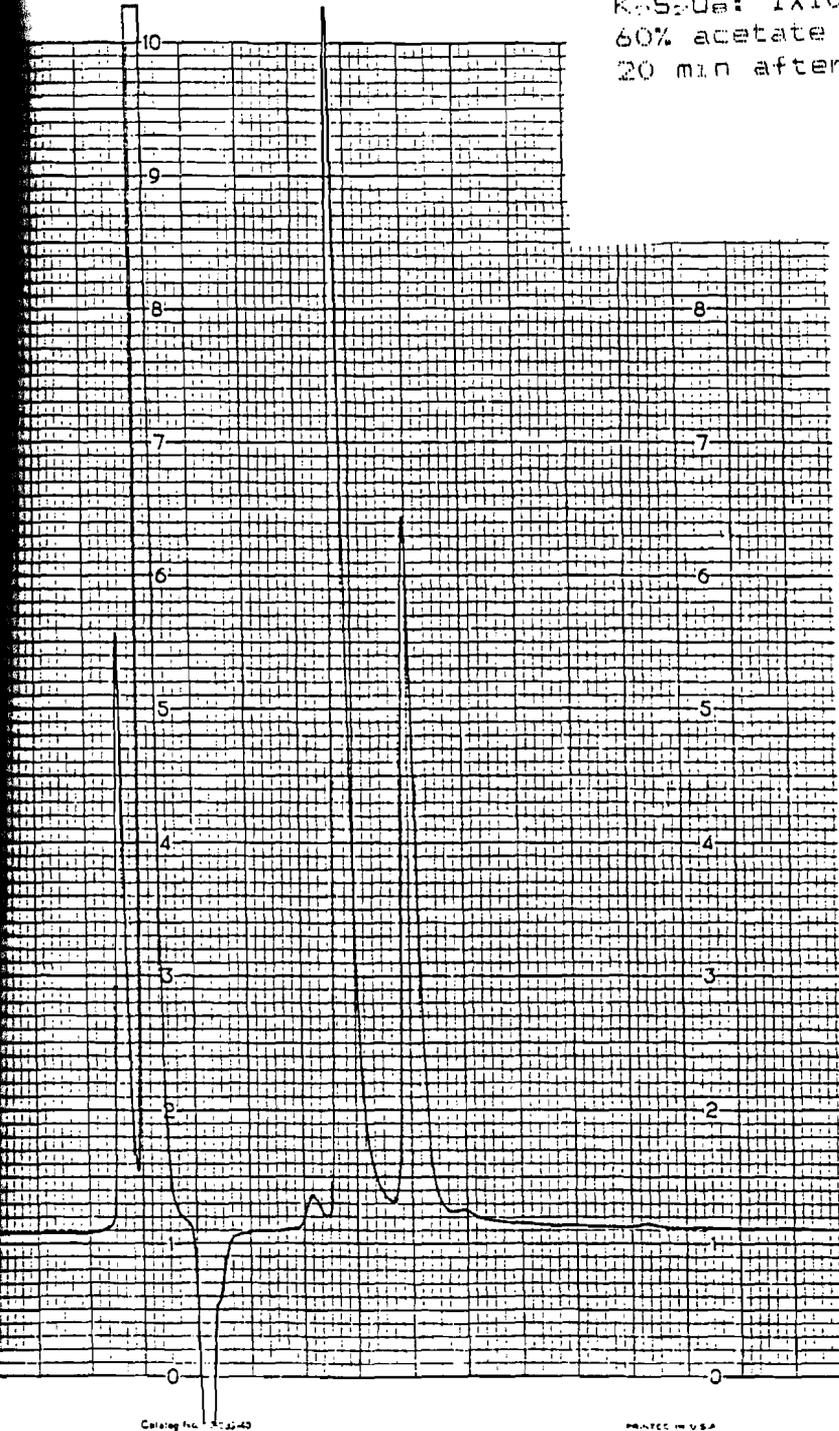
Run 8

NaOH: 4X10⁻⁵ M, 10 mL
DMG: 2X10⁻⁵ M, 10 mL
Cu(NO₃)₂: 1X10⁻⁵ M, 10 mL
K₂S₂O₈:1X10⁻⁴ M, 10 mL
60% acetate buffer/40% methanol, 10 m
30 min after mixing
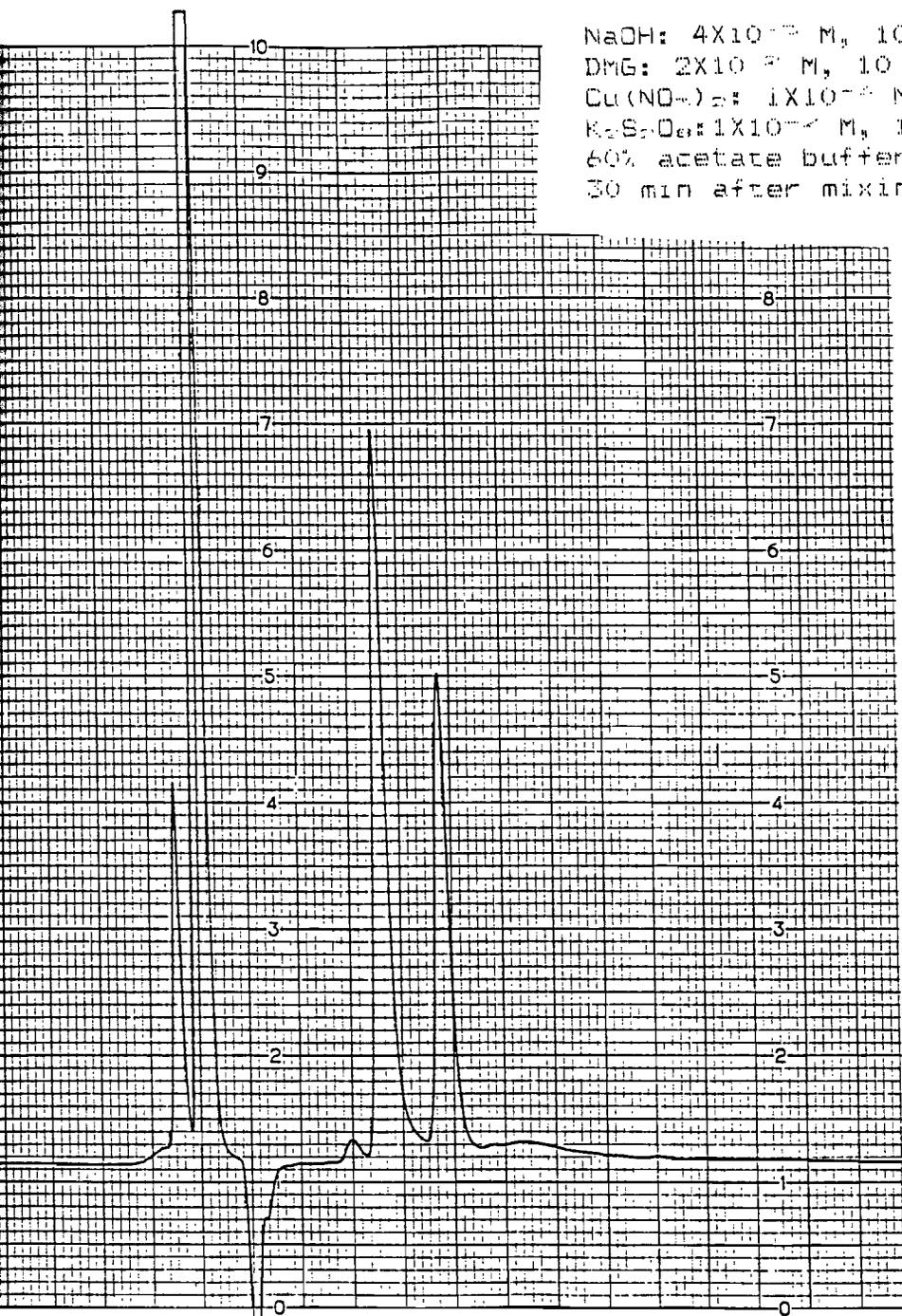
FISHERbrand Recordall Chart Paper

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RUN 9

NaOH: 4×10^{-3} M, 10 mL
DMG: 2×10^{-2} M, 10 mL
Cu(NO$_3$)$_2$: 1×10^{-2} M, 10 mL
K$_2$S$_2$O$_8$: 1×10^{-2} M, 10 mL
60% acetate buffer/40% methanol, 10 mL
40 min after mixing

RUN 10

