COLORIMETRIC METHODS FOR THE DETERMINATION

OF CARBON MONOXIDE IN AIR

by

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CHAPTER I

INTRODUCTION

During the last decade, popular interest in air pollution has been aroused due to increased publicity and increased awareness of the damaging effects that pollutants can have. Carbon monoxide has been a special problem because of its chemical inertness. The problem is made significant by carbon monoxide's potential for chronic and acute physiological distress.[1] The chemist, then, is faced with the problem and responsibility for the analysis of carbon monoxide.

The most recent trends have been towards expensive instrumental methods.[2,3,4,5] Proposed methods use nondispersive infrared spectroscopy techniques,[6] or measurement of CO infrared absorbance at 4.67 μ in a 10 m gas cell.[7] Gas Chromatography,[8,9] conductance,[10] and chemiluminescent methods[11] have also been used to analyze air mixtures for carbon monoxide. Recently, satellite-borne sensors[12] have been investigated for global pollution monitoring.

Indicator tubes have been used to detect CO in the range 25-100 ppm, but a recent study showed that commercially available tubes were unacceptable for giving quantitative results.[13] Many of these tubes are based on the reduction of palladium salts and comparison with a color chart or standard tubes.[14,15]

Good colorimetric methods for carbon monoxide are limited. The reaction of carbon monoxide with diiodine pentoxide releases iodine vapors which can be determined in a variety of ways.[16,17] Carbon monoxide also reacts with hot mercuric oxide to give mercury vapor which can be followed spectrophotometrically.[18] High temperatures and expensive instrumental accessories are required by both methods. The tentative standard manual method measures a silver colloidal dispersion formed by the reaction of carbon monoxide with an alkaline solution of silver and sodium para-sulfaminobenzoate.[19,20,21] Difficulties with the method include the use of strongly alkaline solutions and the measurement of a sol rather than a solution.
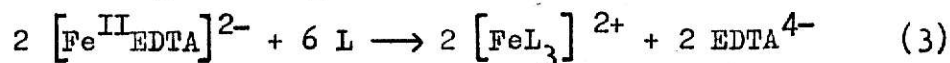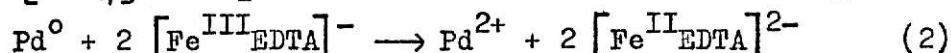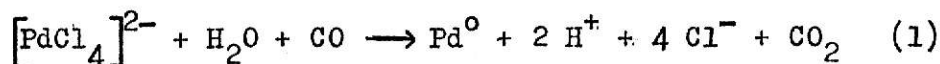
Several methods for the analysis of carbon monoxide have been studied. The methodology used for each study was similar, but each method utilized different reactions. Therefore, the remainder of the thesis is divided into four chapters, each dealing with a different method. The basic methodology will be described in the first section and necessary modifications described in later sections.

CHAPTER II

A FERROUS ORTHO-PHENANTHROLINE METHOD FOR CARBON MONOXIDE

Previous workers in this lab have developed a method for carbon monoxide utilizing tetrachloropalladate(II), ferric(III) EDTA, and a counter complexing ion such as 1,10-phenanthroline or 2,2'-dipyridyl.[22,23] In this study a different sampling method was utilized and several new catalysts and counter ligands were tried.

The reaction sequence is presumed to be

$$\left[PdCl_4\right]^{2-} + H_2O + CO \longrightarrow Pd^o + 2\ H^+ + 4\ Cl^- + CO_2 \quad (1)$$

$$Pd^o + 2\left[Fe^{III}EDTA\right]^- \longrightarrow Pd^{2+} + 2\left[Fe^{II}EDTA\right]^{2-} \quad (2)$$

$$2\left[Fe^{II}EDTA\right]^{2-} + 6\ L \longrightarrow 2\left[FeL_3\right]^{2+} + 2\ EDTA^{4-} \quad (3)$$

where L is a color producing counter ligand. The driving force for the reaction is the reversal of magnitudes of the stability constants for the iron(III) and iron(II) complexes of EDTA and L.

Experimental

Reagents used were reagent grade or the best quality commercially available. The deionized water used was distilled water which had been passed through a column of deionizing resin and prewashed 6-14 mesh activated coconut charcoal (Fisher Scientific Co.).

