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Application of the autoxidation of phenolic compounds to the analysis of cations

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71-14,274

WIEDMANN, Jerome Lee, 1945-
APPLICATION OF THE AUTOXIDATION OF PHENOLIC
COMPOUNDS TO THE ANALYSIS OF CATIONS.

Iowa State University, Ph.D., 1970
Chemistry, analytical

APPLICATION OF THE AUTOXIDATION

OF PHENOLIC COMPOUNDS TO THE ANALYSIS OF CATIONS

by

Jerome Lee Wiedmann

A Dissertation Submitted to the

Graduate Faculty in Partial Fulfillment of

The Requirements for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Analytical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1970

PLEASE NOTE:

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SECTION I. OXIDATION OF MONOHYDROXY PHENOLS

Introduction

Kakita, et al.(1) proposed a method for the analysis of microgram a-mounts of copper by the oxidation of phenol in basic solution in the presence of chloramine-T. The reaction took two hours at $100^{\circ}C$. The method was tried to see if the author's results could be reproduced. Analogous compounds were substituted in an attempt to obtain a more sensitive method for copper with less severe conditions.

Experimental Work

The procedure used by Kakita, et al.(1) was as follows: Standard copper solution (0-1 μg of copper) was diluted to about 30 ml with water, 1 ml of phenol solution (25 g of phenol in 50 ml of 40 % NaOH diluted to 100 ml) and 1.5 ml of 10 % aqueous chloramine-T solution were added and the solution adjusted to pH 11.5-11.6. This solution was placed in a 50-ml conical flask and heated in a boiling water bath for two hours to develop the color. The solution was cooled to room temperature, diluted with water to exactly 100 ml, and the absorbance of this solution was measured at 410 nm.

Initial attempts to reproduce the data given by Kakita, et al.(1) failed because chloramine-T decomposes into a yellow tarry material. The chloramine-T used initially had already decomposed. Fresh chloramine-T was synthesized by the method of Chattaway (2). The synthesis goes as follows: About 50 g p-toluenesulfonamide was added to 500 ml of commercial sodium hypochlorite (chlorox, 5.25 % NaOCl). Some of the sulfonamide failed to dissolve. The mixture was cooled in an ice bath and placed in a hood. Glacial acetic acid was added until no more of the white water-insoluble pre-

cipitate of dichloramine was formed. The dichloramine was rinsed with several portions of water to remove the excess hypochlorite, sodium chloride and p-toluenesulfonamide. About 25 g of dichloramine was dissolved in 125 ml of hot 10 % sodium hydroxide and quickly filtered through a glass funnel with a fritted disc to remove any insoluble material. On cooling, chloramine-T precipitates from the solution as large white crystals.

The purity of the dichloramine and chloramine-T was checked by titration with thiosulfate (3). Aliquots of a standard potassium iodate solution, with potassium iodide, hydrochloric acid and starch added, were used to standardize the thiosulfate. The chloramine-T was dissolved in water, potassium iodide, hydrochloric acid and starch was added and titrated to the starch end point with the standardized thiosulfate. Glacial acetic acid was used to dissolve the dichloramine so no hydrochloric acid was necessary in that case. These titrations indicated that dichloramine contained 2.021 chlorine atoms per molecule and that the chloramine-T contained 1.018 chlorine atoms per molecule.

Copper wire dissolved in nitric acid was used as a source of copper. Liquid phenol was used primarily because of the convenience of measuring the amount of phenol in this state.

The absorption spectra of a solution made up according to Kakita, et al. (1) but with no copper added, and a second solution with 1 μg copper added are shown in Figure 1. The absorption spectra of the various components of the reaction mixture prior to reaction is shown in Figure 2. The increase in absorbance with increasing copper concentration is shown in Figure 3. The effect of time on the production of the colored species,
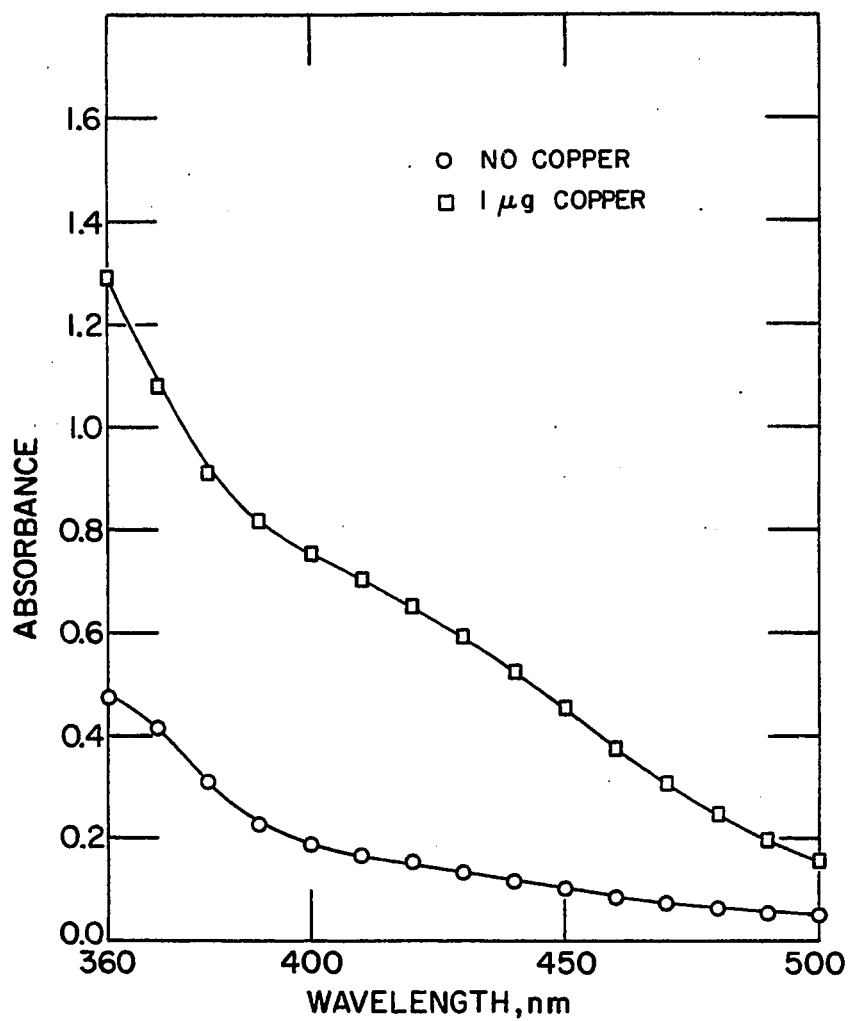
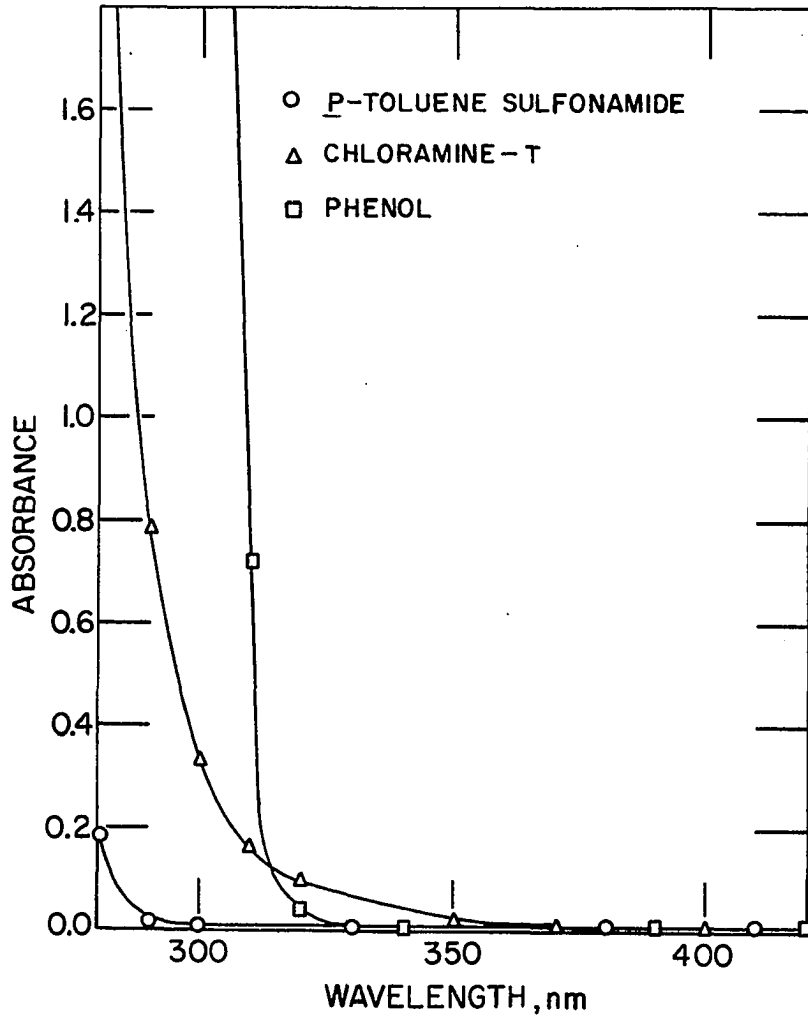Figure 1. Absorption of phenol-chloramine-T reaction products

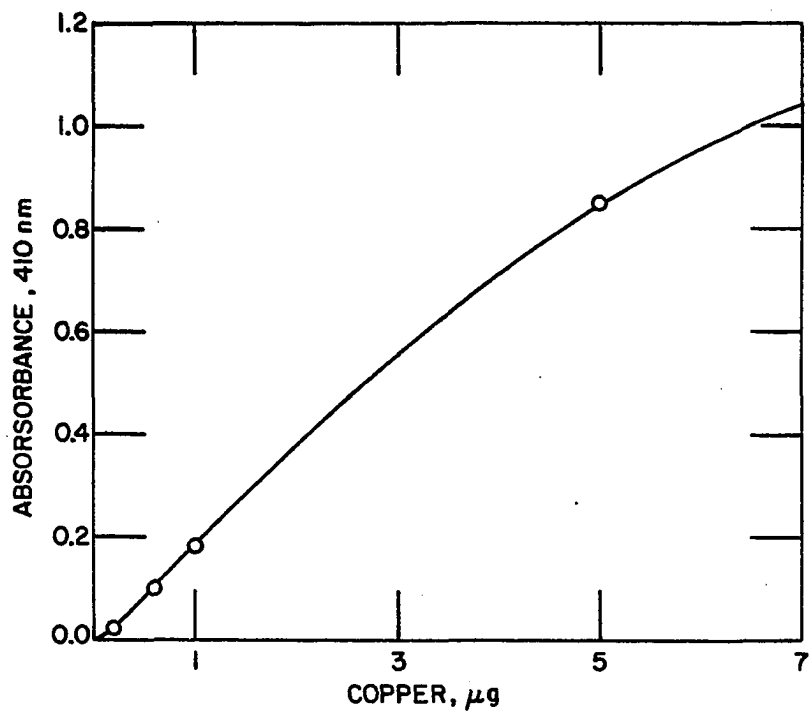Figure 2. Absorption of compounds prior to reaction

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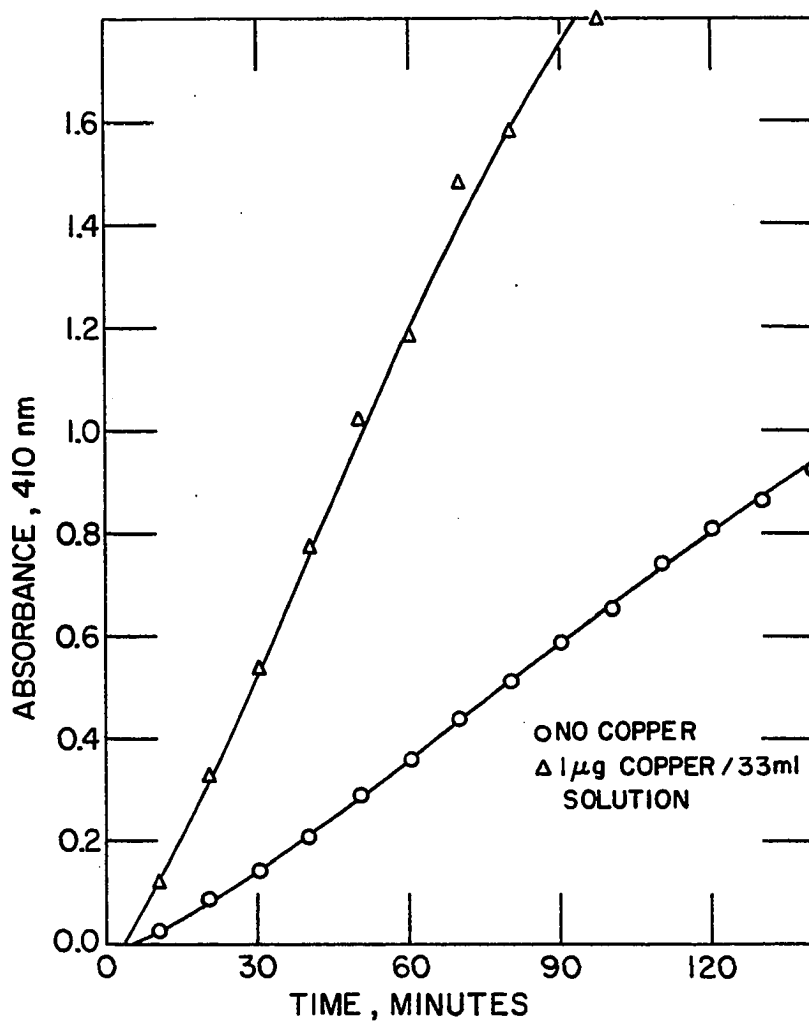
Figure 4. Effect of time on the phenol-chloramine-T reaction

both in the absence of copper and in the presence of $1\,\mu$g copper per 33 ml solution, can be seen in Figure 4. These data were collected by extracting enough solution for an absorbance reading from the reaction vessel at ten minute intervals.

Chloramine-B and p-nitrochloramine-B were synthesized from benzene-sulfonamide and p-nitrobenzenesulfonamide respectively by Chattaway's method (2) which was described previously for the synthesis of chloramine-T. Titration of these chloramines with thiosulfate gave 1.10 and 1.05 active chlorine atoms respectively per molecule of chloramine. The effect of sub-stitution of these compounds for chloramine-T can be seen in Figures 5 and 6.

Derivatives of phenol were obtained and purified by distillation in the case of liquids or recrystallization in the case of solids. The com-pounds tested, and the absorption spectra of their reaction products were as follows: o-cresol, Figure 7; m-cresol, Figure 8; p-cresol, Figure 9; o-bromophenol, Figure 10; m-chlorophenol, Figure 11; p-chlorophenol, Figure 11; o-nitrophenol, Figure 12; p-nitrophenol, Figure 13; thymol, formed a white precipitate; catechol, Figure 14; resorcinol, Figure 15; hydroqui-none, Figure 16; and phloroglucinol, Figure 17.

The methyl and halogen derivatives were run in the same fashion as the phenol-chloramine-T reaction and were studied in the absence of copper and in the presence of $1\,\mu$g of copper. The nitrophenols are colored compounds. Their absorption spectra, unreacted, were compared to the observed spectra after reaction in the absence of copper. Thymol was reacted in the same manner as phenol but formed a white curdy precipitate. The polyhydroxy

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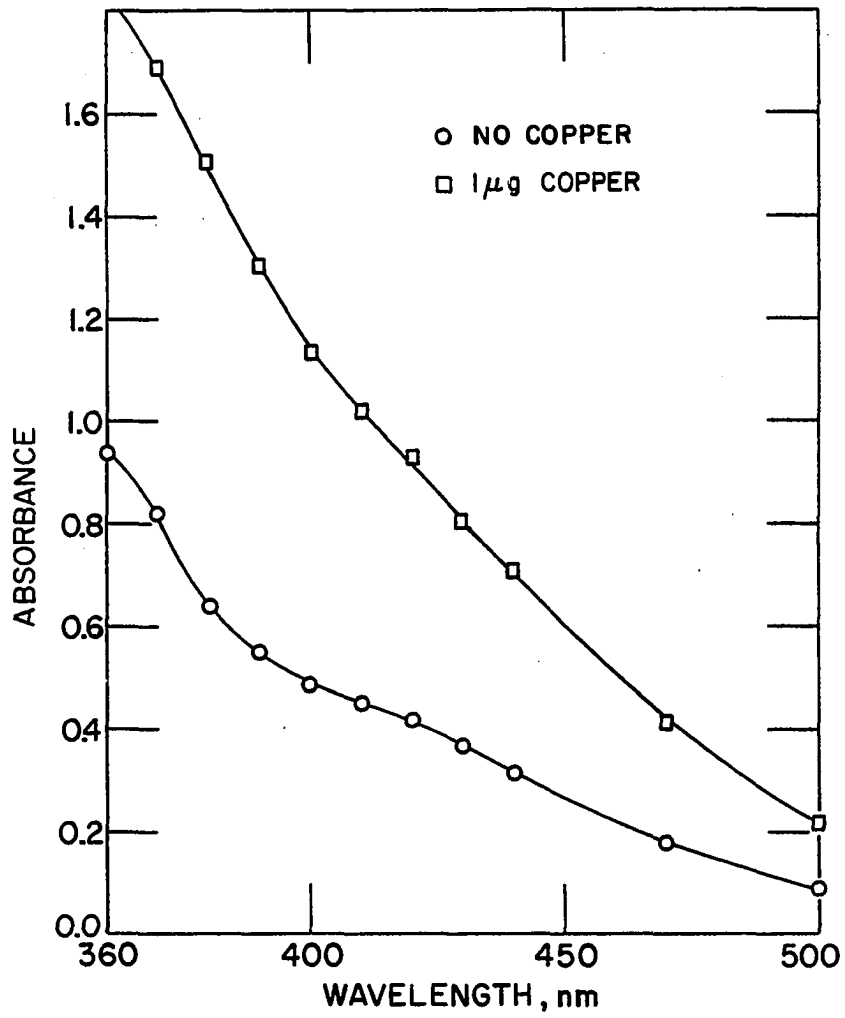
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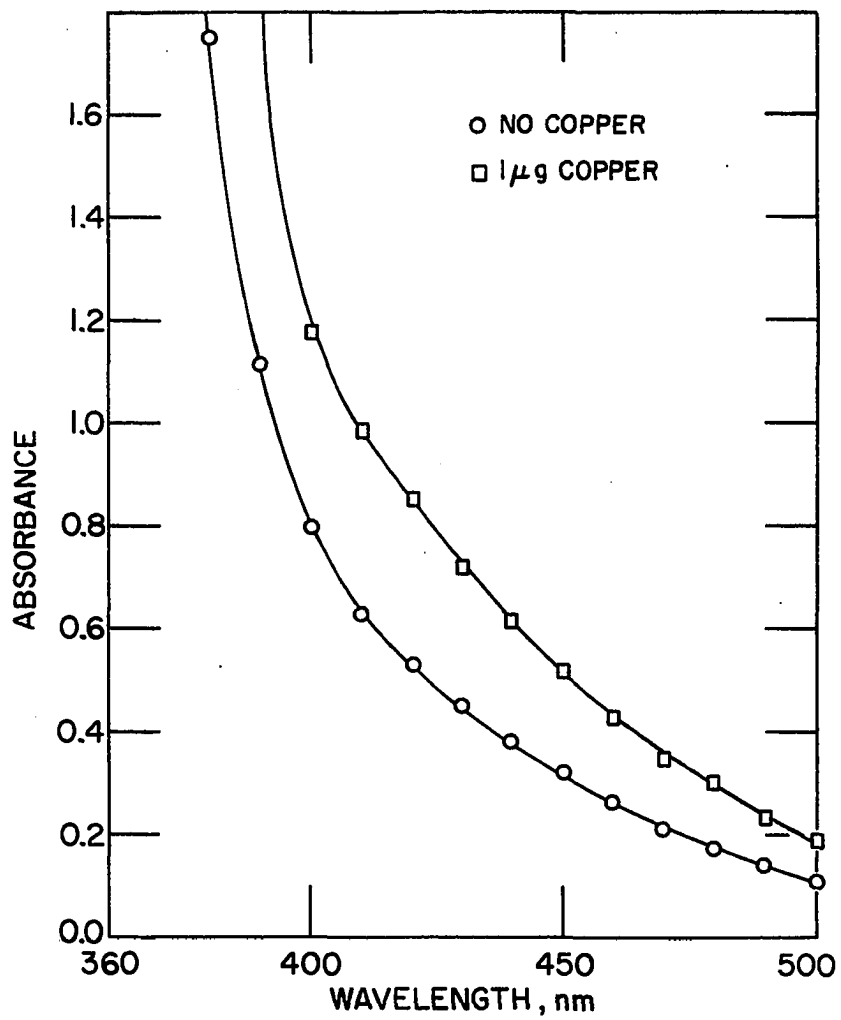
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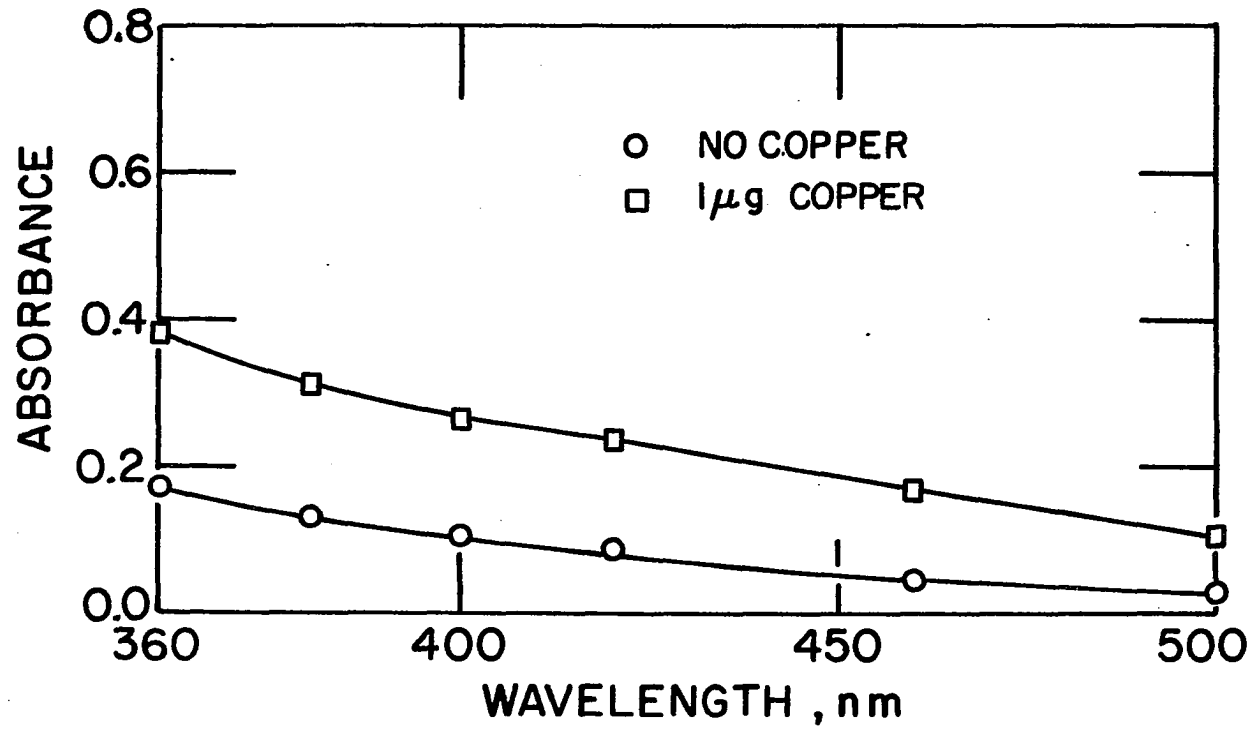
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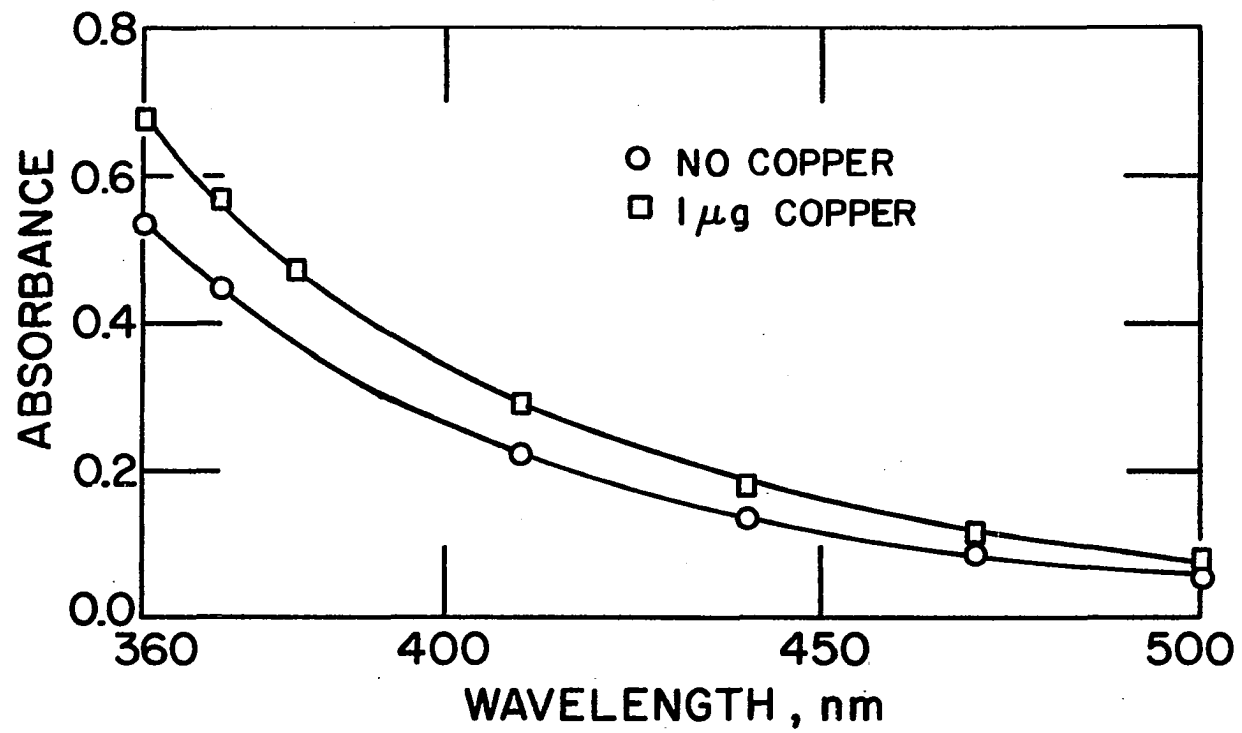
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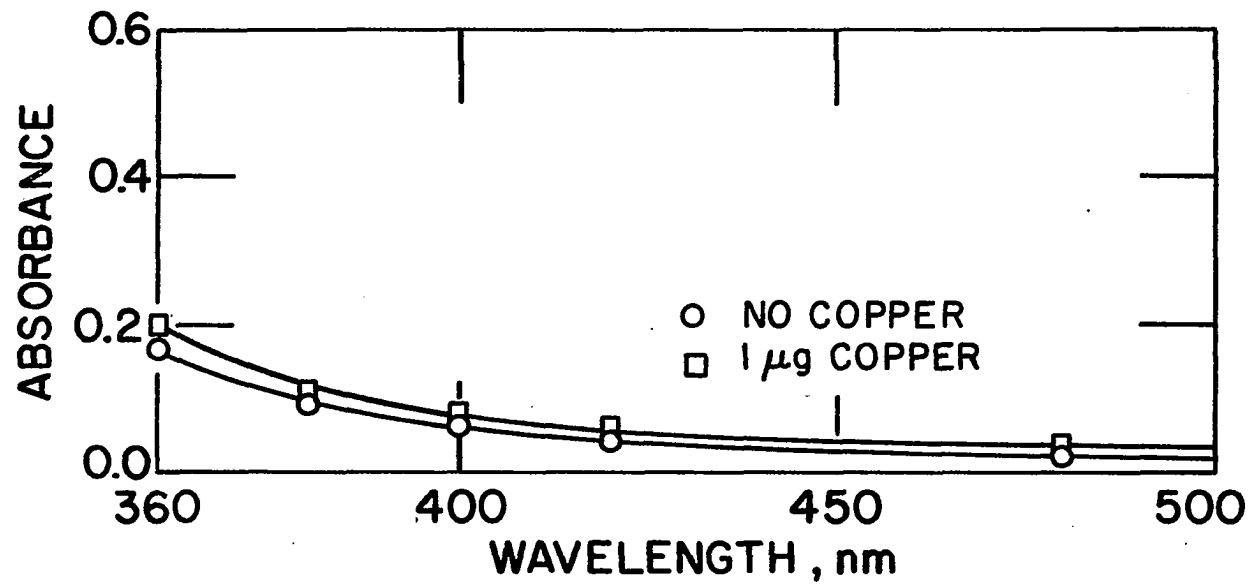
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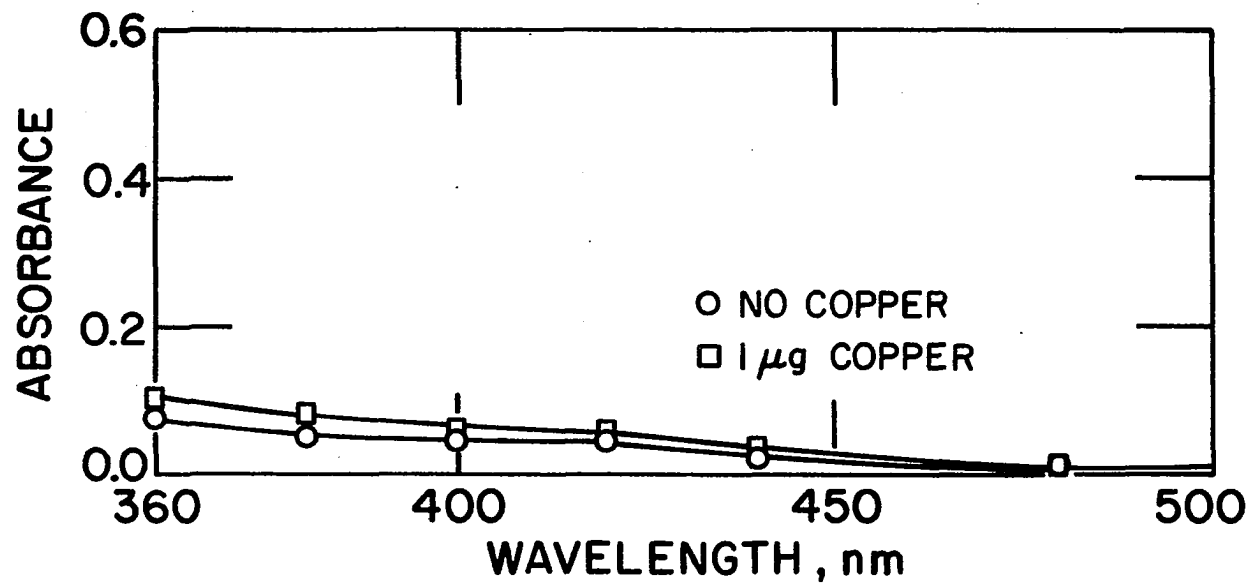
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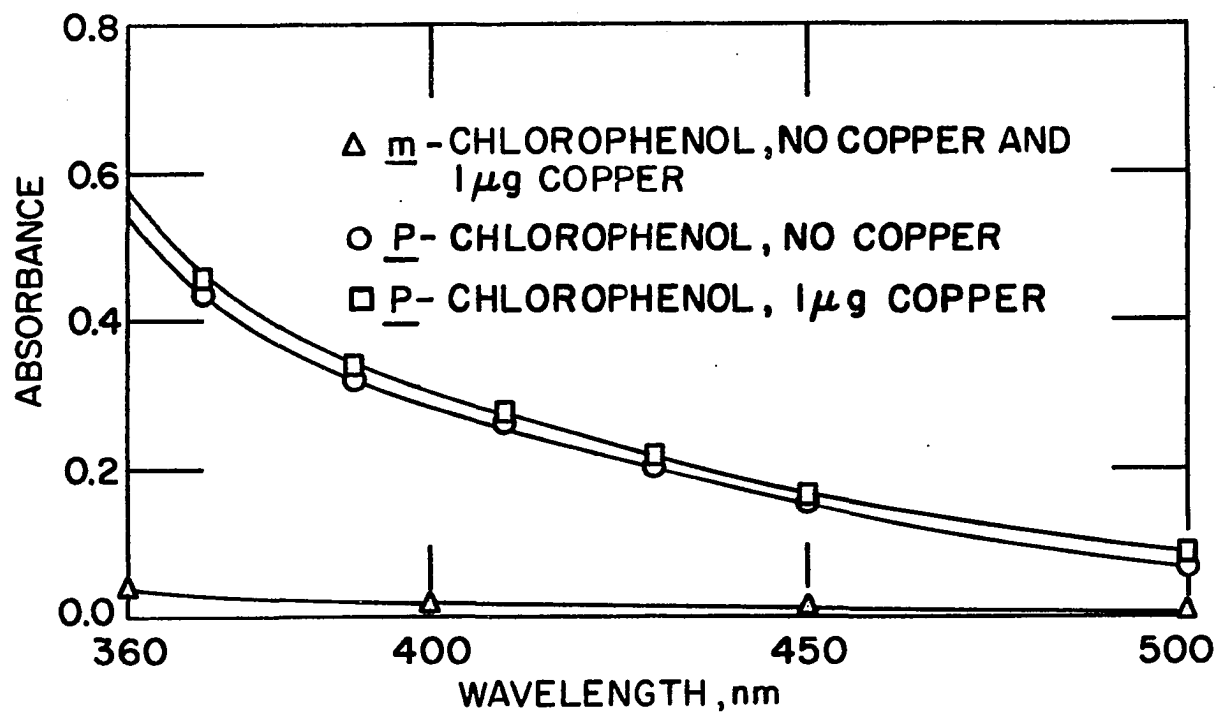
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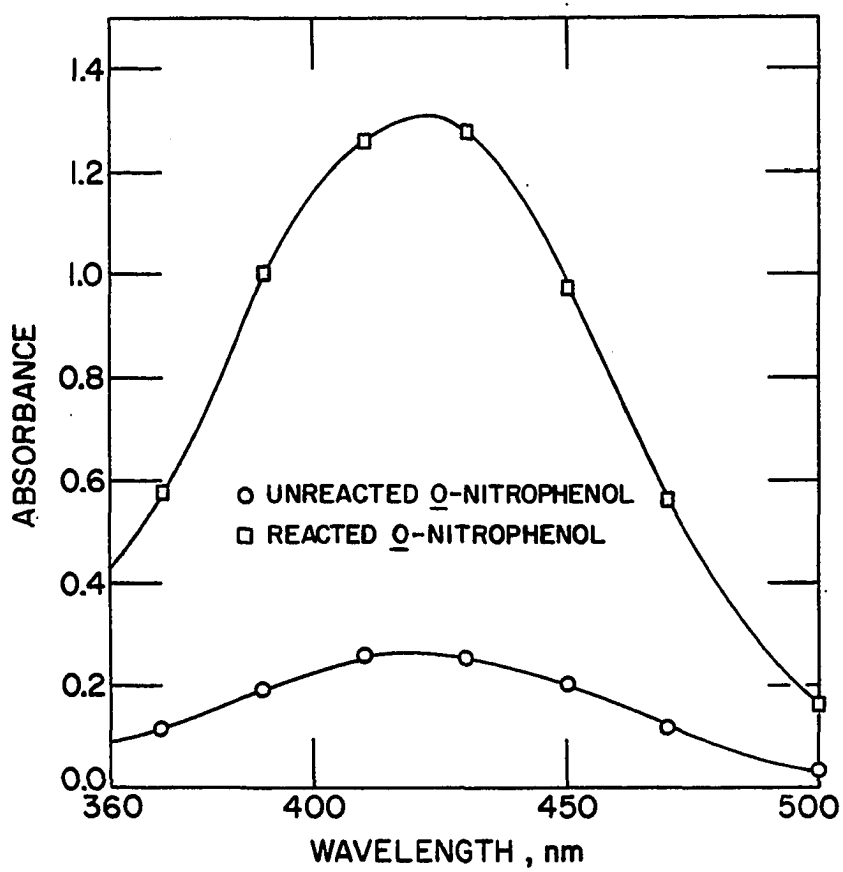
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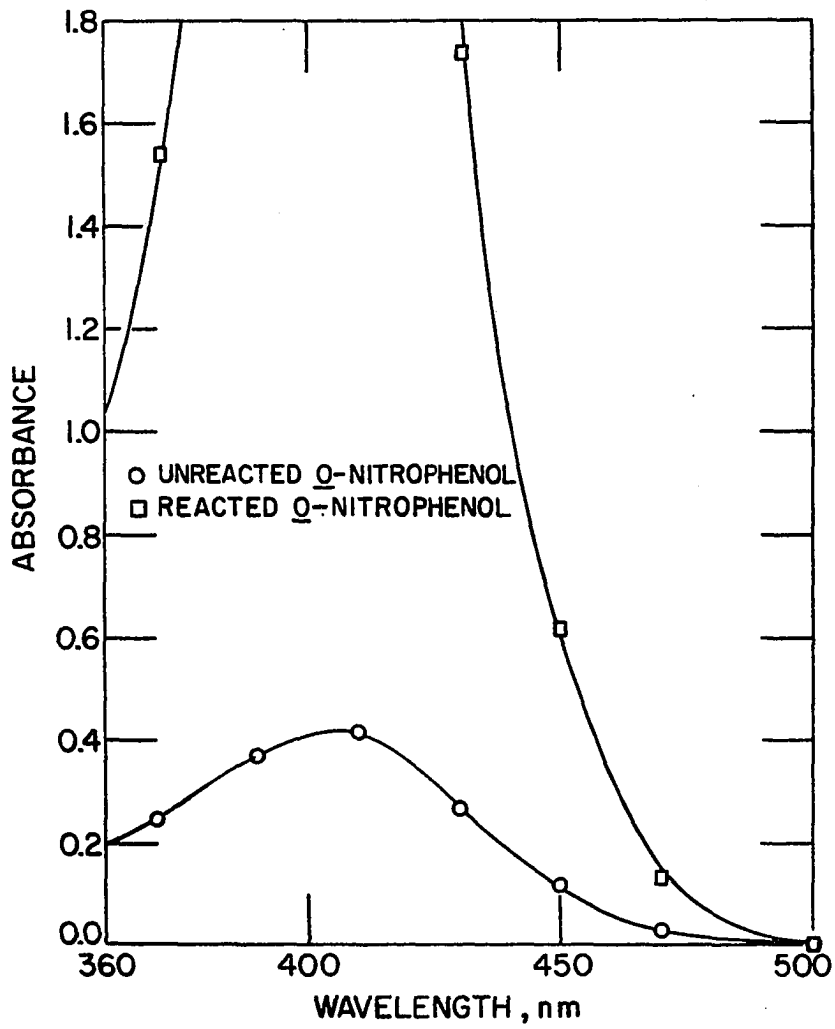
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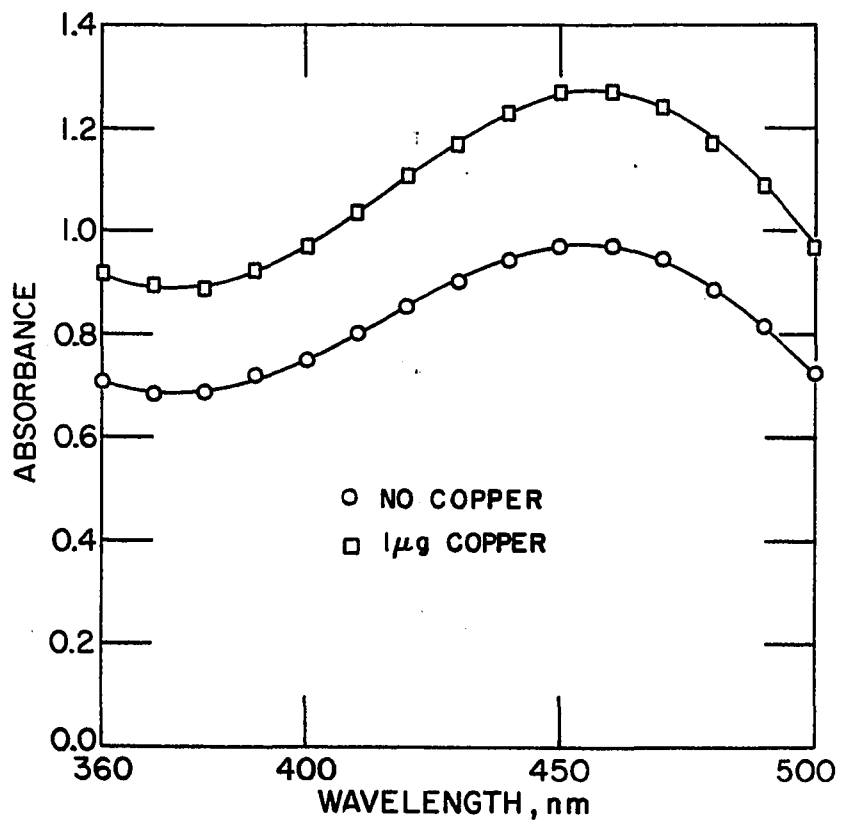
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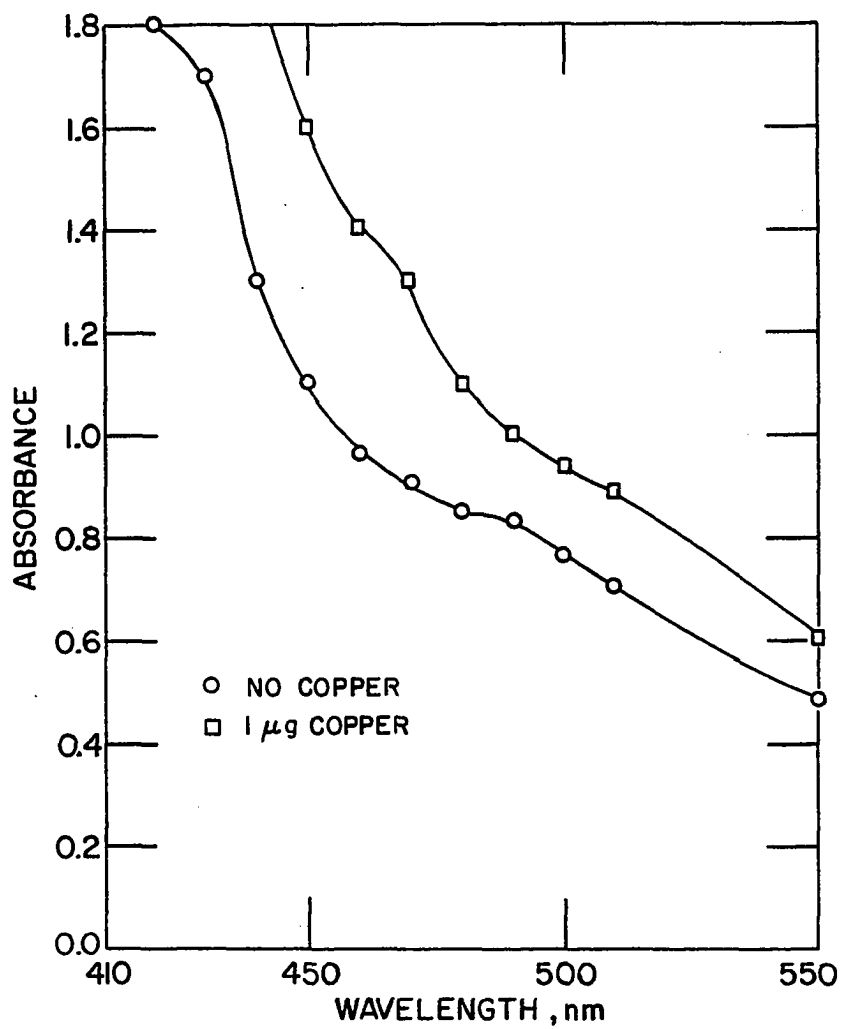
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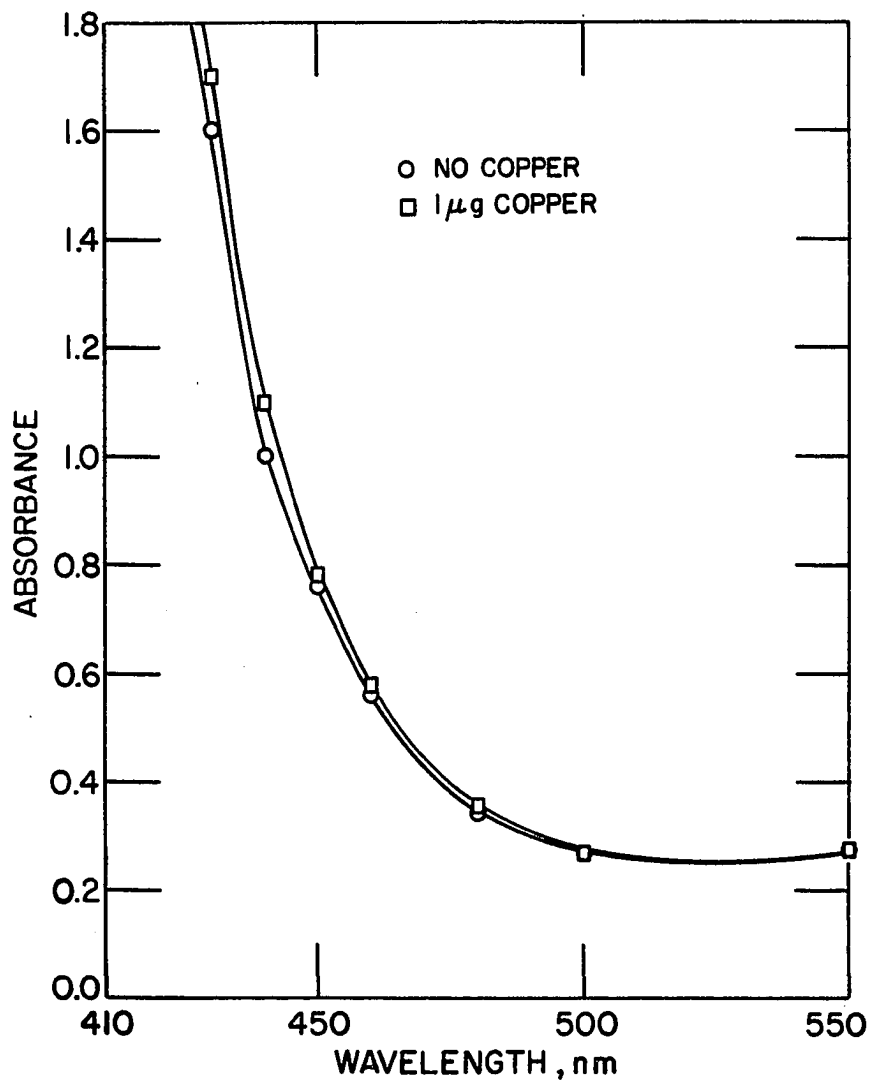
Figure 17. Substitution of phloroglucinol for phenol

derivatives reacted before heat could be applied so they were studied at room temperature. The reaction times for these compounds were two hours for resorcinol, 75 minutes for catechol, 30 minutes for hydroquinone and 20 minutes for phloroglucinol.