NaOH: 4×10^{-3} M, 10 mL
DMG: 2×10^{-2} M, 10 mL
Cu(NO$_3$)$_2$: 1×10^{-3} M, 10 mL
K-S-O$_8$: 1×10^{-2} M, 10 mL
60% acetate buffer/40% methanol, 10 mL
50 min after mixing

RUN 11

NaOH: 4X10⁻⁻ M, 10 mL
DMG: 2X10⁻⁻ M, 10 mL
Cu(NO₃)₂: 1X10⁻⁻ M, 10 mL
K₂S₂O₈: 1X10⁻⁻ M, 10 mL
60% acetate buffer/40% methanol, 10
60 min after mixing

RUN 12

NaOH: 4X10⁻⁻ M, 10 mL
DMG: 2X10⁻⁻ M, 10 mL
Cu(NO₃)₂: 1X10⁻⁻ M, 10 mL
K₂S₂O₈: 1X10⁻ M, 10 mL
60% acetate buffer/40% methanol, 10 mL
30 days after mixing
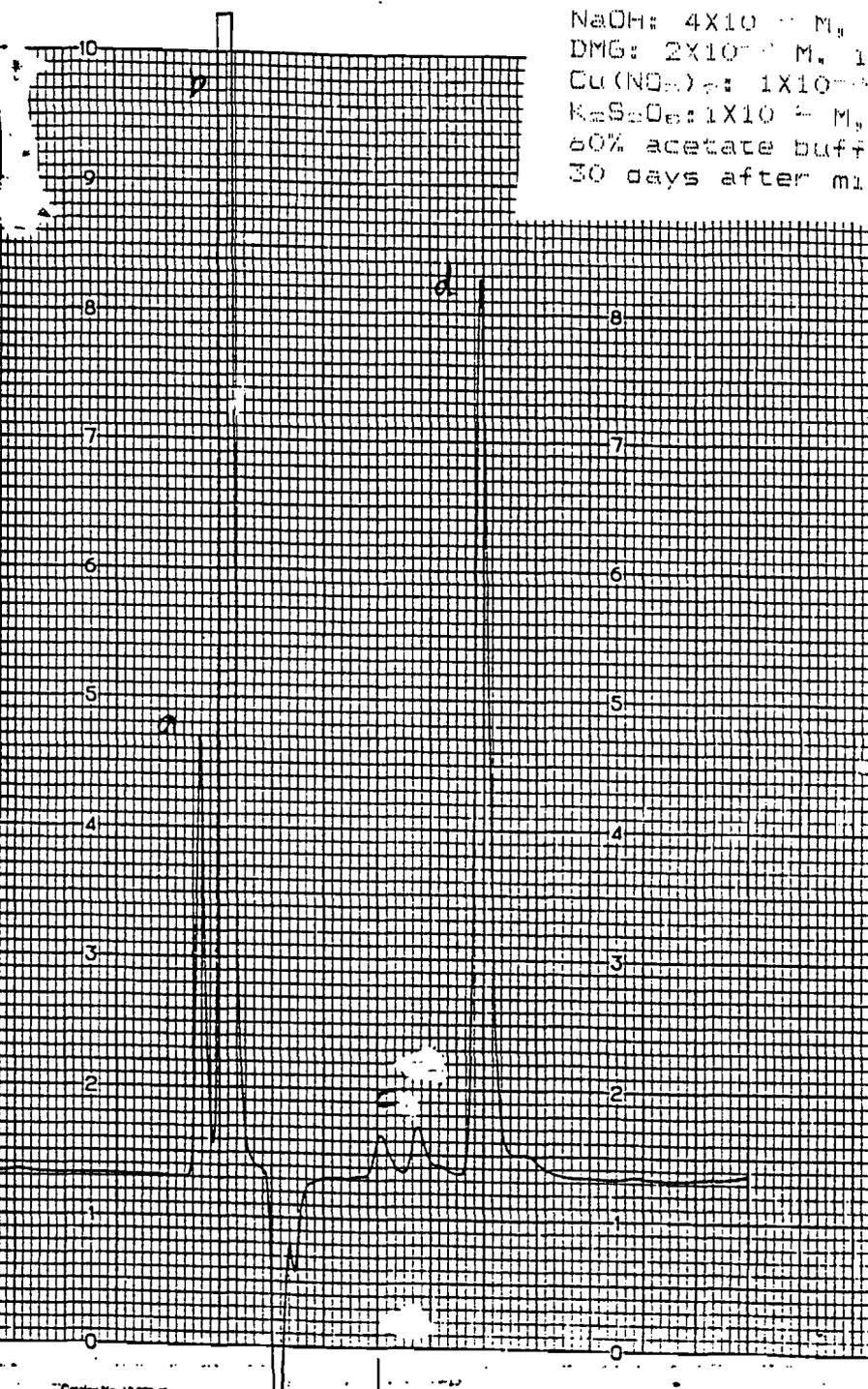
RUN 13