Apparatus used to measure absorbance was a Bausch and Lomb Spectronic 20 spectrophotometer. Absorbtion spectra were recorded on a Coleman 124 spectrophotometer. Hamilton syringes #702 and #1001 were used to prepare test atmospheres. Round bottom flasks (250 ml, S/T 19/22) were outfitted with rubber serum stoppers so that test atmospheres could be easily made and shaken with reagent. A Burrell Model BB Wrist-Action Shaker was used to shake the bottles containing reagent solution and test atmosphere. A Beckman Zeromatic pH meter with glass versus calomel electrodes was used for pH measurements.

<u>Sodium tetrachloropalladate(II)</u> (0.01 M) was prepared by adding 0.177 gm palladium(II) chloride (0.001 mole) and 0.117 gm sodium chloride (0.002 mole) to water. The mixture was stirred with a magnetic stirbar till solution was achieved and diluted to exactly 100 ml.

The following solutions were made by weighing out an appropriate weight of the pure compound and diluting to volume in volumetric flasks: 0.01 M hydrogen ethylenediaminetetraacetate-ferrate(III),[24] 0.16 M sodium molybdate, 8.3×10^{-3} M 1,10-phenanthroline, and 3.2×10^{-3} M 2,2'-dipyridyl. Solutions of other ligands tried were used only for qualitative work.

<u>Reagent Solution A</u> is prepared by pipetting 3.20 ml each of 0.16 M sodium molybdate solution, 0.01 M hydrogen ethylenediaminetetraacetate-ferrate(III) solution and 0.01 M sodium tetrachloropalladate(II) solution to 50 ml of 8.3×10^{-3} M 1,10-phenanthroline solution. The reagents are added in the order listed. The pH is adjusted to 7.0 ± 0.1 with sodium hydroxide solution.

The <u>procedure for qualitative testing</u> was to prepare about 10 ml of the test solution and bubble 100% carbon monoxide through the solution. Generally, test solutions were about 10^{-3} M in each component.

The <u>procedure for quantitative testing</u> is adapted from the technique used with the silver sulfaminobenzoate method.[19] Pipet a volume of reagent into the 250 ml flasks and close with a serum cap. Inject an appropriate volume of 100% carbon monoxide through the cap with a syringe and shake the flask for an appropriate length of time on the wrist-action shaker.

Results and Discussion

The results of qualitative tests are shown in Table I.

Attempts to modify the reagent solution described by Hamlin[22] were unsuccessful. Qualitative tests showed that a solution containing both molybdate ions and ferrous ions was restricted in the usable pH range because of the formation of precipitates in acidic and basic solutions. Several ligands were tried instead of 2,2'-dipyridyl and 1,10-phenanthroline. Either the ligand was insoluble or palladium

metal was formed. The ligand of choice became 1,10-phenanthroline because 2,2'-dipyridyl allowed palladium metal to form during quantitative work. When 1,10-phenanthroline was used, no palladium metal was observed.

Table I. Qualitative Tests of Reagents
Using Palladium(II) and Iron(III)

Reagent	Response[a]
Na_2PdCl_4, HFeEDTA, MoO_4^{2-}	
+ 2,4,6-Tri-(2-Pyridyl)-5-triazine	Pd°
+ 3-(2-Pyridyl)-5,6-Diphenyl-1,2,4-Triazine-	
p,p'-Disulfonic acid, Disodium salt	–
pH 8.5	–
pH 6	–
pH 4	–
+ 1,10-phenanthroline	+
+ 2,2'-Dipyridyl	Pd°
+ Tripyridyl	–
HFeEDTA, 1,10-phenanthroline, $Pd(NO_3)_2$, MoO_4^{2-}	
pH 7 (filter)	–
pH 8 (filter)	–
HFeEDTA, MoO_4^{2-}, 1,10-phenanthroline	–
HFeEDTA, $PdCl_4^{2-}$, 1,10-phenanthroline	–

a   Response to 100% carbon monoxide:

 –   no reaction

 Pd° palladium(0) metal formation

 +   formation of red color

Reagent A was then used for quantitative analysis of carbon monoxide. Time studies show a linear increase in absorbance at 508 nm (Figure 1). A calibration curve was obtained (Table II, Figure 2), and found to be nonlinear but reproducible. These results are consistent with earlier studies.[22]

Table II. Absorbance and Standard Deviations for a Calibration Curve for Reagent Solution A at 508 nm

(30 minutes contact time, 25 ml reagent)

Concentration of CO (ppm)	Absorbance and Standard Deviation
500	0.039 ± 0.013
1500	0.252 ± 0.006
2500	0.625 ± 0.015

Since carbon monoxide is nearly water-insoluble, the linear increase with time is attributed to the nearly constant carbon monoxide concentration. Therefore, longer contact times would have greater sensitivity, and eventually reach a plateau when all carbon monoxide had reacted. The postulated plateau was not observed within four hours.