Discussion

The method of Kakita, et al. (1) was found to be reasonably reproducible but tedious. Study of the variables involved did not suggest any major improvements until other compounds were substituted for the reactants.

Chloramine-B (Figure 5) had an effect nearly identical to that of chloramine-T (Figure 1) in the reaction. p-Nitrochloramine-B (Figure 6) had a much reduced sensitivity for copper in the reaction. If the sulfonamide group was part of the colored species formed in the reaction, the presence of the nitro group should have produced a more intense absorption at a higher wavelength. Since the opposite effect was observed, the effect of substitution of phenolic derivatives was studied.

Comparison of the results for phenol (Figure 1) with those obtained when derivatives of phenol were used yielded the following conclusions. The three cresol isomers (Figures 7, 8 and 9) had much reduced sensitivity to copper, although some increase in absorbance with increased copper concentration was observed in each case. o-Bromophenol (Figure 10), and p-chlorophenol (Figure 11) show even less increase in absorbance in the presence of copper, and m-chlorophenol (Figure 11) shows no change in absorbance. o-Nitrophenol (Figure 12) and p-nitrophenol (Figure 13) absorb at the same wavelengths in the visible region as the reaction products do. No further study of these compounds was made. The much increased absorbance

of the reaction products is a significant indication that the products in some way are formed from the nitrophenols. Thymol or 2-hydroxy-1-isopropyl-4-methylbenzene was investigated. This compound yielded a white curdy precipitate and thus was not studied any further.

Considerable improvement in both the time and temperature necessary for reaction was observed when the series of dihydroxy phenols was examined. Catechol, resorcinol and hydroquinone were all capable of reacting at room temperature. Also it was usually not necessary to allow the color to develop for two hours. An additional problem was of course introduced in that the reaction started as soon as the solution became alkaline. Catechol (Figure 14) exhibited increased reactivity but little response to copper. Resorcinol (Figure 15) and hydroquinone (Figure 16) both had reasonable reactivity and good response to copper. The spectrum of the reacted resorcinol had a convenient absorption maximum at 450 nm while the reacted hydroquinone just gave a shoulder in the visible region.

One further compound, phloroglucinol or 1,3,5-trihydroxybenzene (Figure 17) was studied. This compound also reacted rapidly at room temperature. It did not exhibit much sensitivity for copper so it was not investigated further.

After this series of studies was made it became obvious that resorcinol was the best possibility for further investigation. It was discovered that the presence of chloramine-T was not necessary for the reaction of resorcinol.

SECTION II. AUTOXIDATION OF RESORCINOL

Introduction

The term autoxidation is generally applied to slow oxidations involving oxygen from the air which occur at room temperature (4). These oxidations are contrasted to the rapid processes of inflammatory combustion which require high temperatures. These autoxidations are promoted by light and small amounts of catalysts such as heavy metals and peroxidic substances. This autoxidation process is the reaction which occurs when resorcinol solutions turn green or brown in alkaline media or when white crystals of resorcinol turn brown.

The literature was searched for analytical methods based upon the autoxidation of resorcinol or resorcinol derivatives. The influence of some cations on this autoxidation was first noted by Lavoye (5) in 1921. Triebs (6) studied the absorption of oxygen by an alkaline solution of resorcinol. In 1949 Shapiro (7) suggested using resorcinol as a spot test for copper or silver. In 1952 Lambert (8) proposed a method for the determination of copper based on the autoxidation of resorcinol. Slater (9) in 1961 proposed a similar method for copper using orcinol. In 1968 Ilicheva and Yatsimirskii (10) published some further work on the copper-resorcinol system including a study of the kinetics involved.

Since the copper-resorcinol reaction had been well studied, no further work was done on it. In the available literature, however, no mention was made of the possibility of using resorcinol as a method for determining silver. Lambert (8) listed silver as the most serious interference in his copper method. It was reasoned that if a complexing agent could be found

which would complex copper but not silver, than one could use the autoxidation of resorcinol for an analytical method for silver.

Mechanism of Autoxidation

Further study of the literature was conducted in an effort to learn more about the mechanism involved in the autoxidation and if possible the nature of the colored species formed.

In 1939 Henrich (11,12) proposed that resorcinol was autoxidized by Reaction 1.

Reaction 1
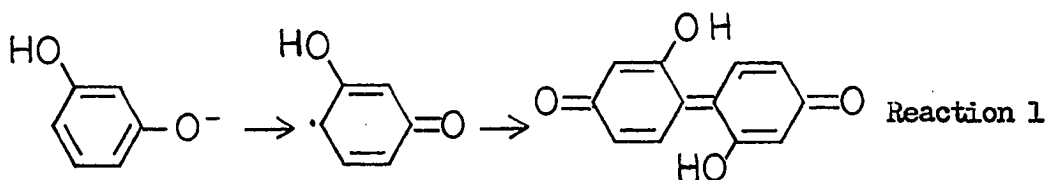
The 2,2'-dihydroxydiphenoquinone was then presumed to be the colored species which was formed. However, the two rings of the 2,2'-dihydroxydiphenoquinone must be coplanar for a diphenoquinone structure. It can easily be seen from models that the two phenolic groups give sufficient steric hinderance to prevent the formation of this intra ring double bond. Indeed no diphenoquinone substituted in the 2,2' or 6,6' positions have ever been synthesized (13-16) although a few erroneous reports have been made. The diphenoquinone structure is even less credible when the visible spectra of known diphenoquinones are studied. Typical 3,3',5,5'-substituted compounds have absorption maxima between 395 to 425 nm and molar absorptivities of 60,000 to 70,000 1/mole-cm (14,17,18). The observed absorption maximum for autoxidized resorcinol is 450 nm (Figure 21). Molar absorptivity calculations based on the concentration of silver give a molar absorptivity of 10-000. Beer's law and the calculations are given below. Consequently the

colored species formed is not a diphenoquinone.

$$A_s - A_b = \epsilon bc \quad \text{and} \quad \epsilon = (.396 - .021)/(1)(3.7 \times 10^{-5}) = 10,000$$

where A_s is the absorbance of the sample (.396 from Figure 23)
      A_b is the absorbance of the blank (.021 from Figure 23)
      ϵ is the molar absorptivity
      b is the cell path length (1 cm)
      c is the silver concentration (100 μg Ag$^+$/25 ml or 3.7x10^{-5} M Ag$^+$)

There is no further literature on mechanisms for the autoxidation of resorcinol. However, orcinol has been studied in some detail. The presence of a methyl group in the five position does not significantly change the reactions involved. The methyl group makes orcinol slightly more receptive to autoxidation (19) and stabilizes the products (20, 21). Consequently it is also easier to study.

Based on earlier work by Musso (20,22,23) and also the ESR studies of Stone and Waters (24), Reaction 2 was proposed for the autoxidation of orcinol.
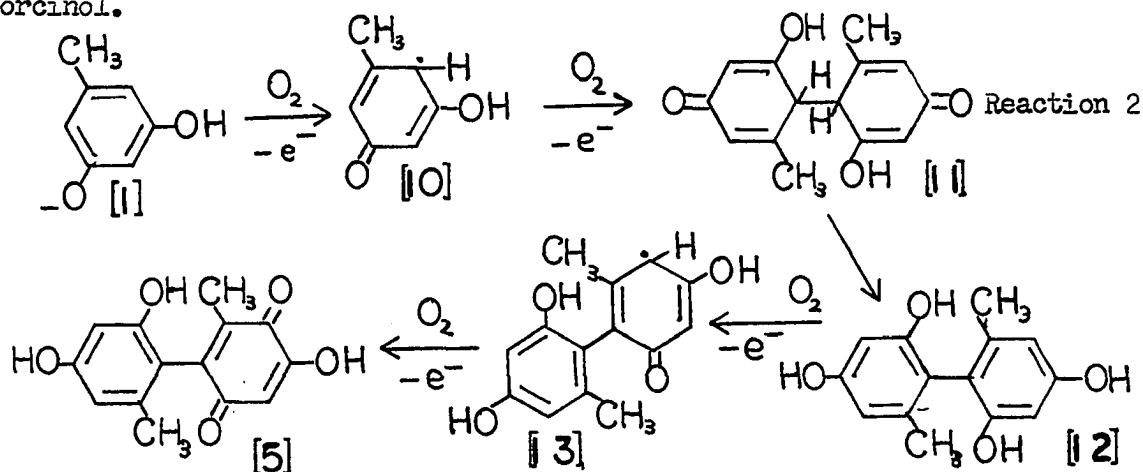
ESR studies of the alkaline oxidation of orcinol with K$_3$Fe(CN)$_6$ give definite evidence of [10] in the solution (24). It is possible to detect [12] chromatographically at any stage of the K$_3$Fe(CN)$_6$ oxidation (25). Boiling with sodium in pyridine causes cleavage of the ether linkages in

the polymer formed by the oxidation. Both [1] and [12] could be isolated in the resulting solution (25). Consequently Reaction 2 is a reasonable explanation of the $K_3Fe(CN)_6$ oxidation.

When the oxidation by oxygen is studied, however, no evidence is found for [10] or [12] (25). Reaction 3 was postulated by Musso and coworkers (19,25-29) to account for this lack of [10] in the autoxidation solution.
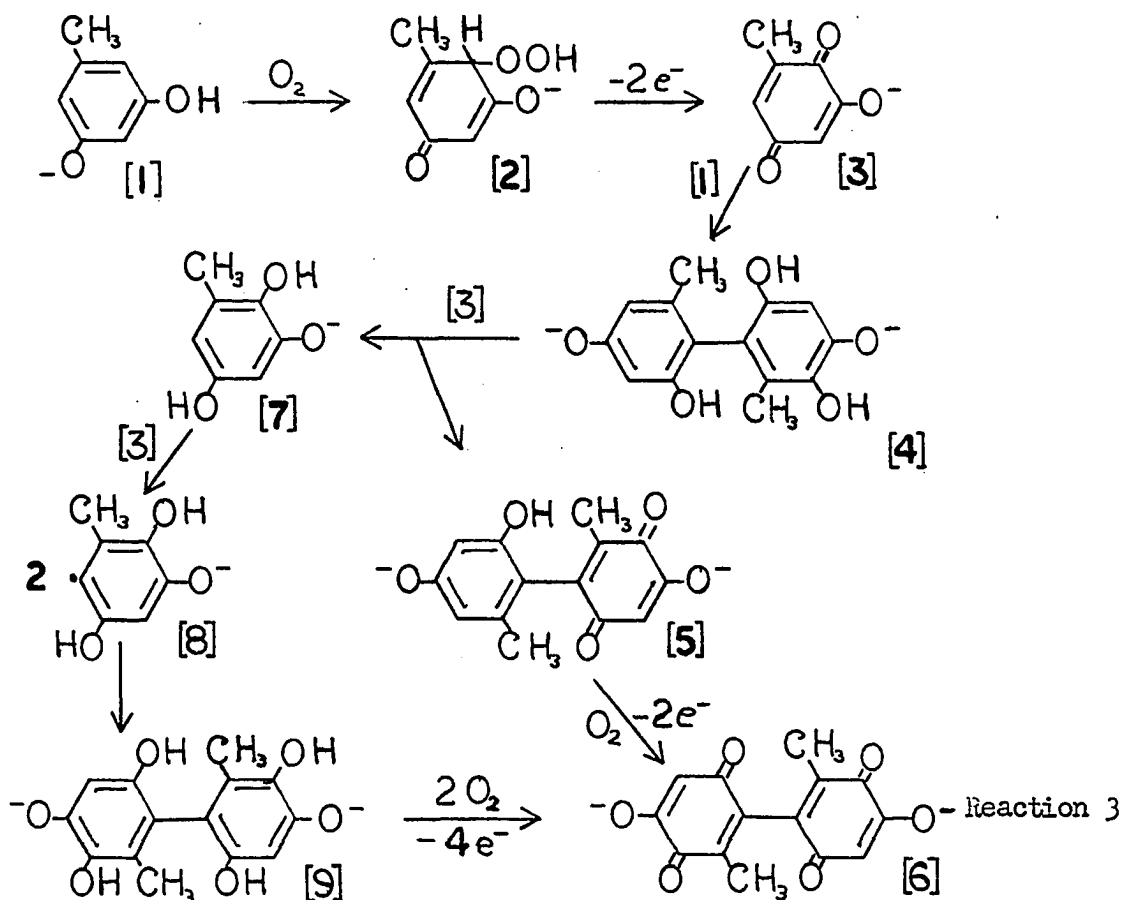
The attack of the oxygen in a position para to one of the phenolic groups on the orcinol anion is expected since the ESR work (24) shows that 95% of the time, the extra electron resides in one of the two positions para to an oxygen.

Specie [3] reacts too quickly with anionic orcinol to be detected in

the solution. However, if more steric hinderance is introduced into the molecule such as a <u>tert</u>-butyl group in position five (25) this monomeric quinone is stabilized to the extent that it can be isolated in the reaction products.

The reaction sequence [1] → [2] → [3] → [4] → [5] → [6] provides nearly all of the product since the solution is dilute enough to prevent two [8] radicals from coming in contact often enough to be a major pathway (25).
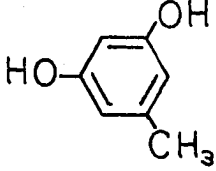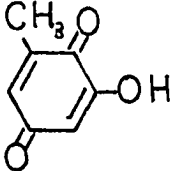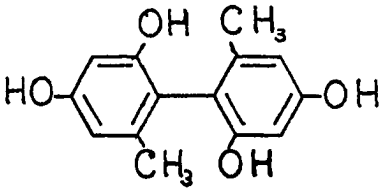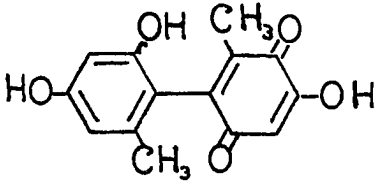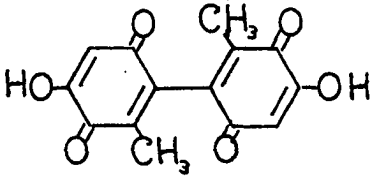
The rate determining step is the electrophilic attack of oxygen on the orcinol anion (26). This follows from the observation that only the products [5] and [6] can be found spectrophotometrically in the reacting solution.

The autoxidized solution of resorcinol has an absorption maximum at 450 nm at pH 11.5. There are no published data on the absorption of possible autoxidation products. Corresponding data has been published for orcinol (22) and can be seen in Table 1. Autoxidized orcinol has an absorption maximum of 475 nm (28). The only compound which has a maximum at 475 nm is the diphenylmonoquinone.

When 5% orcinol and 0.91 M KOH were reacted at room temperature for five days, a 50% yield of diphenylmonoquinone and diphenyldiquinone in a 9:1 ratio was obtained (19).

No bathochromic shift was observed in the spectrum of a reacting orcinol solution during the first ten hours of reaction (30). As [5] is converted to [6], a bathochromic shift in the wavelength of maximum absorption will occur.

Table 1. Absorption spectra in 0.2 $\underline{N}$ NaOH-methanol (22)

Compound	λ_{max} nm	ϵ	λ_{max} nm	ϵ
	291	2900		
	277	8800	494	1900
	293-4	9100		
	288	15000	474	2500
	279-80	20100	494-5	7800

One now raises the question of how do cations catalyze this autoxidation. Ilicheva and Yatsimirskii (10) postulate a copper(II) hydroxide-phosphate-resorcinol complex which then dissociates into a copper(I)-hydroxide-phosphate complex and a resorcinol free radical. Since in 1968

they explain the autoxidation in terms of Henrich's reaction, and since this has been proved incorrect since 1944 (13), their whole work is subject to doubt.

The cations, copper(II) and silver(I), probably act by catalyzing the decomposition of the peroxide, [2], to form a free radical of [3], which would quickly attack an orcinol anion to yield [4]. According to Waters (4) this is the general mechanism for the acceleration of autoxidation by cations.

The copper(II) would remove an electron from the peroxide [2] to yield a copper(I) and the free radical of [3]. Air oxidation would then oxidize the copper(I) back to copper(II).

Silver(I) would also form the free radical of [3] but would be reduced to inactive silver(0) in the process. Thus it would not have a truly catalytic function in the reaction.

Experimental Work

Apparatus

All pH measurements were made using a Corning Model 10 pH meter fitted with a Beckman #40495 glass electrode (0-14 pH, 15-80°C) and a Corning calomel electrode #476002.

Several spectrophotometers were used. Recorded spectral scans of the UV-Visible region were obtained on a Cary Model 14 spectrophotometer. A Beckman Model B spectrophotometer with a constant voltage transformer was used for preliminary work. This instrument was unstable enough to be the major source of error in the method, so it was replaced by a Coleman Hitachi Model 101 spectrophotometer. The Beckman and Coleman instruments

were used only for visible work in the region 340-650 nanometers. The
Coleman spectrophotometer was used with a Bausch and Lomb V. O. M. 5 re-
corder for kinetic work. For the study of temperature dependence a Beckman
DU spectrophotometer was used. The compartment of this instrument was ad-
justed to constant temperature with a water bath reservoir and a varistatic
pump. The samples were reacted in the same water bath.

All spectrophotometric measurements were made using either borosili-
cate one-centimeter cells (Corning #30-310) or quartz one-centimeter cells
(Corning #30-300).

A Rinco Model V. E. 50 rotovac was used in the recrystallization of
organic compounds.

A stopwatch and a Gralab timer Model 171 were used to take accurate
time measurements.

An aluminum block melting point apparatus, standardized with benzoic
acid, was used for all melting points.

A Sargent model XXI polarograph was used for the polarographic meas-
urement of oxygen.

A simple sublimation apparatus was constructed for the purification of
some of the organic compounds. The heat source was a 1-liter heating man-
tle. The sample to be purified was placed in a 115-mm diameter porcelain
evaporating dish. A 100-mm diameter funnel was inverted over the dish in
the heating mantle and the variac on the heating mantle adjusted to provide
a temperature a few degrees below the melting point of the compound. A
piece of 3-mm glass rod was passed through the neck of the funnel, bent in-
to a hook at the top and into a loop at the bottom of the funnel. Then a

7-cm piece of filter paper could be placed on the loop and the height of the loop adjusted by placing the hook on a ring stand and raising or lowering the ring. The filter paper catches sublimed material which falls off of the funnel. This apparatus can purify up to 10 g of resorcinol in 24 hours.

Reagents

Standard copper solutions were prepared by dissolving copper wire in concentrated nitric acid and diluting to volume in a volumetric flask with deionized water. Normally an aliquot of this solution was used to prepare a second solution dilute enough in copper so that several milliliters of this second solution would contain the desired amount of copper.

Standard silver solutions were prepared by dissolving Mallinckrodt Analytical reagent grade silver nitrate in water, adding two to three drops of concentrated nitric acid to stabilize the solution, and diluting to volume with deionized water in a volumetric flask. A second dilution was usually necessary to provide the desired concentration. Pure silver wire, dissolved in concentrated nitric acid, was also used as a source of silver. Both sources of silver gave identical results when used in the resorcinol method.

Adsorption of silver on the vessels used to store dilute standard silver solutions is a serious problem (31, 32). Previous treatment of the vessels is important since it takes seven rinsings to remove the adsorbed silver from the walls (31). The adsorption studies indicate that borosilicate glass is as good as other containers. Silver adsorption can be minimized by allowing the glassware to become saturated with silver and then

never removing this saturated surface. Since no method of preventing this problem has been devised, the magnitude of the error involved was investigated. A solution containing 10 μg Ag$^+$/ml was stored in a 1-liter volumetric flask. A ten-ml aliquot of this solution was analyzed for silver by the resorcinol method. After one month, 3.1 % of the silver had been absorbed onto the wall of the flask and after two months, 4.4 %. The 1.0 mg/ml stock solution used to prepare the two month old solution was (after two months) diluted 1:100 and tested also. Only 0.6 % of it had absorbed onto the wall of the flask.

Fresh silver solutions were prepared when accurate concentrations of silver were needed.

Most phenolic compounds autoxidize in time even in the solid form, so that purification is necessary regardless of the source of the compound. Even pure resorcinol will need annual recrystallization to maintain the purity necessary for stable aqueous solutions. Mallinckrodt USP grade resorcinol was recrystallized from chloroform-ethanol mixtures. After one recrystallization of resorcinol, the melting point was usually 107-109°C, 109-110°C after two recrystallizations, and 110.2°C for crystals which were dried in vacuum over anhydrous magnesium perchlorate. The literature value (33) was 111°C. Sublimed resorcinol melted at 109.4-110.4°C.

Lambert (8) used isopropanol as the solvent for his resorcinol solutions. This was compared to deionized water. Resorcinol quickly deteriorated when it was dissolved in undistilled isopropanol. Resorcinol dissolved in distilled isopropanol and in deionized water both had about the same stability. Deionized water is preferred because the decomposition

product is a lighter color in water than in isopropanol. Aqueous 2 % resorcinol solutions were generally stable for two to three months and 0.2 % solutions for slightly longer. The deterioration was indicated by a yellow color appearing in the stock solution. An aqueous solution of resorcinol has a pH of 5.7. The more alkaline the solution the less stable it is.

The 1 $\underline{M}$ solution of sodium citrate was prepared from 'Baker Analyzed' reagent. It was stable in deionized water for at least two years.

The combination of resorcinol and sodium citrate into one stock solution was studied. This combined solution (0.2 % resorcinol, 1 $\underline{M}$ sodium citrate) had a stability only 24 hours. The addition of acid was not an effective stabilizing agent because so much acid was necessary to provide an acidic pH that the resulting solution was acid enough to overcome the pH 11.5 buffer system. The only way to solve this problem was to keep stock solutions of both resorcinol and sodium citrate and then combine them just prior to use.

The buffer system used to maintain the constant pH necessary in the reaction was prepared by dissolving $Na_3PO_4 \cdot 12H_2O$ (57.0 g) and Na_2HPO_4 (14.2 g) in deionized water and diluting this solution to one liter. The trisodium phosphate used was 'Baker Analyzed' reagent and the disodium hydrogen phosphate was Mallinckrodt Analytical reagent. The resulting solution was 0.1 $\underline{M}$ in disodium hydrogen phosphate and 0.154 $\underline{M}$ in trisodium phosphate. This solution is stable for at least two years. The insolubility of the phosphate salts prevented increasing the strength of the stock reagent. Five ml of this solution buffers the reaction solution at pH 11.5.

The phosphate buffer system can be combined with the sodium citrate

solution by preparing the buffer as directed above and then using this solution as a solvent for the sodium citrate.

Other chemicals such as those used for the interference studies were either 'Baker Analyzed' reagent or Mallinckrodt Analytical reagent.

Oxygen

Waters (4) in his book on oxidation mechanisms states: "It has, in fact, been found, that the rates of autoxidation of almost all purified compounds are independent of the O_2 pressure, until values well below 100 nm total pressure have been reached."

Triebs (6) noted that 0.5 mole of O_2 is absorbed per mole of resorcinol when resorcinol undergoes oxidation. The resorcinol concentration in a typical 25-ml volume of reacting solution is 0.007265 $\underline{M}$. The oxygen concentration of the same solution, assuming air saturation, is only 2.579 x 10^{-4} $\underline{M}$. From this information it would appear that the amount of oxygen in the solution is the limiting factor of the reaction. Since oxygen produces a polarographic wave it was possible to polarographically monitor the oxygen concentration.

Figure 18 shows the polarographic scan of 24 ml of an air-saturated solution of sodium citrate, phosphate buffer and 100 μg silver(I). The polarographic wave was caused by the reactions (34)

$$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^- \text{ and}$$

$$H_2O_2 + 2e^- \longrightarrow 2OH^-.$$
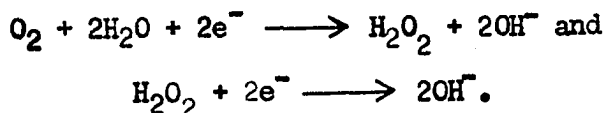
When N_2 was bubbled through the solution for 15 minutes to remove the oxygen, Figure 19 was obtained. When one ml of 2% resorcinol was added, a polarographic wave identical to that of Figure 19 was obtained.
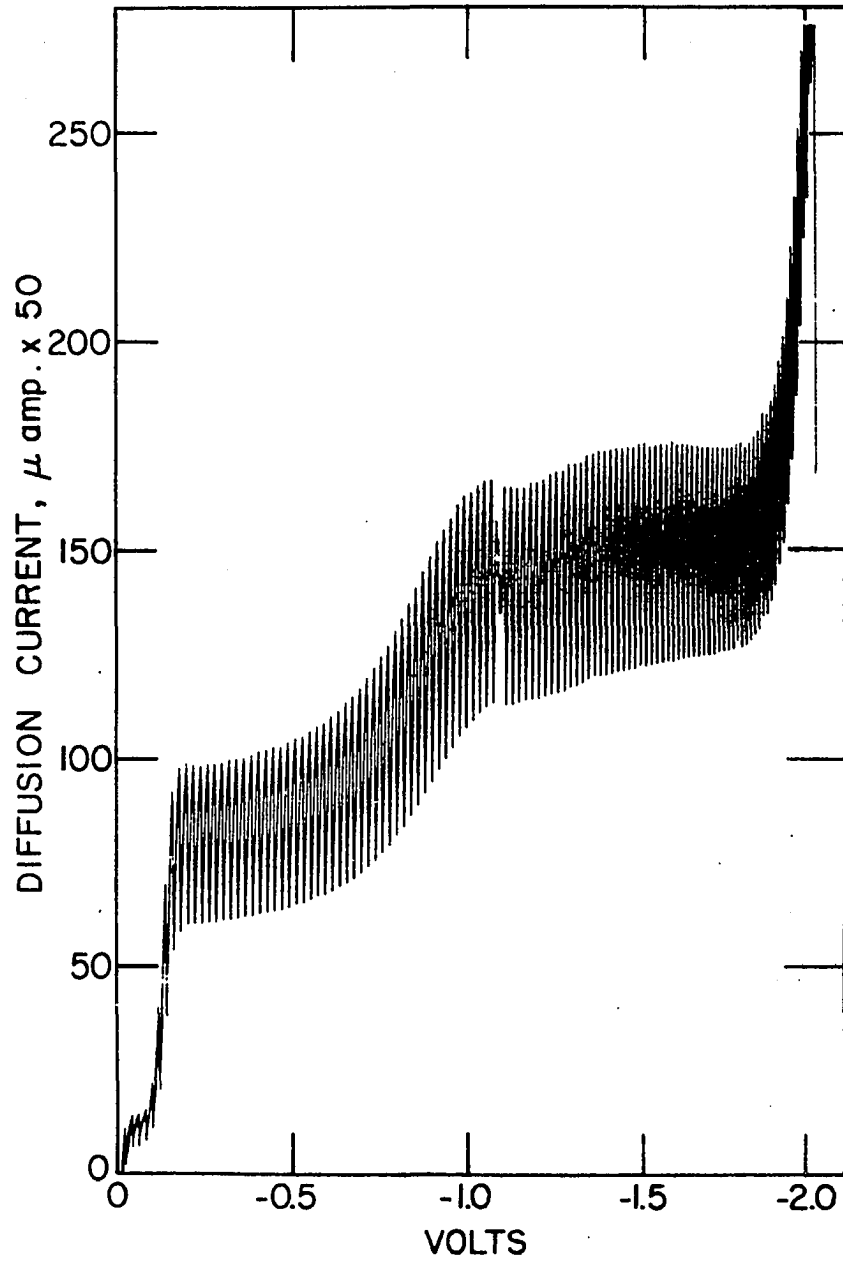
Figure 18. Polarogram of oxygen

36
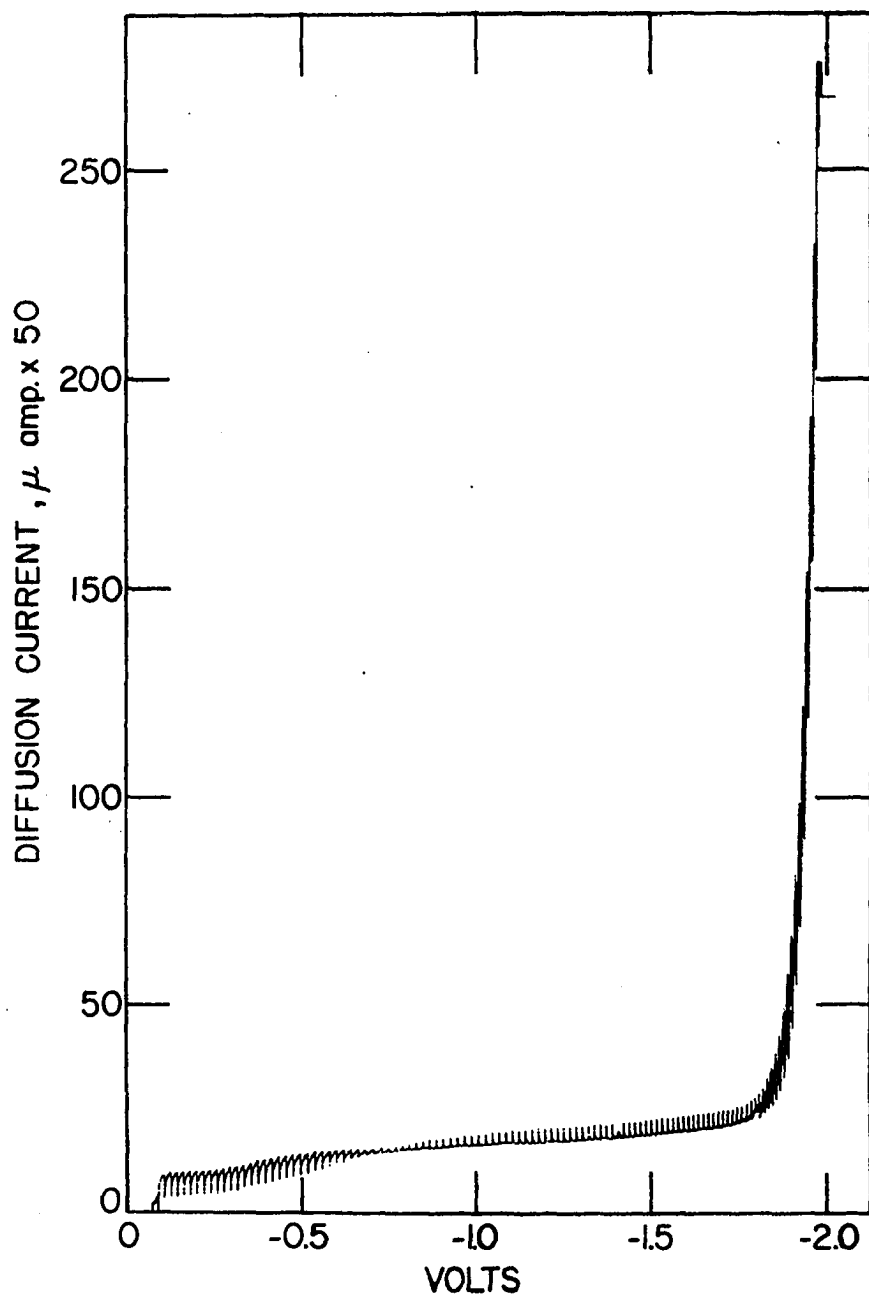
Figure 19. Polarogram in the absence of oxygen

A second solution was prepared and allowed to react while the diffusion current was measured at -0.52v which is at the top of the first oxygen wave. The results for the first 30 minutes and the residual current after the oxygen was removed are shown in Figure 20. From Figure 20 the percentages of oxygen present at 10 and 30 minutes of reaction time were calculated to be 93.75% and 83.8% of the initial oxygen concentration, respectively.

Wavelength

The visible spectrum of a silver-resorcinol reaction after 30 minutes at pH 11.5 is shown in Figure 21. The spectra were the same for the copper-catalyzed product, the silver-catalyzed product, the blank, and the silver-catalyzed product when corrected for the blank. Similar solutions were allowed to react at pH 11.5 and then the pH was adjusted to other values like 9.81 and 5.50 and the spectra recorded.

pH

Three studies of the pH variable were made and are shown in Figure 22. The first study used resorcinol which had reacted to a stable concentration of colored species. The pH of the aliquots of this solution was varied and the absorbance measured. It was learned that the absorbance increased with increasing pH. The second study allowed reactions to occur at various pH values and then the solutions were diluted with acid or base until the final pH and volume were 11.5 and 50 ml respectively for absorbance measurements. A maximum absorbance was obtained at pH 10.30 and decreased only slightly up to about pH 11.30. From these two pieces of data it was decided that over the pH range of 10.90 to 11.50 one should observe fairly con-
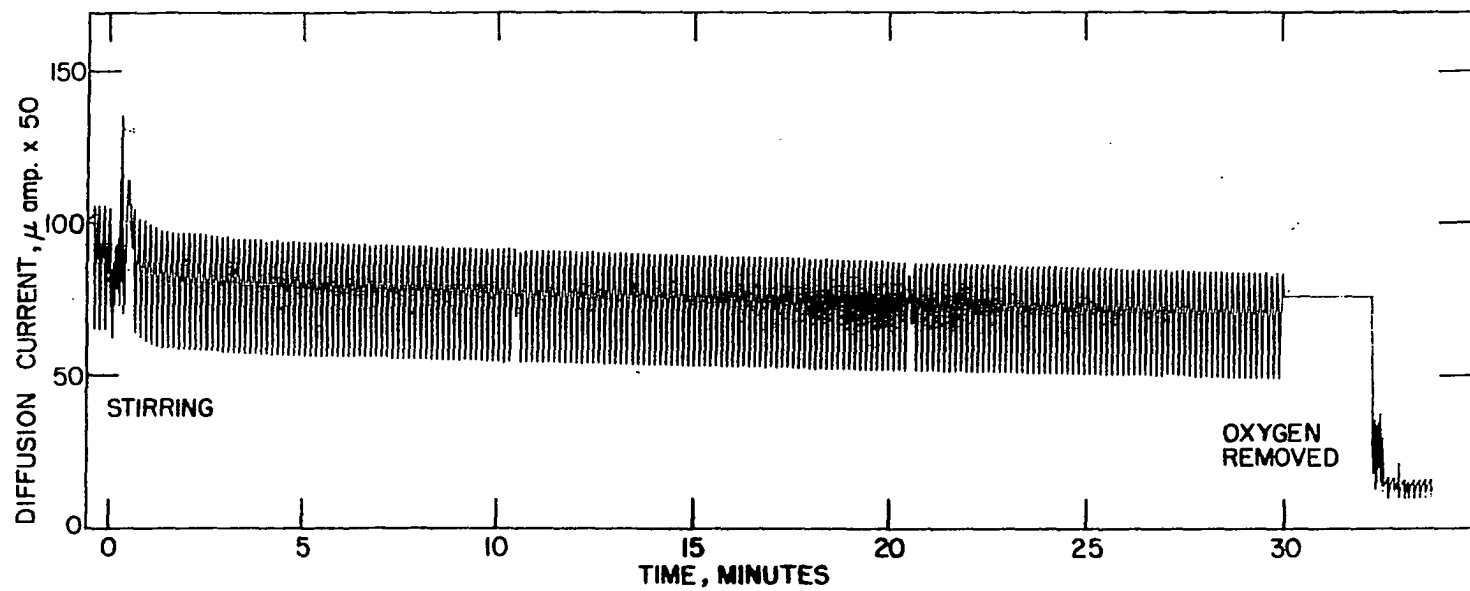
Figure 20. Effect of the silver-resorcinol reaction on the polarographic oxygen wave at -0.13v.
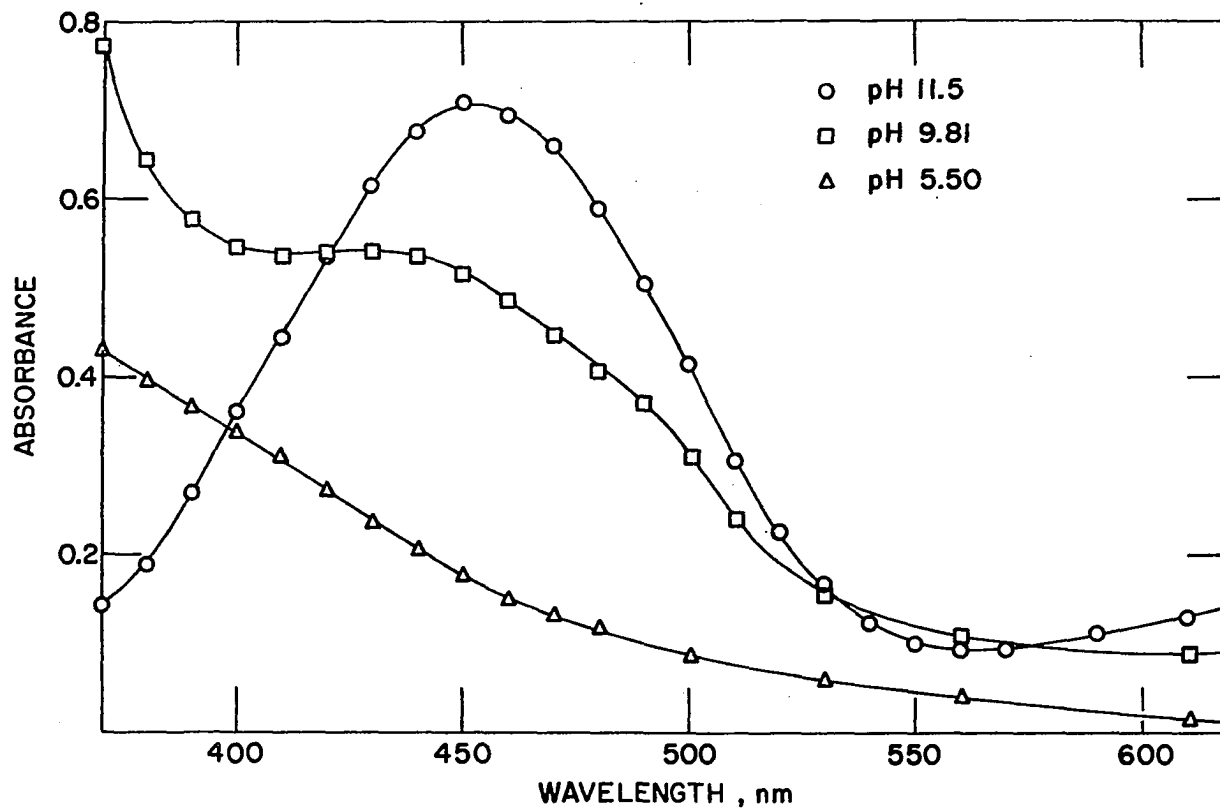
Figure 21. Absorbance of the autoxidation products of resorcinol
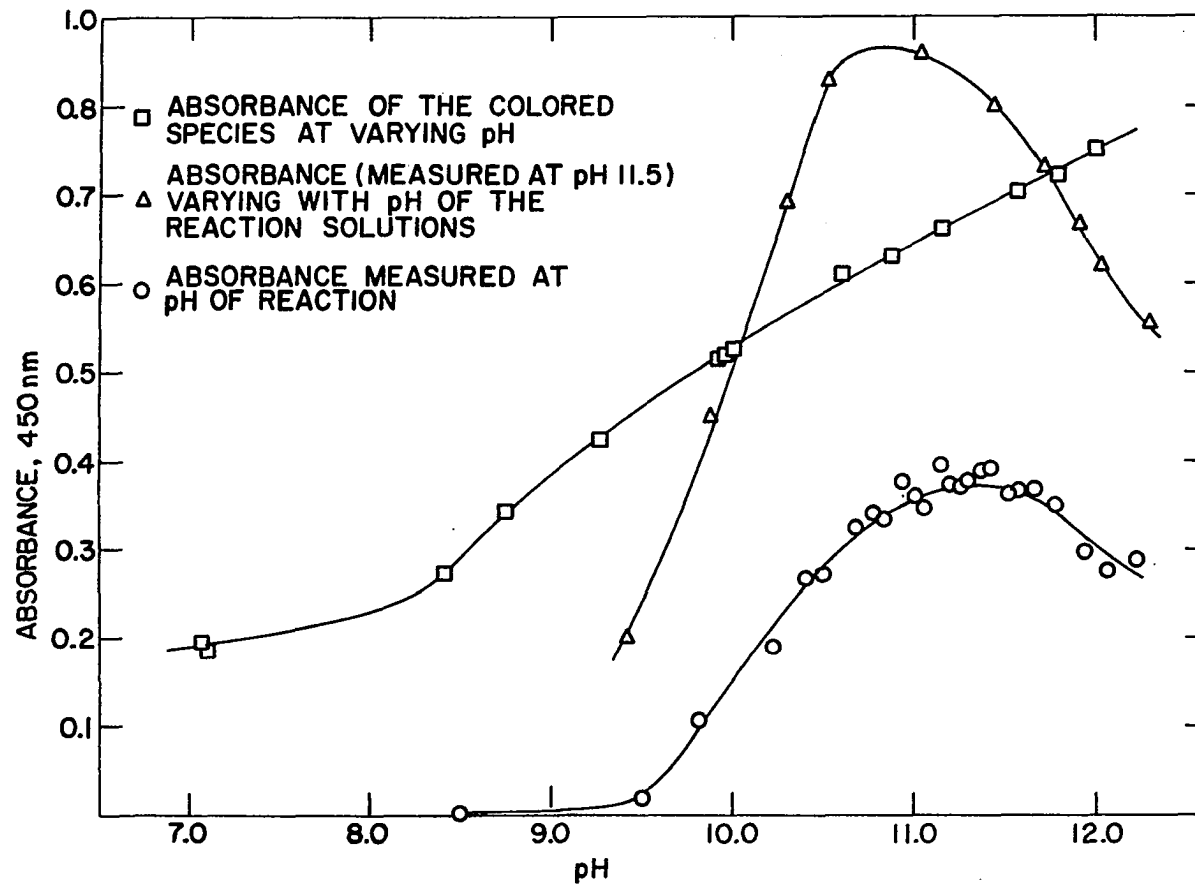
Figure 22. Influence of pH on the silver-resorcinol reaction

stant values for the absorbance. This assumption was checked by reacting solutions at various pH values and then measuring both the pH and the absorbance of each solution. It was found that absorbances of all solutions with pH values between 10.90 and 11.80 fell inside a ± 5% of the average value at pH 11.5 which was the reacting solution with buffer added.