CuSO4: 1X10⁻³ M, 10 mL
60% acetate buffer/40% methanol, 30 m

Conditions:
Varian 2010 pump/2210 system
UV detector, model 2050
column : Alltech C-18 cartridge
         (25 cm X 4.6 mm)
mobile phase : 60% of acetate buffer
                and 40% methanol
wavelength : 235 nm
range : 0.08
flow rate : 1.0 mL/min
chart rate : 1.0 cm/min

RUN 14

KNO₃ : 1X10⁻⁴ M, 10 mL
60% acetate buffer/40% methanol, 30 mL

Conditions:
Varian 2010 pump/2210 system
UV detector, model 2050
column : Alltech C-18 cartridge
         (25 cm X 4.6 mm)
mobile phase : 60% of acetate buffer
               and 40% methanol
wavelength : 235 nm
range : 0.08
flow rate : 1.0 mL/min
chart rate : 1.0 cm/min

RUN 15

K₂SO₄ : 1X10   M, 10 mL
60% acetate buffer/40% methanol, 30 mL

Conditions:
Varian 2010 pump/2210 system
UV detector, model 2050
column : Alltech C-18 cartridge
          (25 cm X 4.6 mm)
mobile phase : 60% of acetate buffer
                and 40% methanol
wavelength : 235 nm
range : 0.08
flow rate : 1.0 mL/min
chart rate : 1.0 cm/min