The nonlinear correlation of carbon monoxide concentration to the absorbance of iron(II) 1,10-phenanthroline indicates a more complex reaction mechanism than that proposed. An unknown active species may be the problem or the reaction may not go to completion as well as is required by good analytical procedures.

Further study was deemed unfeasible because other methods are more sensitive, require less time and have linear calibration curves.

THIS BOOK CONTAINS NUMEROUS PAGES WITH DIAGRAMS THAT ARE CROOKED COMPARED TO THE REST OF THE INFORMATION ON THE PAGE.

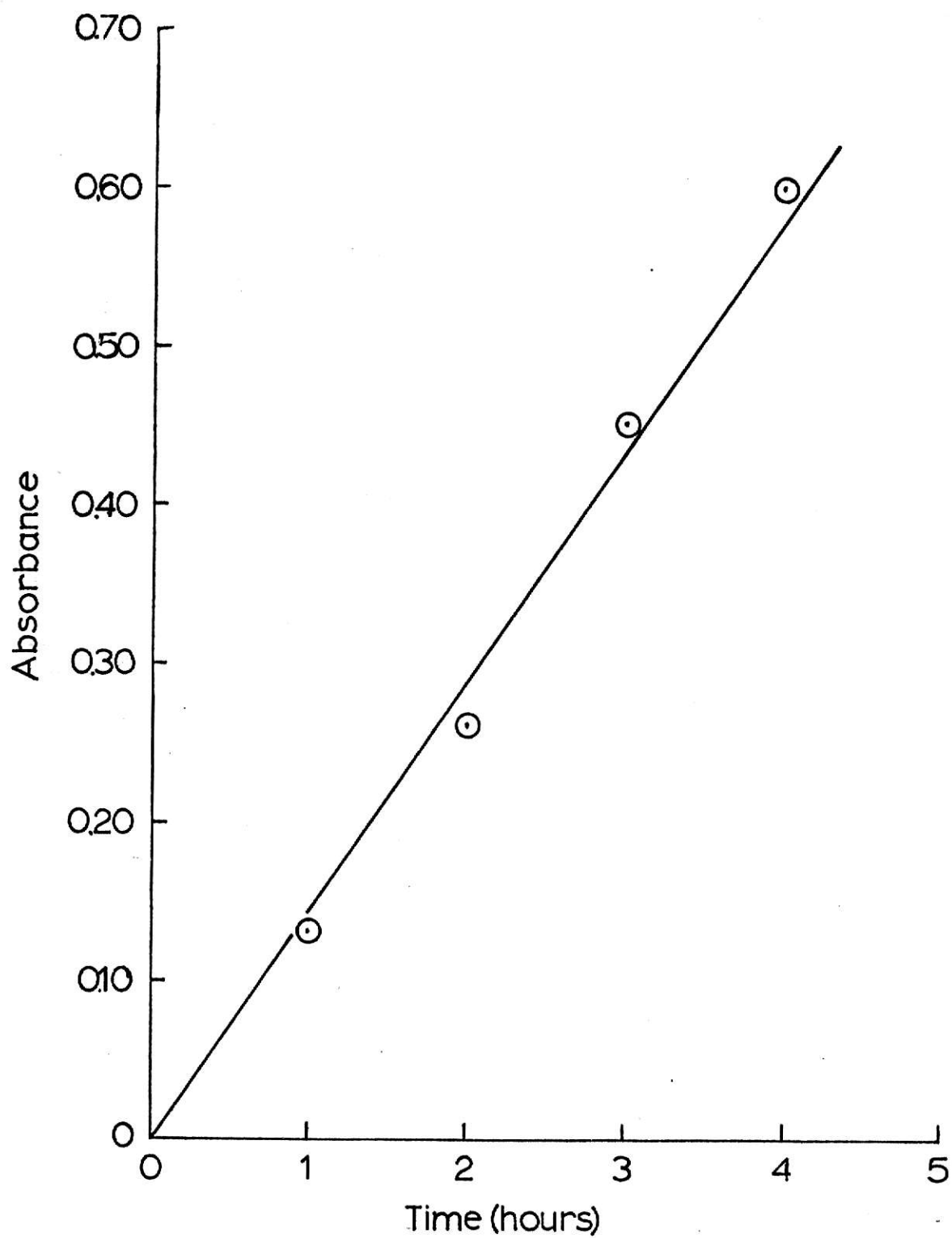THIS IS AS RECEIVED FROM CUSTOMER.