Buffer

As can be seen from Figure 22, careful pH control is necessary. Lambert (8) used a 0.25 $\underline{M}$ phosphate buffer to maintain a pH of 11.5. Since 11.5 is the optimum pH for the silver-resorcinol reaction as well as the copper-resorcinol reaction, this same buffer was used. The effect of the concentration of the buffer was investigated by adding 10 or 15 ml of buffer solution instead of the normal 5 ml. There was no change in absorbance when the phosphate was increased.

An attempt was made to make a more concentrated buffer solution but the solubility of the phosphate salts did not allow more concentrated solutions at room temperature.

Since silver ores are normally dissolved in a concentrated acid, and since the reacting medium must be at pH 10.90 to pH 11.80, it was necessary to determine the maximum amount of hydrogen ion which could be tolerated without interference. This was determined by preparing a silver nitrate solution from pure silver nitrate and deionized water. Then 0.32 $\underline{M}$ nitric acid was used to add varying amounts of H^+ to the solutions. The maximum allowable amount was 0.0029 mole of H^+ for 5 ml of buffer solution in 25 ml of total volume.

Order of addition

Several orders of addition of reagents were tried to determine the most reproducible sequence. Since the resorcinol begins to react above pH 10, either the buffer or the resorcinol must be added last. No change in absorbance was observed for variations in the order of addition of silver, resorcinol, sodium citrate and buffer as long as this rule was followed.

Time

Figure 23 shows the effect of time on the absorbance of reacting resorcinol solutions containing 0, 20, 40, 60, 80, 100, and 150 μg silver. The resorcinol concentration was 0.04% in each reacting solution. Figure 24 shows a family of curves produced by varying the reaction time between 5 and 40 minutes for 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160 and 170 μg of silver.

Resorcinol

Measuring the absorbance of various silver concentrations (0-200 μg) for three different resorcinol concentrations (0.04%, 0.08% and 0.12%) produced three smooth curves suitable for analysis of silver. The absorbance was measured after a reaction time of ten minutes and plotted in Figure 25. A series of resorcinol concentrations, 0.016, 0.04, 0.08, 0.12 and 0.16%, were reacted for 35 minutes and the absorbance recorded. The same series was also studied with 50 and with 100 μg silver present. The results are shown in Figures 26, 27, and 28, respectively. Figures 29 and 23 show the reaction of 0.016% and 0.04% resorcinol respectively in the presence of 0, 20, 40, 60, 80, 100, and 150 μg silver.

The amount of resorcinol was varied to study the effect of concentra-
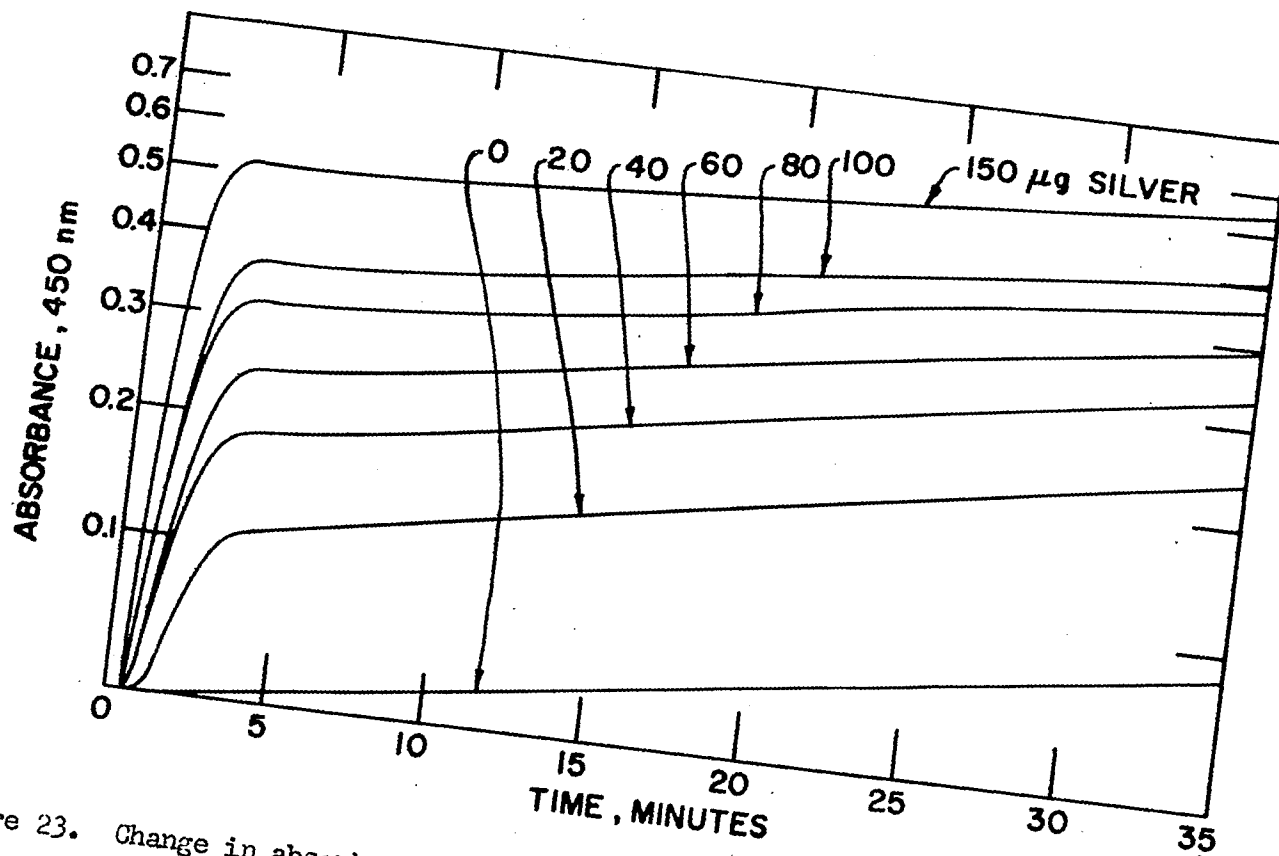
Figure 23. Change in absorbance with time for 0.04% resorcinol (25 ml)
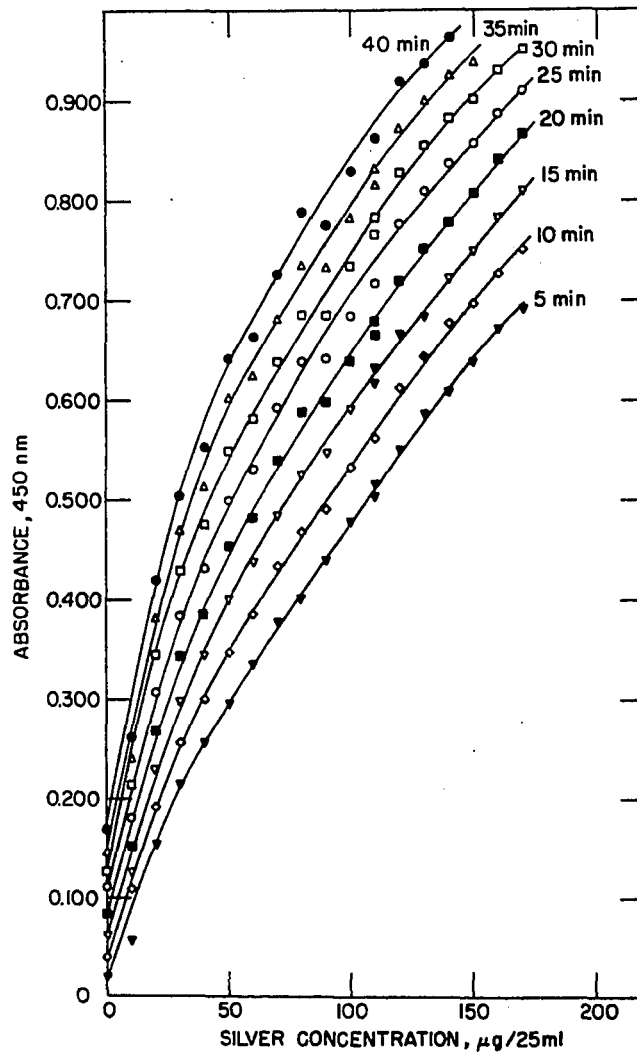
Figure 24. Variation of absorbance of 0.08% resorcinol with concentration of silver and reaction time
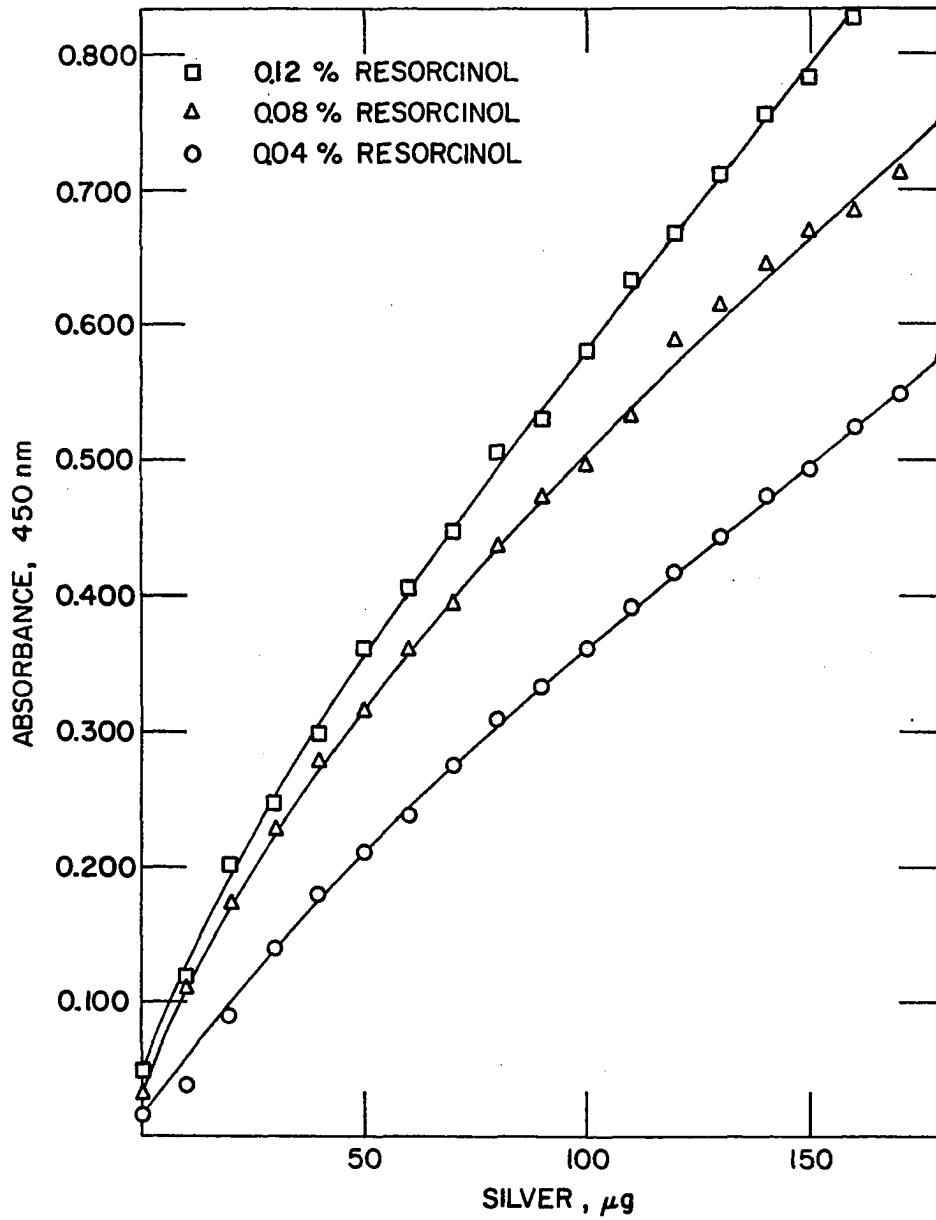
Figure 25. Calibration curves for silver
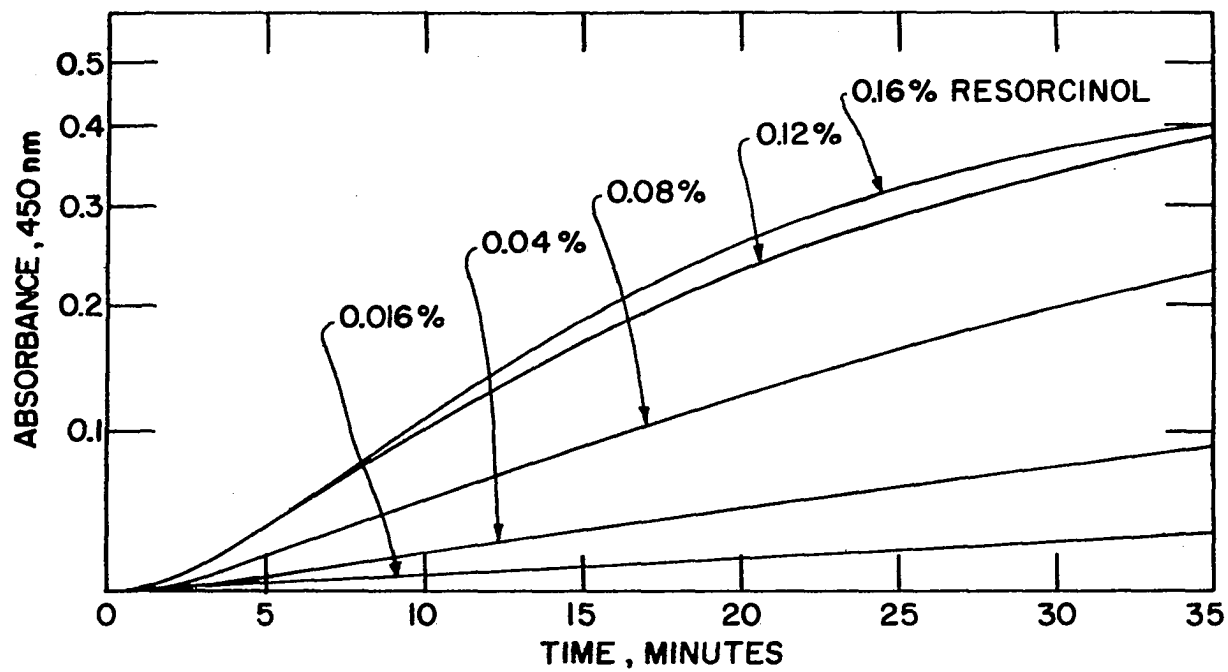
Figure 26. Change in absorbance of resorcinol with time (25 ml)
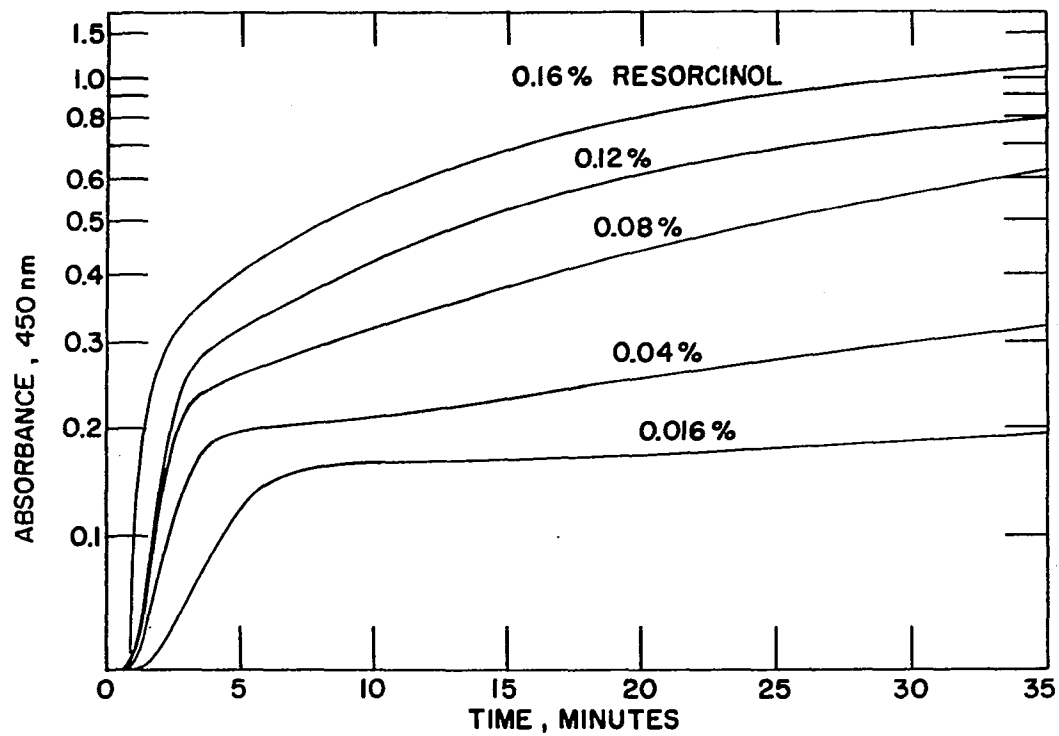
Figure 27. Change in absorbance of resorcinol with time in the presence of 50 μg silver/ 25 ml
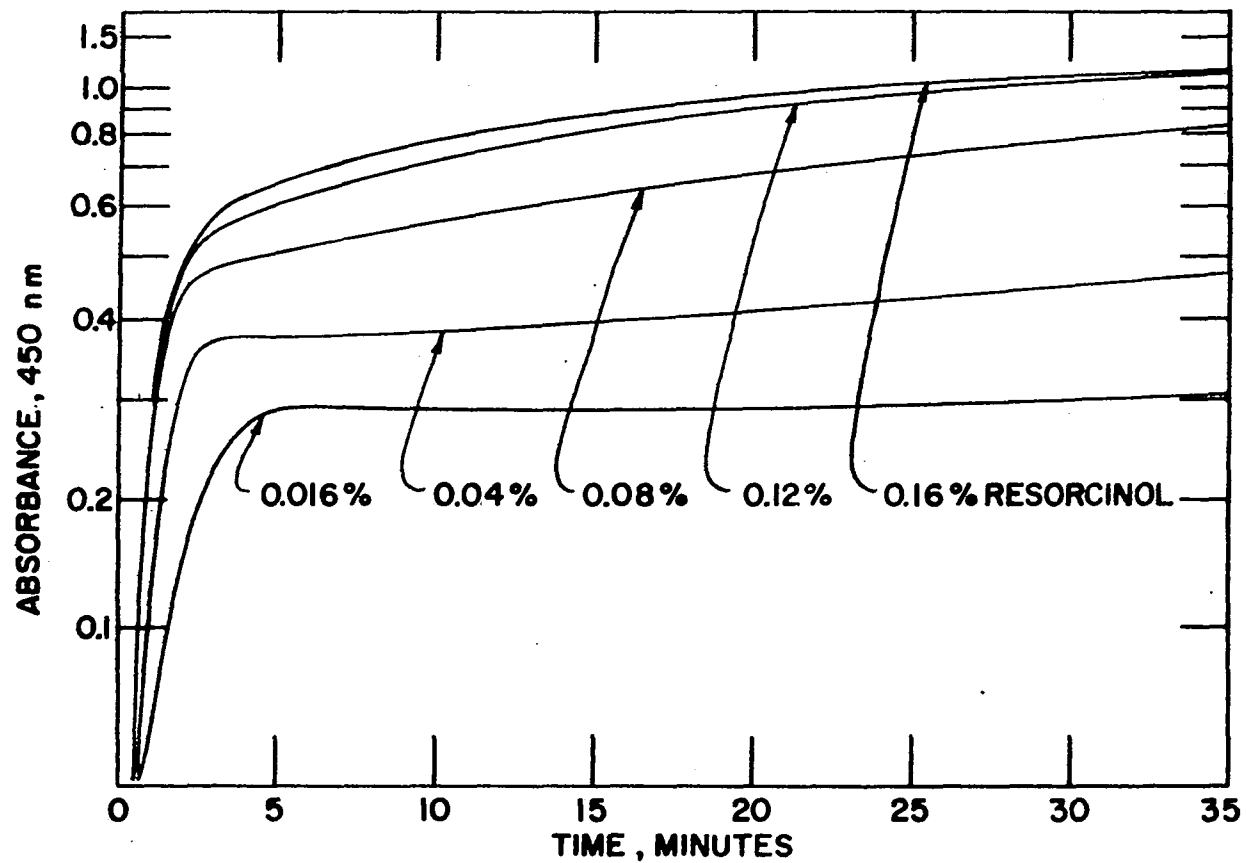
Figure 28. Change in absorbance of resorcinol with time in the presence of 100 μg silver/
25 ml
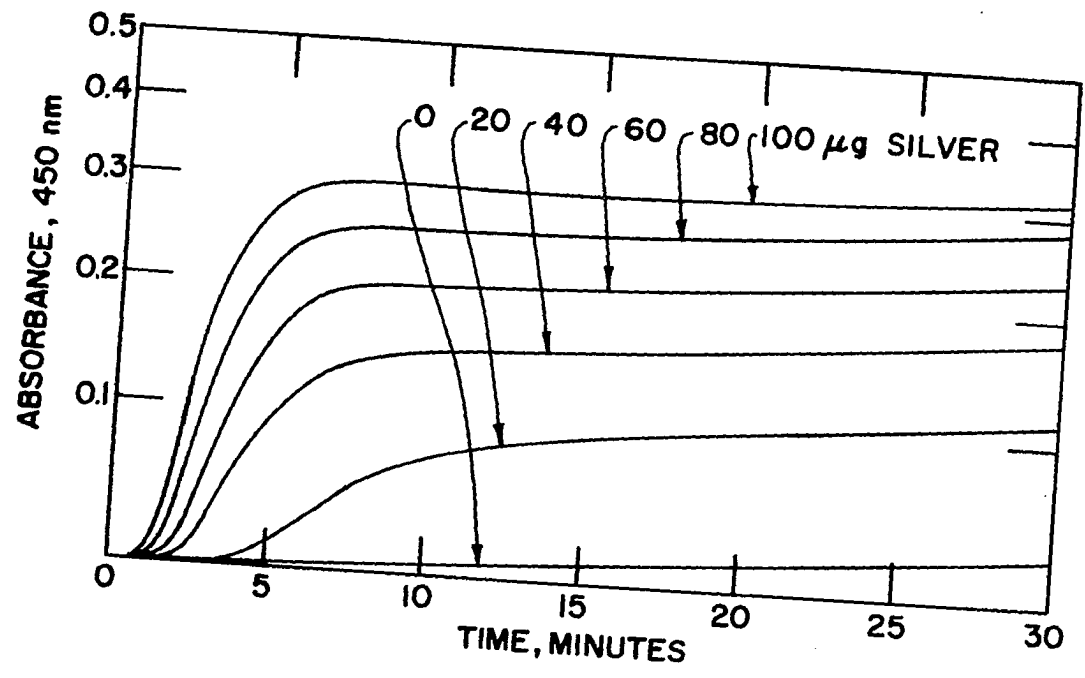
Figure 29. Change in absorbance with time for 0.016% resorcinol (25 ml)

tion of resorcinol on samples containing 0 to 10 μg of silver. The concentrations of resorcinol used were 0.04, 0.08, 0.12, 0.16 and 0.20%. These solutions of resorcinol were reacted in the absence of silver (Figure 30) and in the presence of ten μg of silver (Figure 31). At ten minutes of reaction time the differences in absorbance between the corresponding solutions of resorcinol in Figure 30 and Figure 31 are 0.07, 0.09, 0.103, 0.111, and 0.057, respectively. From these data it appears that either 0.12% or 0.16% should be the best resorcinol concentration for the analysis of less than ten μg of silver. The four resorcinol concentrations, 0.08, 0.12, 0.16, and 0.20%, were studied further. They were reacted with 0, 1, 2, 4, 6, 8, and 10 μg silver. The resulting absorbances for the first 35 minutes are shown in Figures 32 to 35.

Silver

The silver is present initially in the reaction solution as silver(I). Addition of sodium chloride right after the addition of buffer produces a white cloudiness in the solution. After ten minutes, when the activity of the silver in the solution has disappeared, no cloudiness was detectable on the addition of sodium chloride. Thus the silver(I) is apparently reduced to silver(0) by the reaction.

The effect of silver on the autoxidation of resorcinol has been illustrated in Figures 24 and 25. The useful range of the silver can be extended to higher concentrations as shown in Figure 36. The resorcinol concentration used in obtaining Figure 36 was 0.04%.

Calibration curves for 0 to 10 μg silver after ten minutes reaction time were prepared from the data in Figures 32 to 35. These calibration
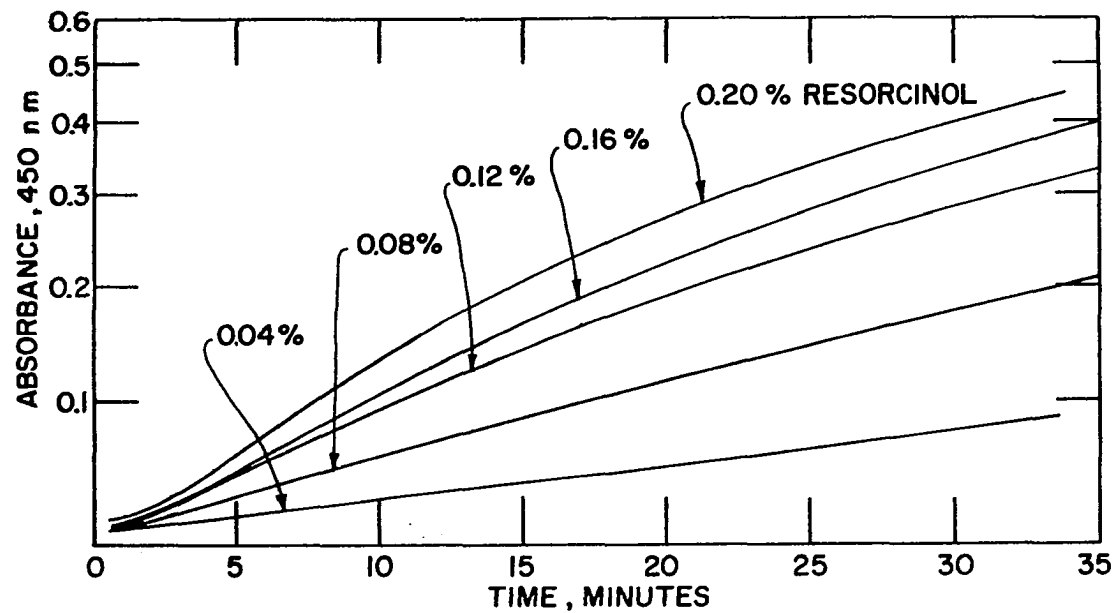
Figure 30. Change in the absorbance of solutions of resorcinol with time
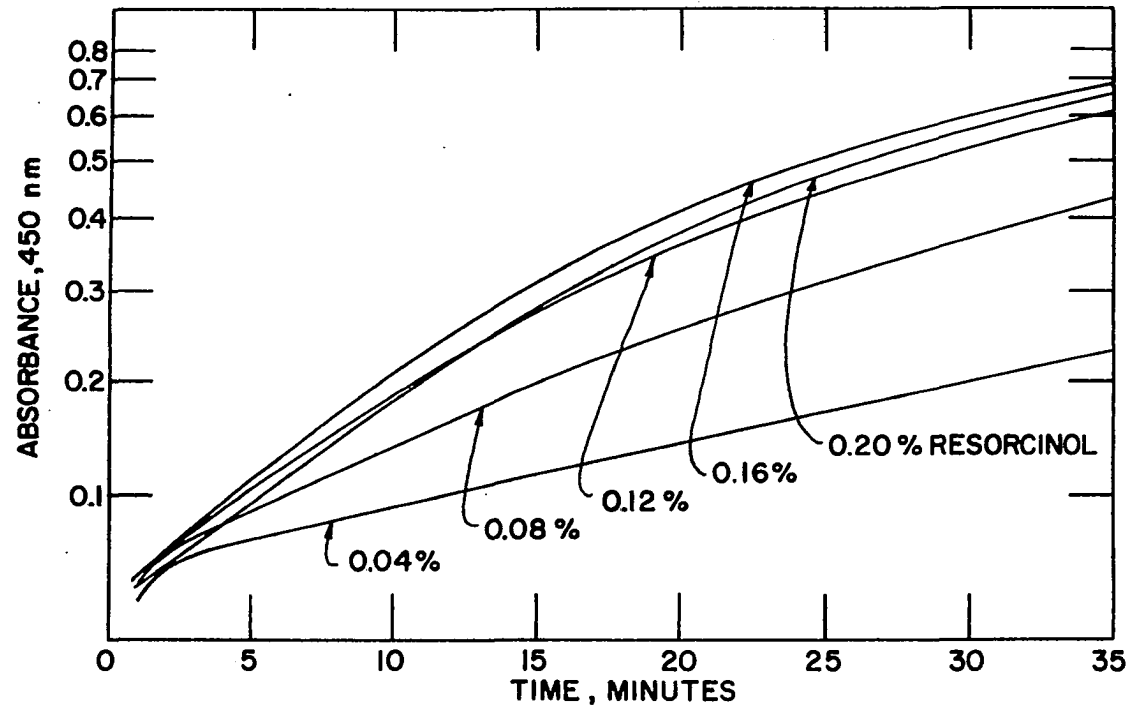
Figure 31. Change in the absorbance of solutions of resorcinol with time in the presence of 10 μg silver
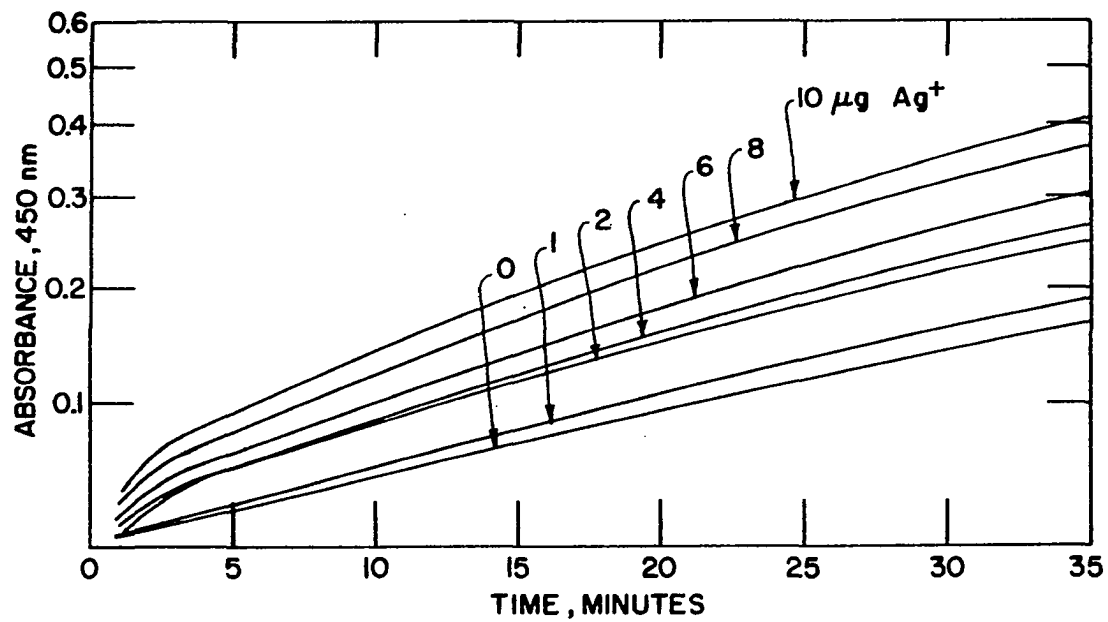
Figure 32. Change in the absorbance of solutions 0.08% in resorcinol with silver and time
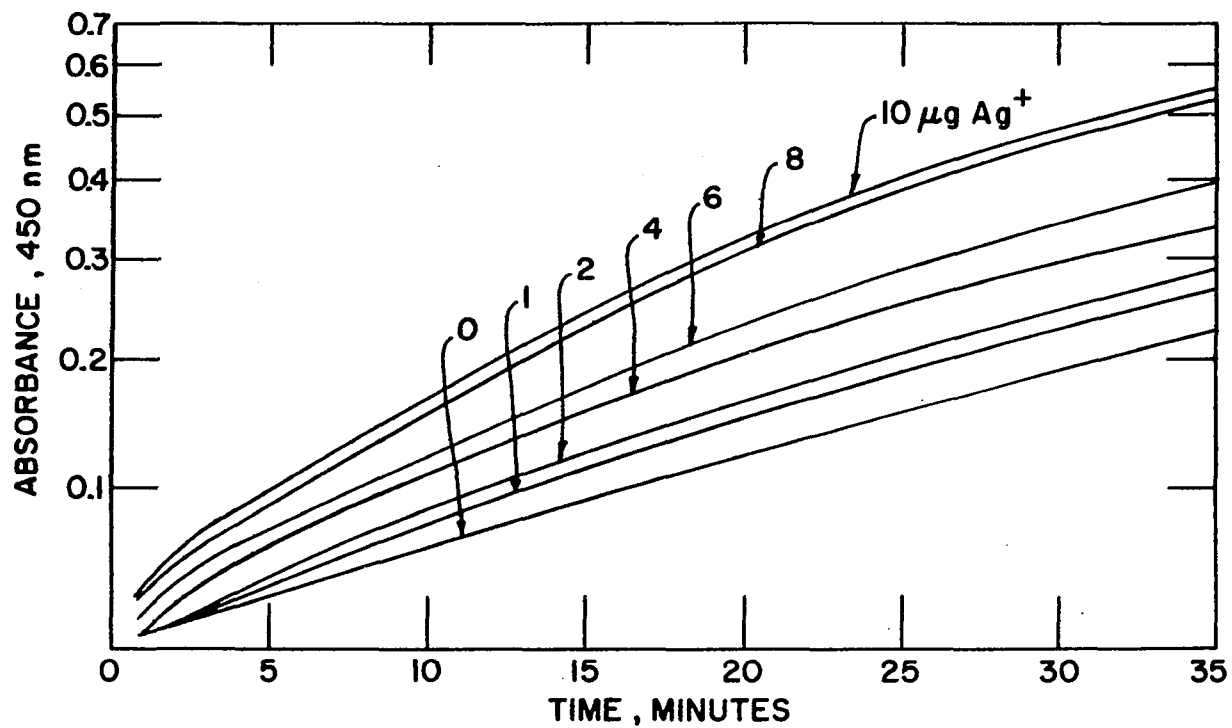
Figure 33. Change in the absorbance of solutions 0.12% in resorcinol with silver and time

54

Figure 34. Change in the absorbance of solutions 0.16% in resorcinol with silver and time

TIME, MINUTES

ABSORBANCE, 450 nm

10 μg Ag+

8

6

4

2

1

0
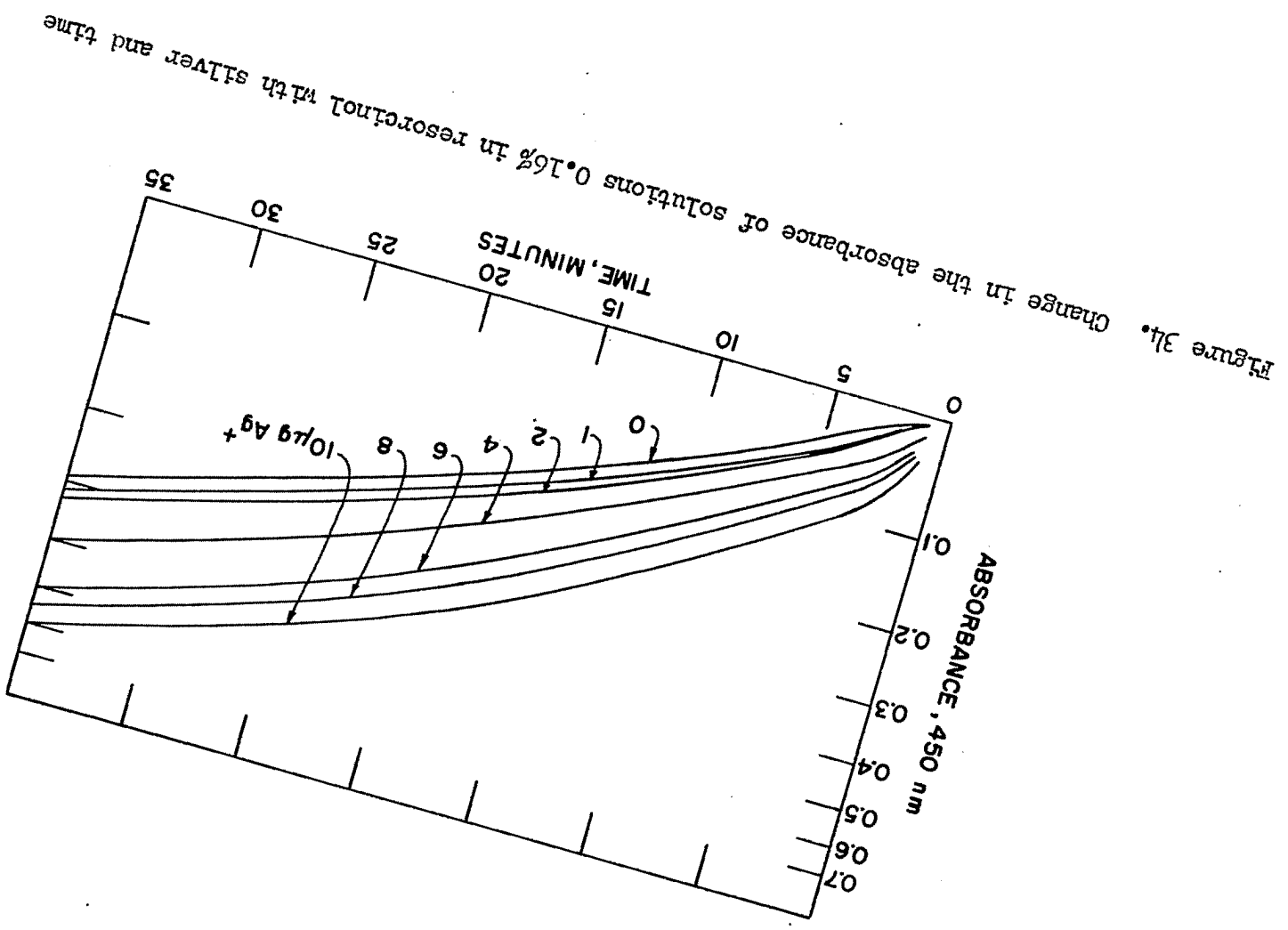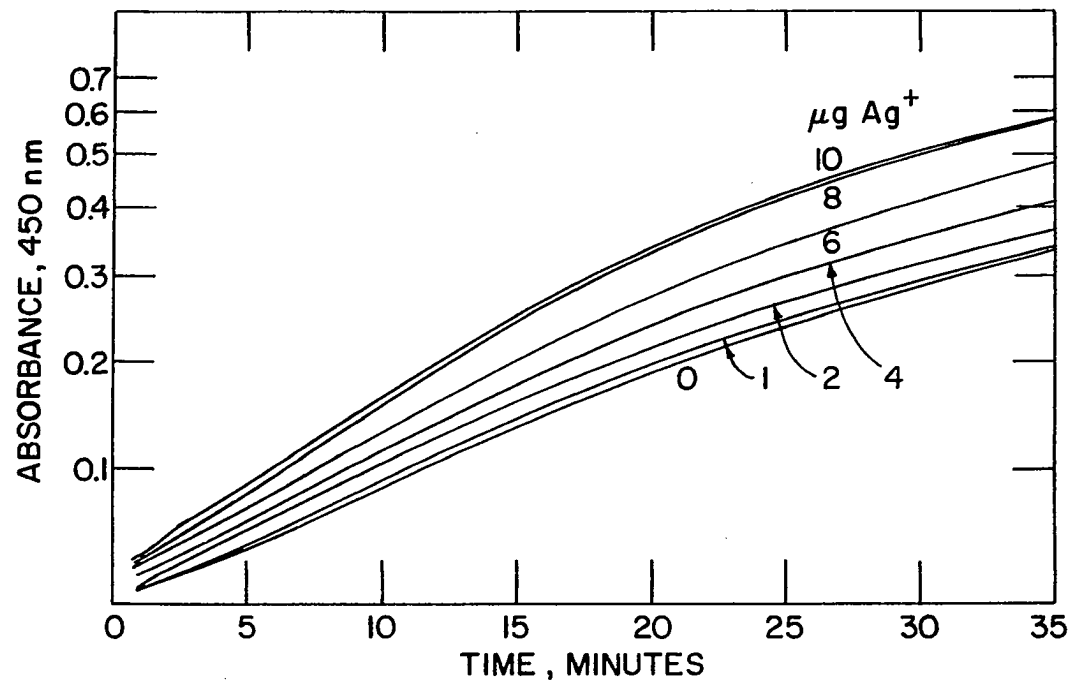
Figure 35.   Change in the absorbance of solutions 0.20% in resorcinol with silver and time
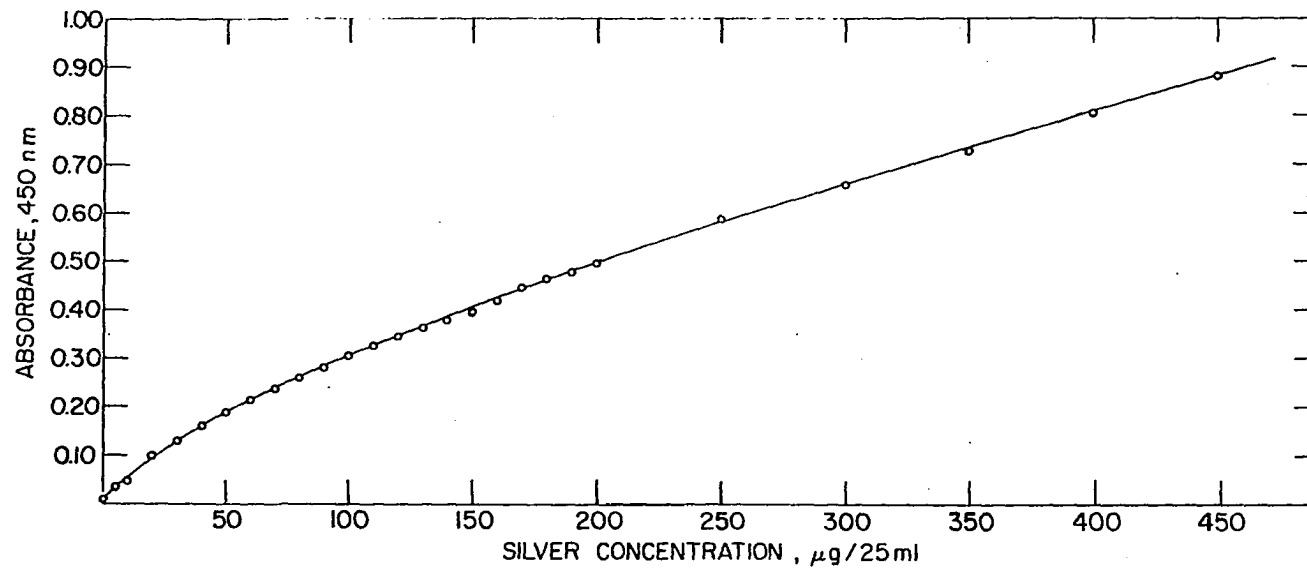
Figure 36. Calibration curve for the determination of silver using a 0.04% solution of resorcinol

curves are shown in Figure 37.