APPENDIX C

–
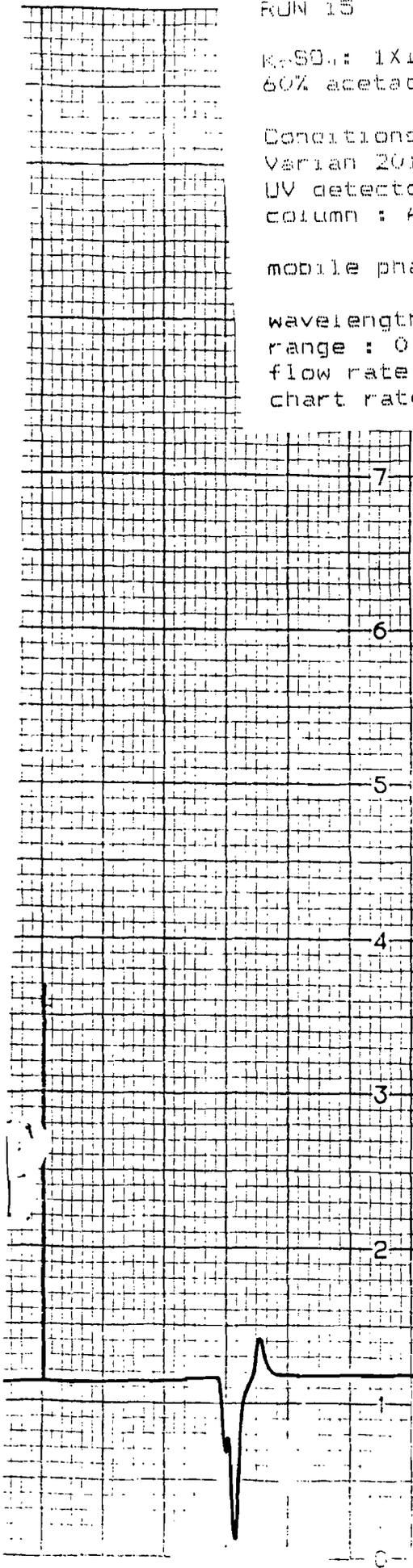
$_2S_2O_8$: $1X10^{-2}$ M, 10 mL
0% acetate buffer/40% methanol, 40 mL
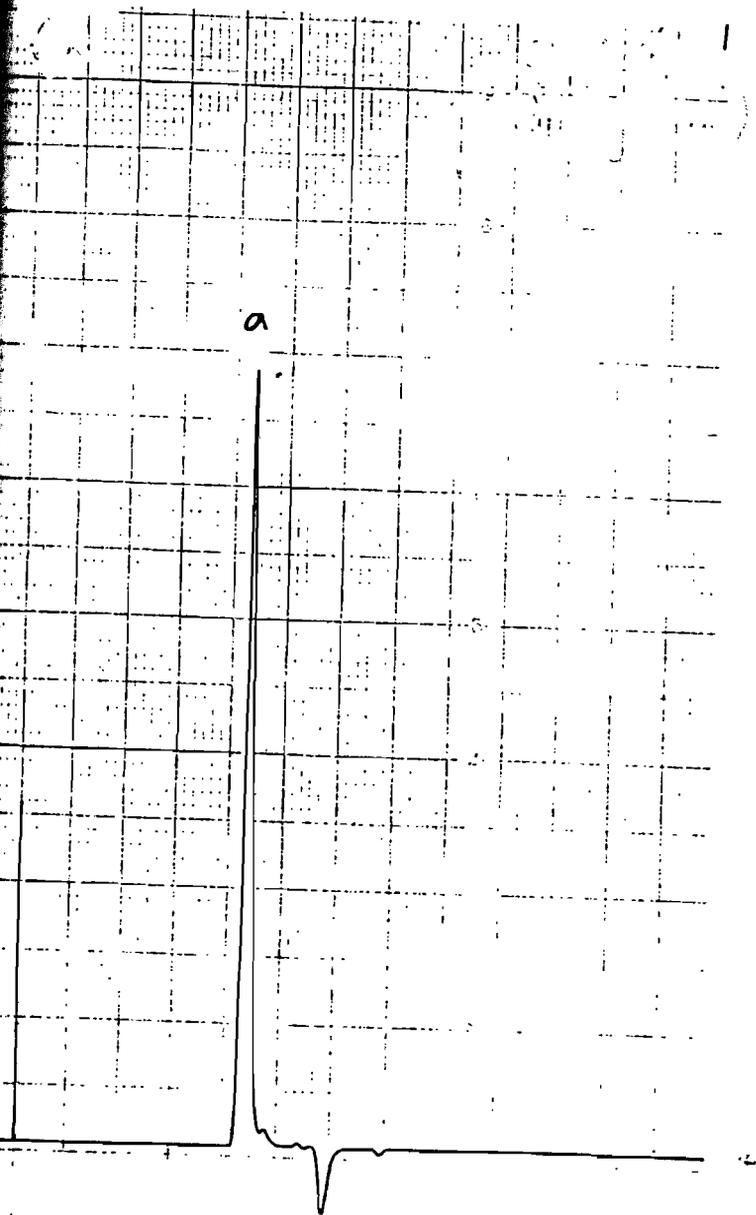
CU 12.5
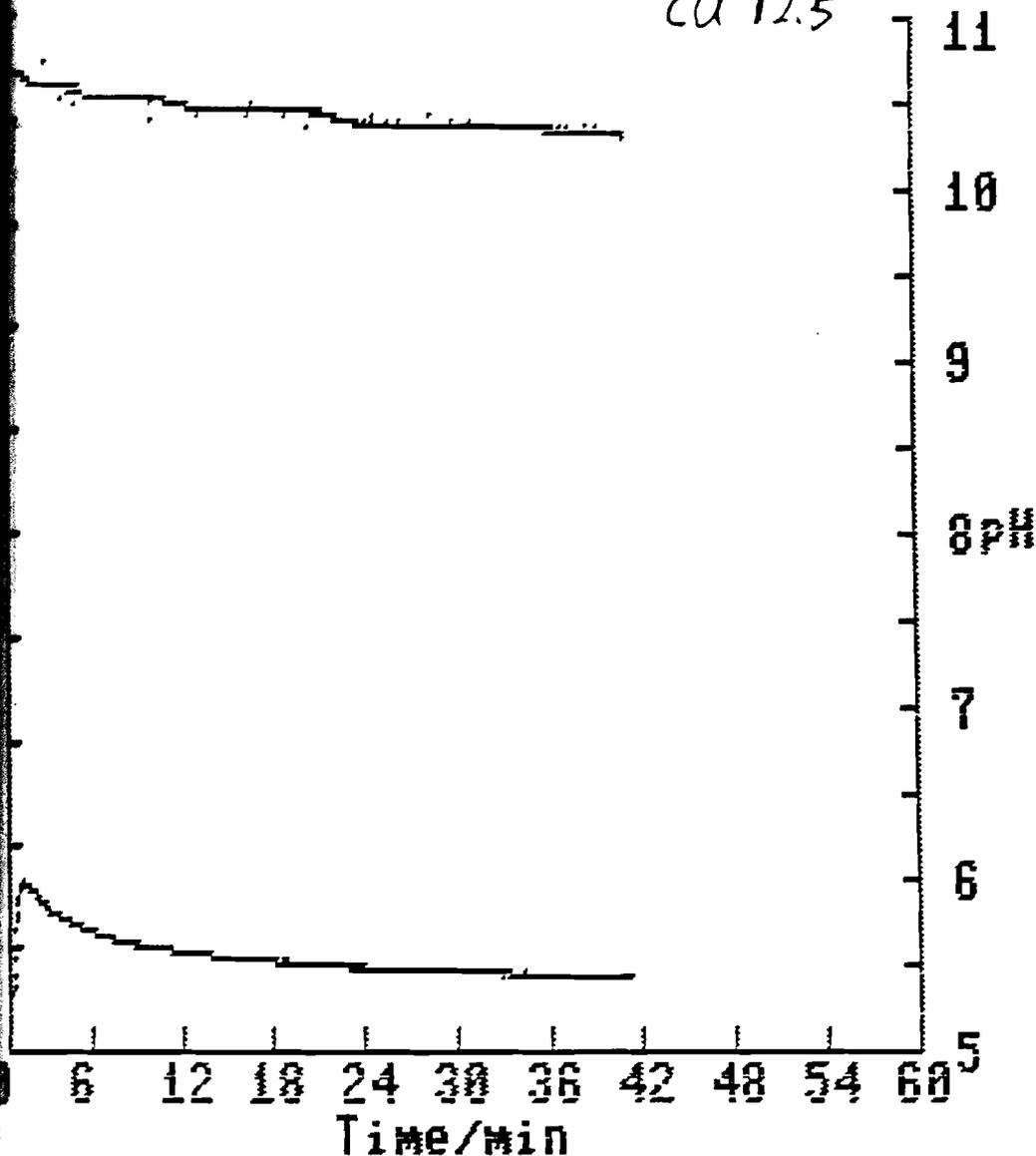
CU12.5