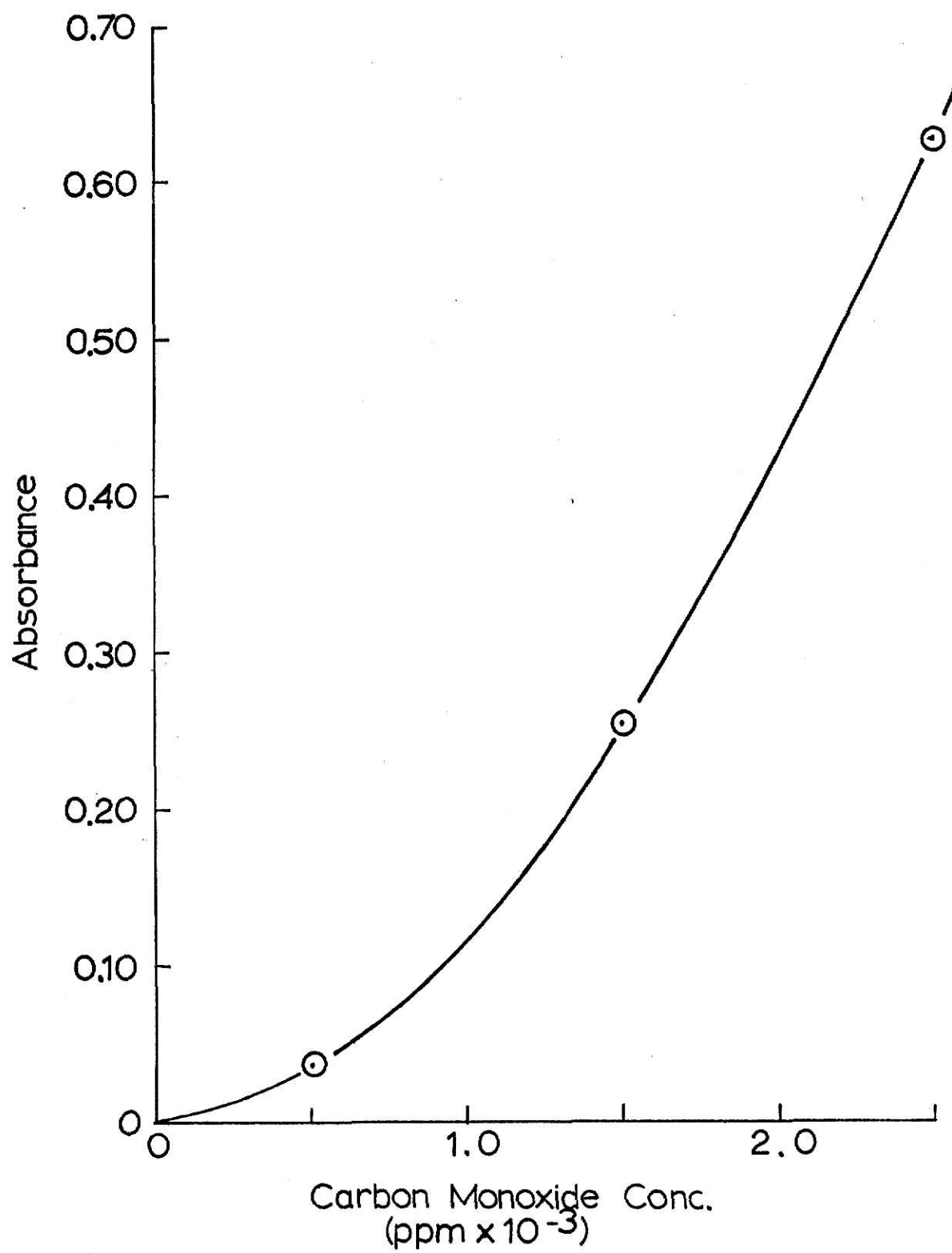Figure 1. Response versus contact time for reagent solution A (820 ppm CO)