Temperature

The effect of temperature on the absorbance of autoxidizing solutions of resorcinol was studied using a Beckman DU spectrophotometer with a water-cooled sample compartment. The cooling water was circulated from a constant temperature reservoir by a varistatic pump. The procedure used was to study a series of solutions containing a constant amount of resorcinol and different concentrations of silver at each temperature. Five temperatures covering the range 20 to 30°C were studied. Thus there were five points showing the increase in absorbance with increasing temperature for each concentration of silver. The concentrations of silver studied were 0, 0, 2, 5, 10, 15, 20, 20, 50, 100, 150, and 200 μg of silver/25 ml of reacting solution. Since each set of points described a straight line, the slopes of these lines represent the effect of the temperature in terms of absorbance units (A.U.)/°C. See Figures 38 and 39. The slopes of these lines are 0.0013, 0.0008, 0.0011, 0.0016, 0.0024, 0.0023, 0.0014, 0.0022, 0.0018, 0.0022 and 0.0024 A.U./°C, respectively. The solutions containing 0 to 2 μg silver have an average slope of 0.001 A.U./°C. The solutions between 5 to 200 μg silver range from 0.0014 to 0.0024 A.U./°C with an average of 0.0020 A.U./°C.

Reaction volume

One ml of 2% resorcinol and 100 μg of silver when reacted in a 50-ml volume gave an absorbance of 0.3 and when reacted in a 25-ml volume gave an absorbance of about 0.6. Thus the volume of the reaction mixture was somewhat arbitrary. Volumes of 25 ml were consistently used in this study for
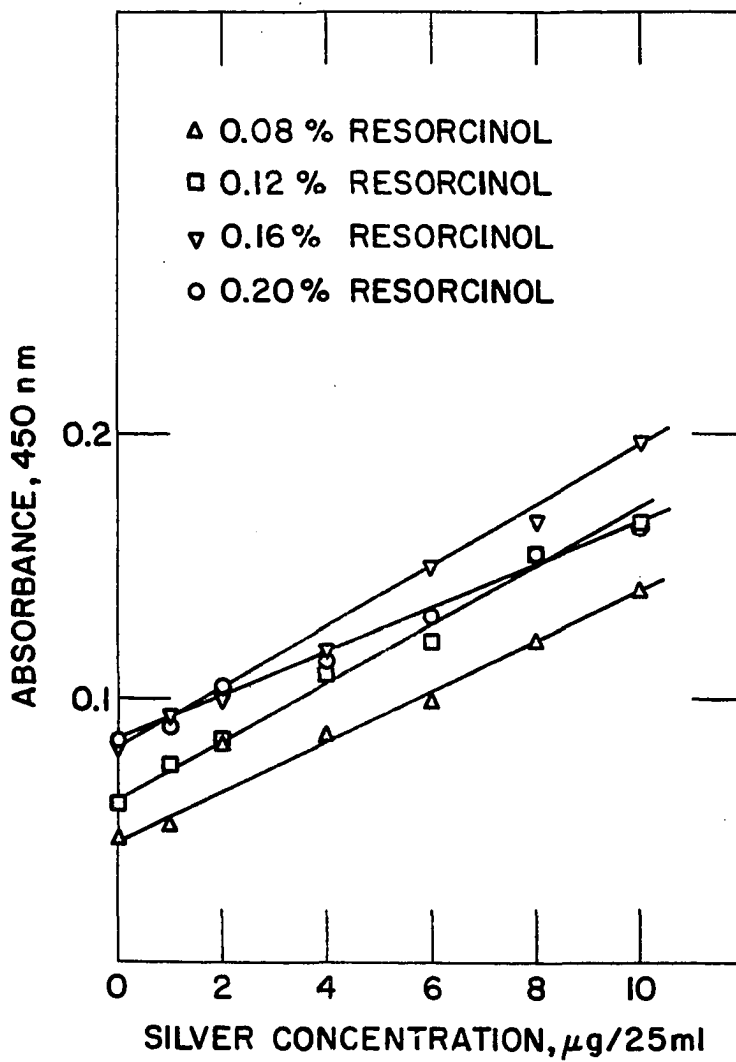
Figure 37. Comparison of the absorbance data from figures 33 to 36 at a reaction time of ten minutes
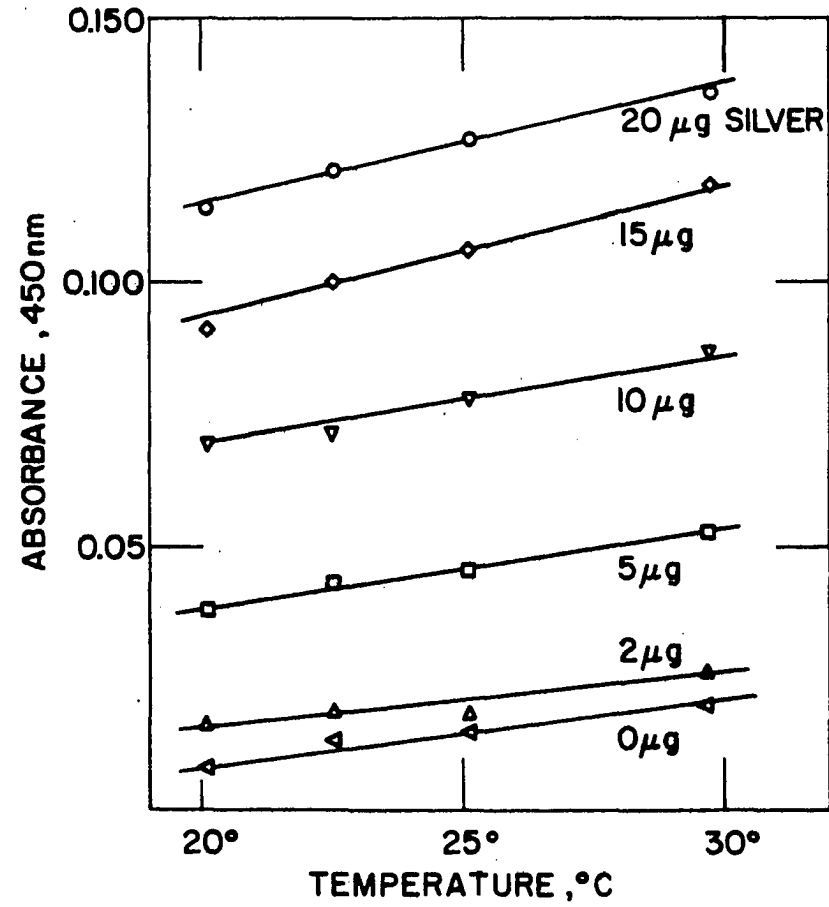
Figure 38. Effect of temperature on absorbance
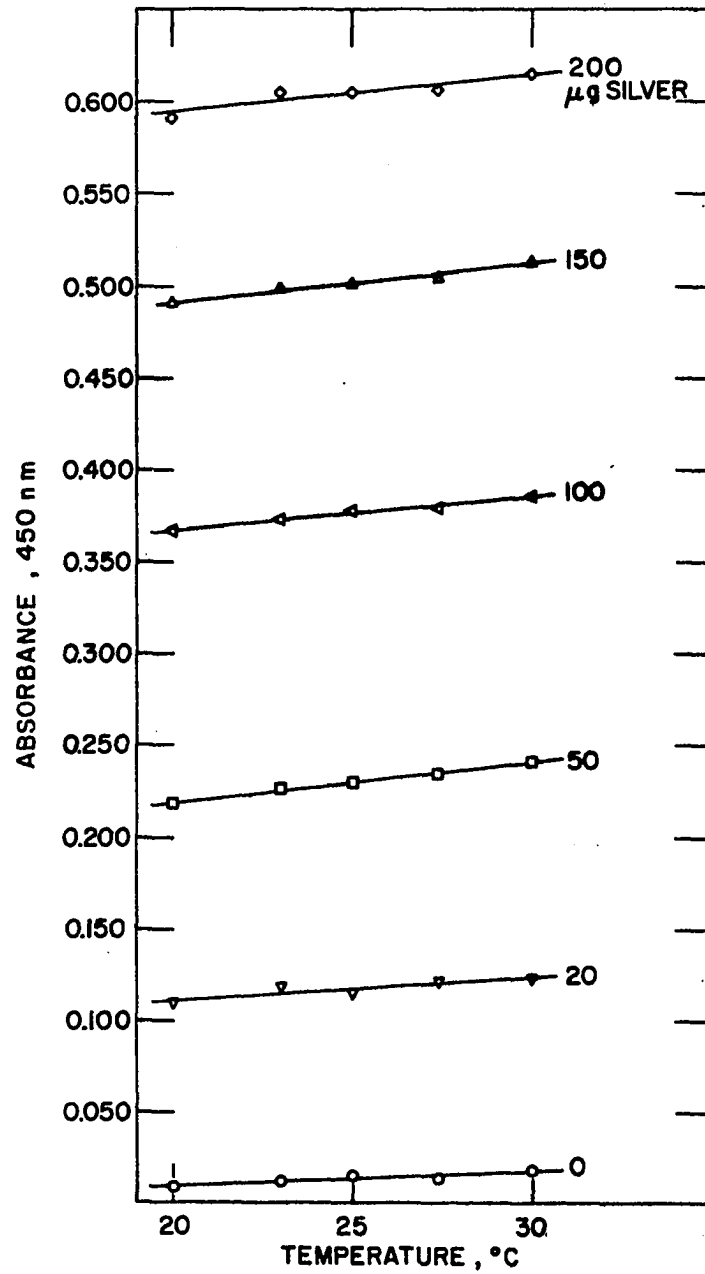
Figure 39. Effect of temperature on absorbance

convenience, since volumetric flasks were used as reaction vessels.

Light

Since compounds of silver are sometimes light sensitive, it was thought that light might have an effect on the reaction, but there was no apparent change in absorbance due to daylight, darkness or artificial light.

Copper

Figure 40 was obtained by reacting 0.016, 0.04, 0.08, 0.12, and 0.16% resorcinol in the presence of 0.5 µg copper(II). A 0.4% stock solution of resorcinol and a solution containing 0.1 µg/ml copper(II) were used. The change in absorbance was measured periodically for 35 minutes after the phosphate buffer was added to initiate the reaction.

Figures 40 and 26 were compared to determine the optimum concentration of resorcinol. Since the reaction becomes more sensitive to copper with increasing concentrations of resorcinol instead of leveling off like silver does, 0.08% resorcinol was selected to study the variation of copper at one concentration of resorcinol. This is shown in Figure 41. The concentrations of copper used were 0, 0.2, 0.4, 0.6, 0.8, and 1.0 µg copper(II)/25 ml volume.

Figure 42 shows a calibration curve for copper with 0.08% resorcinol and 30 minutes reaction time. Concentrations of copper measured were 0, 0.4, 0.6, 1.0, 1.2, and 1.4 µg of copper/25 ml. Each absorbance value except the 1.4 µg value is an average of three samples.

Masking copper

In order to make the autoxidation more selective for silver it was necessary to find a reagent which would destroy the activity of the copper
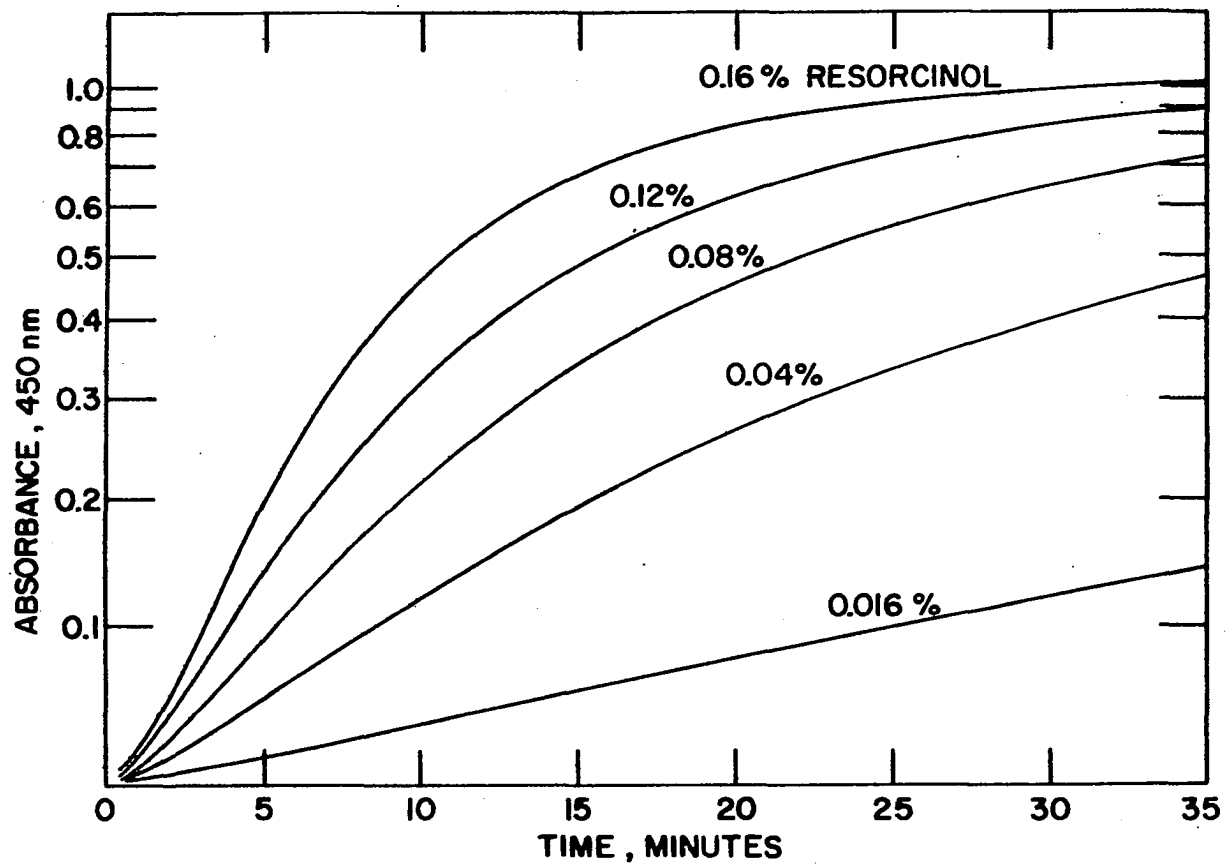
Figure 40. Change in the absorbance with time for 0.5 μg copper/25 ml
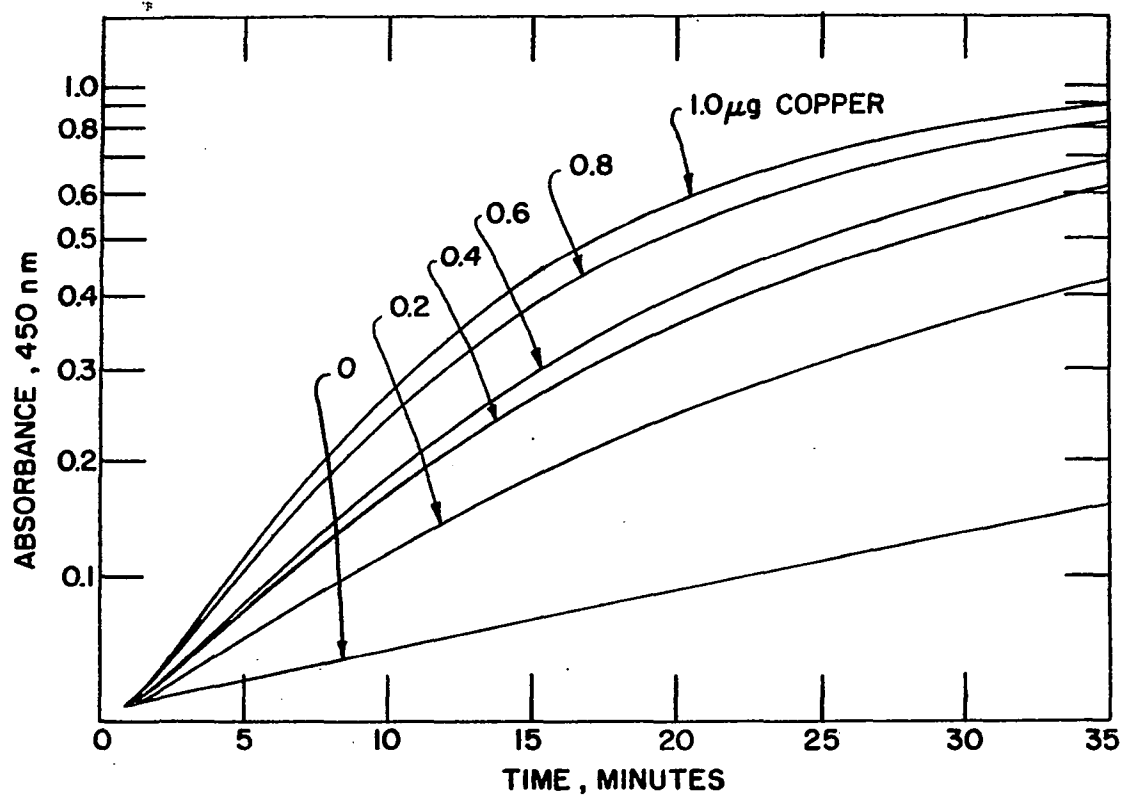
Figure 41. Change in the absorbance with time for 25 ml of 0.08% resorcinol
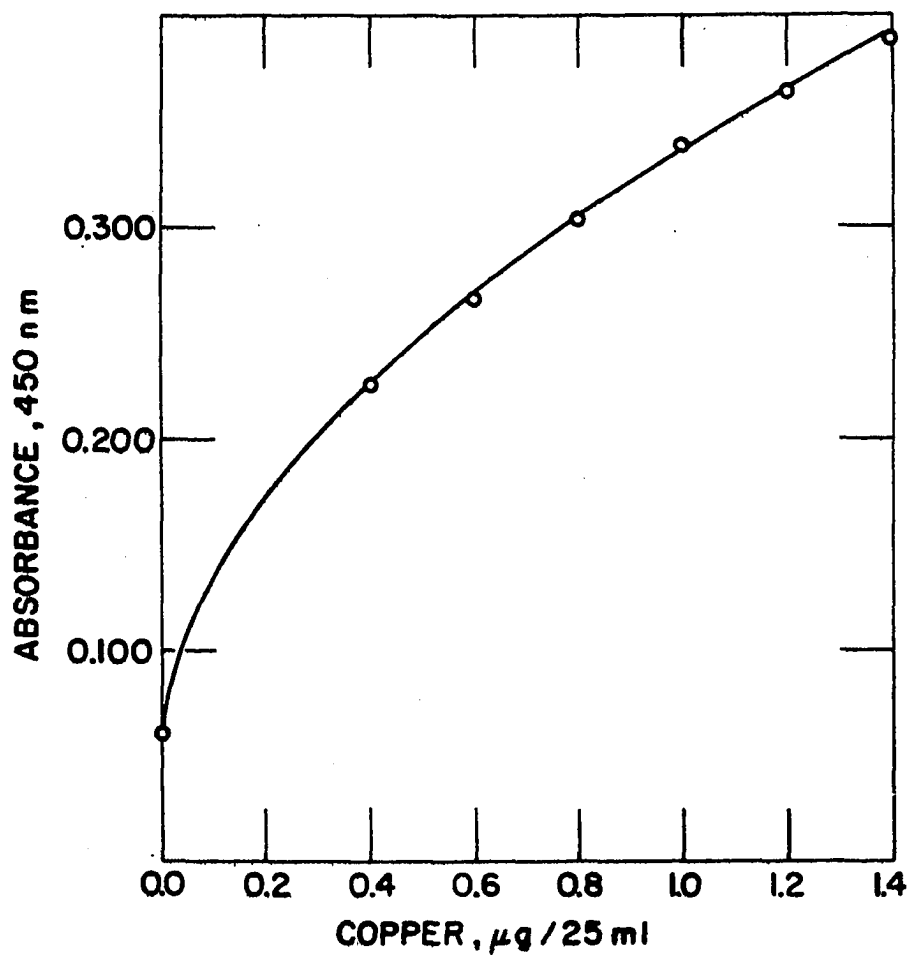
Figure 42. Calibration curve for the determination of copper in 0.08% resorcinol

but not interfere with the silver-resorcinol reaction.

Cuproine was tried as a method of extracting the copper (35). Copper (II) must be reduced to copper(I) to be extracted into isoamyl alcohol by the cuproine. Hydroxylamine hydrochloride and sodium sulfite were used as reducing agents. This was unsuccessful since the silver was reduced with the copper (36).

EDTA was used by Slater (9) to quench the copper reaction. There is a substantial difference in the conditional formation constants for the silver-EDTA (log K = 5.9) and copper-EDTA (log K = 17.7) complexes (37) at pH 11.5. The effect of EDTA on the blank, copper and silver-resorcinol reactions are shown in Figure 43.

In order to locate other complexing agents the book by Martell and Sillen (38) on stability constants was consulted. Ascorbic acid, histidine, sodium tartrate and sodium citrate all appeared to have large separations between the formation constants of the copper and silver complexes. Ascorbic acid retarded the action of both copper and silver on the resorcinol. Histidine (Figure 44) complexed the copper first but its range of usefulness was no greater than that of EDTA. The effect of sodium tartrate on the reaction can be seen in Figure 45. Sodium citrate masked copper below 10 µg/ 25 ml and did not interfere with the silver-resorcinol reaction at any concentration up to 0.4 M. The effect of citrate on the copper-resorcinol reaction is shown in Figure 46.

Interferences

A literature survey was made to determine the ores which contain silver and the elements commonly found with it in nature (39-43). The common
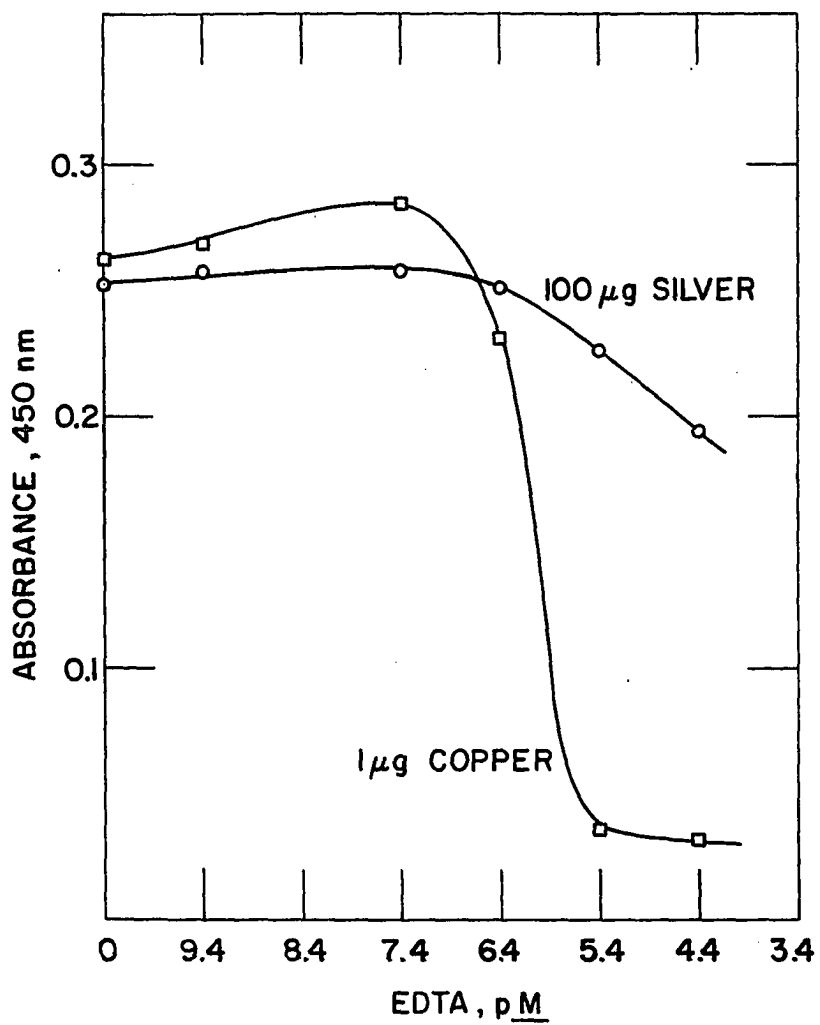
Figure 43. Effect of EDTA on the copper-resorcinol and silver-resorcinol reactions
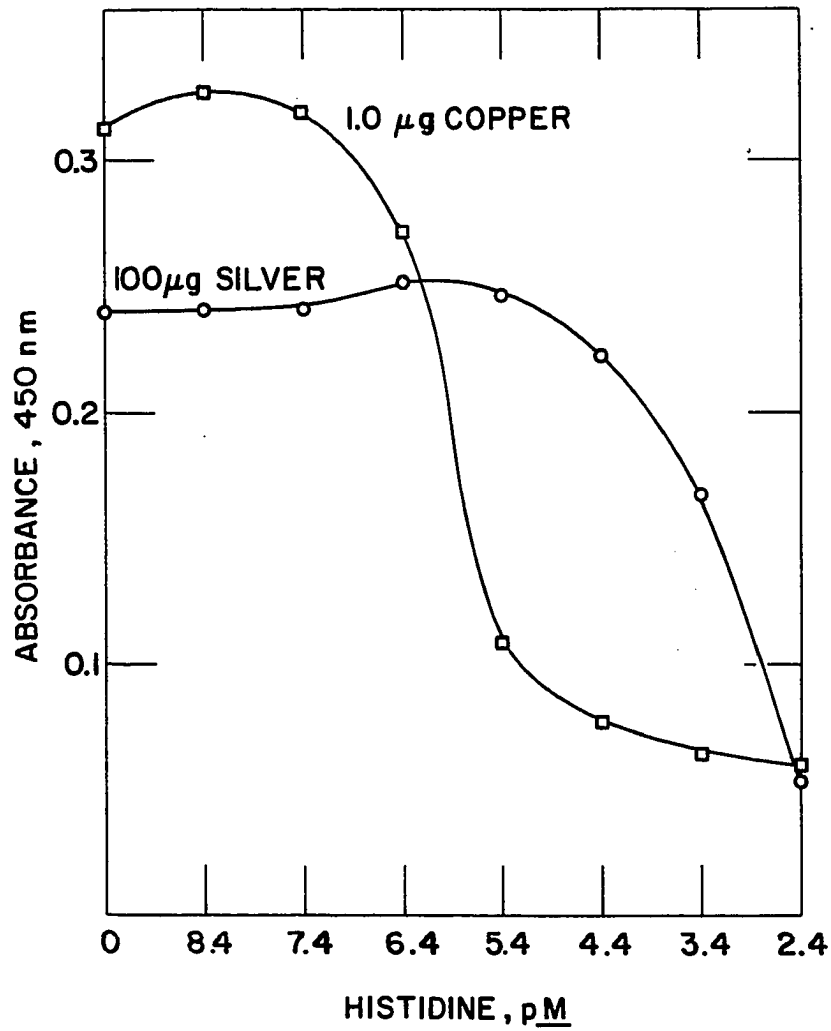
Figure 44. Effect of histidine on the silver-resorcinol and copper-resorcinol reactions
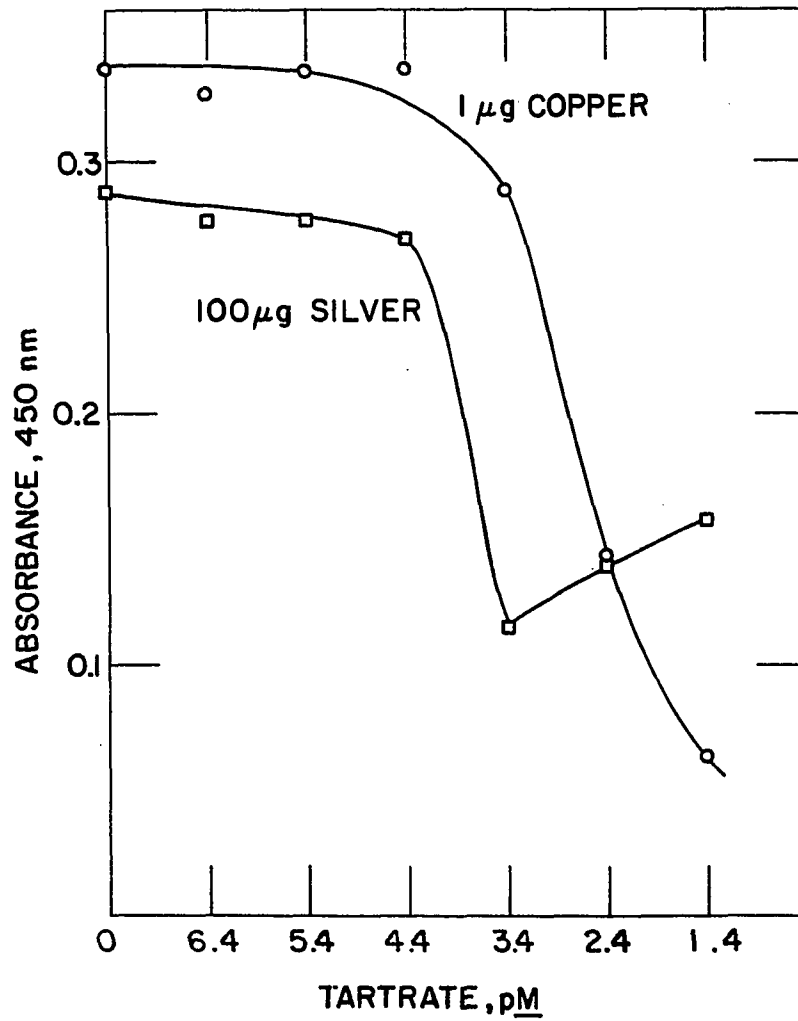
Figure 45. Effect of tartrate on the copper-resorcinol and silver-resorcinol reactions
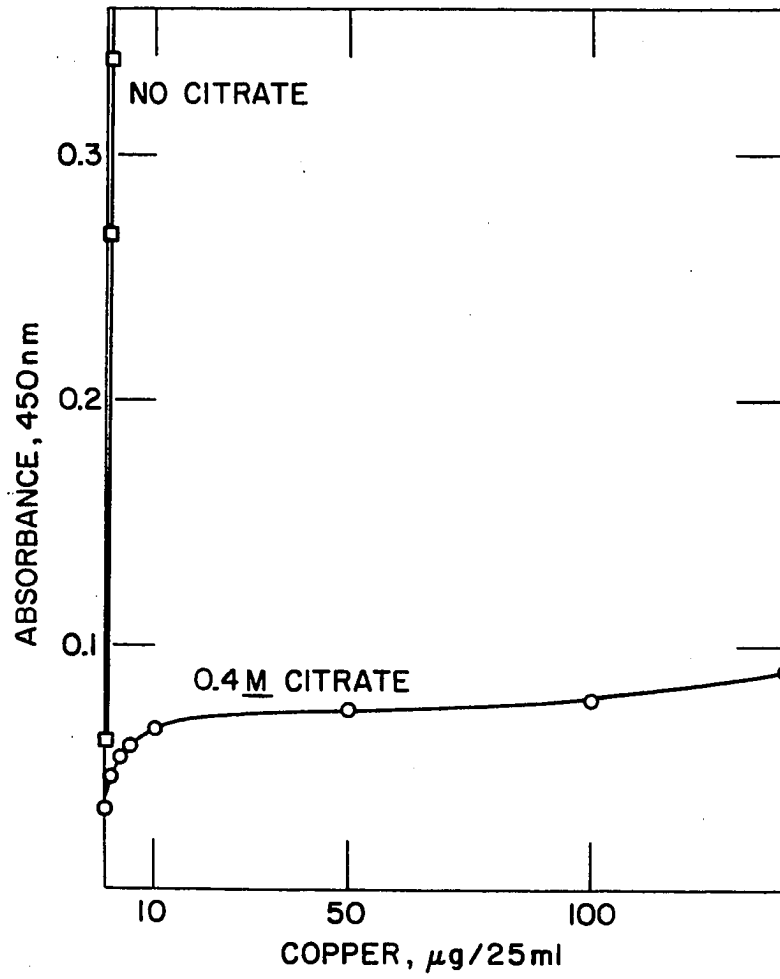
Figure 46. Effect of citrate on the copper-resorcinol reaction

silver-bearing ores are: native silver, Ag; native gold, Au; chalcocite, Cu_2S; argentite, Ag_2S; galena, PbS; proustite, Ag_3AsS_3; stephanite, Ag_5SbS_4; pyrargyrite, Ag_3SbS_3; tetrahedrite, $(Cu,Fe,Ag,Zn)_{12}Sb_4S_{13}$; tennantite, $(Cu,Fe,Ag,Zn)_{12}As_4S_{13}$; and niccolite, NiAs. The elements found in these and associated minerals are Pb, As, Sb, Au, Hg, Cu, Ni, Fe, Zn, Mg, Mn, Ca, Ba, U, Bi, Al, Se, Te, Tl, Ge, Sn, S, Cl, Br, I, Si, and C. Since these elements are the most likely to interfere, attempts were made to test their levels of interference.

The solubility of the ores was also investigated. Silver halides are soluble in ammonium hydroxide. Almost all of the sulfide minerals containing silver are soluble in nitric acid. The selenide and telluride minerals and many of the miscellaneous minerals are soluble in nitric acid.

The levels at which various anions and cations interfered with the silver method were determined for the ions listed in Tables 2 and 3. The procedure used to determine the interference levels of these ions was to run a sample containing 100 μg of silver by the normal procedure with the amount of interfering ion added prior to the addition of the buffer. For convenience solutions of resorcinol and silver were combined such that the stock solution was 0.1% in resorcinol and 10 μg/ml in silver. With 10 ml of this solution and 5 ml of buffer-citrate solution added to initiate the reaction, 10 ml of volume was available for the addition of the interfering ion. Usually this was done for ion concentrations of 5, 50, and 500 μg/25 ml and 5, 50, and 500 mg/25 ml. The level of interference used here is the concentration of the ion at which the absorbance of the solution no longer falls within $\pm$ 5% of the correct value.

Table 2. Levels of interference of cations

Cation	mg/25 ml	Means of interference[*]	Cation	mg/25 ml	Means of interference[*]
Na^+	1110		Fe^{+3}	5	d
K^+	500	a	Al^{+3}	5	b
Li^+	50	c	Tl^{+3}	0.5	b
NH_4^+	0.5	b	Cr^{+3}	0.5	a
Hg^+	0.5	b	Bi^{+3}	0.5	b
Cu^+	0.05	b	Dy^{+3}	5	b
Hg^{+2}	0.5	b	Er^{+3}	5	
Ba^{+2}	5	c	Eu^{+3}	0.5	b
Sr^{+2}	5	c	Ho^{+3}	5	b
Ca^{+2}	5	b	La^{+3}	0.5	a
Mg^{+2}	50	c	Lu^{+3}	0.5	a
Co^{+2}	0.05	d	Pr^{+3}	5	c
Zn^{+2}	5	b	Tm^{+3}	50	b
Pb^{+2}	0.05	c	Tb^{+3}	0.5	a
Ni^{+2}	0.5	d	Yb^{+3}	50	b
Cu^{+2}	0.015	a	Sm^{+3}	0.5	b
Fe^{+2}	0.5	b	Nd^{+3}	0.05	a
Cd^{+2}	5	b	Gd^{+3}	0.5	b

[*]a means high results; b means low results; c means precipitate formed; d means colored complex or ion.

Table 3. Levels of interference of cations and anions

Ion	mg/25 ml	Means of interference[*]	Anion	mg/25 ml	Means of interference[*]
Au^{+3}	0.05	a	IO_3^-	500	b
Th^{+4}	50	c	SO_4^{-2}	500	
Sn^{+4}	0.05	b	S^{-2}	0.005	b
Ce^{+4}	0.5	b	SO_3^{-2}	5	b
Pt^{+4}	0.5	a	CO_3^{-2}	500	b
UO_2^{+2}	0.5	d	CrO_4^{-2}	5	a
NO_3^-	500		MoO_4^{-2}	500	
ClO_4^-	500		$S_2O_8^{-2}$	0.5	a
Ac^-	500		$S_2O_3^{-2}$	0.005	b
Cl^-	0.5	c	$C_2O_4^{-2}$	50	
Br^-	0.05	c	AsO_4^{-3}	5	b
I^-	0.05	b	PO_4^{-3}	327	
NO_2^-	0.5	a	$Fe(CN)_6^{-3}$	0.05	b
CN^-	0.05	b	$Fe(CN)_6^{-4}$	0.005	b
F^-	500		EDTA	0.0037	b
VO_3^-	0.5		Tartrate	0.23	b
CNS^-	0.05	b	Citrate	1890	
ClO_3^-	500				

[*]a means high results; b means low results; c means precipitate formed; d means colored complex or ion.

Applications

Three 0.02-g portions of silver solder were weighed out, dissolved in a few drops of nitric acid, diluted to one liter and 10-ml aliquots used for analysis. Three aliquots of each sample were analyzed and the average value was used in each case. To an additional three aliquots of each sample, 5-μg portions of silver were added. The silver concentrations of these spiked aliquots were determined from the calibration curve just like the other aliquots except 5 μg was subtracted before the calculation of the percentage of silver. Results for the first three determinations were 51.65, 52.04 and 51.46% silver. Results for the silver spiked determinations were 51.55, 51.94 and 51.36% silver. The overall average was 51.67%. When this is compared to the gravimetric result of 50.92% by Diehl and Butler (44), the error was +1.5%. Other constituents of the silver solder according to Diehl and Butler (44) are 15.74% copper, 17.0% cadmium and 15.9% zinc.

Two lead ores were obtained from Professor Harvey Diehl. The one ore was 0.9% copper and 0.2% silver while the other was 0.8% copper and 0.5% silver as determined by emission spectrographic analysis by Mr. Ed De Kalb. Since standards were not available, the accuracy of the analysis is probably not better than ±30%. Qualitatively the analysis indicated that the same elements were present in both ores. Aluminum, iron, calcium, lead and silicon were major constituents of both ores. The first ore had more lead, less silica and also had zinc as a major constituent. Minor components of both ores included silver, copper, magnesium, manganese, antimony and titanium. The second ore also had barium and zinc present in small

amounts. Traces of arsenic, boron, cadmium, cobalt, chromium, tin, molybdinum, nickel, phosphorus, and strontium were present also.

The large amount of silica present led to difficulties in dissolving the ore samples. An equivolume mixture of perchloric and nitric acids, perchloric acid alone, sodium carbonate fusion, and treatment with HF were all found unsatisfactory for the dissolution of the ores. An equivolume mixture of perchloric and phosphoric acids was found to do the best job of dissolving the ore samples. The first ore contains 9.6% silica and 4.2% other insoluble residue left after HF treatment of the material which did not dissolve in the perchloric-phosphoric acid mixture. The second ore contained 41.3% silica and 15.5% other insoluble residue after HF treatment. Emission spectrographic analysis of the residues left after digestion with equivolume perchloric-phosphoric acid indicated that the insoluble material is mostly silica with some lead, titanium, aluminum, barium, and silver present also.

A violet colored solution was obtained when the ores were digested with the perchloric-phosphoric acid mixture. When water was added this solution changed from violet to pink. The pink goes to colorless when reduced with metallic zinc and to wine red when oxidized by periodate so it is caused by Mn(III). The manganese present in the ore is oxidized to Mn(III) by the perchloric acid and stabilized by the phosphate present. The pink color interferes with the spectrophotometric silver-resorcinol method. Addition of a small amount of ferrous carbonate reduced the Mn (III) to Mn(II). Subsequent analysis of the samples indicated no reactivity in the resorcinol method, even when silver was added to the solutions.

Apparently some component of the ore solution was causing interference. The ores were not studied further.

Discussion

Introduction

The effect of silver on the autoxidation of resorcinol has never been studied previously. This effect was studied and a method for analyzing 1-400 μg of silver in 15 ml of solution was proposed and tested.

Mechanism of autoxidation

The colored product of the reaction, which was measured spectrophotometrically, was 2(4-resorcyl),5-hydroxyhydroquinone which was formed when the monoanion of resorcinol reacted with hydroxyquinone. The hydroxyquinone was the product of air oxidation of another molecule of resorcinol. ESR studies, ultraviolet spectra and studies of derivatives of resorcinol indicated that this was the mechanism which occurred. The rate determining step was the electrophilic attack of oxygen on the anion. All further steps were fast until the diphenomonoquinone was formed. This species was stable in terms of hours rather than seconds at pH 11.5.