NaOH: 4×10^{-2} M,   50 mL
DMG: 2×10^{-2} M,   50 mL
Cu(NO$_3$)$_2$: 1×10^{-2} M, 12.5 mL
K$_2$S$_2$O$_8$: 4×10^{-2} M, 50 mL
H$_2$O: 87.5 mL
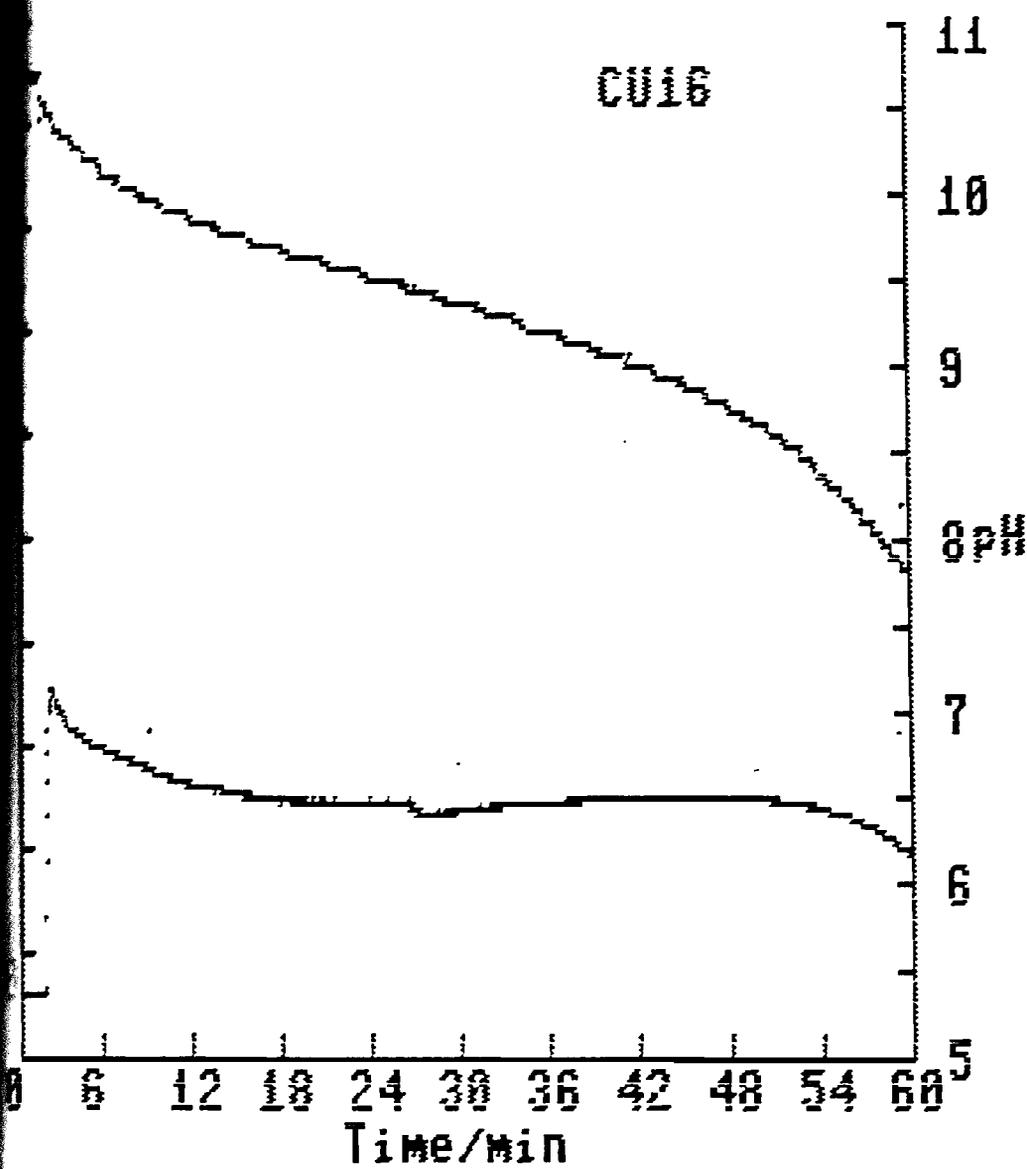
CU16

NaOH :4X10⁻³ M,   50 mL
DMG: 2X10⁻³ M,   50 mL
Cu(NO₃)₂:1X10⁻³ M, 16 mL
K₂S₂O₈: 4X10⁻² M,   50 mL
H₂O: 84 mL