Figure 2. Absorbance versus carbon monoxide concentration for reagent solution A

CHAPTER III

A FORMAZAN METHOD FOR CARBON MONOXIDE

Few compounds are known which may be reduced to give a colored species. Tetrazolium salts are such compounds, because they can be reduced to colored formazans (Equation 4). Several reviews of the

$$R''-C \underset{N-N-R}{\overset{N=\overset{+}{N}-R'}{\lessgtr}} \quad \xrightarrow{[H]} \quad R''-C \underset{N-NH-R}{\overset{N=N-R'}{\lessgtr}} \quad (4)$$
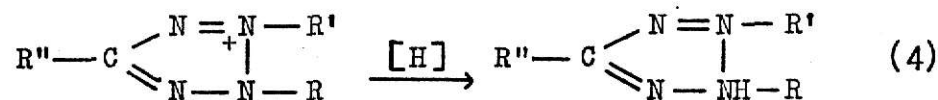
synthesis, reactions and uses of these compounds have been published.[25,26] In biological applications, tetrazolium salts have been used to determine dehydrogenase activity in soils,[27] and for early diagnosis of the presence of tumour cells.[26] Since the formazans are usually water-insoluble species, there is little diffusion into nonreducing tissues and dehydrogenase activity can be more precisely located. Tetrazolium salts have also been used to determine carbonyl groups in paper pulp[28,29] and ketones in phenol.[30] Color reactions of formazans with several transition metals[31] and the extraction of metals with 2,3,5-triphenyltetrazolium chloride (TTC) have been examined.[32]

This study examined the use of tetrazolium compounds to oxidize silver metal produced when silver nitrate is reacted with carbon monoxide in alkaline solutions.

Experimental

Procedures used were similar to those described in Chapter II. Because the formazans produced were light sensitive, the 250 ml round bottom flasks were spray painted black.

Qualitative experiments showed the need for a water soluble formazan. Therefore, efforts were made to synthesize several derivatives of 2,3,5-triphenyltetrazolium chloride. The primary synthesis route[33] involved the addition of a diazonium salt (1) to the hydrazone (2) of an aldehyde and a hydrazine to form a formazan (3). Tetrazolium salts were then formed by oxidation of the formazan.

$$X \overbrace{\bigcirc} CHO + NH_2NH \overbrace{\bigcirc} Y \longrightarrow X \overbrace{\bigcirc} CH=NNH \overbrace{\bigcirc} Y \quad (5)$$

$$\underline{2}$$

$$\underline{2} \quad + \quad {}^+N_2 \overbrace{\bigcirc} Z \quad \longrightarrow \quad X \overbrace{\bigcirc} C \overset{N=N \overbrace{\bigcirc} Y}{\underset{NNH \overbrace{\bigcirc} Z}{}} \quad (6)$$