Cations which stimulate the reaction would presumably have to speed up the slow step in the reaction sequence. Copper(II) and silver(I) can both influence the reaction by forming free radicals of resorcinol or the subsequent peroxide. Thus their function in the solution is probably oxidation-reduction in nature. The air oxidation of copper(I) would account for the catalytic effect of copper. The silver is converted to metallic silver after 3 to 5 minutes of reaction and then no longer reacts.

Oxygen

One can see from the polarograms shown in Figures 18 to 20 that the oxygen in the solution is sufficient for the amount of reaction which occurs in the first 30 minutes. Since the silver responsive reaction is completed in about five minutes, control of the amount of oxygen is unnecessary.

Wavelength

Since 450 nanometers was the wavelength of maximum absorption for both the silver-resorcinol reaction product and the resorcinol autoxidation product, this was the preferred wavelength for measurements of absorbance. No maximum was available in the visible region of the spectrum at lower pH values, thus an alkaline pH must be maintained for the measurement of absorbances.

pH

Based on the data of Figure 22 the pH must remain between pH 10.9 and pH 11.8 in order to get consistent absorbance measurements. In practice it is convenient to use a buffer at the high end of this range, pH 11.5 for example, because the silver is added as an acidic solution and a larger pH range is available in case too much acid is added. Solutions only slightly too acidic for the buffer system can be measured by adding 10 or 15 ml of buffer instead of 5 ml. If the solution is too acidic to be adjusted to pH 11.5 with 15 ml of buffer, concentrated sodium hydroxide can be added to reduce the amount of acid present. Care must be taken to adjust this pH before the resorcinol has been added and if the silver solution becomes more basic than pH 10 the resorcinol must be kept separate until the reac-

tion is started.

Buffer

The same phosphate buffer used by Lambert (8) met all of the require-
ments of a good buffer system for the reaction so no attempt was made to
try other buffers. It was inexpensive, available in high purity, had a
high buffer capacity, was readily soluble and did not interfere with the
reaction.

Order of addition

The desired reaction will not begin until the resorcinol has been made
basic with the buffer solution. Obviously, one of these two components
must be added last, and the reaction timed from this last addition. The
resorcinol must be accurately measured while the amount of buffer added can
be approximate so it is convenient to add the buffer last. Also silver(I)
is probably more stable in acidic solution. An exception to this method
would be a sample of silver ion which is already basic. In this case the
resorcinol solution must be added last. Other changes in the order of ad-
dition have no effect on the reaction.

Time

The optimum time is somewhat dependent on the silver concentration.
Higher concentrations of silver normally react within three minutes. For
these solutions, five minutes may be the best time. Reaction times over
15 minutes have more scatter in a set of results as can be seen in Figure
24 and consequently they should be avoided. Also when copper is present,
the copper is slower reacting than silver so a short time period favors an
accurate determination of silver. For more dilute solutions of silver the

reaction is slower and ten minutes or more must be used. For this reason

ten minutes is recommended for all concentrations.

Resorcinol

It was found from the data of Figures 26, 27, and 28 that the slope in

the absence of silver parallels the slopes of the 50 and 100 μg silver/25

ml reactions only for the solutions containing 0.016% and 0.04% resorcinol.

These data are shown in Table 4. The more concentrated the resorcinol, the

more divergent the slopes become.

Table 4. Change in absorbance for a $2\frac{1}{2}$ minute interval on either side of
ten minutes reaction time

Concentration of resorcinol %	$7\frac{1}{2}$ to 10 minutes			10 to $12\frac{1}{2}$ minutes		
	No Ag$^+$	50 μg Ag$^+$	100 μg Ag$^+$	No Ag$^+$	50 μg Ag$^+$	100 μg Ag$^+$
.016	.002	.005	.000	.002	.001	.000
.040	.007	.009	.004	.007	.011	.008
.080	.017	.030	.027	.018	.030	.031
.120	.032	.052	.054	.033	.054	.049
.160	.038	.072	.064	.039	.070	.048

With 0.016% resorcinol, Figure 29, the reaction is so slow (ten min-

ute minimum) for the low concentrations of silver that the 0.016% concen-

tration could not conveniently be used. The reaction with 0.04% resorcin-

ol is as fast as higher concentrations (three minute minimum) so that this

is the optimum concentration of resorcinol.

Concentrations of silver of 0 to 10 μg/25 ml are best determined in

0.16% resorcinol. The higher the concentration of resorcinol the larger

the slope of the calibration curve for silver. This effect is observed in Figure 37 and holds true until 0.2% resorcinol is reached. In the solution containing 0.2% resorcinol the absorption peak at 450 nm is slower forming and causes a reduced slope at ten minutes reaction time.

Silver

Excellent calibration curves for silver were obtained when the recommended concentrations of resorcinol were used. Figures 32 and 37 show typical results.

Temperature

The temperature studies, Figures 31 and 32, strongly indicate that for concentrations of silver above 5 μg/25 ml, there is no trend. The temperature effects on absorbance are small enough to be difficult to measure. Consequently the values obtained are of the same order of magnitude as the errors in the measurements. Both high and low values are observed at high and low concentrations of silver. Thus the average value, 0.002 A. U./$^{\circ}$C, is more relevant than any individual result.

The most dilute concentration of silver measured, 2 μg/25 ml, was approaching the value obtained in the absence of silver, 0.001 A. U./$^{\circ}$C. This is reasonable since the reaction rate in very dilute solutions of silver is very slow in comparison to more concentrated solutions of silver.

Copper

Comparison of the data shown in Figure 26, which had no copper present, with that shown in Figure 40, where 0.5 μg copper/25 ml was present, was made to determine the optimum concentration of resorcinol for the determination of copper. These data are given in Table 5 for 10 and 30 min-

ute reaction times. It can be seen from the increasing differences in absorbance that the sensitivity increases with time and with increasing concentration of resorcinol. This suggests that there is no real optimum concentration of resorcinol. The selection of a concentration for resorcinol depends on the range of concentrations of copper being measured. The concentration, 0.08%, which is ideal for 0.1 to 1 μg copper/25 ml, gave good results as can be seen in Figure 42.

Masking copper

Of the various methods of masking the copper, the only one which was really effective was the addition of sodium citrate. The reason is that higher concentrations of the other reagents interfere with the silver-resorcinol reaction but higher concentrations of sodium citrate do not interfere. It appears from Figure 46 that silver could be determined in the presence of large excesses of copper if the amount of copper is known.

Interferences

Most cationic interferences appear to be caused by coprecipitation of silver with the other cation which is precipitating as a hydroxide, citrate, or phosphate. Citrate complexes most cations, usually making them more soluble and reducing the interference by precipitation by a factor of ten. The principal use of the citrate is to complex copper(II). Uranium interferes by forming a yellow complex with citrate and with resorcinol. Some colored ions like cobalt, nickel, and iron(III) interfere when they become concentrated enough to exhibit an appreciable absorbance at 450 nm. Some cations like gold and lanthanum interfere by increasing the rate of reaction. Anions interfere by complexing the silver (chloride, bromide),

by oxidation of the resorcinol (peroxidisulfate), by reduction of the colored reaction product (sulfite, thiosulfate), and by absorbtion at 450 nm (chromate).

Table 5. Absorbance caused by 0.5 µg copper/25 ml at various concentrations of resorcinol

Percentage resorcinol	After ten minutes	After 30 minutes
0.016	0.027	0.092
0.040	0.099	0.324
0.080	0.162	0.444
0.120	0.219	0.498
0.160	0.353	0.624

Applications

The method was successfully applied to the determination of silver in a silver solder. The error, +1.5% in the determination is within the ±2% limits of accuracy normally accepted for routine spectrophotometric work.

An attempt was made to apply the method to two lead ores. The high silica content caused problems with dissolution of the ores. The best solvent, concentrated phosphoric acid and 70% perchloric acid in a 1:1 mixture, provided the additional problem of pink $Mn(III)$ phosphate. It was possible to reduce this with iron(II). Even with a colorless solution, however, it was not possible to determine the silver present. Interference was established by spiking a known amount of silver into the solution and then observing that even this amount of silver could not be detected.

Thus it appears that some agent in the solution was retarding the reaction with resorcinol.

Proposed procedure

The following is the proposed analytical procedure which was decided upon after thorough study of the variables involved in the silver-resorcinol system. The sample to be determined was dissolved and made up to volume in such a way that 15 ml or less contained 10-400 μg of silver. To a 25-ml volumetric flask was added 5 ml of 0.2% resorcinol solution and the aliquot of the sample to be determined. If the sample was 15 ml, the reaction was started by diluting the solution to volume with citrate-phosphate buffer. If less than 15 ml of sample solution was used, water was added to produce 20 ml total volume and then the buffer was added. A quick shake of the stoppered flask provided adequate mixing. A timer was used to record the exact time at which the buffer was added. Exactly 10 minutes after the buffer was added the solution was read in a spectrophotometer at 450 mm. This means that the solution was poured into the spectrophotometer cell prior to the end of the ten minutes. For a large number of determinations it was convenient to start the first three samples at once and start the reaction in the second set of three samples after five minutes. Additional sets of samples were started at 9, 14, 18, 23, 27, 32, and 36 minutes. It was necessary to measure out the solutions prior to adding the buffer to the first set of three. Only three samples were run at one time since one cell was needed for water to adjust the 100% T point and conventional spectrophotometers will only hold four cells at one time. For example, buffer was added to the first flask at zero time, to the second at zero

plus ten seconds, to the third at zero plus 20 seconds and to the fourth at five minutes, to the fifth at five minutes plus ten seconds and so on. The same procedure is used for 1 to 10 μg portions of silver except that five ml of 0.8% resorcinol is added instead of the 0.2% resorcinol.

Since a large number of samples can be quickly determined by this procedure, there are several advantages of this method. One can conveniently include numerous standards with the samples to be determined. Several duplicate analyses can be made if higher accuracy is desired. One can apply the temperature corrections given in the section on temperature and use one carefully determined calibration curve for all future analyses. Speed is also an advantage when unknown samples are being determined since one quickly learns if the aliquot of solution added contains a measurable concentration of silver. The reaction should be suitable for adaptation to continuous flow analysis in any situation where concentrations of silver between 1 and 400 μg/15 ml need to be analyzed continuously.

SECTION III. AUTOXIDATION OF DERIVATIVES OF RESORCINOL

Introduction

The use of orcinol suggested by Slater (9) and the use of resorcinol recommended by Lambert (8) are the only two phenolic autoxidation methods in the literature. A comparison of the interferences in these two methods indicated that cations do not necessarily have the same response with resorcinol and orcinol. To investigate the possibility of methods for other cations by using derivatives of resorcinol, eleven of these compounds were obtained and studied.

Cresorcinol was difficult to prepare in quantity and 2-nitroresorcinol absorbed strongly in the visible region making measurements difficult so these two derivatives were not studied further. 4,6-Dichlororesorcinol was found to be quite unstable and seemed to warrant only a cursory study. The other eight derivatives, orcinol, 2-methylresorcinol, 4-ethylresorcinol, 4-chlororesorcinol, phloroglucinol, 3,5-dihydroxybenzoic acid, 2,4-dihydroxybenzoic acid, and 2,6-dihydroxybenzoic acid were studied in detail.

Two factors were considered in selection of the compounds for further study. First, the availability of the compounds through manufacturers of research chemicals. It should be noted that with the exception of cresorcinol, all of the compounds investigated are readily available and inexpensive. Second, the positions substituted were varied to gain insight about the reactivity as related to the position of substitution. The 2-, 4-, and 5- positions were all blocked by an alkyl group and also by a carboxyl group. Also the 4- position was studied using a chlorine atom as the blocking group and going one step further, blocking both 4- and 6- posi-

tions on the same molecule. Phloroglucinol was studied to observe the effects of complete symmetry in the molecule as well as an additional 5-substituent.

Presumably all of the derivatives studied have a pK_1 value (or pK_2 in the case of the benzoic acids) within about one pH unit of resorcinol. It can be seen from the resorcinol case that a range of several pH units will produce substantial autoxidation. The assumption was thus made that reaction at pH 11.0-11.5 would be typical of the activity of all the compounds studied.

Experimental work on each derivative is given in a separate section for each derivative. Since the reactions of the derivatives are quite similar they are all discussed in the same discussion section.

Mechanism of Autoxidation

The mechanism proposed by Musso and coworkers (19, 25-29) for the autoxidation of orcinol can be applied to most of the other derivatives studied since the presence of a methyl, chlorine or carboxyl group on the resorcinol ring does not significantly change the nature of the reactions involved. This mechanism is discussed in detail in the section on resorcinol and consequently will not be discussed further in this section.

However the third hydroxyl group which is present on phloroglucinol does make a significant change in the reactivity of the ring. For instance sodium borohydride will reduce phloroglucinol to resorcinol (45). NMR studies (46) of solutions of the mono-, di- and trisodium salts of phloroglucinol indicate from the chemical shift of the protons that the di- and tri-substituted compounds are no longer aromatic. In IR measurements (46)

of the solids, the lack of aromatic peaks for these two compounds is ob-
vious. The difference is also evident when the acid dissociation constants

(47) of resorcinol (pK_1=9.15 and pK_2=11.32) and phloroglucinol (pK_1=8.45

and pK_2=8.88) are compared. The rate of exchange of the 2-, 4- and 6-posi-
tion protons with deuterium is much faster for resorcinol than for catechol

and hydroquinone (48) and the rate increases by a factor of six going from

pH 8 to pH 11. Phloroglucinol exchanges the 2-, 4- and 6-position protons

even faster. The usual explanation (46) for this behavior is that the di-

anion of phloroglucinol has a resonance stabilized, dihydro form as shown

below.

The oxidation of phloroglucinol by potassium ferricyanide at pH 7 was

investigated by Stein and Tendeloo (49-53). The reaction was first order

in both phloroglucinol and ferricyanide, the initial reaction was reversi-

ble and resulted in free radical formation but the second reaction was ir-

reversible (49). Diffusion coefficient measurements indicated a 2- or 3-

benzene ring product (50). Electrophoresis in 0.1 N NaOH in the absence of

oxygen was used to separate the products of the ferricyanide oxidation.

With the electrophoresis velocity of the phloroglucinol equal to 1.0, the

velocities and colors of the products were: 0.9 to 1.0, yellow brown; 0.6

to 0.7, red purple; 0.2 to 0.3, brown. There was no further investigation

of the products given in the literature. The autoxidation of phloroglucin-

ol which occurs at more alkaline pH values has apparently never been stud-

ied.

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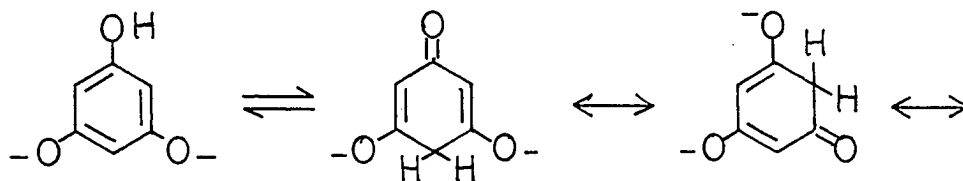
Cresorcinol

Cresorcinol is not commercially available. An attempt was made to prepare it by diazotizing 2,4-diaminotoluene. This was unsuccessful when attempted as a one-step reaction. The procedure given by Henrich (54) was then used. The reaction sequence is as follows:
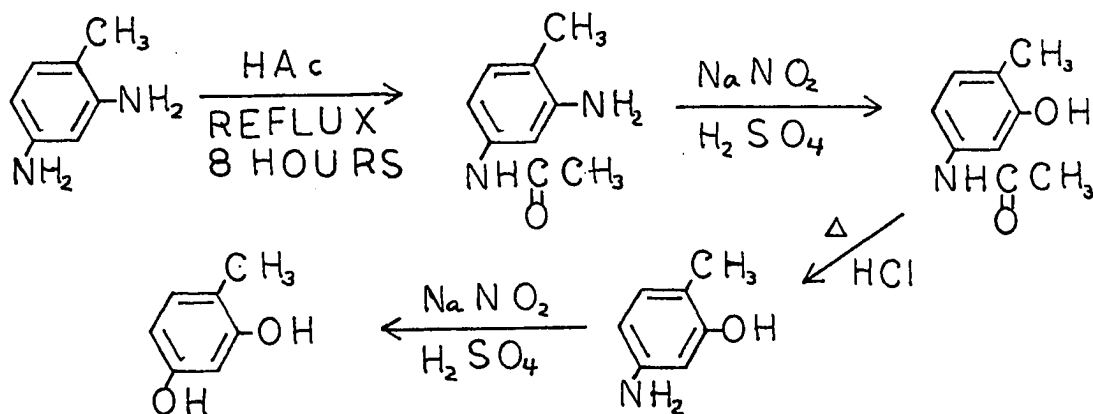
The first reaction was run using 30 g 3,4-diaminotoluene, 25 g glacial acetic acid and 20 ml H_2O. This mixture was refluxed for eight hours, cooled and filtered and then refluxed for eight hours and again cooled and filtered. The product was a dull white color and was insoluble in cold water. Crystals which melted at 152-154°C were obtained after several recrystallizations from water. Wallach (55) reports 159-161°C for the melting point of this compound.

Twenty grams of this amide was dissolved in 400 ml water and 24 g concentrated HCl and cooled in an ice bath. Then 8.8 g sodium nitrite dissolved in 500 ml water was slowly added using a long-tipped dropping funnel. The temperature was kept below 5°C and very little foam formed. After the sodium nitrite was added, the solution was warmed up to 45°C at which time nitrogen was given off and a red solid formed. The red crystals

melted at 185-190°C but a white solid sublimed out of the crystals at 170°C and these white crystals melted at 224-6°C. Wallach (55) reported a melting point of 224-225°C for the colorless compound. The red color was probably due to a small amount of an azo dye impurity. Yield of this step was about 85%.

Ten grams of the red crystals were added to 250 ml of water and 70 ml of concentrated HCl and heated in an open beaker for 15 minutes. Fine blackish crystals formed when this solution was cooled. The yield of this step was usually so small that the next step was run on the same solution by cooling the mixture to below 5°C in an ice bath and adding 4 g of sodium nitrite in 300 ml water via a dropping funnel. The products of this solution were a small amount of black tarry material and a dark red solution. The solution, after filtration, was saturated with NaCl and extracted with 2 to 3 volumes of diethyl ether until no more colored material was extracted. The ether was removed with the rotovac leaving a dark red oil. Extraction of this oil with petroleum ether and subsequent evaporation of the petroleum ether provided a small amount of red crystalline material from which white needles slowly sublime at room temperature. The crystals smell like pine tar and are volatile enough to be difficult to keep in an open beaker. The crystals melted at 103-105°C. The literature value (54) for cresorcinol was 105-107°C.

Cresorcinol was not studied further since the synthesis was involved, the yield was poor and the compound was more unstable than other resorcinol derivations.

4,6-Dichlororesorcinol

The 4,6-dichlororesorcinol was obtained from Pfaltz & Bauer Chemical Company. The commercially available material was reddish colored. It was learned that 4,6-dichlororesorcinol could be extracted into benzene leaving most of the red impurity behind. The benzene was then removed with a roto-vac and white crystals were obtained. When suction filtration was used to remove the remaining benzene, the white compound turned red. The commercial compound melted at 66-76°C. When recrystallized from $CHCl_3$ the melting point was 74-84°C. The sublimed material had a melting point of 80-82°C. After recrystallization from benzene it melted at 82-86°C. The literature value is 113°C (33).

A few preliminary investigations of the response to cations were made using the benzene-purified material. The 4,6-dichlororesorcinol solution used was prepared by dissolving 8.149 g in water and diluting to 250 ml. Assuming pure compound this was 0.182 $\underline{M}$. In the reaction 5 ml of this stock solution was diluted to 50 ml and thus the final molarity of the reaction was 0.0182 $\underline{M}$. This is five times the recommended resorcinol concentration of 0.04% given in the previous section. The 4,6-dichlororesorcinol solution used was not pure since droplets of benzene were present after dissolution of the compound. Thus the molarity was somewhat lower than 0.0182 $\underline{M}$. Figure 47 shows the absorption spectra of autoxidized 4,6-dichlororesorcinol and also autoxidized 4,6-dichlororesorcinol with silver present, both spectra measured after ten minutes of reaction time. The cations were added in 1 to 10-ml aliquots and deionized water was used to dilute to 45 ml. A 5-ml portion of phosphate buffer was added to initiate
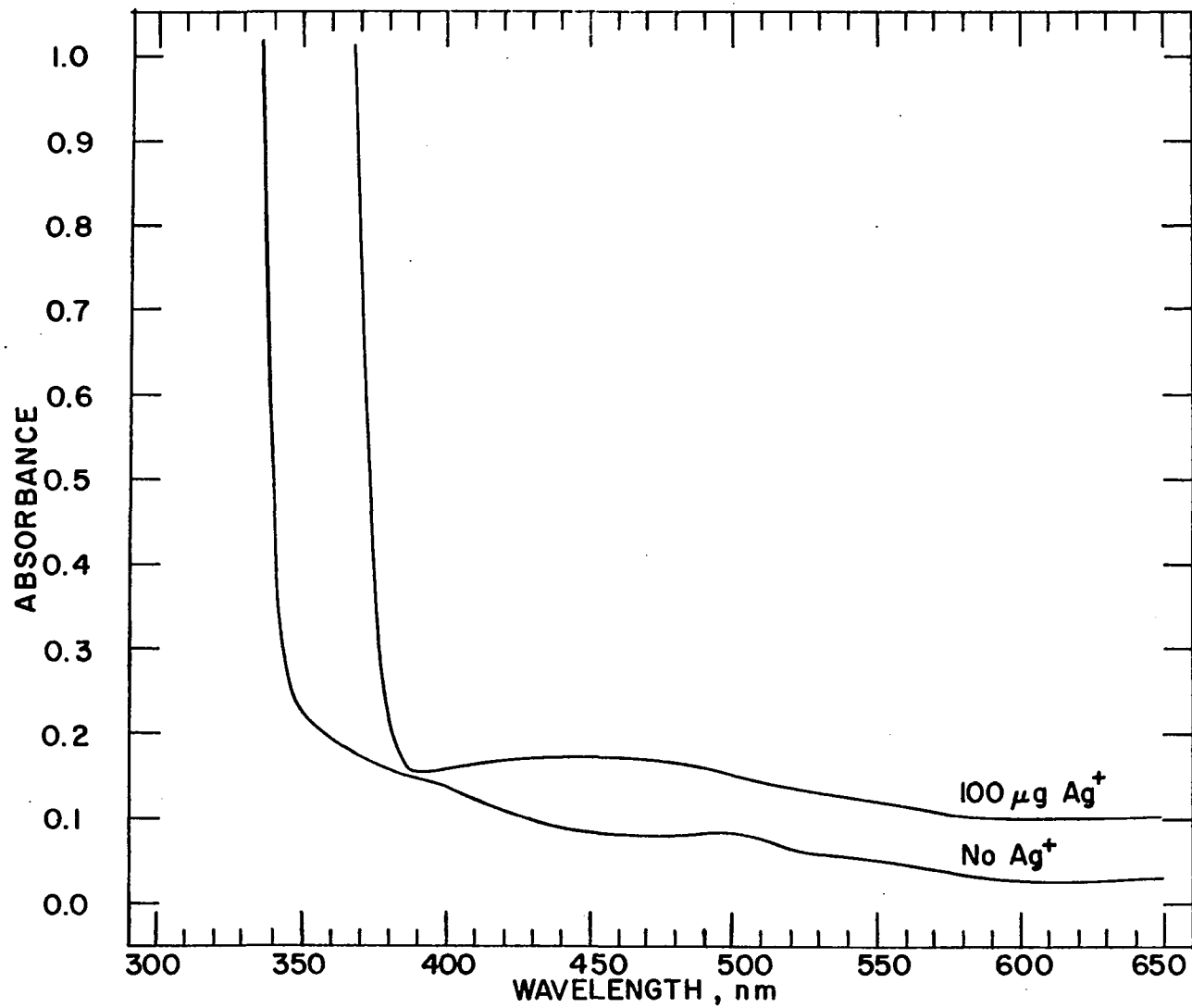
Figure 47. Visible absorption spectrum of 25 ml of autoxidized 4,6-dichlororesorcinol

the reaction. The absorbance was measured at 470 nm after 30 minutes of reaction time. The results of each averaged set of three determinations is given in Table 6. The range on the 15 blank results was from 0.036 to 0.063.

Since this compound was hard to purify and was quite unstable, it was not studied in detail. Silver and copper definitely stimulate the reaction and cadmium appears to interfere at the concentrations studied.

2-Nitroresorcinol

The 2-nitroresorcinol was obtained from Pfaltz and Bauer. It was purified by recrystallization from hot absolute ethanol. Twice recrystallized material melted at 81-83°C. The literature value (33) for the melting point was 83.5°C.

Figure 48 shows the visible spectra of 0.0004 $\underline{M}$ 2-nitroresorcinol after an autoxidation period of ten minutes at pH 11.5. The rate of autoxidation appears to be much slower than the other resorcinol derivatives studied. No change in the spectra is observed in alkaline medium after ten minutes. As can be seen from Figure 48 silver has no effect on the autoxidation. The absorbance maximum at 390 nm, which is present prior to any autoxidation, is so intense that increased dilution must be used to make absorbance measurements in the visible region. The increased dilution necessary to make absorbance measurements appears to have reduced the autoxidation rate to below a measureable degree in the first ten minutes. This derivative was not studied further because of this complicating factor.

Table 6. Effect of cations on the autoxidation of 4,6-dichlororesorcinol

Cation	Concentration in $\mu g/50$ ml	Absorbance
Blank[a]		0.048
Cu^{+2}	1	0.072
Ag^{+}	100	0.137
NH_4^{+}	100	0.063
Cd^{+2}	100	0.030
Pb^{+2}	100	0.038
Hg^{+2}	100	0.040
Ca^{+2}	100	0.053
Fe^{+3}	100	0.049
Mg^{+2}	100	0.052
Co^{+2}	100	0.050
Zn^{+2}	100	0.040

[a]Absorbance of the blank is an average of 15 determinations. The other values are averages of three determinations.

4-Chlororesorcinol

The 4-chlororesorcinol was obtained from Pfaltz and Bauer. It was purified by sublimation and melted at 103-105°C. Aldrich (56) lists a melting point of 106.5-107.5°C for their product. The literature value (33) of 89°C is probably an error.

Figure 49 shows the visible spectra of 0.010 M 4-chlororesorcinol after 10 and 130 minutes at pH 11.5. The visible spectra after ten minutes in the presence of 100 µg of silver is also shown in Figure 49.
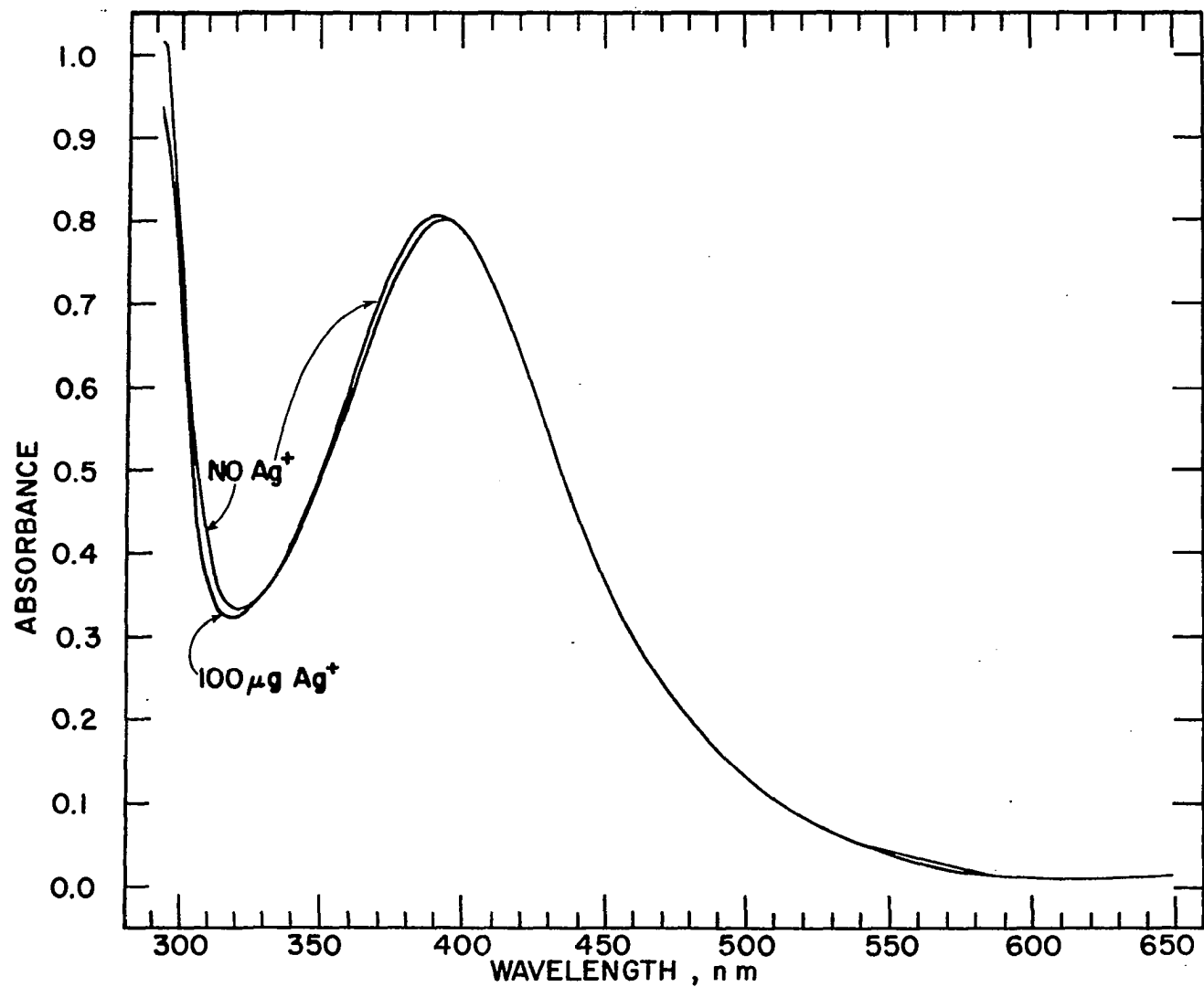
Figure 48. Visible absorption spectrum of autoxidized 2-nitroresorcinol (25 ml)
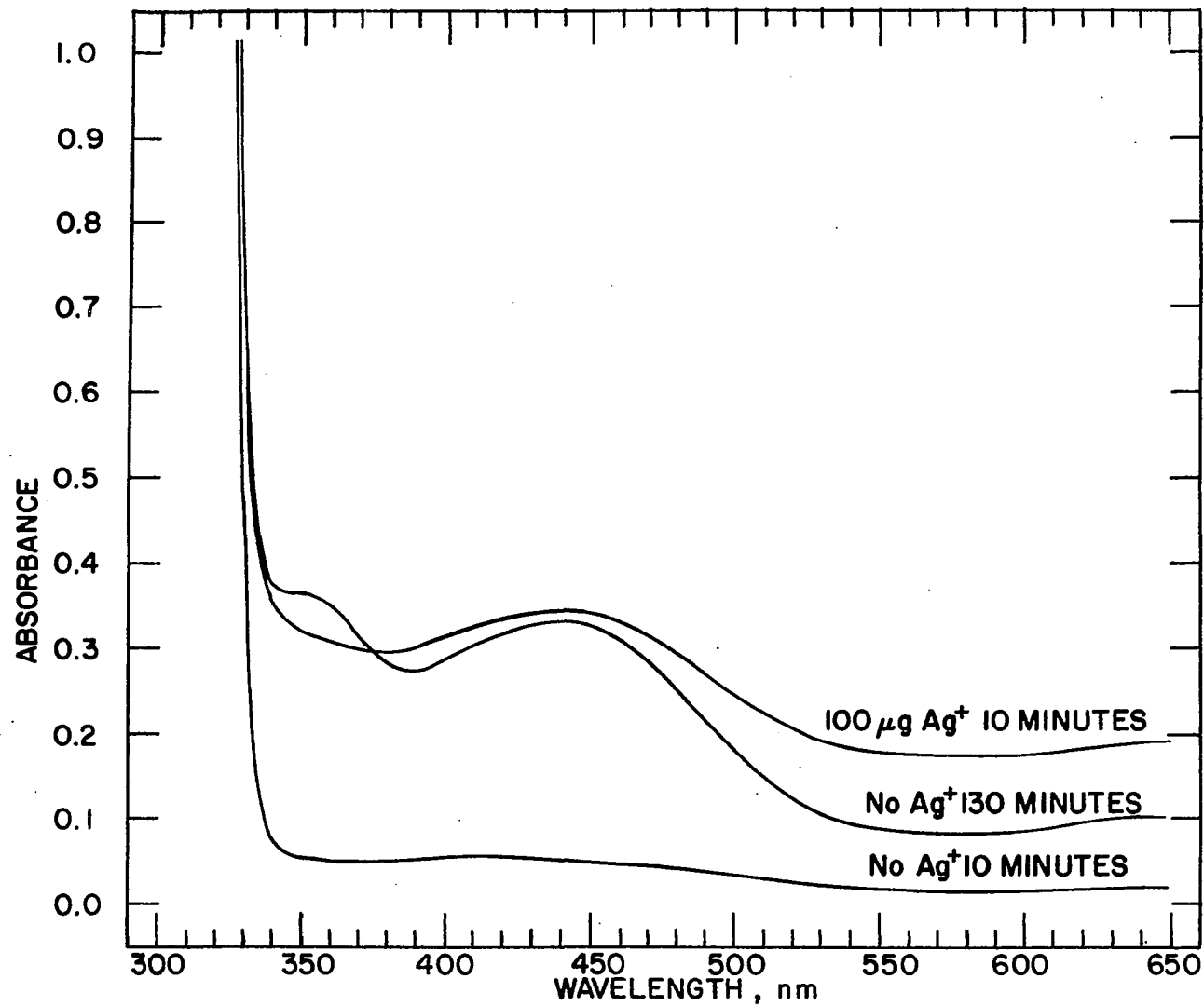
Figure 49. Visible spectrum of autoxidized 4-chlororesorcinol (25 ml)

The wavelength of maximum absorption is 440 nm.

The effect of various cations on the autoxidation was studied by addition of 0.1 to 10 ml of solutions containing these cations to 10 ml of 0.025 M 4-chlororesorcinol and then addition of 5 ml of phosphate buffer to initiate the reaction. The results are shown in Table 7 along with similar data for resorcinol and the three dihydroxybenzoic acids. The only cations showing definite increase in autoxidation of 4-chlororesorcinol are Ag^+, Cu^{+2}, Cu^+, Mn^{+2}, and Pt^{+4}. Figure 50 shows the increase of absorbance with time for the blank and these five cations.

3,5-Dihydroxybenzoic Acid

The 3,5-dihydroxybenzoic acid was obtained from Aldrich Chemical Company. It is not volatile enough for convenient sublimation. The acid is fairly insoluble in cold water but much more soluble in hot water so recrystallization from water was the method of purification used. Fifty ml of deionized water was heated to boiling, 20 grams of the acid added and as soon as the solid dissolved, the solution was suction filtered into a warm flask. This solution was allowed to cool to room temperature and filtered. Further cooling in ice removes more of the acid from solution. The crystalline solid can be further purified by rinsing several times with small portions of cold water. Usually about 80% of the initial material is recovered as pure acid in this procedure. The melting point after two such recrystallizations was 240.4°C. The literature value (33) for the melting point is 237-240°C.

Figure 51 shows the visible absorption spectra of 0.010 M 3,5-dihydroxybenzoic acid after seven minutes of reaction and also after ten min-

Table 7. Effects of cations on the absorbance of resorcinols after 10 minutes of autoxidation [a]

μg	Cation	Resorcinol	4-Chloro resorcinol	3,5-Dihydroxy benzoic acid	2,4-Dihydroxy benzoic acid	2,6-Dihydroxy benzoic acid
	Blank[b]	.063	.036	.010	.003	.092
100	Ag^+	.615	.316	.168	.117	.684
5×10^5	Na^+	.076	.048	.011	.003	.081
5×10^5	K^+	.070	.041	.010	.002	.096
5000	Li^+	.055	.032	.008	.008	.096
50	NH_4^+	.048	.030	.008	.002	.081
50	Hg^+	.224	.042	.012	.008	.128
50	Cu^+	1.46	.376	.038	.021	1.28
50	Hg^{+2}	.104	.052	.021	.014	.124
500	Ba^{+2}	.089	.056	.027	.025	.103
500	Sr^{+2}	.083	.050	.026	.024	.098
500	Ca^{+2}	.063	.045	.025	.018	.096
500	Mg^{+2}	.060	.032	.010	.004	.106
5	Co^{+2}	.124	.045	.009	.001	.164
500	Zn^{+2}	.112	.046	.011	.001	.113
5	Pb^{+2}	.068	.038	.008	.002	.090
50	Ni^{+2}	.053	.030	.008	.001	.091
1	Cu^{+2}	.191	.120	.010	.002	.190

[a]Measurements were all made on 25 ml of solution.

[b]The absorbance of the blank is the average of four values.

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Table 7 (Continued)

μg	Cation	Resorcinol	4-Chloro resorcinol	3,5-Dihydroxy benzoic acid	2,4-Dihydroxy benzoic acid	2,6-Dihydroxy benzoic acid
500	Cd^{+2}	.063	.042	.018	.014	.093
50	Fe^{+2}	.087	.067	.029	.016	.148
50	Mn^{+2}	.717	.239	.010	.013	.838
5	Pd^{+2}	.076	.047	.007	.000	.092
500	Ti^{+3}	.014	.019	.006	.001	.017
500	Sb^{+3}	.043	.041	.009	.003	.070
50[c]	Fe^{+3}	.071	.041	.017	.014	.148
500	Al^{+3}	.132	.079	.009	.002	.148
38.5	Tl^{+3}	.065	.043	.006	.005	.073
50	Cr^{+3}	.036	.025	.006	.002	.058
50	Bi^{+3}	.068	.035	.007	.000	.096
5[c]	Au^{+3}	.176	.071	.023	.030	.135
500	Dy^{+3}	.044	.026	.013	.007	.066
500	Er^{+3}	.033	.027	.011	.004	.051
50	Eu^{+3}	.050	.040	.005	.000	.072
500	Ho^{+3}	.043	.027	.013	.006	.075
500	Lu^{+3}	.038	.026	.010	.007	.060
500	La^{+3}	.045	.036	.014	.006	.066

[c]With a ten fold increase in concentration the cation reacts with the compound to form a colored species prior to the addition of buffer.

Table 7 (Continued)

μ g	Cation	Resorcinol	4-Chloro resorcinol	3,5-Dihydroxy benzoic acid	2,4-Dihydroxy benzoic acid	2,6-Dihydroxy benzoic acid
50	Tb^{+3}	.042	.026	.009	.001	.060
500	Yb^{+3}	.034	.028	.011	.005	.050
50	Sm^{+3}	.046	.028	.007	.001	.073
50	Nd^{+3}	.061	.036	.010	.006	.090
50	Gd^{+3}	.054	.029	.008	.004	.074
500	Pr^{+3}	.041	.029	.011	.007	.070
500	Tm^{+3}	.033	.025	.009	.002	.051
50	Ce^{+4}	.048	.031	.013	.005	.065
500	Th^{+4}	.053	.035	.014	.008	.085
5	Sn^{+4}	.041	.026	.007	.001	.078
50	Pt^{+4}	.103	.091	.018	.010	.100
50	UO_2^{+2}	.075	.033	.006	.001	.090
500	$AsO_4^{\equiv}$	.032	.048	.009	.000	.080
500^d	$CrO_4^{=}$	.048	.029	.003	.000	.078
500	VO_3^{-}	.072	.061	.020	.004	.201
500	$MoO_4^{=}$	.107	.071	.010	.001	.240
500	$WO_4^{=}$	.068	.038	.008	.001	.141

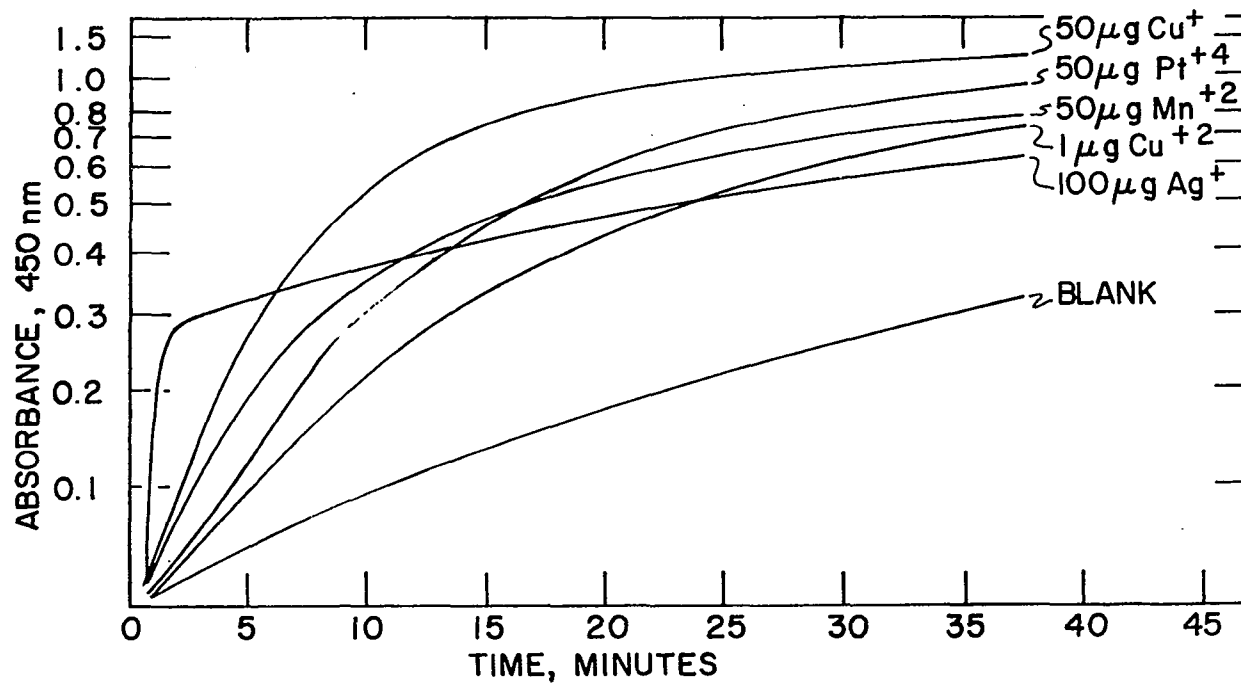^{d}Absorbance was corrected for the natural absorbance of $CrO_4^{=}$.