CU17

11

10

9

8pH

7

6

5

6 12 18 24 30 36 42 48 54 60

Time/min
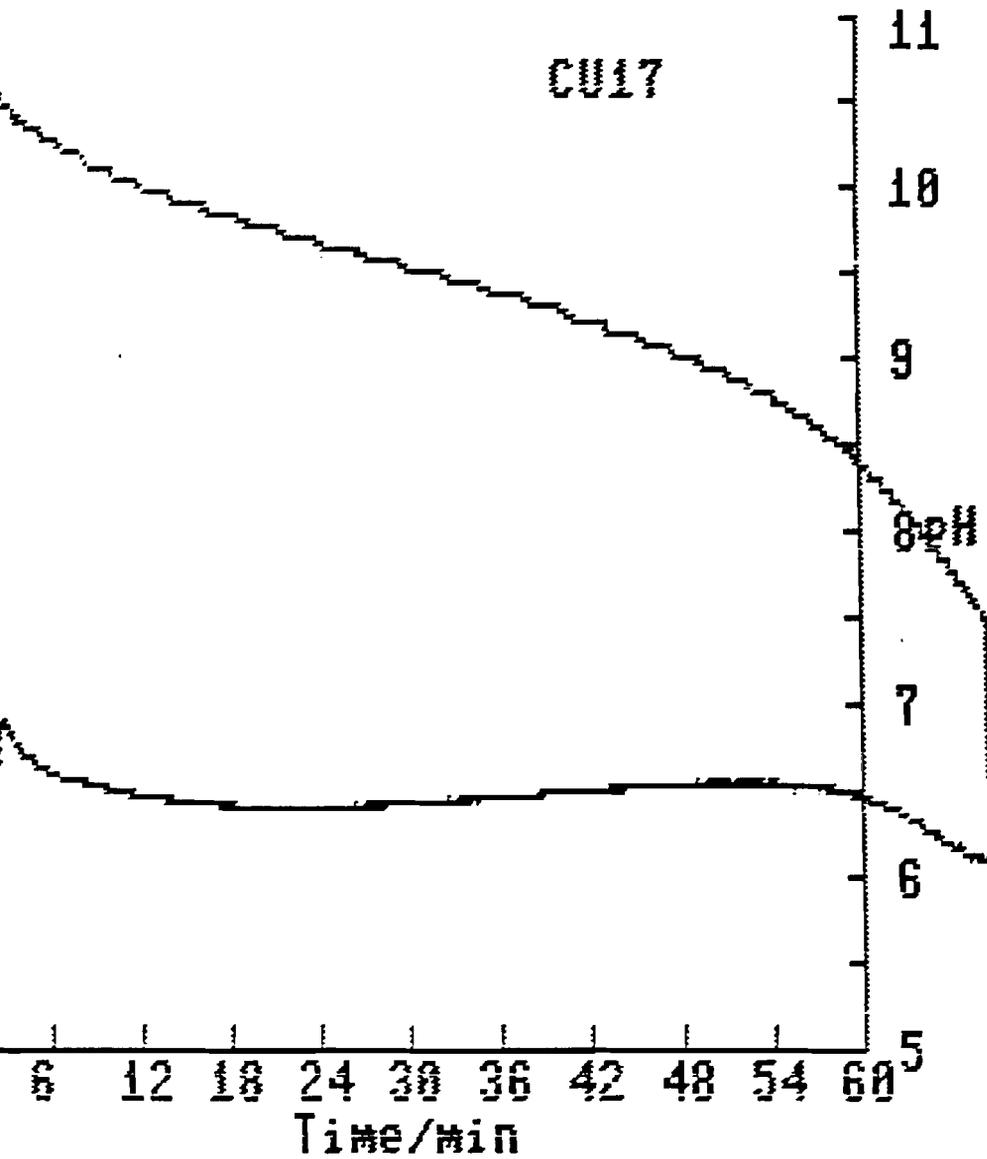
NaOH: 4X10⁻³ M,   50 mL
DMG: 2X10⁻³ M,   50 mL
Cu(NO₃)₂:1X10⁻³ M,   17 mL
K₂S₂O₈: 4X10⁻² M,   50 mL
H₂O: 83 mL