$$\underline{1} \qquad\qquad\qquad \underline{3}$$

$$\underline{3} \quad + \quad [O] \quad \longrightarrow \quad X \overbrace{\bigcirc} C \overset{N=N \overbrace{\bigcirc} Y}{\underset{N-N \overbrace{\bigcirc} Z}{}} \quad (7)$$
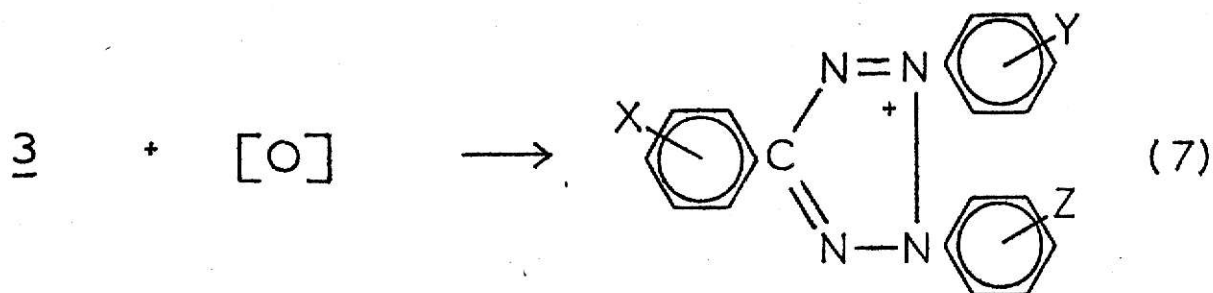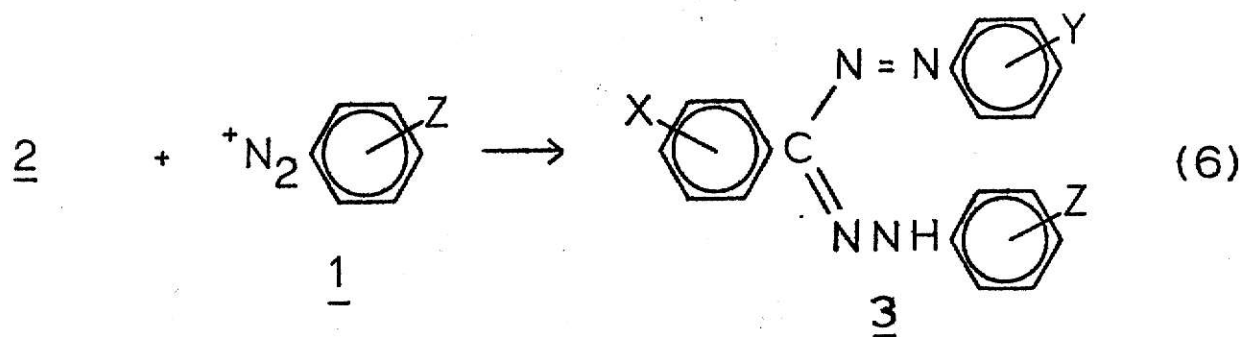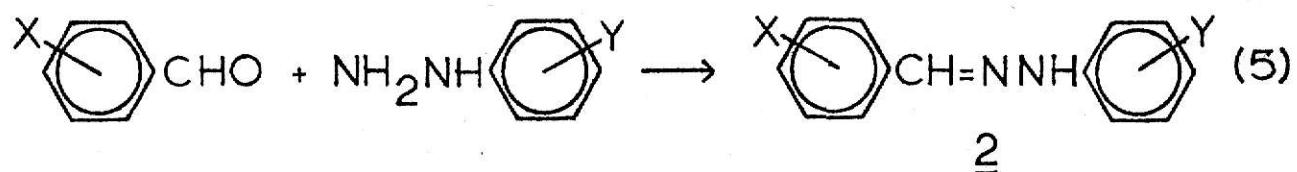
Table III shows the substituents (X, Y, and Z) of the compounds which were synthesized. Synthesis procedures are given.

Table III. Formazan Derivatives Synthesized

Compound	X	Y	Z
8	H	H	p-COOH
9	H	H	p-SO_3H
10	H	p-SO_3H	p-SO_3H

<u>Benzaldehyde phenylhydrazone</u> (<u>4</u>) - Dissolve 0.1 mole of freshly distilled benzaldehyde in 125 ml methanol and add 0.1 mole phenylhydrazine with agitation.

<u>Benzaldehyde p-sulfophenylhydrazone</u> (<u>5</u>)[34] - Dissolve 0.1 mole p-hydrazinobenzene sulfonic acid in 50 ml water with the addition of sodium bicarbonate, heat to boiling, and add slightly more than 0.1 mole freshly distilled benzaldehyde. Cool quickly and extract with ether.

<u>p-Sulfobenzenediazonium chloride</u> (<u>6</u>) - Dissolve 0.1 mole sulfanilic acid in 100 ml water with the addition of sodium bicarbonate and add 6.9 gm sodium nitrite. Cool in ice-salt bath to 0-5° C and carefully add the solution to 50 ml 1:1 hydrochloric acid with stirring. Stir continuously, do not allow any precipitate to dry.

<u>p-Carboxylbenzenediazonium chloride</u> (<u>7</u>) - Follow the synthesis of <u>6</u> except use p-aminobenzoic acid instead of sulfanilic acid.

<u>3,5-diphenyl-1-p-carboxyphenyl formazan</u> (<u>8</u>)[35] - Dissolve <u>4</u> in 500 ml methanol and add to 500 ml methanol containing 25 gm sodium hydroxide and 35 gm sodium acetate. Cool to 20° C and slowly add to <u>7</u> with continuous agitation. Filter the red crystals which form.

<u>3,5-diphenyl-1-p-sulfophenyl formazan</u> (<u>9</u>)[36] - Follow the procedure for <u>8</u> except add <u>6</u> instead of <u>7</u>.