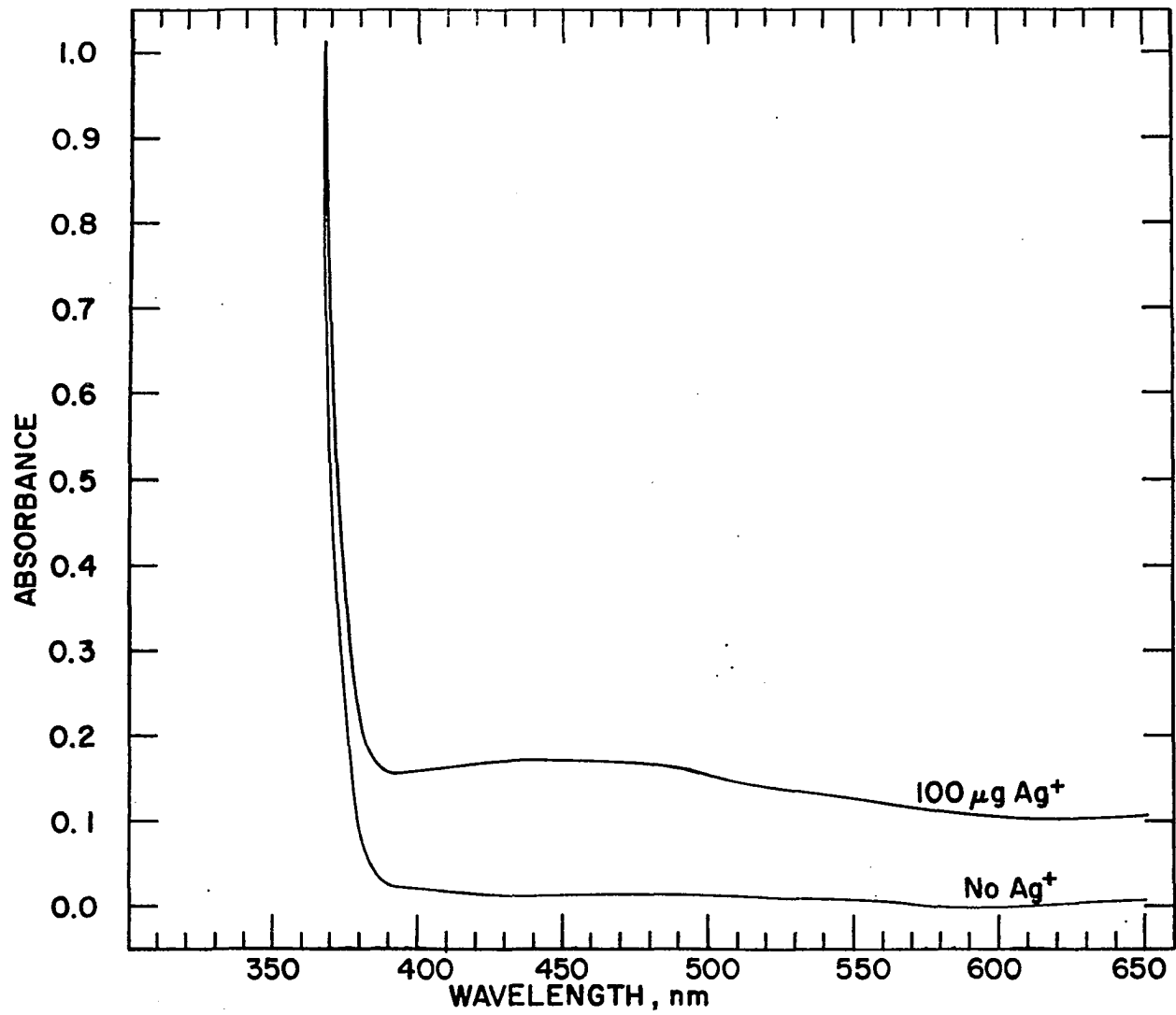Figure 50. Change in the absorbance with time for 25 ml of 4-chlororesorcinol

Figure 51. Visible absorption spectrum of 25 ml of autoxidized 3,5-dihydroxybenzoic acid

utes of reaction in the presence of 100 μg silver/25 ml. No absorption

maximum is observed in the blank after seven minutes but the silver reac-

tion has a maximum at 450 nm.

The effect of various cations on the autoxidation was studied by add-

ing from 0.1 to 10 ml of solutions of the cations to 10 ml of 0.025 $\underline{M}$ 3,5-

dihydroxybenzoic acid, adding sufficient water to bring the volume up to

20 ml and then adding 5 ml of phosphate buffer to adjust the pH to 11.5

and initiate the reaction. The data obtained are given in Table 7. The

only cation which substantially increases the rate of autoxidation is sil-

ver. Other cations giving some increase in autoxidation are Cu^+, Hg^{+2},

Fe^{+2}, Ba^{+2}, Sr^{+2}, Ca^{+2}, Pt^{+4}, and VO_3^-. Figure 52 shows the increase in

absorbance with time for Ag^+, Cu^+, Hg^{+2}, Ba^{+2}, Pt^{+4}, and the blank.

2,4-Dihydroxybenzoic Acid

The 2,4-dihydroxybenzoic acid was obtained from Aldrich Chemical Com-

pany. It was purified by recrystallization from water. Twenty grams of

the acid will dissolve in 150 ml of hot water and reprecipitate on cool-

ing. After two recrystallizations the compound melted at 230.4°C. The

handbook value (33) is 235-236°C.

Figure 53 shows the visible spectra of 0.010 $\underline{M}$ 2,4-dihydroxybenzoic

acid after ten minutes of reaction and of a similar solution in the pres-

ence of 100 μg Ag^+/25 ml. The silver speeds up the reaction sufficiently

so that an absorption maximum at 450 nm can be observed after ten minutes.

Various cations were added to the 0.01 $\underline{M}$ 2,4-dihydroxybenzoic acid

solution to determine the effect on the autoxidation. The results of this

study are shown in Table 7. The effect of Ag^+, Mn^{+2}, Ba^{+2}, Cu^+, and Pt^{+4}
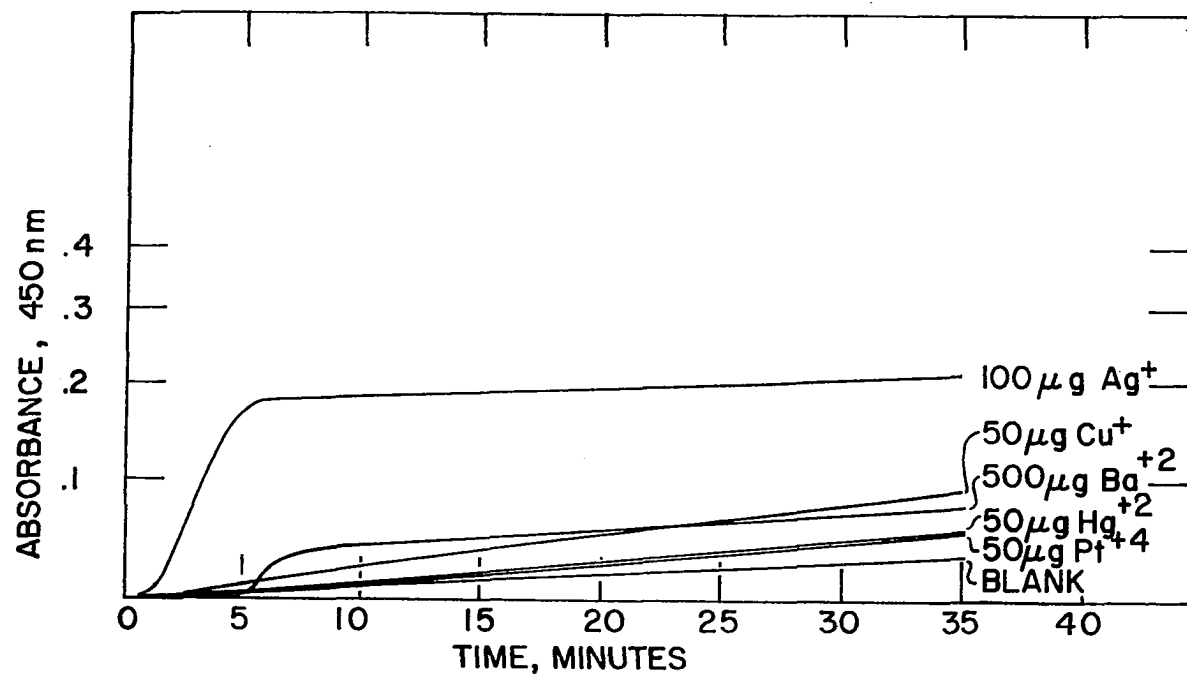
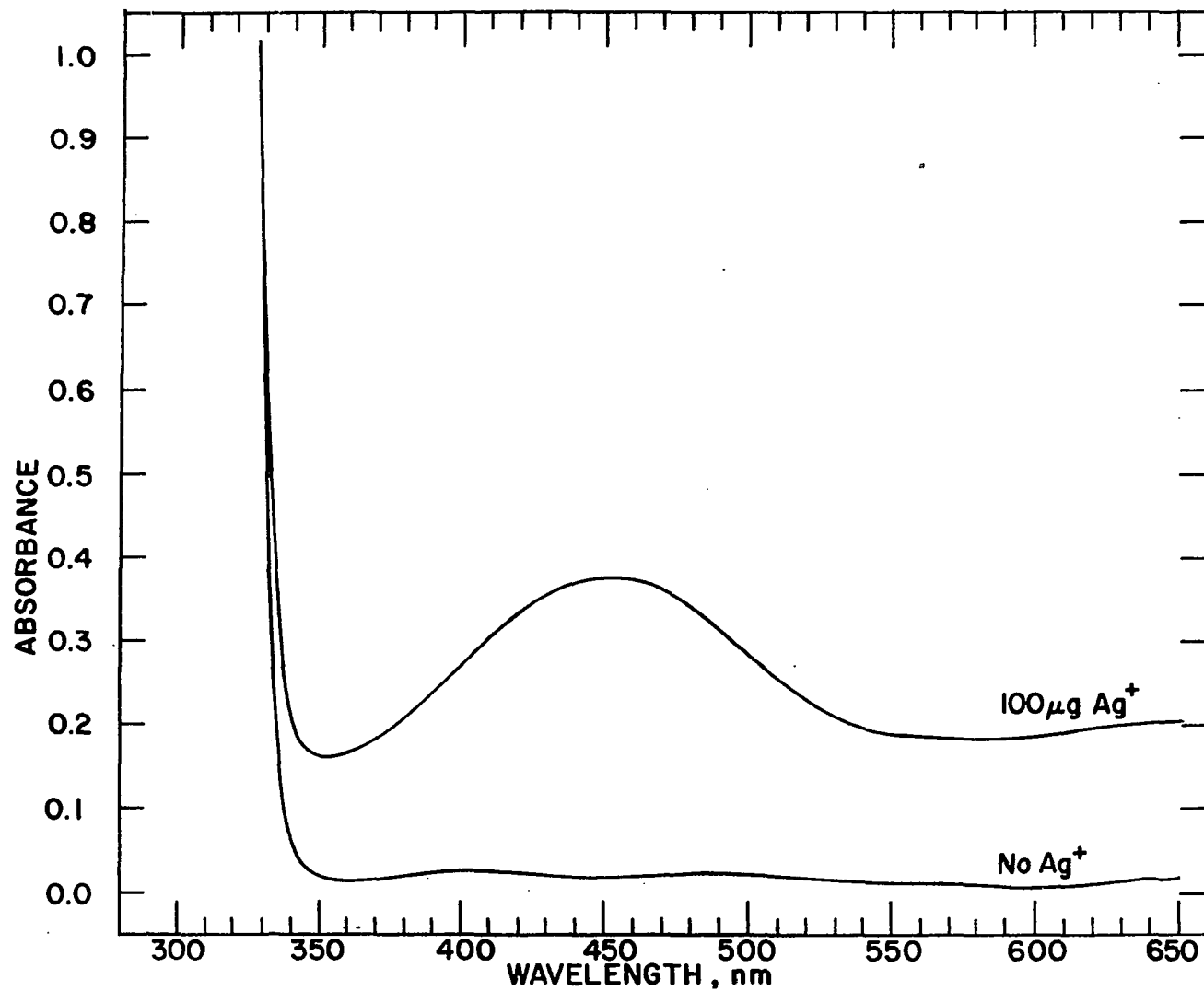Figure 52. Change in the absorbance with time for 25 ml of 3,5-dihydroxybenzoic acid

Figure 53. Visible absorption spectrum of autoxidized 2,4-dihydroxybenzoic acid (25 ml)

on the absorbance for the first 35 minutes of reaction time is shown in Figure 54.

2,6-Dihydroxybenzoic Acid

The 2,6-dihydroxybenzoic acid was obtained from Aldrich Chemical Company. Unlike the other two dihydroxybenzoic acid derivatives, this acid was volatile enough to be sublimed. The sublimed material melted at 106.4-108.4°C. The acid melted at 167-169°C when recrystallized from water. The literature (33) indicates decomposition at 167°C.

The autoxidation of this compound proceeds through a violet colored step to a green solution as can be seen from the spectra in Figure 55. Some cations, like the silver also shown in Figure 55, speed up the reaction. Others either have no effect or decrease the reaction rate. In nearly all cases the solution is green after reacting for 20 minutes. The effects of various cations on the first ten minutes of autoxidation are shown in Table 7. The absorbance values given in Table 7 are measured at 450 nm which is the absorption maximum of the green solution. Consequently lower values sometimes indicate a slower reaction rate rather than decreased catalytic activity. Figure 56 illustrates the effect of time on the absorption of reacting 2,6-dihydroxybenzoic acid. The effects of 100 μg Ag^+, 50 μg Cu^+, 1 μg Cu^{+2}, 50 μg Mn^{+2}, and 500 μg $MoO_4^{-2}/25$ ml on the autoxidation are also shown in Figure 56.

2-Methylresorcinol

The 2-methylresorcinol was supplied by Aldrich Chemical Company. The 2-methylresorcinol can be recrystallized from ethanol-chloroform mixtures. A more convenient means of purification was sublimation. The sublimed ma-
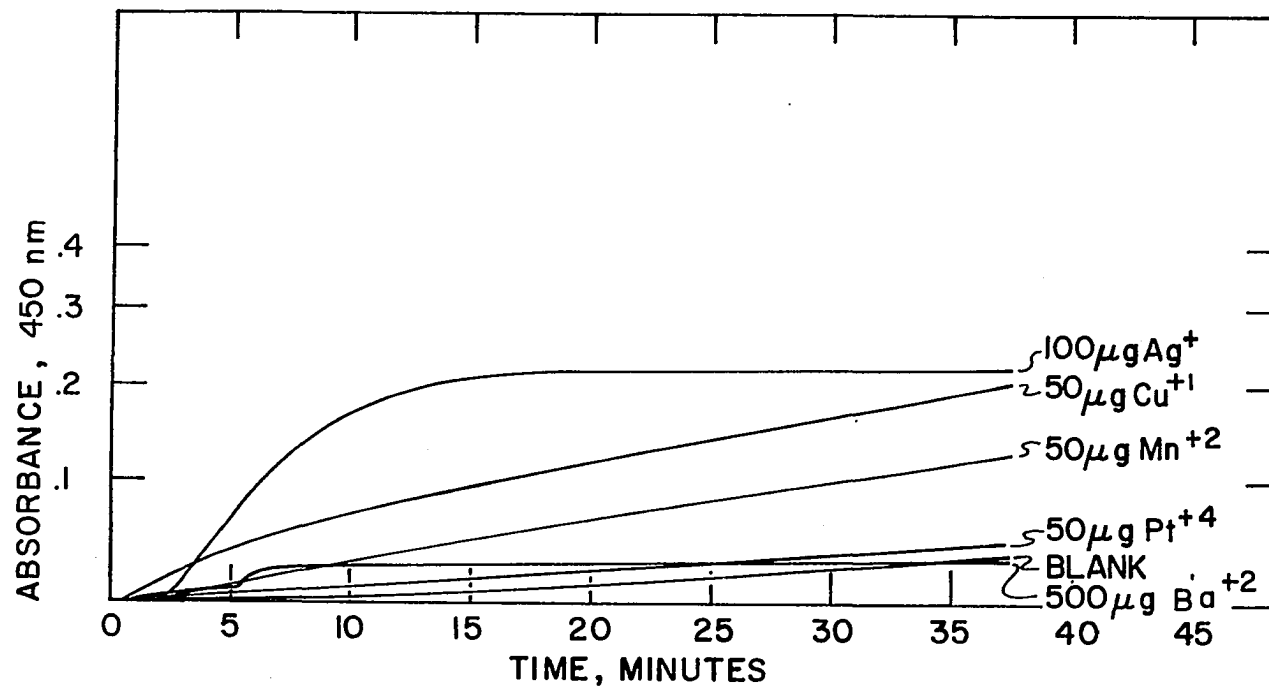
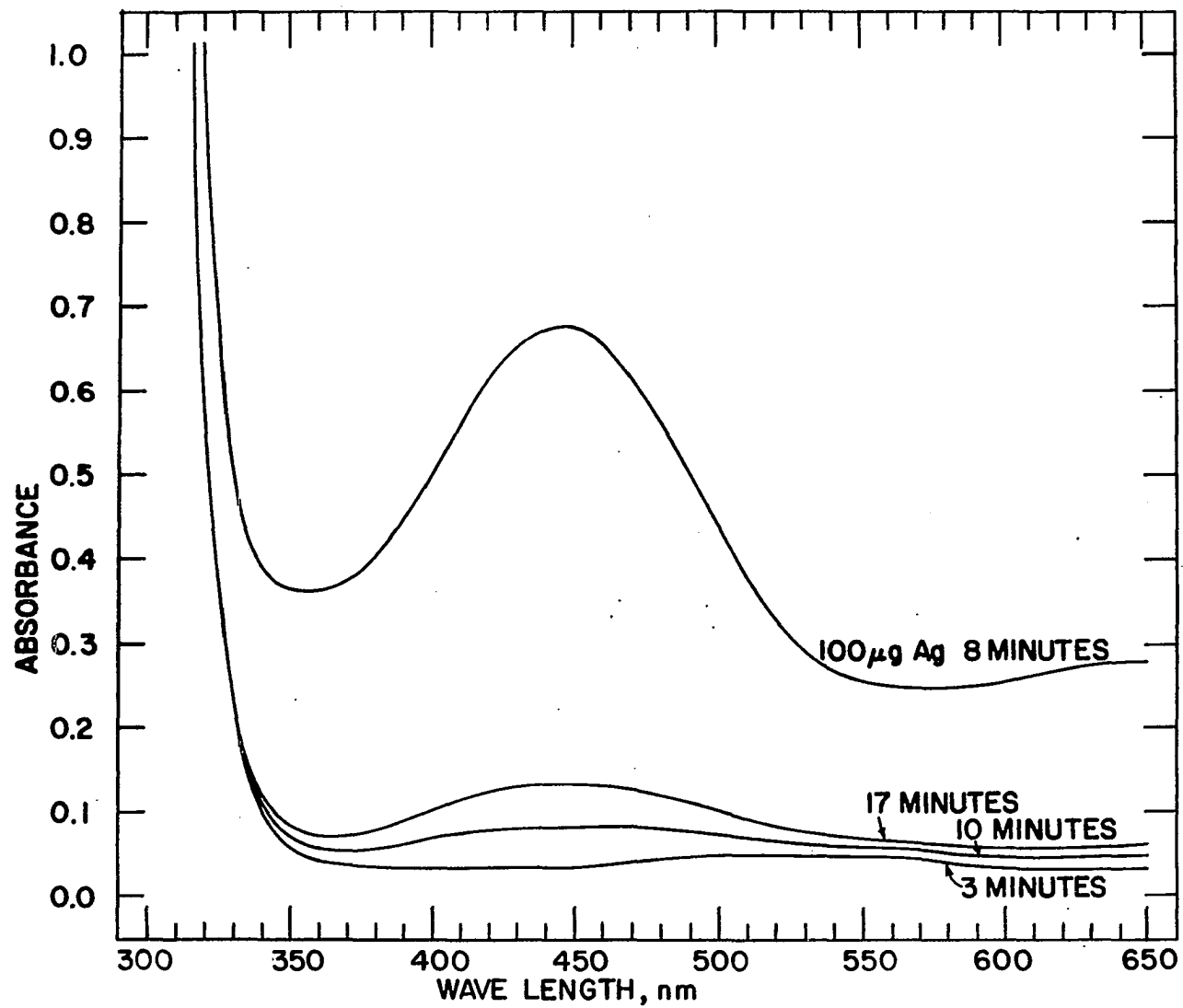Figure 54. Change in the absorbance with time for 25 ml of 2,4-dihydroxybenzoic acid

Figure 55. Visible absorption spectrum of autoxidized 2,6-dihydroxybenzoic acid (25 ml)
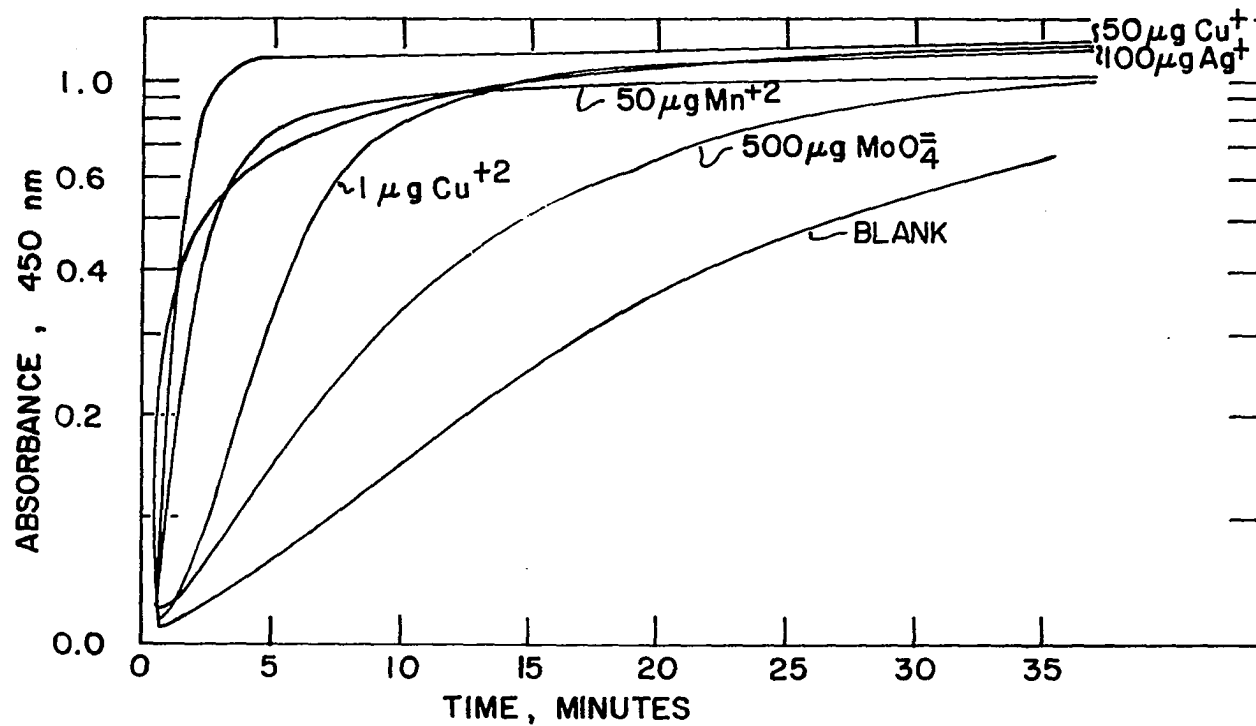
Figure 56. Change in the absorbance with time for 25 ml of 2,6-dihydroxybenzoic acid

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terial melted at 120°C. The literature value (33) for the melting point is 119°C.

The visible spectra for 0.01 $\underline{M}$ 2-methylresorcinol after ten minutes at pH 11.5 is shown in Figure 57 both for the absence and the presence of 100 μg Ag^+. The absorption maximum at 470-480 nm is present in both solutions.

The effects of various cations on the reaction were tested by adding 0.1-10 ml of solutions of these cations to 10 ml of 0.025 $\underline{M}$ 2-methylresorcinol, diluting to 20 ml with deionized water and then initiating the reaction by adding 5 ml of phosphate buffer. The results of the study are presented in Table 8. Figure 58 illustrates the effect of time on the absorbance of the reagent blank and in the presence of 100 μg Ag^+, 1 μg Cu^{+2}, 50 μg Mn^{+2}, and 500 μg Al^{+3}.

Orcinol

Orcinol monohydrate was obtained from Aldrich Chemical Company. Purification by sublimation produced the anhydrous orcinol which melted at 106.4-108.4°C. The Merck Index (57) shows the melting point of the monohydrate at 58°C and 107°C for the anhydrous compound.

The absorption spectra of 0.01145 $\underline{M}$ orcinol after 10 and 120 minutes of reaction at pH 11.5 is shown in Figure 59. The effect of 100 μg Ag^+ on the first ten minutes of reaction is also shown in Figure 59. The wavelength of maximum absorption is 470 nm in all three cases.

The effects of various cations on the reaction were tested by adding 0.1 to 10 ml of solutions of these cations to 10 ml of 0.025 $\underline{M}$ orcinol, diluting to 20 ml with deionized water and then adding 5 ml of phosphate buffer to initiate the reaction. Absorbance measurements which were taken
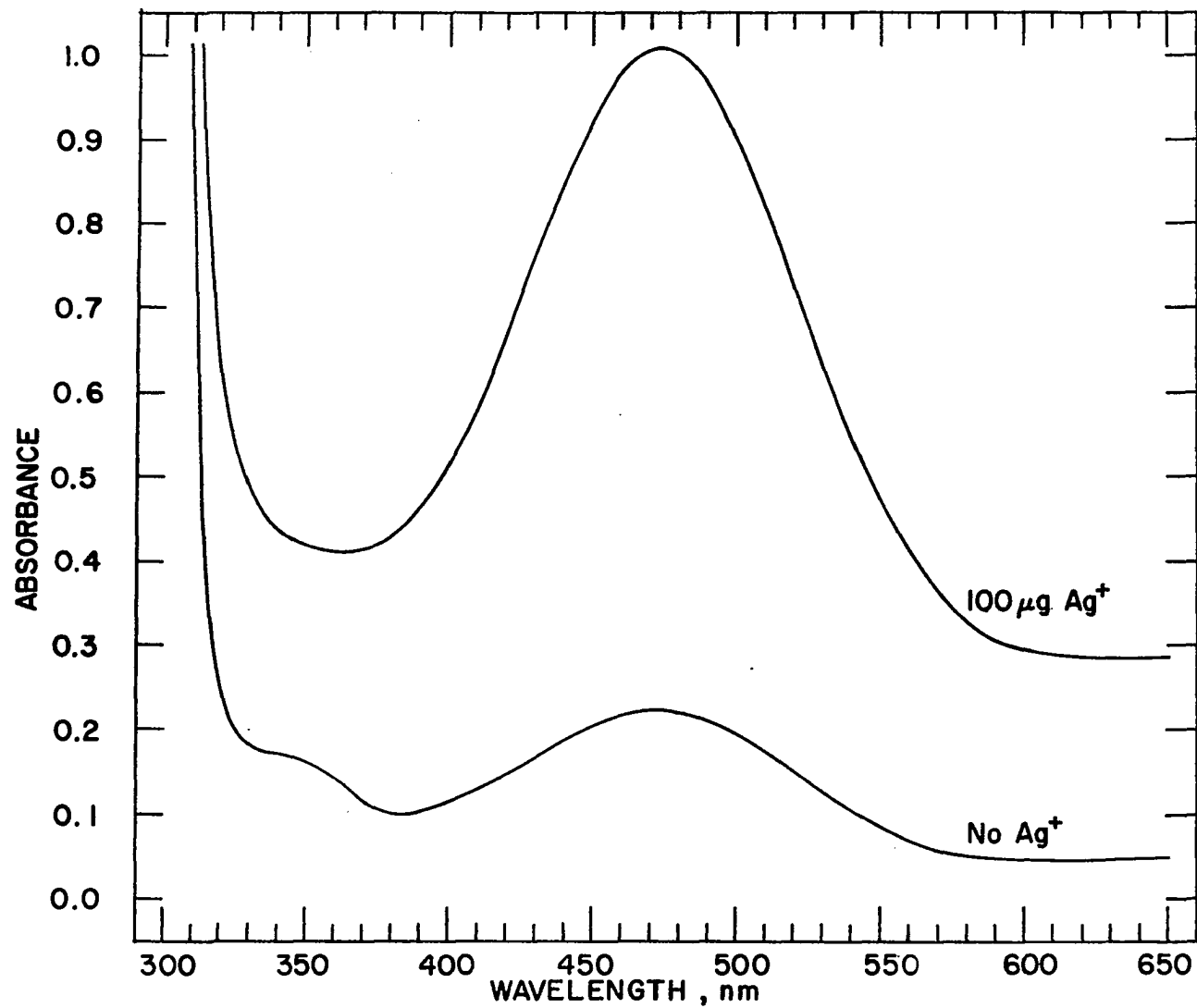
Figure 57. Absorption spectrum of autoxidized 2-methylresorcinol (25 ml)

Table 8. Effects of cations on the absorbance of resorcinols after 10 minutes of autoxidation [a]

μg	Cation	2-methylresorcinol	orcinol	4-ethylresorcinol	phloroglucinol
	Blank[b]	.234	.080	.101	.008
100	Ag^+	.930	.374	.208	.139
500000	Na^+	.244	.124	.083	.006
500000	K^+	.252	.086	.094	.008
5000	Li^+	.163	.067	.088	.007
50	NH_4^+	.150	.052	.067	.010
50	Hg^+	.148	.070	.092	.046
50	Cu^+	.165	.393	.121	.005
50	Hg^{+2}	.288	.096	.107	.022
500	Ba^{+2}	.205	.080	.112	.042
500	Sr^{+2}	.205	.078	.119	.031
500	Ca^{+2}	.178	.063	.101	.027
500	Mg^{+2}	.207	.064	.080	.011
5	Co^{+2}	.320	.125	.100	.027
500	Zn^{+2}	.428	.098	.103	.006
5	Pb^{+2}	.168	.052	.090	.008
50	Ni^{+2}	.165	.050	.078	.006
1	Cu^{+2}	.693	.213	.103	.025

[a]Measurements were all made on 25 ml of solution.

[b]The absorbance of the blank is the average of four values.

Table 8 (Continued)

μg	cation	2-methylresorcinol	orcinol	4-ethylresorcinol	phloroglucinol
500	Cd^{+2}	.150	.068	.100	.016
50	Fe^{+2}	.245	.100	.090	.036
50	Mn^{+2}	.885	.293	.081	.051
5	Pd^{+2}	.198	.076	.101	.007
500	Ti^{+3}	.052	.021	.024	.007
500	Sb^{+3}	.134	.036	.093	.009
50^{c}	Fe^{+3}	.190	.093	.086	.030
500	Al^{+3}	.425	.145	.104	.013
38.5	Tl^{+3}	.184	.071	.090	.072
50	Cr^{+3}	.093	.035	.068	.005
50	Bi^{+3}	.196	.053	.093	.005
50^{c}	Au^{+3}	.142	.109	.110	.036
500	Dy^{+3}	.104	.045	.075	.008
500	Er^{+3}	.085	.039	.064	.006
50	Eu^{+3}	.162	.160	.092	.005
500	Ho^{+3}	.115	.046	.071	.013
500	La^{+3}	.120	.048	.032	.010
500	Lu^{+3}	.101	.046	.072	.010

cWith a ten fold increase in concentration the cation reacts with the compound to form a colored species prior to the addition of buffer.

Table 8 (Continued)

μ g	cation	2-methylresorcinol	orcinol	4-ethylresorcinol	phloroglucinol
500	Pr^{+3}	.110	.045	.076	.013
500	Tm^{+3}	.081	.036	.066	.005
50	Tb^{+3}	.126	.047	.084	.004
500	Yb^{+3}	.084	.038	.064	.007
50	Sm^{+3}	.142	.048	.073	.008
50	Nd^{+3}	.127	.094	.091	.012
50	Gd^{+3}	.147	.051	.087	.012
50	Ce^{+4}	.091	.051	.081	.006
500	Th^{+4}	.183	.052	.082	.012
5	Sn^{+4}	.153	.054	.086	.012
50	Pt^{+4}	.250	.063	.090	.022
50	UO_2^{+2}	.183	.086	.091	.014
500	AsO_4^{-3}	.330	.108	.102	.005
500^d	CrO_4^{-2}	.151	.054	.086	.004
500	VO_3^-	.132	.067	.089	.046
500	MoO_4^{-2}	.343	.205	.101	.019
500	WO_4^{-2}	.219	.129	.095	.005

[d]Absorbance was corrected for the natural absorbance of $CrO_4^=$.
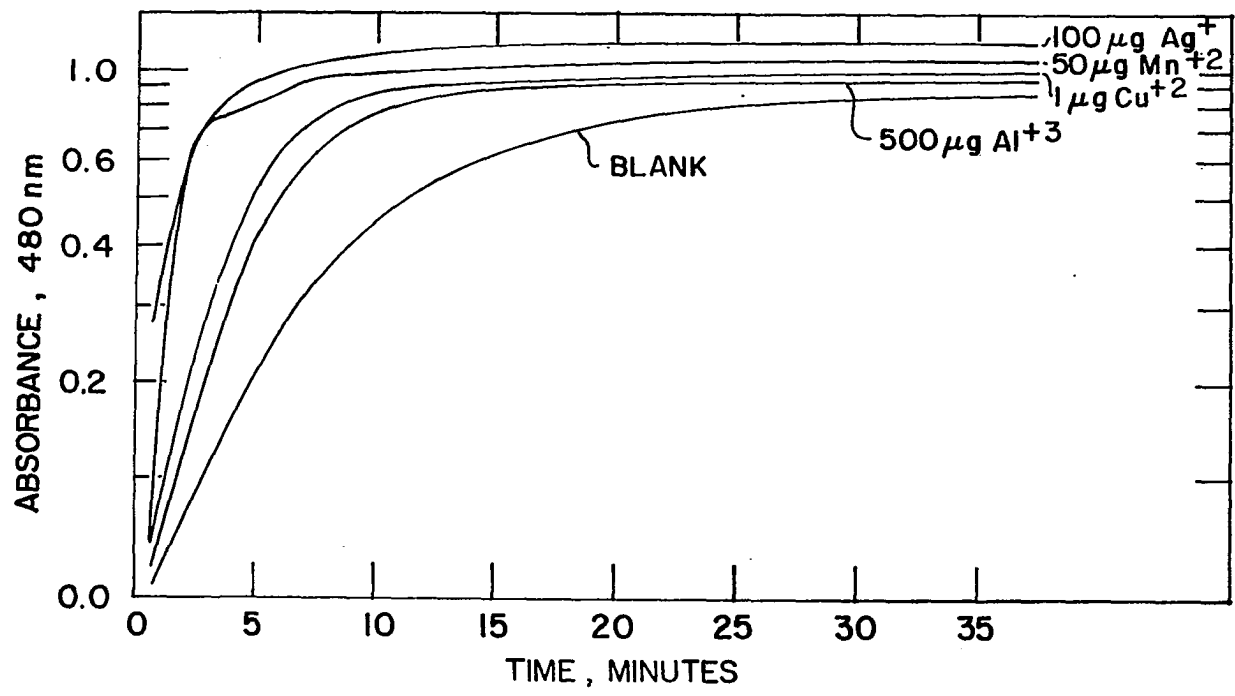
Figure 58. Change in the absorbance with time for 25 ml of 2-methylresorcinol
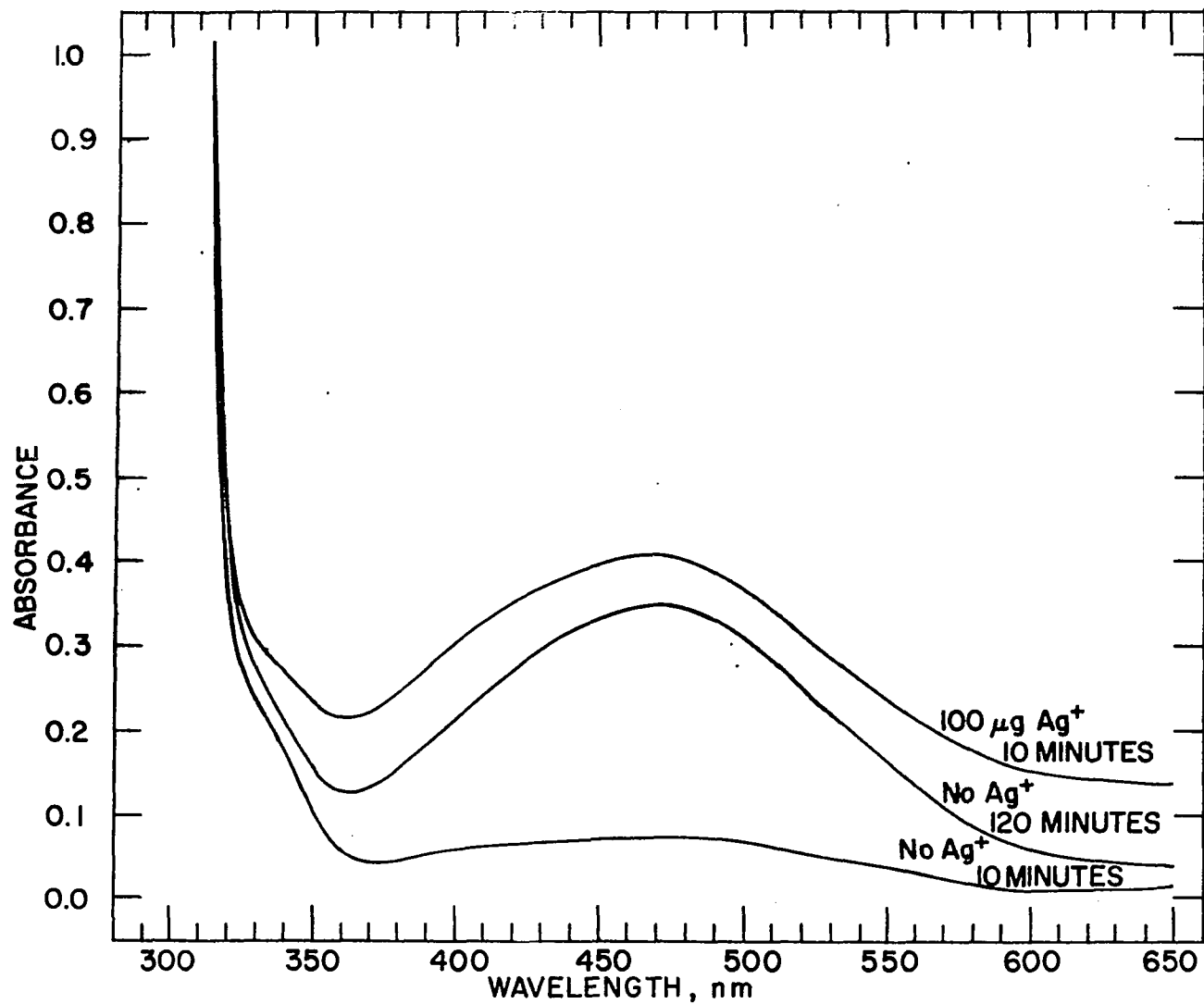
Figure 59.   Absorption spectrum of 25 ml of autoxidized orcinol

after ten minutes at 430 nm are shown in Table 8.

Figure 60 shows the effects of 100 μg Ag^+, 1 μg Cu^{+2}, and 5 μg Co^{+2} on the absorbance during the first 35 minutes. The blank reaction is also shown on Figure 60. Figure 61 shows the effects of 50 μg Cu^+, 50 μg Eu^{+3}, 500 μg Al^{+3}, and 500 μg WO_4^{-2}.

4-Ethylresorcinol

Aldrich Chemical Company was the source of the 4-ethylresorcinol used. Sublimation was used to purify the compound. Small white branched crystals were obtained which melted at $95.4^\circ C$. The literature value (33) for the melting point was $98-99^\circ C$ and Aldrich provided a melting point range of $93-97^\circ C$ with the sample.

The visible spectrum produced by ten minutes of autoxidation of 0.01 M 4-ethylresorcinol at pH 11.5 is shown in Figure 62. The same figure also shows the spectrum produced when 100 μg Ag^+ was present. The wavelength of maximum absorption in both cases is 480 nm.

The effects of various cations on the reaction were tested by addition of 0.1 to 10 ml of solutions of these cations to 10 ml of 0.025 M 4-ethyl-resorcinol, dilution to 20 ml with deionized water and then addition of 5 ml of phosphate buffer to initiate the reaction. The absorbance measurements which were taken after ten minutes are presented in Table 8.