CU18
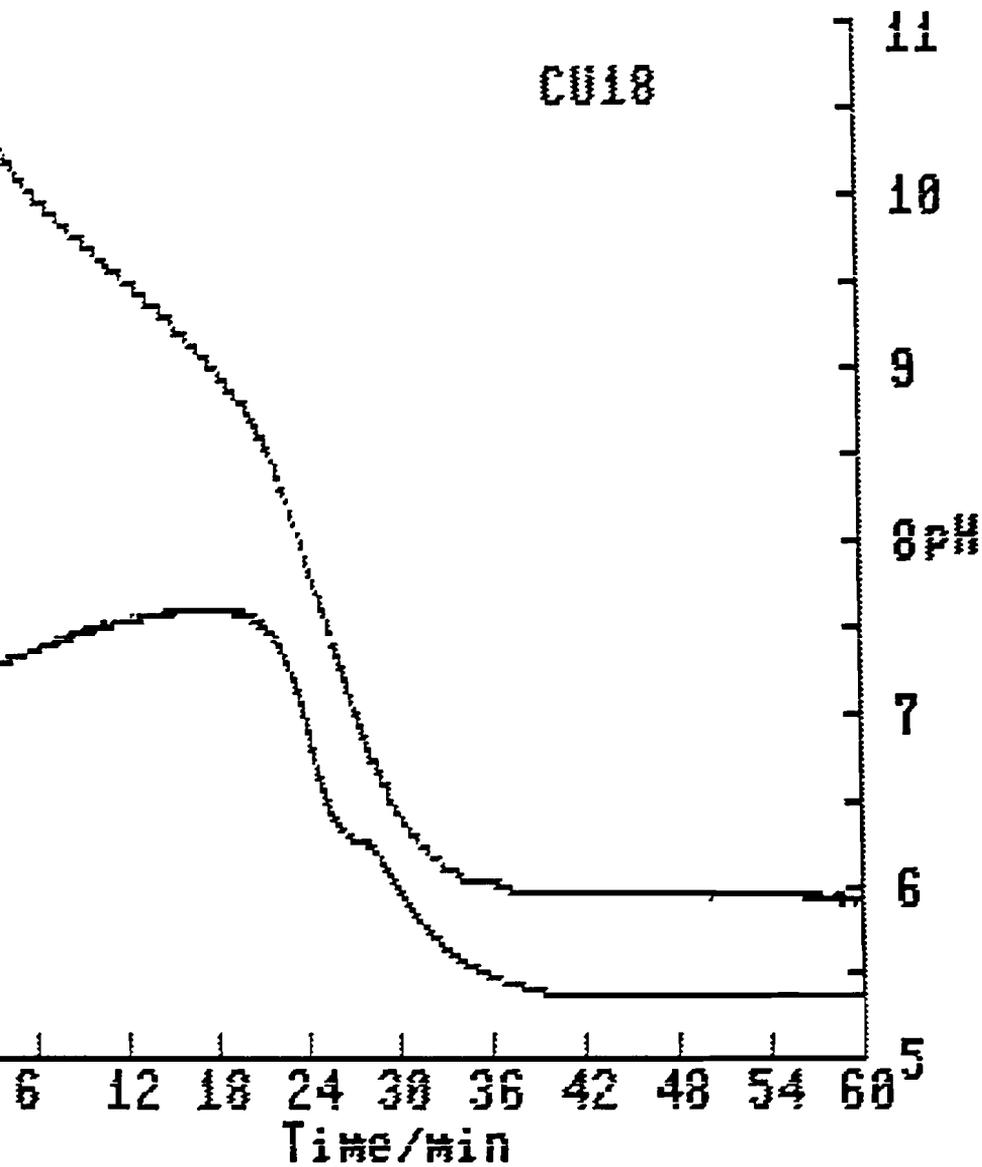
NaOH: 4×10^{-3} M, 50 mL
DMG: 2×10^{-2} M, 50 mL
Cu(NO$_3$)$_2$: 1×10^{-3} M, 18 mL
K$_2$S$_2$O$_8$: 4×10^{-2} M, 50 mL
H$_2$O: 82 mL

CU 19

Time/min
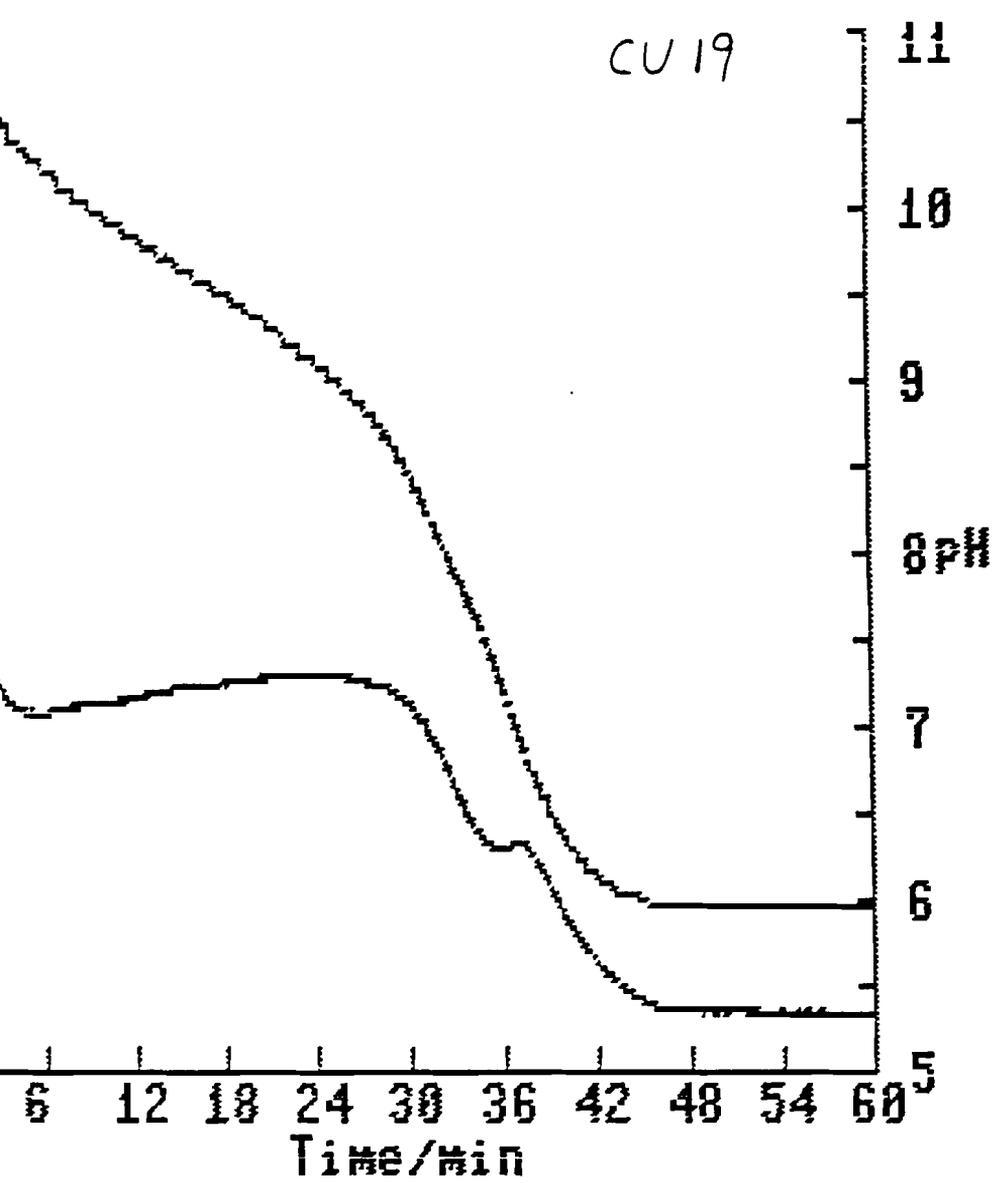
OH :4X10⁻ M,   50 mL
G: 2X10⁻⁻ M,   50 mL
(NO₃)₂:1X10⁻⁻ M, 19 mL
S₂O₈: 4X10⁻⁻ M,   50 mL
D: 81 mL