<u>3-phenyl-1,5-di-p-sulfophenyl formazan</u> (<u>10</u>) - Dissolve <u>5</u> in a minimum volume of sodium bicarbonate solution and cool to less than 15° C. Add the diazonium salt (<u>6</u>) slowly, avoiding the addition of excess water by using a separatory funnel. Isolation of the red product proved difficult. Partial isolation of product occurred with the addition of barium chloride, but pure product was not obtained.

The mother liquour was oxidized directly with lead dioxide or sodium bismuthate. These oxidizing agents are insoluble, so excess oxidant was avoided. The solution containing tetrazolium salts was used directly in experiments with carbon monoxide even though a pure product had not been isolated.

The fact that desired reactions had occurred was shown by the characteristic color changes of the solution. Oxidation to a light

yellow solution with several oxidizing agents, including H_2O_2, HgO, PdO_2 and $NaBiO_3$,[37] indicated the formation of a tetrazolium compound. Reduction to a red or pink color in alkaline solution occurred with the addition of hydroxylamine hydrochloride. This indicated reduction to the formazan.

Reagent Solution B is prepared by combining 25.0 ml of 1 M sodium hydroxide, 1.00 ml of 0.1 N silver nitrate, 0.4 gm of succinimide and trace amounts of a tetrazolium salt, and diluting to 50.00 ml with water. The concentration of tetrazolium salt was adjusted so that the blank had an absorbance less than 0.10.

Results and Discussion

Qualitative results are shown in Table IV. Initial experiments showed that a mixture of silver nitrate, succinimide and 2,3,5-triphenyl-tetrazolium chloride gave a pink color in alkaline solution on reaction with carbon monoxide. Since the formazan precipitated and appeared to have low absorbtivity, substituents were added to the phenyl rings. Since the reactions with carbon monoxide occurred in basic solutions, the addition of sulfonic acid groups or carboxylic acid groups appeared to have the greatest chance of success.

Table IV. Qualitative Results for Reagents Containing Tetrazolium Salts

Reagents	Response[a]
TTC + HFeEDTA	−
+ $PdCl_4{}^{2-}$	−
TTC + $(AgCN_4)^{3-}$	−
alkaline	−
neutral	−
TTC + $AgNO_3$	
+ p-sulfaminobenzoic acid	+ (yellow)
+ aminobenzoic acid	−
+ nicotinic acid	Ag^o

Table IV. Continued

TTC + AgNO$_3$

    + saccarine   Ag^o

    + EDTA   Ag^o

    + succinimide   + (pink)

        + Hg^{2+} —

        + Pb^{2+} —

TTC + succinimide

    + Ni(II)SO$_4$ —

    + Hg(II)(NO$_3$)$_2$ —

    + HgI$^+$ —

    + HgI$_4^{2-}$ —

a   Response to 100% carbon monoxide

    —   no reaction

    Ag^o silver metal precipitated

    +   color indicated was developed

Compound <u>10</u> had good solubility and fair absorbtivity. Isolation of the products was a major problem. In addition, formazans are decolorized by visible light.[25] This proved to be a big problem when quantitative work was attempted (Table V) since red form formazan developed in the darkened flasks would isomerize to the yellow form upon exposure to room light or spectrophotometer radiation.

Table V. Response of Reagent B to Carbon Monoxide

Concentration of Carbon Monoxide	Contact Time (minutes)	Absorbance (at 520 nm)
0.16%	30	0.07
0.24%	30	0.15
0.32%	30	0.05
0.40%	30	0.28
0.40%	30	0.36
0.40%	30	0.27
0.40%	55	0.55
0.40%	55	0.44

The use of tetrazolium salts, though initially promising, was found to have several deficiencies. Sensitivity was less than desired since 0.40% carbon monoxide gave an absorbance of about 0.3. At higher concentrations and longer contact times silver metal was precipitated. The reaction was found to occur in strongly alkaline solution. Reproducibility was difficult to achieve because of the light-catalyzed color loss and the formation of silver metal.

CHAPTER IV

CARBON MONOXIDE REAGENTS USING PERMANGANATE ION

OR ORTHO-DINITROBENZENE

Qualitative experiments were done to take advantage of carbon monoxide as a reducing agent. However, few compounds are known which can be reduced to colored products. Tetrazolium compounds were examined in Chapter III. Reduction gave pink or red formazans. Molybdate complexes reduce to molybdenum blue[39] but are decomposed by base[39] and were not examined. The reduction of o-dinitrobenzene[40] was studied for use in the detection of carbon monoxide. The reduction of permanganate ion in alkaline solution was also studied.