Figures 63 and 64 show the effects of the more reactive cations on the absorbance for the first 35 minutes of reaction. The blank reaction, 100 μg Ag^+, 10 μg Cu^{+2}, and 50 μg Cu^+ are presented in Figure 63 while the effects of 50 μg Mn^{+2}, 50 μg Hg^{+2}, 500 μBa^{+2}, and 500 μg Sr^{+2} are shown in Figure 64.
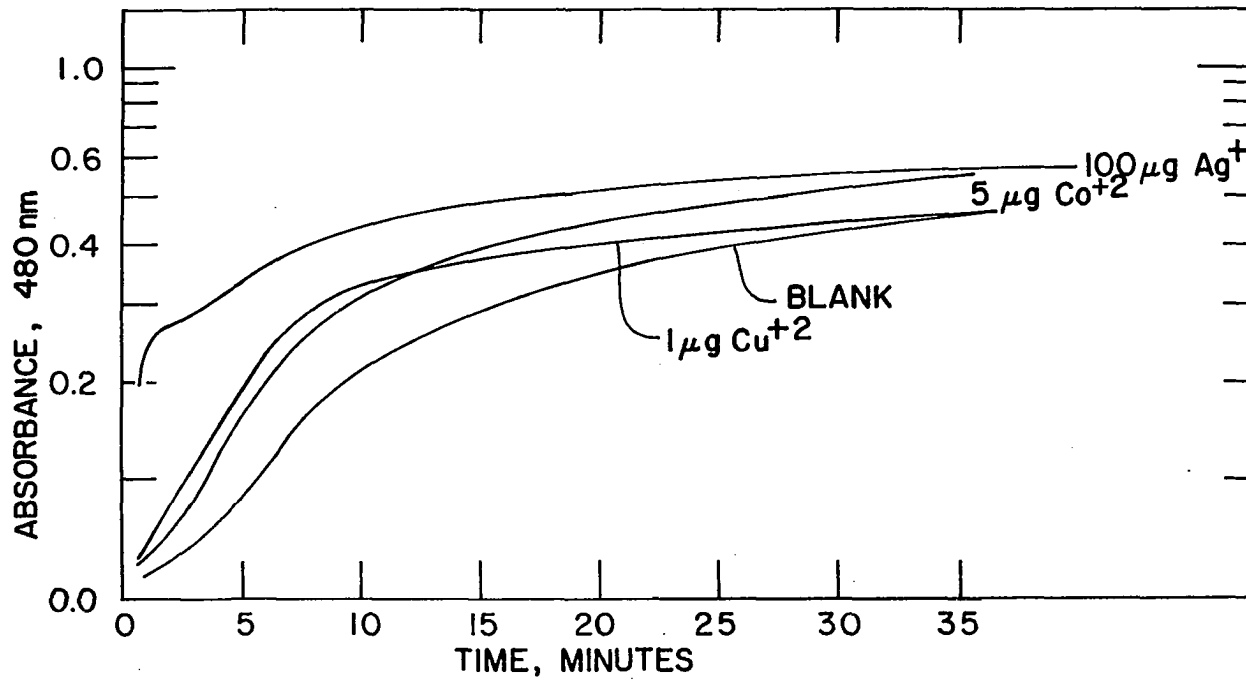
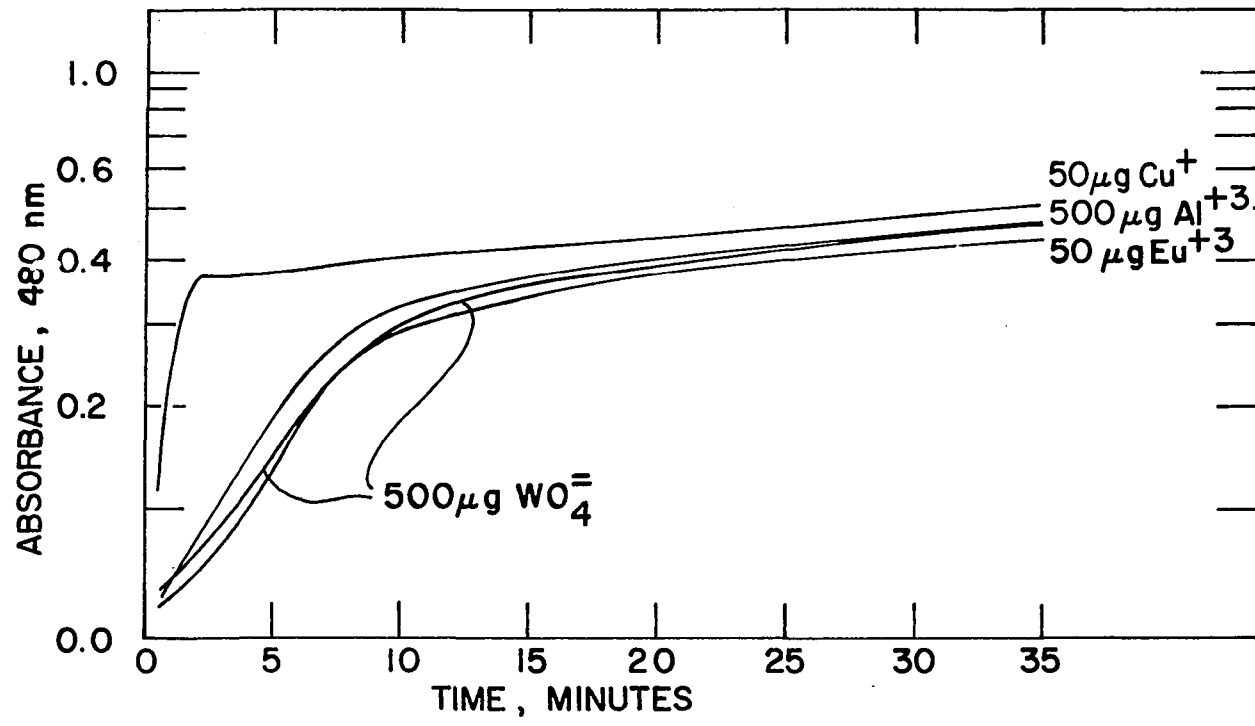Figure 60. Change in the absorbance with time for 25 ml of orcinol

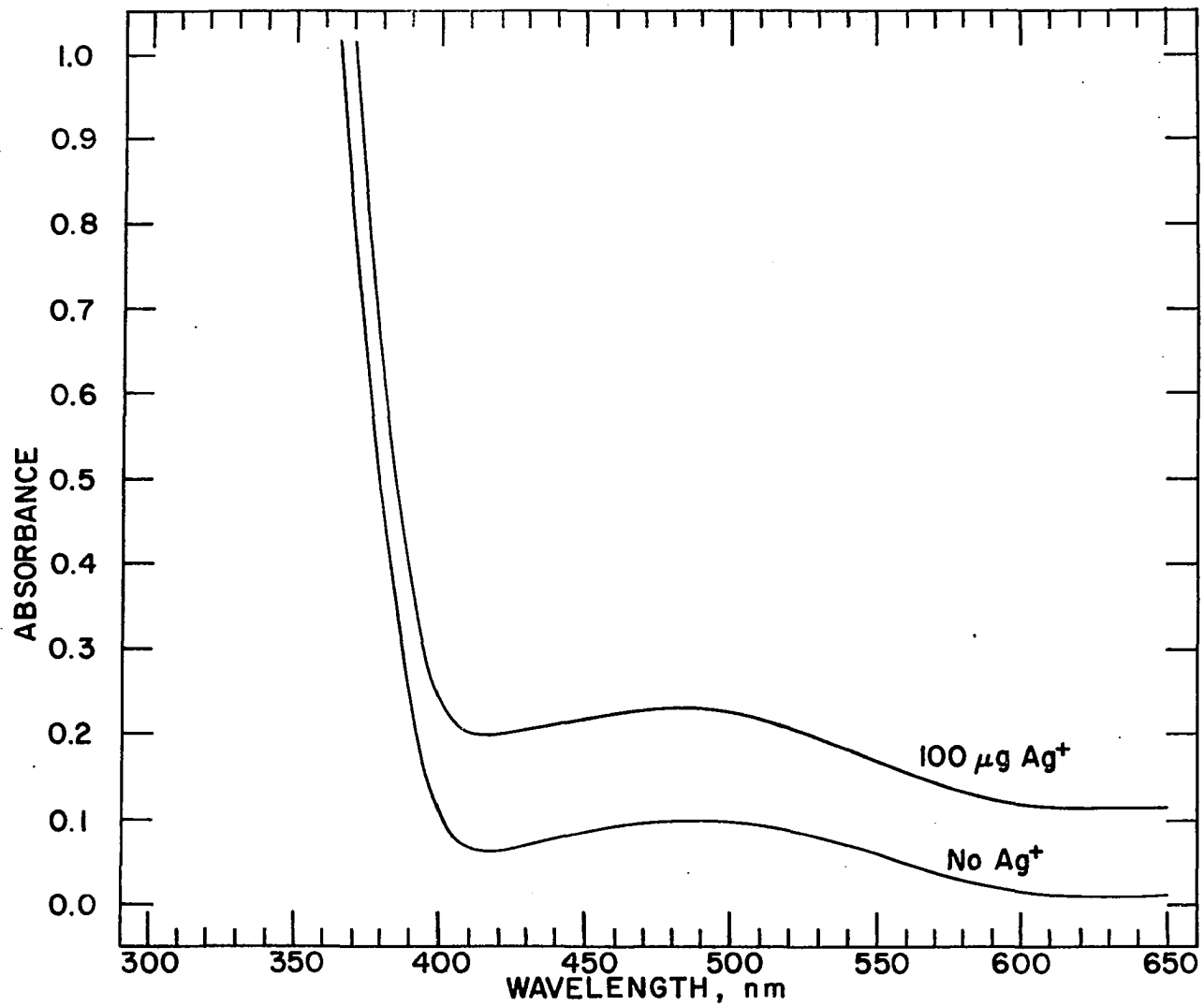Figure 61. Change in the absorbance with time for 25 ml of orcinol

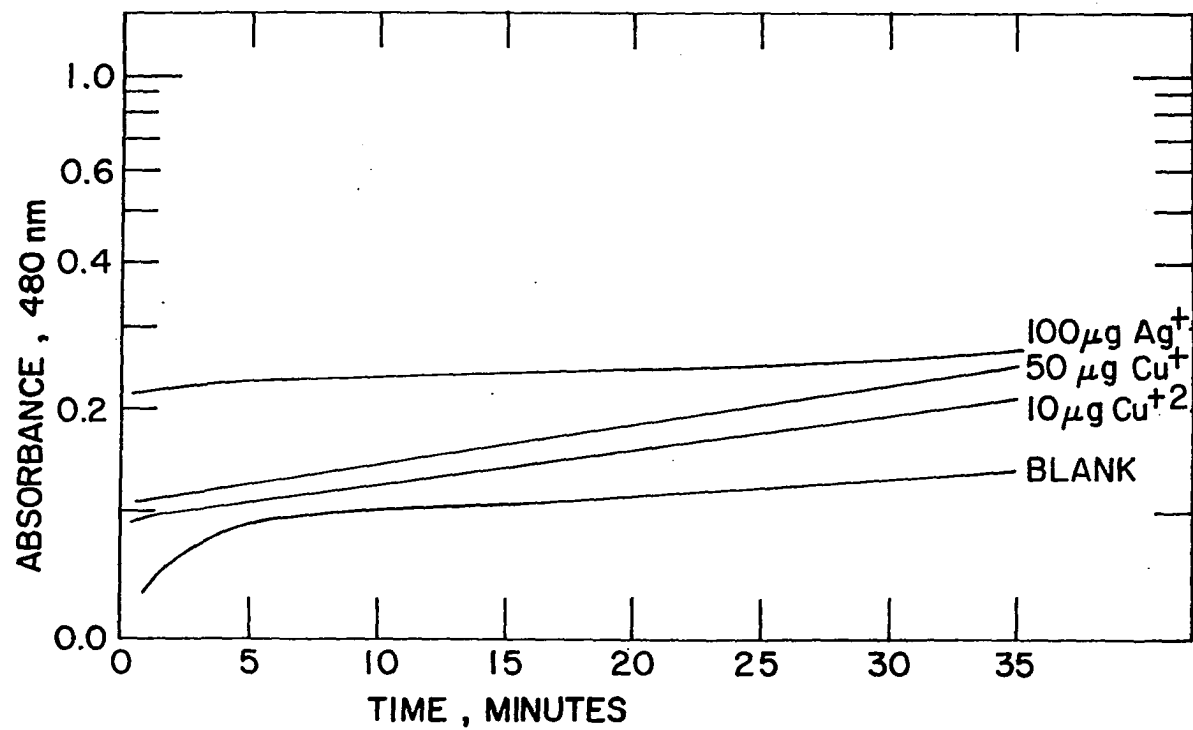Figure 62. Absorption spectrum of 25 ml of autoxidized 4-ethylresorcinol

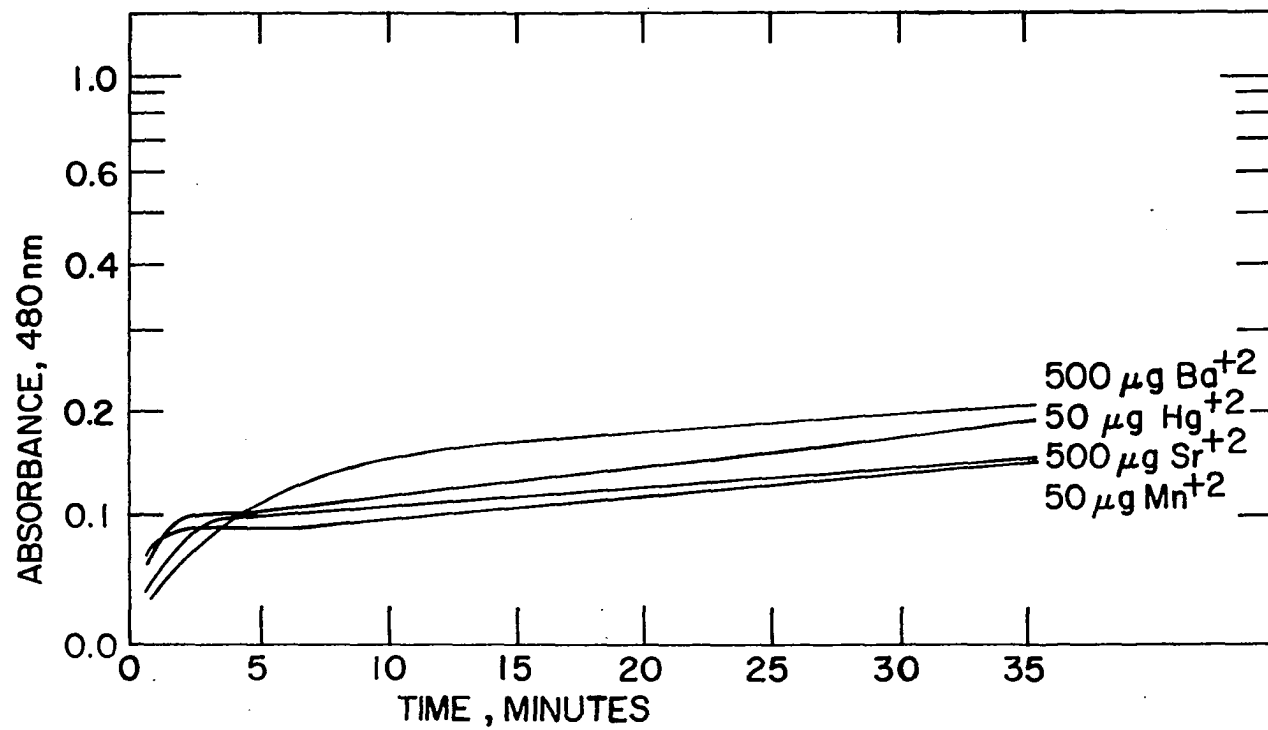Figure 63. Change in the absorbance with time for 25 ml of 4-ethylresorcinol

Figure 64. Change in the absorbance with time for 25 ml of 4-ethylresorcinol

The 4-ethylresorcinol-silver reaction appeared to have less interferences than the resorcinol-silver reaction so it was studied further. The effect of pH is shown in Figure 65. These data were obtained by addition of up to 10 ml of 0.1 $\underline{N}$ nitric acid or 0.1 $\underline{N}$ sodium hydroxide to 10 ml of a stock solution of silver and 4-ethylresorcinol, dilution to 20 ml with deionized water and addition of 5 ml of buffer to initiate the reaction. The absorbance was measured at 10 minutes of reaction time and the pH of the solution measured. The stock solution was prepared by addition of 2.5 ml of 1 mg/ml Ag^+ solution to a 250 ml volumetric flask containing 0.86356 g of 4-ethylresorcinol and then dilution to volume with deionized water. Thus the concentration of silver in each reaction was 100 $\mu g/25$ ml and the concentration of 4-ethylresorcinol was 0.010 $\underline{M}$.

The 4-ethylresorcinol concentration was varied (0.002, 0.004, 0.006, 0.008, and 0.010 $\underline{M}$) and the absorbance measured for the first 35 minutes of reaction time. Figure 66 shows these data. A similar series of 4-ethylresorcinol solutions was caused to react in the presence of 100 μg $Ag^+/25$ ml. These data are shown in Figure 67. Since very little change in absorbance was observed with changing 4-ethylresorcinol concentration, further study of this variable was conducted by measuring a series of 0, 20, 40, 60, 80, and 100 μg $Ag^+/25$ ml at each of 0.001, 0.002, 0.003, 0.004, and 0.005 $\underline{M}$ 4-ethylresorcinol concentrations. These data are shown in Figures 68 to 72, respectively. The most sensitive 4-ethylresorcinol concentration was then determined by plotting these absorbance data at ten minutes of reaction time against the concentration of silver and drawing a straight line through the points from each concentration of 4-ethylresorcinol. See Fig-
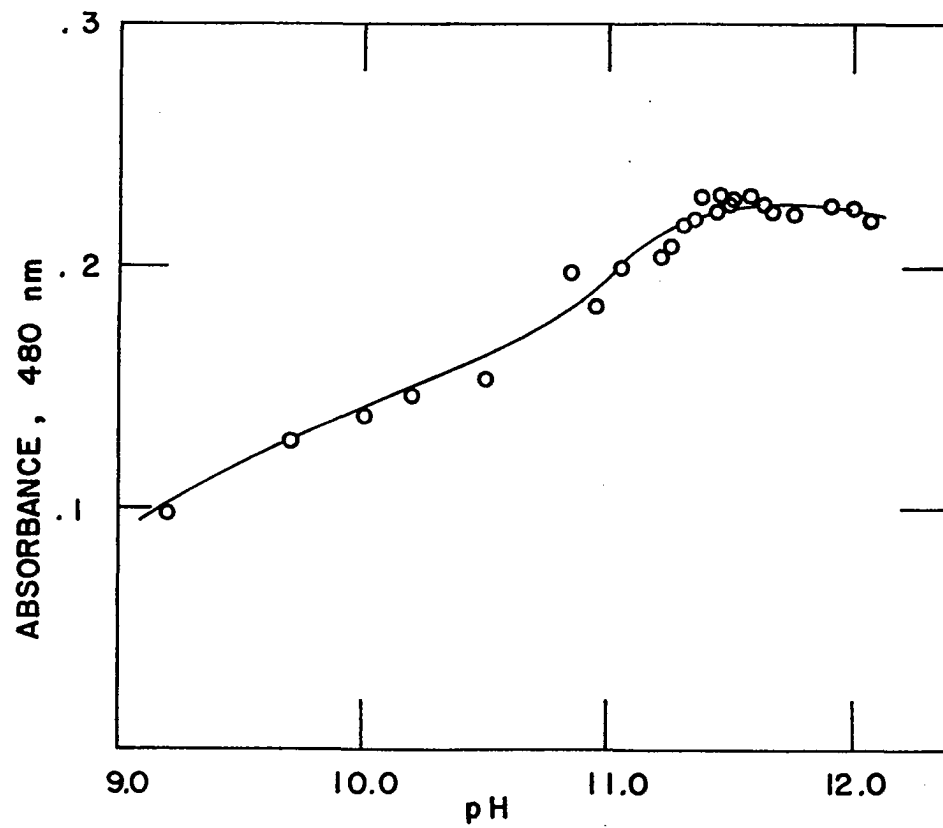
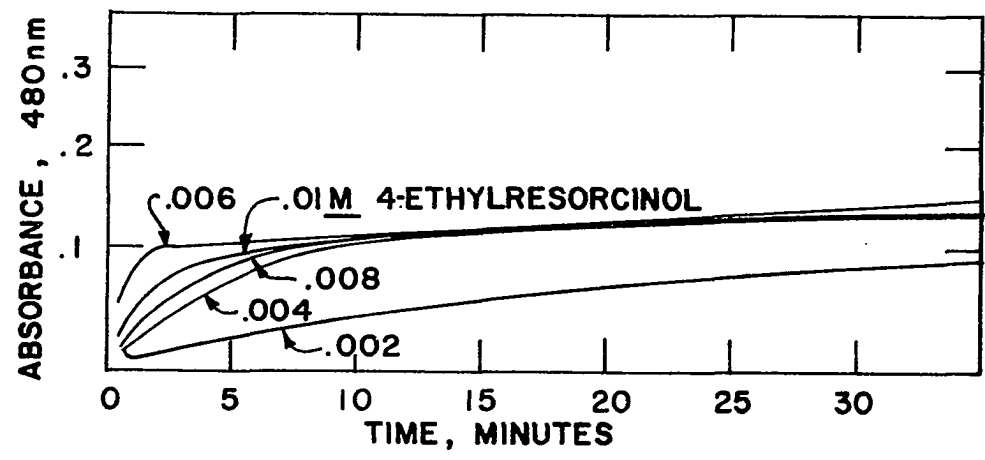Figure 65. Effect of pH on the absorbance of 0.01 M 4-ethylresorcinol autoxidized for ten minutes

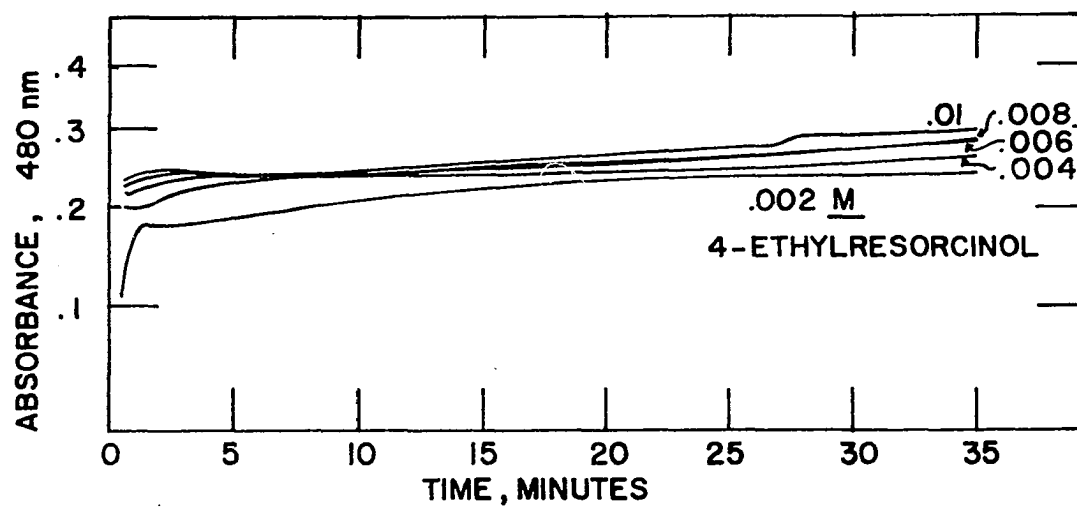Figure 66. Change in absorbance with time for 4-ethylresorcinol

Figure 67. Change in absorbance with time for 4-ethylresorcinol and 100 μg Ag$^+$/25 ml

Figure 68. Change in absorbance with time and concentration of silver for 0.001 $\underline{M}$ 4-ethylresorcinol
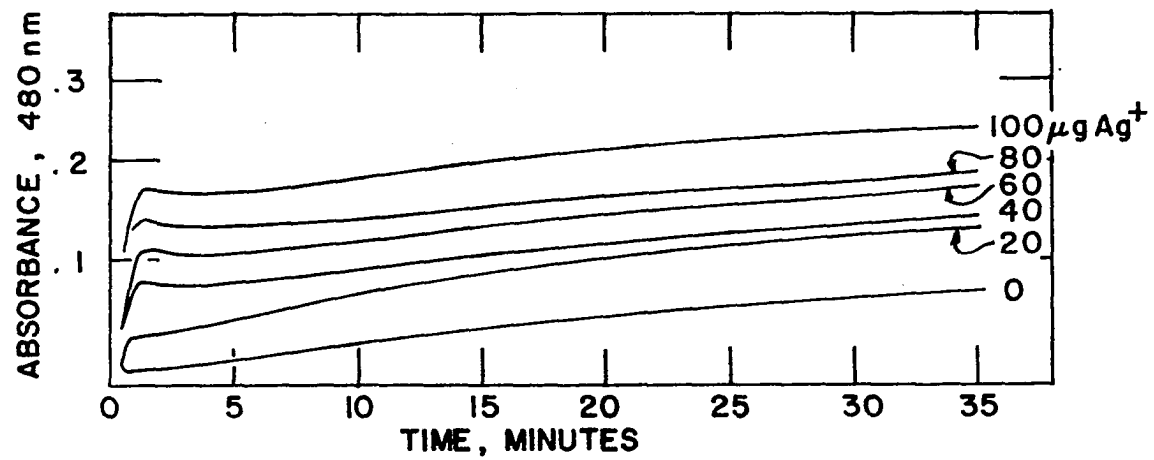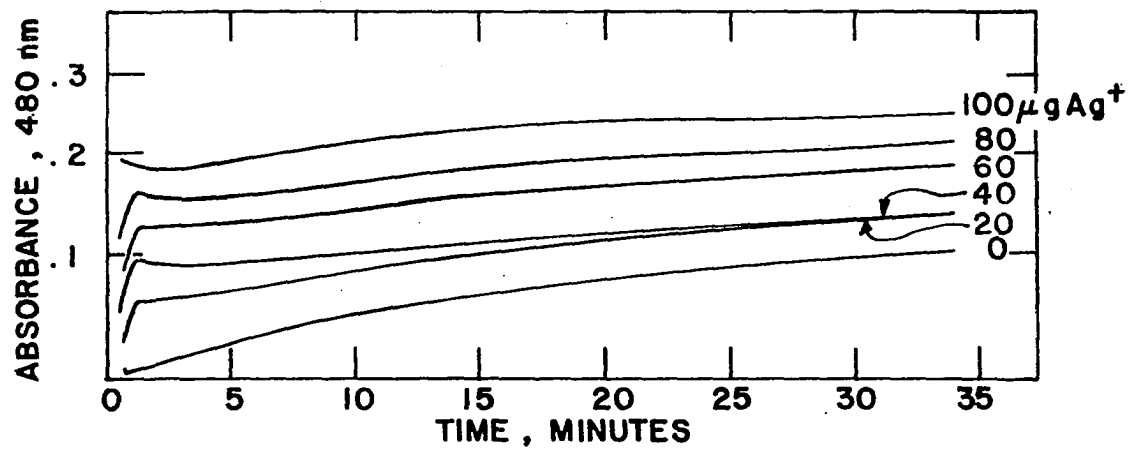
Figure 69. Change in absorbance with time and concentration of silver for 0.002 M 4-ethylresorcinol
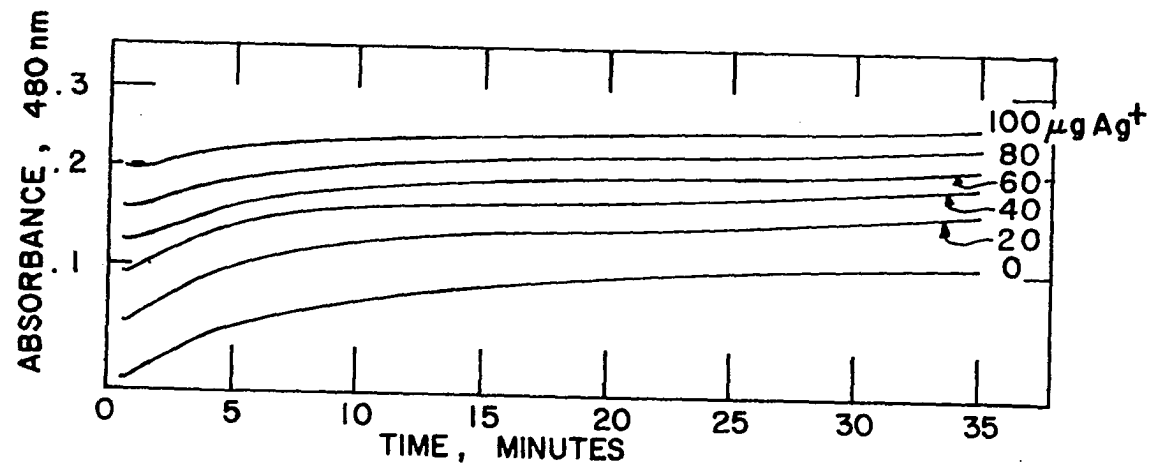
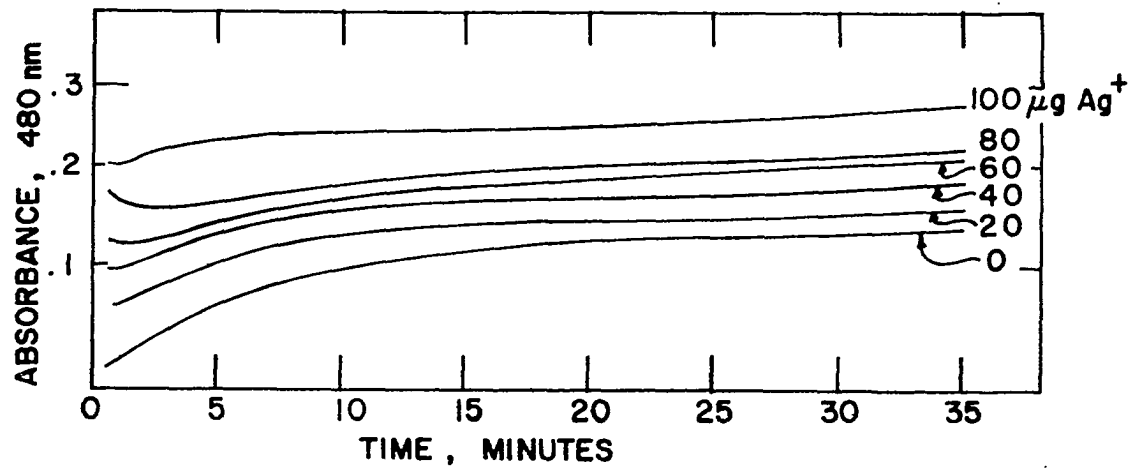Figure 70. Change in absorbance with time and concentration of silver for 0.003 M 4-ethylresorcinol

Figure 71.   Change in absorbance with time and concentration of silver
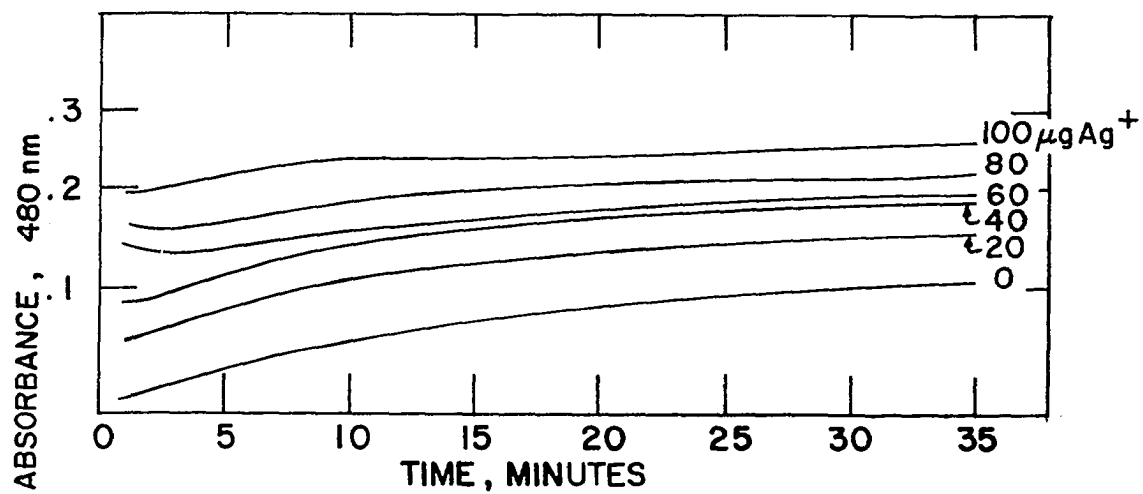
for 0.004 M 4-ethylresorcinol

Figure 72. Change in absorbance with time and concentration of silver
for 0.005 M 4-ethylresorcinol

ure 73. The slopes are 0.00148, 0.00160, 0.00162, 0.00145, and 0.00135, respectively. The most sensitive of the five concentrations has the largest slope, so either 0.002 or 0.003 $\underline{M}$ 4-ethylresorcinol is the optimum concentration. Figure 74 is a calibration curve for the determination of silver with 0.003 $\underline{M}$ 4-ethylresorcinol.

Phloroglucinol

Phloroglucinol was obtained from Matheson Coleman and Bell. According to Merck (57) phloroglucinol undergoes partial decomposition on sublimation so this method of purification was not attempted. Recrystallization from water was used to purify the compound. Twenty grams were dissolved in 150 ml of hot water, filtered and allowed to cool and reprecipitate. After being recrystallized twice the phloroglucinol melted at 217.4-218.4°C. The Merck Index (57) gives 218°C as the melting point.

The spectra of 0.01 $\underline{M}$ phloroglucinol after ten minutes of autoxidation is shown in Figure 75. Figure 75 also shows the effect of 100 μg Ag$^+$ and 38.5 μg Tl^{+3} on the autoxidation. The absorption maximum in all three cases is 550 nm.

The effects of various cations on the reaction were tested by adding 0.1-10 ml of solutions of these cations to 10 ml of 0.025 $\underline{M}$ phloroglucinol, diluting to 20 ml with deionized water and then adding 5 ml of phosphate buffer to initiate the reaction. The absorbance values which were measured after ten minutes of 450 nm are shown in Table 8.

Figure 76 shows the effects of 100 μg Ag$^+$, 1 μg Cu^{+2}, 20 μg Tl^{+3}, 500 μg Ba^{+2} and also the blank on the absorption during the first 35 minutes of reaction time. Figure 77 shows the effects of 50 μg Hg^{+2}, 50 μg
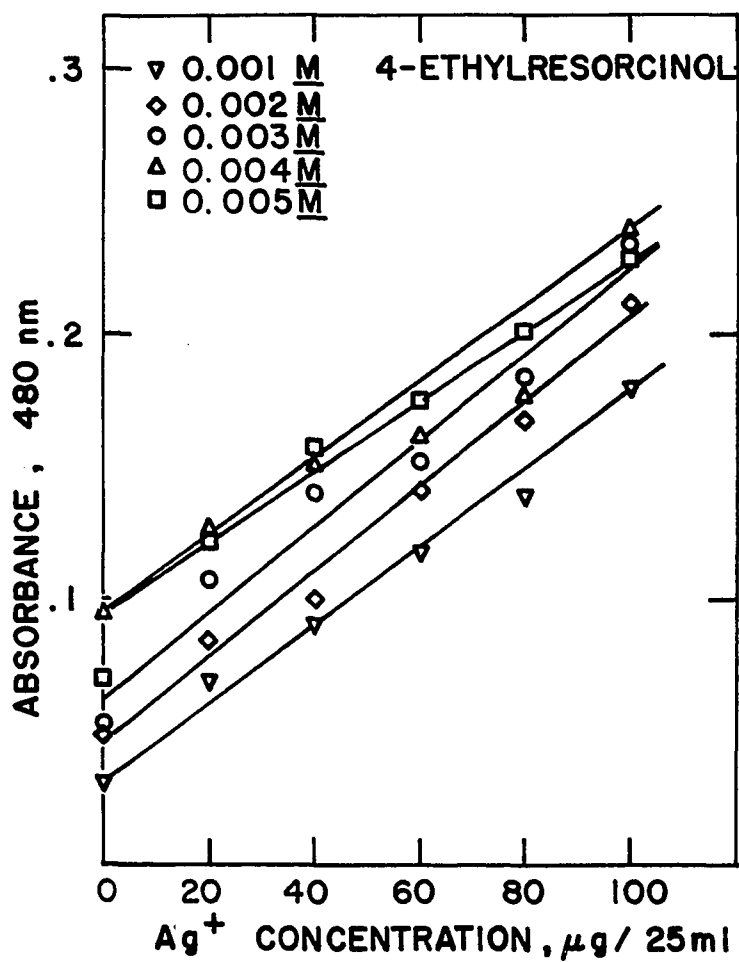
Figure 73. Comparison of the absorbance data in Figures 68-72 at a reaction time of ten minutes
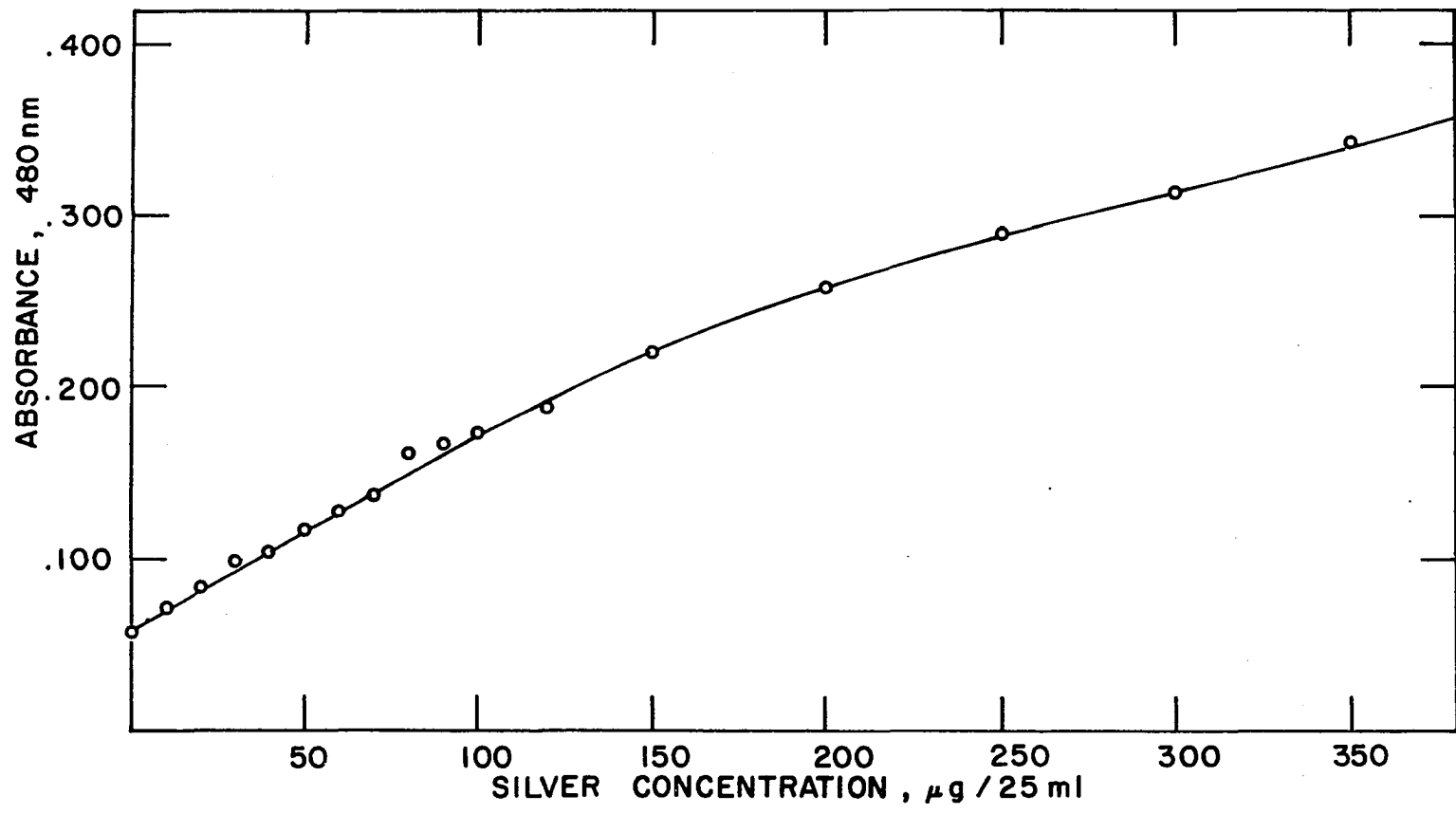
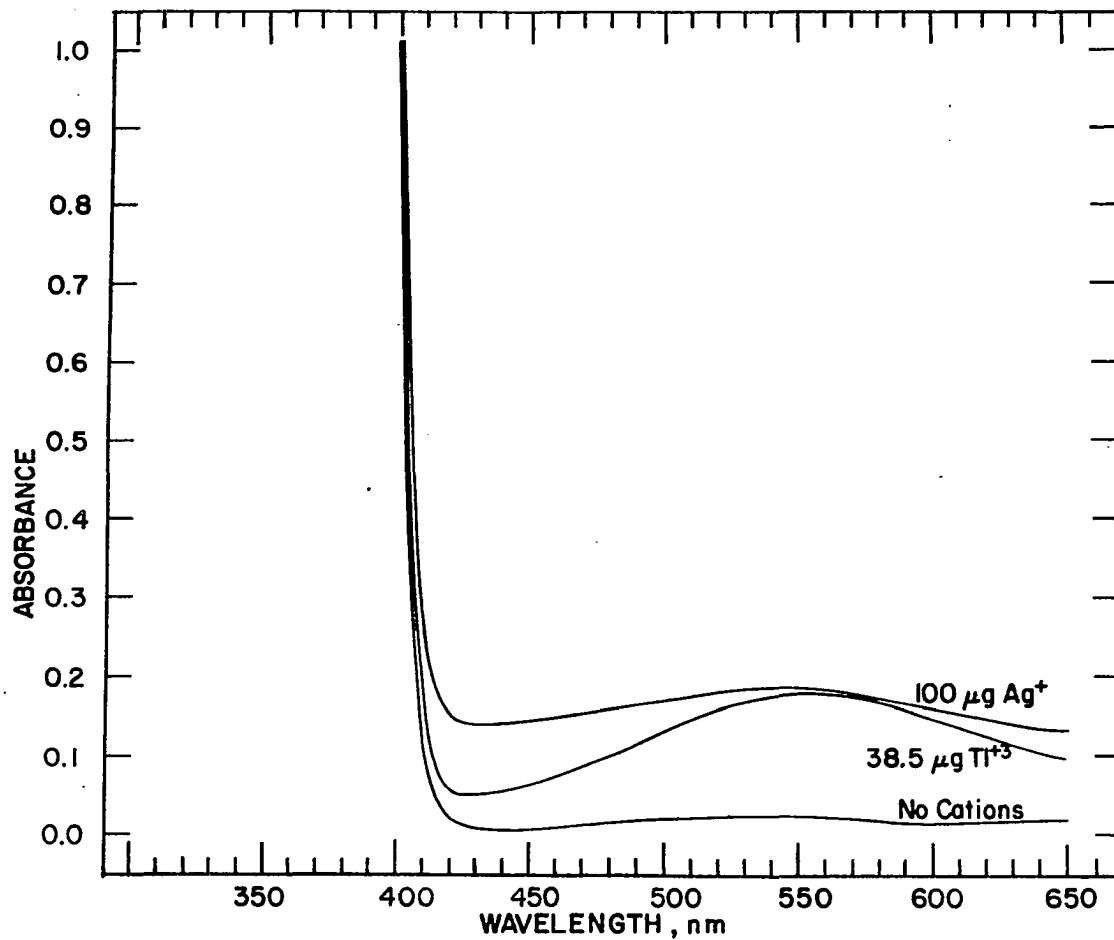Figure 74. Calibration curve for the determination of silver with 0.003 M 4-ethylresorcinol

Figure 75. Absorption spectrum of 25 ml of autoxidized phloroglucinol
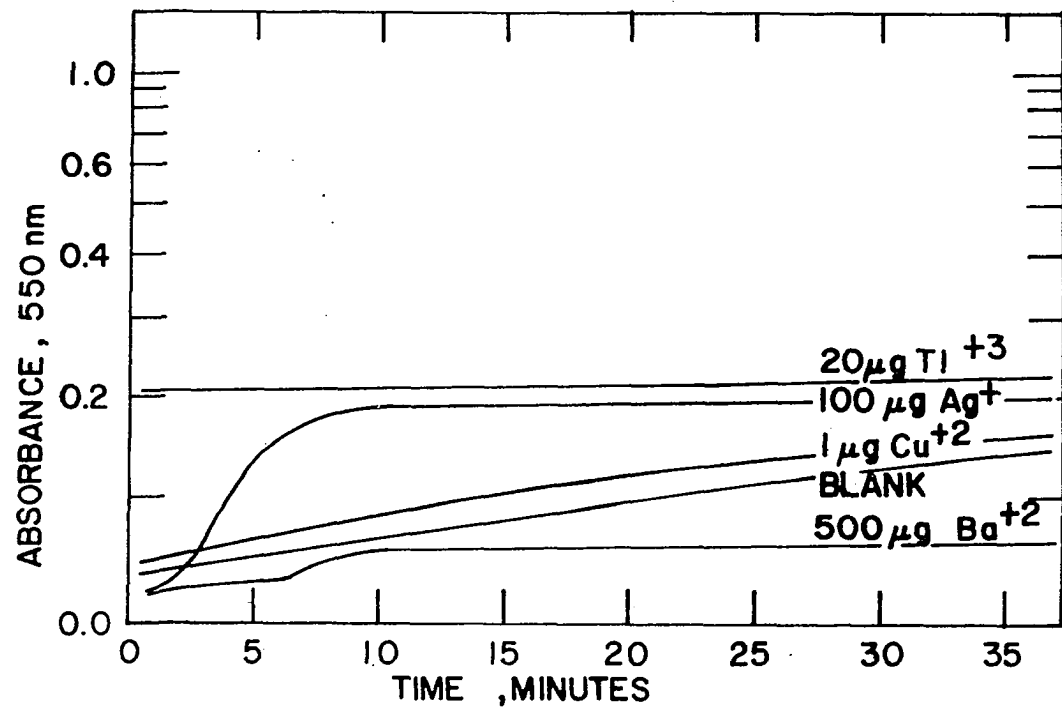
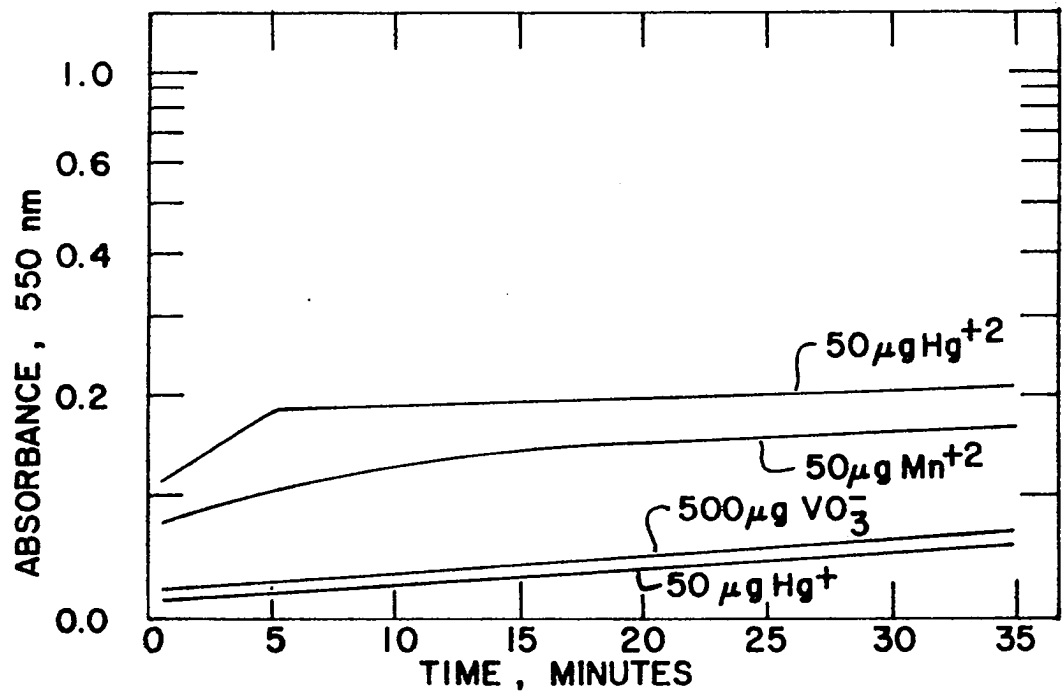Figure 76. Change in the absorbance with time for 25 ml of 0.01 M phloroglucinol

Figure 77. Change in the absorbance with time for 25 ml of 0.01 $\underline{M}$ phloroglucinol autoxidized in the presence of cations

Mn^{+2}, 500 μg VO_3^- and 50 μg Hg^+.