CU 20

OH: 4X10⁻⁻ M,   50 mL
G: 2X10⁻⁻ M,   50 mL
(NO₋)₋:1X10⁻⁻ M, 20 mL
S₂O₈: 4X10⁻⁻ M,   50 mL
O: 80 mL

CU 25

NaOH: 4X10⁻³ M,   50 mL
DMG: 2X10⁻³ M,   50 mL
Cu(NO₃)₂:1X10⁻³ M, 25 mL
K₂S₂O₈: 4X10⁻² M,   50 mL
H₂O: 75 mL

APPENDIX D

CU17A

Time/min

NaOH :4X10⁻ᵐ M,   50 mL
DMG: 2X10⁻ᵐ M,   50 mL
Cu(NO₃)₂:1X10⁻ᵐ M,   17 mL
K₂S₂O₈: 4X10⁻ᵐ M,   50 mL
H₂O: 83 mL

CU18A-1

Time/min

```
aOH:4X10⁻³ M,      50 mL
MG: 2X10⁻⁵ M,      50 mL
u(NO₃)₂:1X10⁻³ M   18 mL
₂S₂O₈: 4X10⁻² M,   50 mL
₂O:               82 mL
```

CU20A

NaOH: 4X10⁻³ M, 50 mL
DMG: 2X10⁻³ M, 50 mL
Cu(NO₃)₂: 1X10⁻³ M, 20 mL
K₂S₂O₈: 4X10⁻³ M, 50 mL
H₂O: 80 mL

CU21A

8pH

Time/min

CU22A

NaOH : 4X10^{-2} M,   50 mL
DMG: 2X10^{-2} M,   50 mL
Cu(NO$_3$)$_2$:1X10^{-2} M, 22 mL
K$_2$S$_2$O$_8$: 1X10^{-2} M, 50 mL
H$_2$O: 78 mL

-87-

CU23A

Time/min

NaOH: 4X10⁻³ M,   50 mL
DMG: 2X10⁻³ M,   50 mL
Cu(NO₃)₂:1X10⁻³ M,   23 mL
K₂S₂O₈: 1X10⁻² M,   50 mL
H₂O: 77 mL

CU22DM50NA40

```
NaOH: 4X10⁻² M,        40 mL
DMG: 2X10⁻² M,         50 mL
Cu(NO₃)₂: 1X10⁻² M,   22 mL
K₂S₂O₈: 1X10⁻² M,      50 mL
H₂O:                   88 mL
```

CU22DM50NA50

Time/min

NaOH: 4×10^{-3} M,   50 mL
DMG: 2×10^{-3} M,   50 mL
Cu(NO$_3$)$_2$: 1×10^{-3} M,   22 mL
K$_2$S$_2$O$_8$: 1×10^{-2} M,   50 mL
H$_2$O: 78 mL

CU22DM25NA50
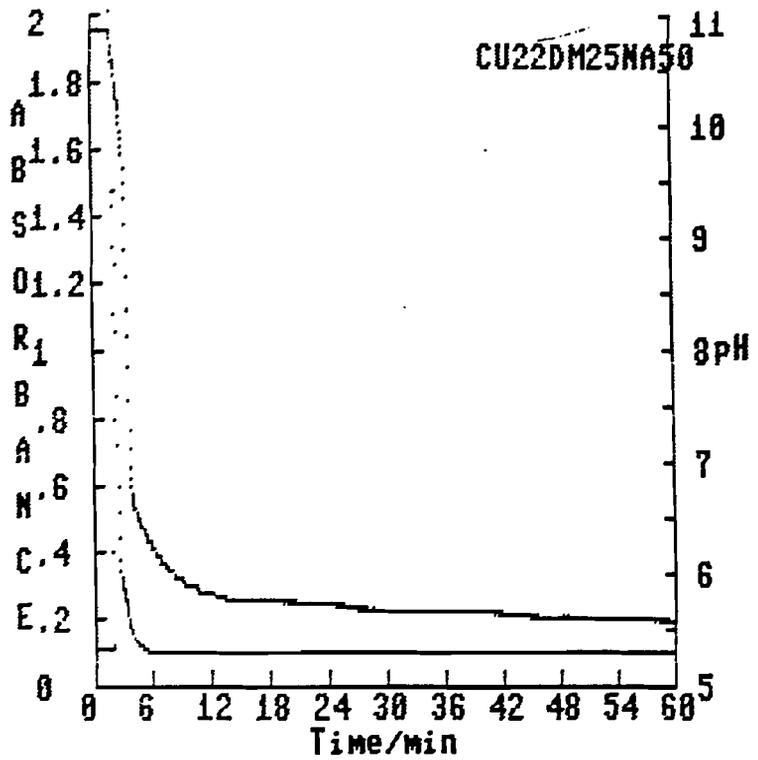
NaOH: 4×10^{-2} M,   50 mL
DMG: 2×10^{-2} M,   25 mL
Cu(NO₃)₂: 1×10^{-2} M,   22 mL
K₂S₂O₈: 1×10^{-2} M,   50 mL
H₂O: 103 mL

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