The sensitivity and speed of reaction of thallium with phloroglucinol (Figure 76) indicated that this could be a potential method for the determination of thallium, so the system was studied in more detail. The thallium (III) sulfate which was used was obtained from City Chemical Corporation of New York. Since the waters of hydration on the compound were unknown the solution was standardized by titration with thiosulfate in the presence of excess KI, HCl and starch indicator. The thiosulfate was standardized against primary standard potassium iodate. It was found that 50 μg thallium(I)/25 ml did not influence the reaction so the trivalent form of thallium was the active species. The thallium(III) sulfate solution was stable for at least two years according to thiosulfate titrations.

The effect of pH is shown in Figure 78. There data were obtained by addition of up to 10 ml of 0.1 $\underline{N}$ nitric acid or 0.1 $\underline{N}$ sodium hydroxide to 10 ml of a stock solution of thallium(III) and phloroglucinol, dilution to 20 ml with water and addition of 5 ml of buffer to initiate the reaction. The absorbance was measured at a reaction time of three minutes and the pH of the solution was measured. The stock solution was prepared by addition of 50 ml of 50 μg/ml Tl^{+3} solution to a 250 ml volumetric flask, addition of 0.78819 g of phloroglucinol and dilution to volume with deionized water. The concentrations in the reacting solutions were 10 μg/25 ml for Tl^{+3} and 0.004 $\underline{M}$ for phloroglucinol. Color developed in the solutions below pH 10.2 but faded quickly. Since the measurements were taken after three minutes, this is reflected in the reduced absorbance for solutions reacting at lower pH values. Difficulty was observed with the reactions using NaOH.
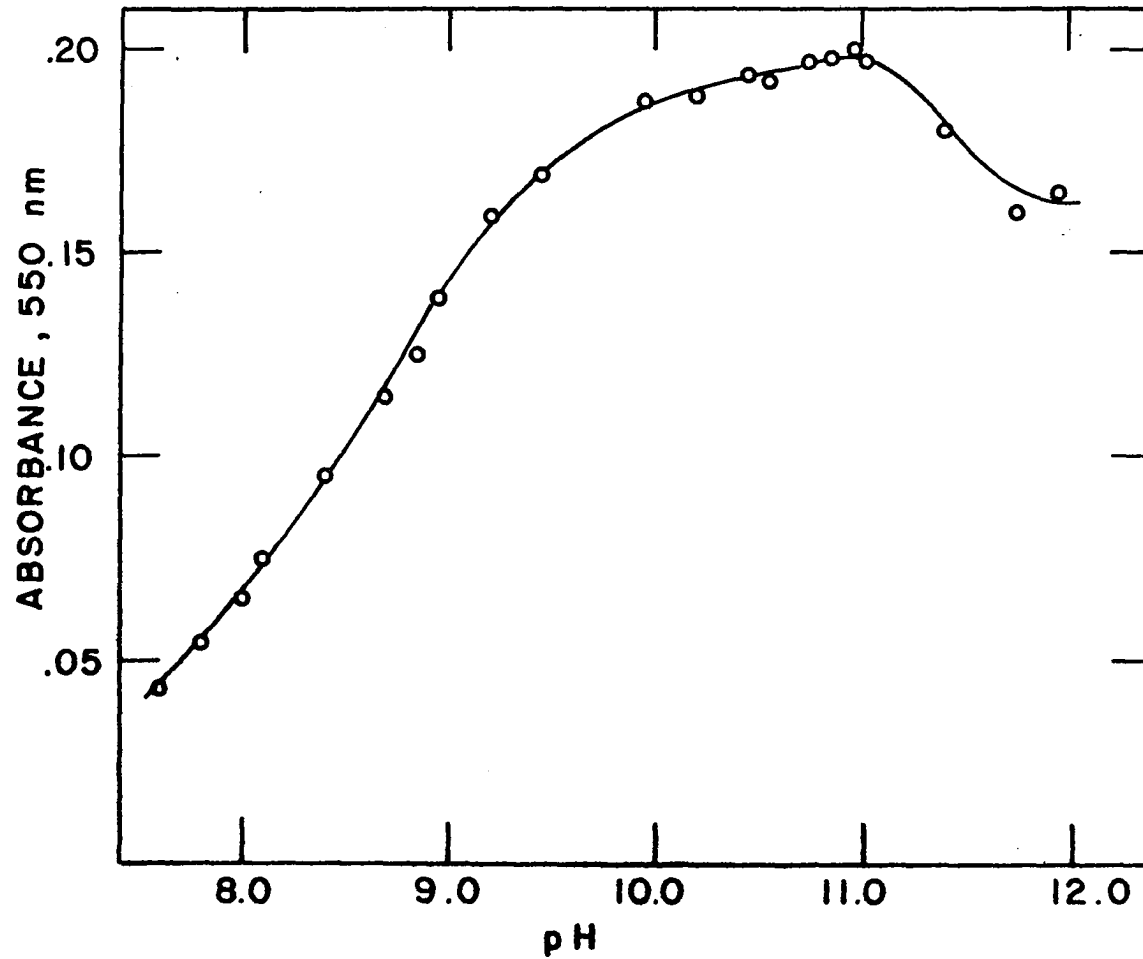
Figure 78. Effect of pH on the Tl^{+3}-phloroglucinol reaction

Very little reaction was observed if the Tl^{+3} or the phloroglucinol was added last (absorbance of 0.022-0.028). When the buffer was added last some improvement was noted in the absorbance (0.079) and better results (0.112) were obtained if the NaOH was added last. Further increase in absorbance was observed (0.135) if the buffer and NaOH were combined and then added. None of these values were reasonably close to the absorbance of 0.153 obtained in the absence of NaOH. Since the pH change was only 0.13 it appeared that the NaOH interfered in the reaction. For development of color in the Tl^{+3}-phloroglucinol reaction both phosphate buffer and oxygen must be present.

The phloroglucinol concentration was varied (0.002, 0.004, 0.006, 0.008, and 0.01 $\underline{M}$) and the absorbance of each solution measured for the first 35 minutes of reaction time. These data are shown in Figure 79. A similar series of phloroglucinol solutions was reacted in the presence of 10 μg Tl^{+3}/25 ml and these data are shown in Figure 80. Not much change was observed between the 0.006, 0.008, and 0.01 $\underline{M}$ concentrations. The series 0.003, 0.004, 0.005, 0.006, and 0.007 $\underline{M}$ was selected for further study. Each of these concentrations of phloroglucinol was reacted in the presence of 0, 2, 4, 6, 8 and 10 μg Tl^{+3}/25 ml. The data are shown in Figures 81 to 85, respectively. Only 20 minutes of reaction time was used since the color produced in the Tl^{+3}-phloroglucinol reactions of Figure 80 were stable for more than 35 minutes.

Figure 86 was obtained by plotting the absorbance values from Figures 81 to 85 at five minutes of reaction time. Since the concentration range of 0 to 10 μg Tl^{+3}/25 ml did not produce a straight line at each of the
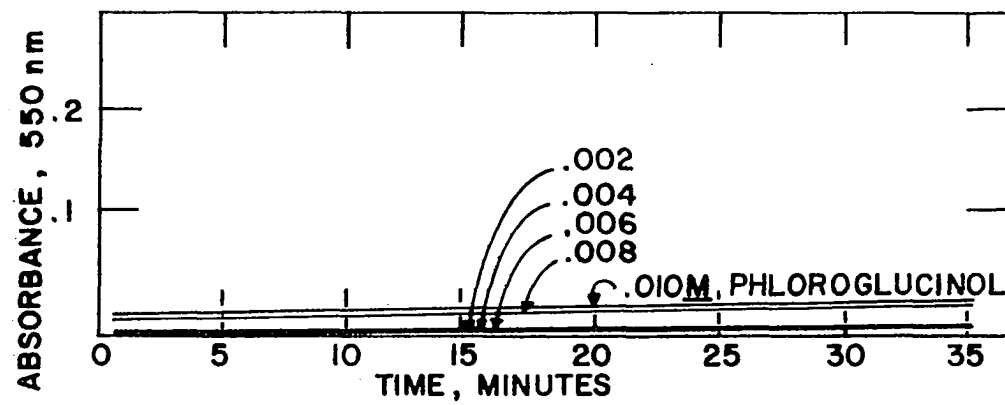
Figure 79. Change in absorbance with time for phloroglucinol
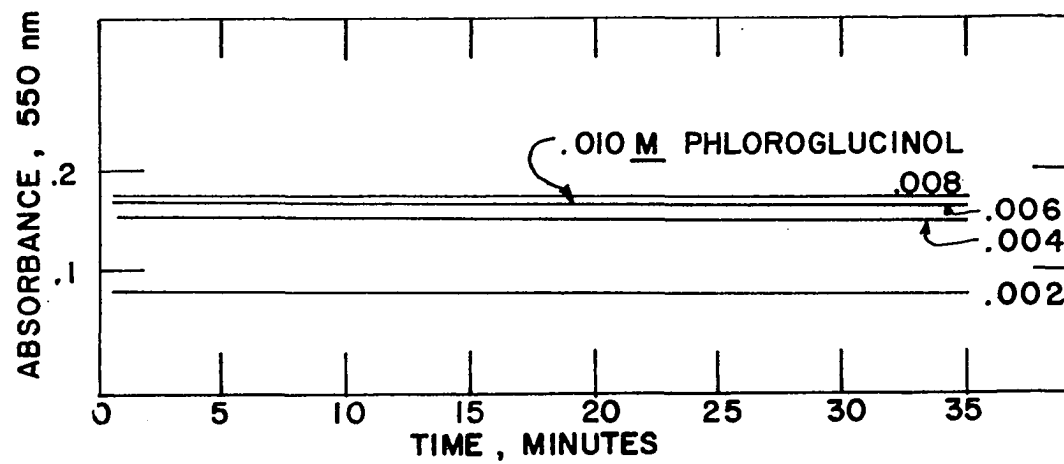
Figure 80. Change in absorbance with time for phloroglucinol and 10 μg Tl^{+3}/25 ml

Figure 81. Change in absorbance with time and concentration of Tl^{+3} for 0.003 $\underline{M}$ phloroglucinol

Figure 82. Change in absorbance with time and concentration of Tl^{+3}

for 0.004 $\underline{M}$ phloroglucinol

Figure 83. Change in absorbance with time and concentration of Tl^{+3} for 0.005 $\underline{M}$ phloroglucinol

Figure 84. Change in absorbance with time and concentration of Tl^{+3} for 0.006 $\underline{M}$ phloroglucinol

Figure 85. Change in absorbance with time and concentration of Tl^{+3}

for 0.007 $\underline{M}$ phloroglucinol

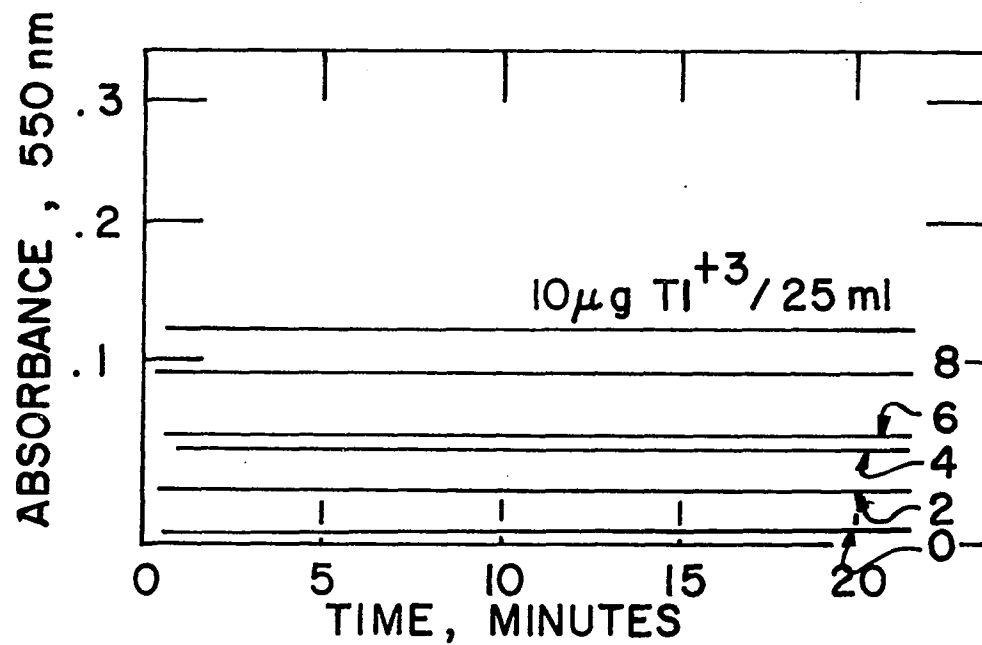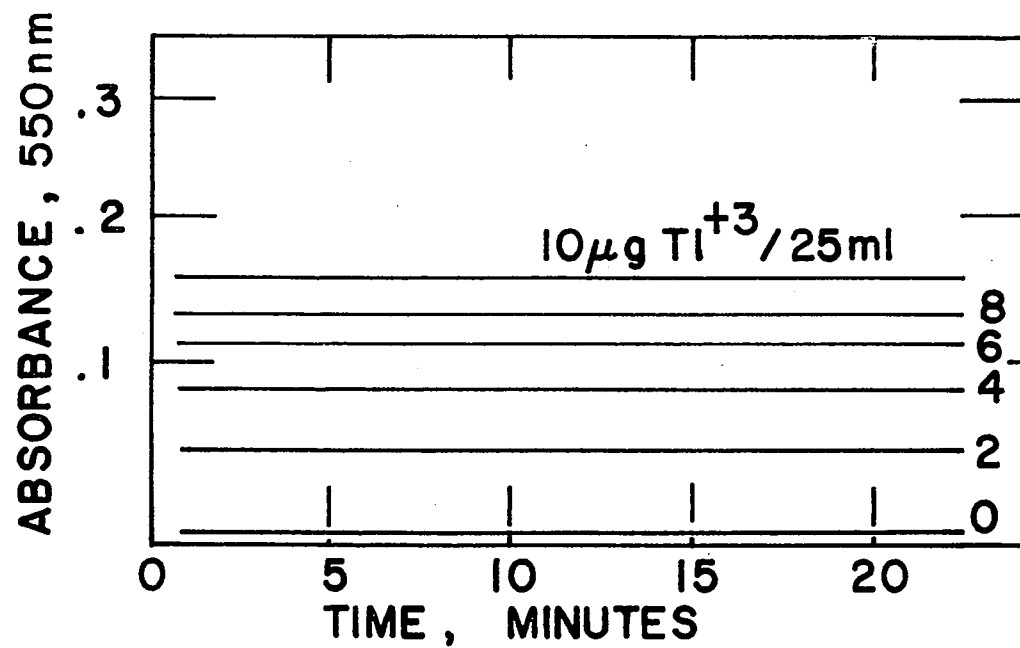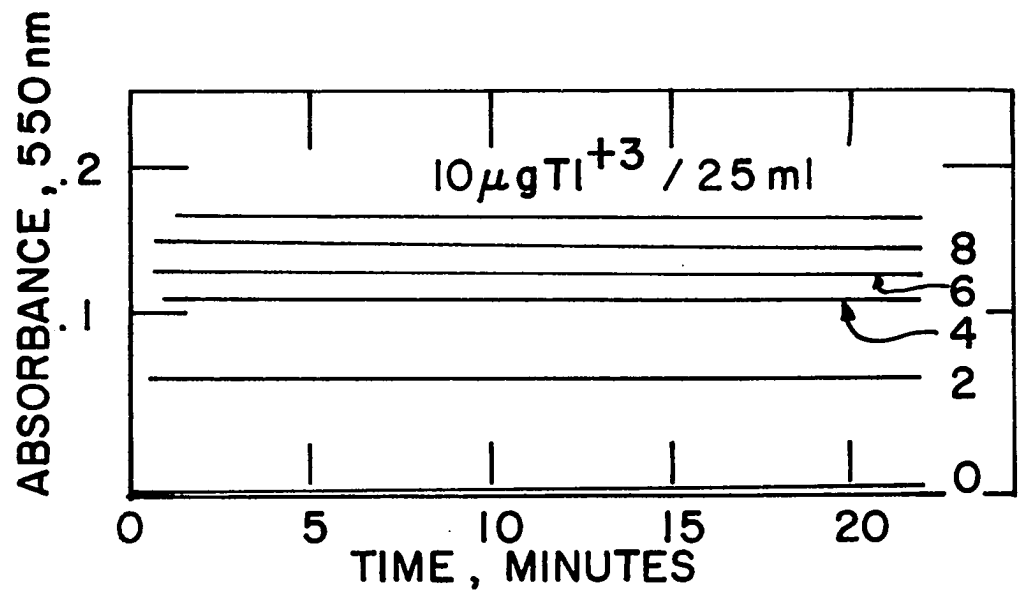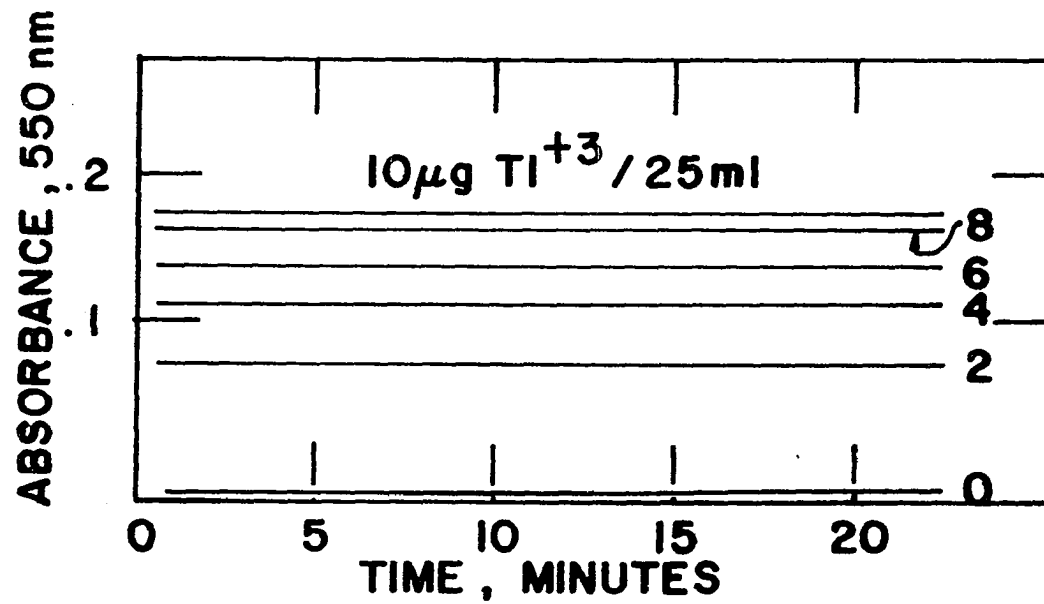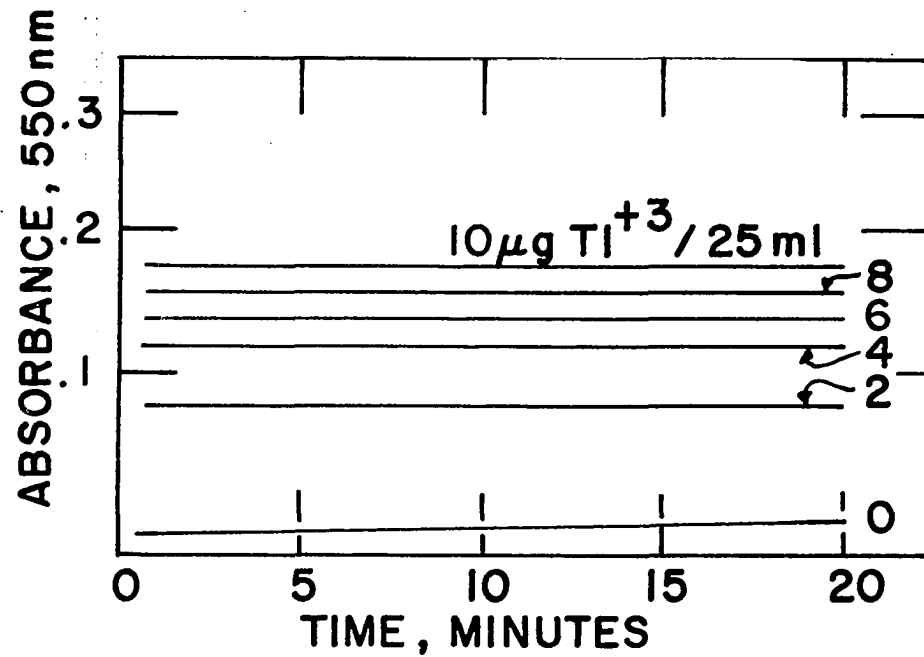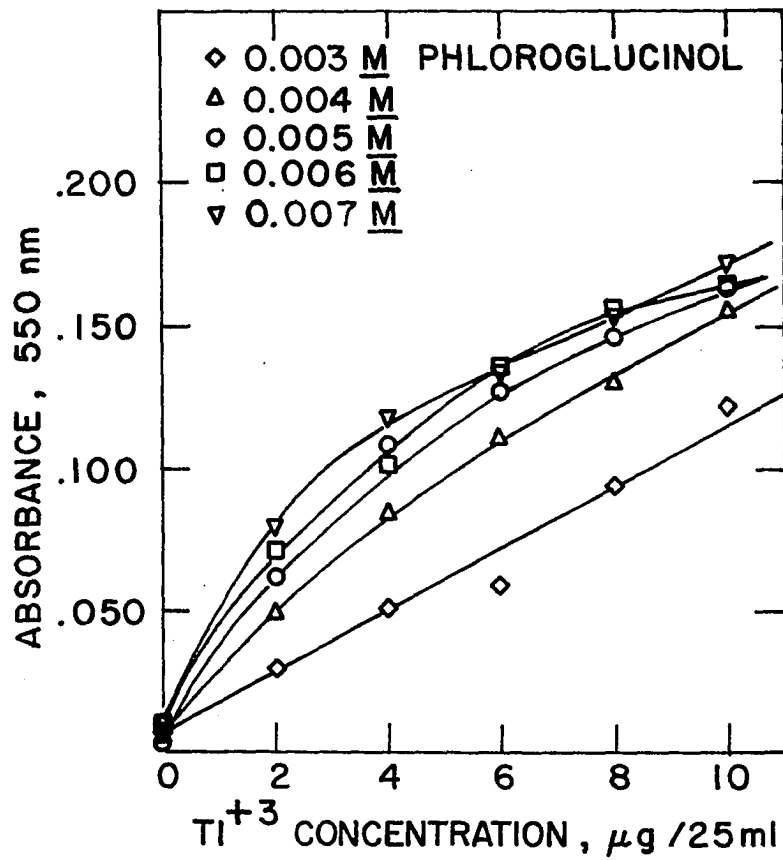Figure 86. Comparison of the absorbance data in Figures 81 to 85 at a reaction time of five minutes

five phloroglucinol concentrations, determination of the slope of each line was difficult. The slopes were estimated to be 0.010, 0.0118, 0.0092, 0.0125 and 0.0090, respectively. The 0.004 $\underline{M}$ solution appeared to be better for higher Tl^{+3} concentrations than the 0.006 $\underline{M}$ solution so it was used for the calibration curve which is shown in Figure 87.

<center>Discussion</center>

Spectra

The ten derivatives of resorcinol whose autoxidation behavior was studied were all colorless solids yielding colorless aqueous solutions except the 2-nitroresorcinol which yielded red crystals and a red solution. Previous experience with resorcinol indicated that solutions below 0.001 $\underline{M}$ did not autoxidize well. This is probably due to the free radical step which requires that a resorcinol anion come in contact with the free radical. More concentrated solutions favor this process. The 2-nitroresorcinol (Figure 48) had such an intense maximum at 390 nm that it was necessary to dilute the solution down to 0.0004 $\underline{M}$ to keep the maximum on scale. Hence no autoxidation was observed in ten minutes. The other compounds all yielded a colored product although in several cases no absorption maximum was obvious in the first ten minutes. However, a maximum developed in all cases during the first two hours of reaction. The spectra of orcinol shown in Figure 59 is a good example. The maximum observed in the autoxidation was always the same maximum observed in the presence of 100 μg $Ag^+/25$ ml. Silver was typical of most cations in yielding spectra similar to the spectra of the blanks. The exceptions were Fe^{+3} and Au^{+3} which will be discussed in more detail later. Resorcinol when allowed to
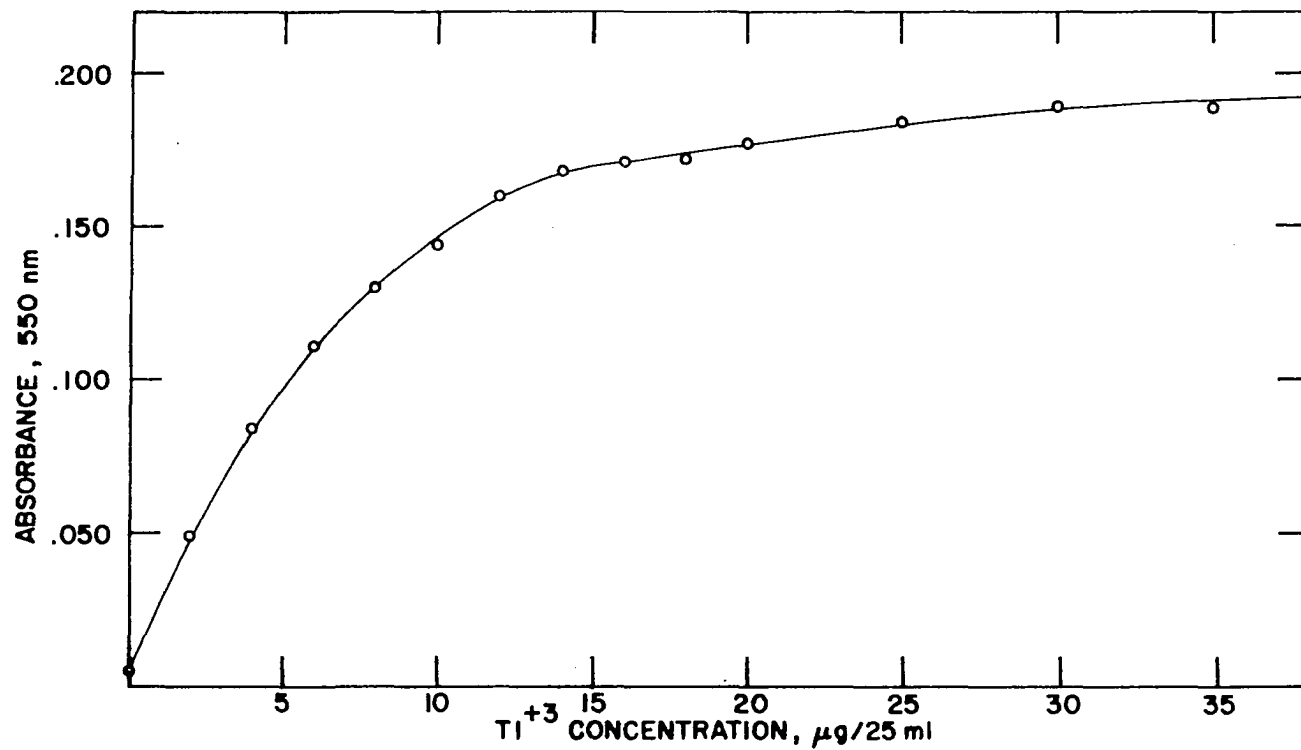
Figure 87. Calibration curve for the determination of Tl^{+3} with 0.004 $\underline{M}$ phloroglucinol

autoxidize exhibited an absorption maximum at 450 nm. The chloroderiva-

tives shown in Figures 47 and 49 also absorbed at 450 nm. The same was

true of the three benzoic acid derivatives whose spectra are shown in Fig-

ures 51, 53, and 55. However, the maxima of the two methyl derivatives and

4-ethylresorcinol were shifted bathochromically to 470, 470 and 480 nm, re-

spectively as can be seen from Figures 57, 59, and 62. The spectra of

phloroglucinol was shifted much more by the extra hydroxyl group and exhib-

ited its maximum absorption at 550 nm (Figure 75). The maximum at 450 nm

normally produced a green colored solution, the 470 nm maximum a brown

colored solution, the 480 nm a red-brown colored solution, and the 550 nm

maximum a violet colored. The 2,6-dihydroxybenzoic acid quickly formed a

violet colored solution which gradually turned green over about the first

20 minutes of reaction. Even resorcinol had a violet colored transition

phase but this phase lasted for only a few seconds. The 2,4- and 3,5-di-

hydroxybenzoic acids had yellow-brown colored transition phases before

turning green.

Influence of cations

Resorcinol, 2-methylresorcinol, orcinol, 4-ethylresorcinol, 4-chloro-

resorcinol, 2,4-, 2,6- and 3,5-dihydroxybenzoic acid and phloroglucinol

were used to study the effects of 52 cations on the autoxidation process.

The absorbance values are recorded in Tables 7 and 8. The large variation

in cation concentrations was largely due to previous experience with the

interference studies for the silver-resorcinol system where many of them

were found to precipitate at pH 11.5 at higher concentrations. Some like

Cu^{+2} were purposely tested in low concentration because they were known to

react with resorcinol at this concentration.

Some cations reacted with all or nearly all of the derivatives. These cations are: 100 μg Ag^+ with activity in all cases; 50 μg Mn^{+2} which affected all except 4-ethylresorcinol and 3,5-dihydroxybenzoic acid; 1 μg Cu^{+2} which did not affect 4-ethylresorcinol, 3,5- and 2,4-dihydroxybenzoic acid; 50 μg Cu^+ which affected all except 2-methylresorcinol and phloroglucinol; and 50 μg Pt^{+4} which did not affect orcinol, 4-ethylresorcinol, and 2,6-dihydroxybenzoic acid. There were five other ions which had activity with five of the nine compounds. These ions were 5 μg Co^{+2}, 500 μg Al^{+3}, 50 μg Hg^{+2}, 50 μg Fe^{+2} and 500 μg MoO_4^{-2}. None of them exhibited activity with 4-ethylresorcinol. The Hg^{+2} did not react with resorcinol, orcinol or 4-chlororesorcinol. Iron(II) did not react with resorcinol, orcinol or 2-methylresorcinol. Cobalt, aluminum and molybdinum all failed to react with 3,5- and 2,4-dihydroxybenzoic acid. Molybdinum did not react with resorcinol, cobalt did not react with 4-chlororesorcinol, and aluminum did not react with phloroglucinol.

Several other ions produced activity worthy of mention with one or two of the derivatives. These were: 50 μg Hg^+ with resorcinol; 500 μg Zn^{+2} and 500 μg AsO_4^{-3} with 2-methylresorcinol; 500 μg WO_4^{-2} with orcinol and 2,6-dihydroxybenzoic acid; 38.5 μg Tl^{+3} with phloroglucinol; and 500 μg of Ca^{+2}, Sr^{+2}, or Ba^{+2} with phloroglucinol, 3,5- and 2,4-dihydroxybenzoic acid.

The most reactive cations were those which were members of oxidation-reduction couples although there was no obvious pattern about the derivatives which did not react with these cations. This trend disappeared with the less reactive ions. The activity of ions like AsO_4^{-2}, WO_4^{-2}, VO_3^-,

MoO_4^{-2} and the alkaline earth metals was difficult to explain.

The change in absorbance with time was studied for several of the most reactive ions with each derivative (Figures 50, 52, 54, 56, 58, 60, 61, 63, 64, 76, and 77). As expected the silver always reacted rapidly and then the reaction leveled off indicating exhaustion of the silver(I) in the solution. The other ions with true catalytic activity reacted more slowly. However, rapid reactions which leveled off in 5 to 10 minutes appeared to be characteristic of 2-methylresorcinol, 4-ethylresorcinol and phloroglucinol. Barium exhibited odd behavior by showing a negligible reaction for the first five minutes and then showing much increased reaction rate for the next five minutes and then leveling off again to the blank rate (Figures 52, 54, 64, and 76).

Trends of reactivity

Since silver was the only cation which increased the degree of autoxidation for all nine of the compounds studied, it was useful in judging the relative reactivities of the compounds. As expected substitution in the 4-position resulted in the least reaction since it blocked one of the sites para to a hydroxyl group. Substitution in the 2-position produced by far the most reaction primarily since it caused no additional steric hinderance which was undoubtedly the reason for the low reactivity of 3,5-dihydroxybenzoic acid. Steric hinderance could also account for orcinol being less than half as reactive as 2-methylresorcinol. It should be noted that in the presence of silver only the 2-position derivatives were more reactive than resorcinol.

The same trend was present but less obvious when the reactions were

studied in the absence of reactive cations. Substitution in the 2-position still produced the most reactive alkyl and carboxyl derivatives. However, the increased reactivity of the alkyl derivatives was apparent since all three had blank reactions which absorbed more intensely than resorcinol. However, since molar absorptivities of the autoxidation products are unknown except for orcinol, these conclusions could be in error.

Increased reactivity was not necessarily the most desirable characteristic since it usually resulted in a much larger increase in the blank than in the catalyzed reactions. For example, 4-chlororesorcinol had an absorbance with 100 μg Ag^+ which was almost three times that of 2,4-dihydroxybenzoic acid but the Ag^+ to blank absorbance ratios were 8.9 and 39, respectively. Also the more reactive compounds usually had more interferences. 2,6-Dihydroxybenzoic acid and 2-methylresorcinol reacted with more cations than any of the 4- or 5-position derivatives. Consider the other extreme, 4-ethylresorcinol, one of the four least reactive compounds which reacted significantly with only two cations compared to the 10 to 13 cations which reacted with each of the compounds substituted in the 2-position.

The data accumulated for 4,6-dichlororesorcinol were difficult to compare with the other derivatives since the concentration was uncertain. However, this compound was definitely the least reactive with silver. The difficult purification leaves doubt about whether the blank was truly as high as the experimental values indicated.

Silver-4-ethylresorcinol reaction

The reaction of silver and 4-ethylresorcinol was studied because it was much more selective than the silver-resorcinol reaction. The increase in selectivity, however, was balanced by a loss in sensitivity so there were merits to both reactions.

It can be seen from Figure 63 that any reaction time greater than or equal to five minutes was suitable. All of the cations which were tested reacted within the first three minutes except Ba^{+2} which characteristically reacted from 5 to 10 minutes after the reaction was initiated. The blank had a faster initial reaction than was usually observed for the autoxidation of derivatives of resorcinol and this was the reason for the high absorbance of the blank.

Figure 65 illustrates the effect of pH on the reaction. Results in the pH range 11.3 to 12.1 were consistently within ±2% of the average absorbance. Absorbances were lower in the pH 10.85 to 11.3 range but pH 10.85 was definitely the lower pH limit since the absorbance decreased rapidly at pH values below this. No reactions were run above pH 12.1 so this was not really an upper limit but merely the maximum pH value at which measurements were made.

The study of varying 4-ethylresorcinol concentrations as shown in Figures 66 and 67 indicated that this was not an important variable. In fact no significant difference was observed between 0.006 M and 0.010 M 4-ethylresorcinol. Since the blank absorbance decreased faster than the absorbance of the 100 μg Ag^+/25 ml samples as the concentration of 4-ethylresorcinol decreased, the lower end of the concentration range (0.001 to 0.005

M 4-ethylresorcinol) was used for further study. As the absorbance values for varying 4-ethylresorcinol concentrations were nearly superimposed, each concentration was run separately with the silver concentrations varied. These data (Figures 68 to 72) were then replotted. The slopes of these lines indicated that 0.002 or 0.003 M 4-ethylresorcinol was the optimum concentration. This could be compared to the optimum resorcinol concentration of 0.04% or 0.00363 M. Comparison of Figures 36 and 74 showed that resorcinol was $2\frac{1}{2}$ times more sensitive to 100 μg Ag^+/25 ml than 4-ethylresorcinol.

The primary advantage of 4-ethylresorcinol over resorcinol could be seen by comparing Figures 42 and 63. The increase in absorbance due to 1 μg Cu^{+2}/25 ml in Figure 42 was 0.54 and the increase due to 10 μg Cu^{+2}/25 ml in Figure 63 after ten minutes was 0.022. This means that 4-ethylresorcinol was 245 times less sensitive to Cu^{+2} than resorcinol. Presumably the amount of copper which can be tolerated in the 4-ethylresorcinol reaction could be increased by a factor of ten by the addition of sodium citrate. Copper(II) is the most serious interference in the silver-resorcinol reaction but the other interfering ions are also less reactive with 4-ethylresorcinol as can be seen from the data of Tables 7 and 8.

Thallium(III)-phloroglucinol reaction

The thallium(III)-phloroglucinol reaction was anomolous in several respects. The color formation was almost instantaneous on the addition of the phosphate buffer. The color was stable for several hours as long as the pH was above 10.45. The color formed but faded out if the pH was below 10.45. The phosphate buffer was essential for the color formation. These

facts were contrary to the behavior observed in the other autoxidation reactions studied. It was definitely an autoxidation, however, since no color developed in the absence of oxygen.

Thallium(III) is extensively hydrolyzed to $TlOH^{+2}$ and to the colloidal oxide even at pH 1-2.5 (58). Consequently the standard solutions must contain sufficient acid to keep the pH below one. When the phosphate buffer is added no precipitation is apparent so the Tl^{+3} must be present as a complex at pH 11.5.

The concentration range 0.003-0.007 M was studied to determine the optimum concentraion of phloroglucinol. The interpretation of these data were complicated by the narrow concentration range of Tl^{+3} over which the absorbance was a linear function of Tl^{+3} concentration. The best concentration for phloroglucinol appeared to be 0.004 M.

Figure 87 shows a calibration curve for the determination of Tl^{+3}. The thallium range of 1 to 10 μg/25 ml gives the most sensitive results. Higher concentrations of Tl^{+3} do not affect the absorbance as much and consequently the reaction is less suitable for their determination.

Suggestions for Future Work

The trends in activity of autoxidation were reasonable and well substantiated with two or three compounds for each position of substitution. It would be interesting to study the 2- and 5-chlororesorcinols. Also the sulfonic acid derivatives should provide additional confirmation to the trends. Further study on disubstituted resorcinols would also prove worthwhile, particularly on compounds such as 2,5-dimethylresorcinol, 2,4-dimethylresorcinol, and the 2,5- and 4,6-disulfonic acid derivatives of re-

sorcinol. In view of the success with 4-ethylresorcinol and silver, checking other higher alkyl derivatives would probably also prove rewarding.

With all of the derivatives studied, 500 μg Fe^{+3} and 50 μg Au^{+3} reacted at nearly neutral pH to form colored species. This behavior was probably due to either slow complex formation or the oxidizing ability of these two ions. Further study of these systems could lead either to analytical methods or ways to prevent their interference in other methods.

Since many cations influence the autoxidation of derivatives of resorcinol, and since the autoxidations themselves have not been investigated, this field should be paradise for a kineticist. Certainly some reactions such as the unexplained delayed reactivity of 500 μg Ba^{+2}/25 ml (see Figures 52, 54, 64, and 76) merit further study.

The 4-ethylresorcinol-silver reaction appeared to be rather straight forward but further work on the system is necessary to polish up the method. The effect of interferences on the reaction has not been determined. It is likely that sodium citrate could be used to complex interfering ions as was done in the silver-resorcinol method. Temperature dependence and the order of addition are other variables which have not been studied. Switching to cells with a 10-cm path length should provide added sensitivity. Obtaining ore samples or alloys for the testing of both methods would be desirable. When 4-ethylresorcinol solutions deteriorated on the shelf they formed precipitates instead of the normal clear colored solutions like other derivatives of resorcinol, so this might be a good system for the identification of reaction products.

Much additional work should be done on the Tl^{+3}-phloroglucinol method.

The nature of the reaction and the structure of the species producing the violet color are not well understood. There has been almost no work on identification of the autoxidation products. No measurements were made on the temperature dependance. Interferences were not studied either although most of these should be kept to a minimum by taking absorbance measurements at 30 seconds before the interfering ions have had a chance to react (see Figures 76 and 77). The phosphate appeared to be a necessary component for the development of color and this variable was not studied at all. Also the effect of different orders of addition has not been sufficiently investigated. The analysis of thallium in ores, alloys or other samples would be desirable for proving the method. It is likely that thallium can be determined in the 0.1 to 1 μg/25 ml range and perhaps even lower with cells having a 10-cm path length. This method should be even easier than either of the silver methods to be modified for automated analysis.

It is possible that a derivative of phloroglucinol such as 2-methyl- or 2-chlorophloroglucinol would have better sensitivity or selectivity to thallium than phloroglucinol has. It is also likely that the autoxidation products would be easier to isolate and study for derivatives than for the compound itself.

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