A solution of silver(I) nitrate, succinimide, and o-dinitrobenzene in alkaline ethanol was exposed to 100% carbon monoxide. No color change was observed. If acid groups like -COOH or -CH$_2$COOH can be added to the ring, water could be used as a solvent system and higher reagent concentrations could be reached. This would increase the chance for success.

During qualitative tests, 100% carbon monoxide was observed to change alkaline permanganate(VII) solution from violet to blue. The color change occurred in solutions that were one half to three molar in sodium hydroxide. The color change is attributed to the formation of blue MnO$_3^-$. Stronger base causes a spontaneous change to green manganate(VI) and in weaker base carbon monoxide did not produce the blue color. Since analytical reactions require better peak separation, the observations were not studied any further.

CHAPTER V

A CRYSTAL VIOLET METHOD FOR CARBON MONOXIDE

A sensitive, colorimetric reagent for carbon monoxide has been discovered which takes advantage of the selective oxidation of leuco crystal violet (4,4',4"-methylidynetris(N,N-dimethylaniline) or LCV) by hypoiodous acid, HOI.[41] Carbon monoxide reduces potassium iodate to HOI through a palladium(II) catalyst. The crystal violet produced is then measured spectrophotometrically to determine the amount of carbon monoxide in the air.

LCV has previously been used to determine hydrogen peroxide,[42] and iodide[43] or total iodide, iodine, and hypoiodite.[44] The mechanism of LCV oxidation to crystal violet is described as either hydride (H^-) extraction,[41,45] of free radical oxidation at the free amine groups of LCV. Although mechanism studies were not done, a hydride extraction mechanism is more plausible.

Experimental

Procedures used and techniques described in Chapter II were also used for this reagent. In addition, a technique utilizing a dynamic gas dilution apparatus (Appendix) was used to show that syringe dilution of 100% carbon monoxide was accurate (Table VI).

Table VI. Comparison of Dynamic and Static Dilution Systems

	Carbon Monoxide Concentration	Absorbance
Dynamic dilution system	80 ppm	0.75
Static dilution system	80 ppm	0.80

Leuco Crystal Violet solution was made by dissolving 0.25 gm of leuco crystal violet (LCV) in 200 ml of water and 2.5 ml 85% phosphoric acid. Dilute to exactly 1 liter.

Potassium Iodate solution (0.1 M) was made by diluting 0.1 mole potassium iodate to exactly 1 liter with H_2O.

Sodium monohydrogenphosphate (0.1 M) was made by diluting 0.1 mole of sodium monohydrogenphosphate to exactly 1 liter with water.

Sodium tetrachloropalladate(II) solution (0.01 M) was made by adding 0.002 mole hydrochloric acid and 0.001 mole palladium(II) chloride to water with stirring and diluting to exactly 100 ml.

Reagent Solution C is made by pipetting 1.00 ml of leuco crystal violet solution, 1.00 ml of 0.1 M potassium iodate, and 1.00 ml of 0.01 M tetrachloropalladate solution into 25.0 ml of water. Adjust the pH to $3.10 \pm .02$ with 0.1 M sodium monohydrogenphosphate. The absorbance maximum is at 587 nm.

Results and Discussion

Qualitative results are reported in Table VII. Chlorate(V) and bromate(V) solutions did not produce crystal violet at pH 1-5.

Table VII. Qualitative Tests of Reagents Containing LCV

Reagent	Response[a]
$LCV + PdCl_4^{2-} + ClO_3^-$	
pH 2.0	Pd^o
pH 3.0	Pd^o
pH 4.0	Pd^o
pH 5.0	$-, LCV$
pH 6.0	$-, LCV$
$LCV + PdCl_4^{2-} + BrO_3^-$	
pH 1.5	Pd^o
pH 2.0	Pd^o
pH 3.0	Pd^o
pH 4.0	Pd^o
pH 5.0	$-, LCV$
$LCV + PdCl_4^{2-} + IO_3^-$	$+, Pd^o$
$+ Hg^{2+}$	$-$

a   Response to 100% carbon monoxide reported as:

-        no reaction

-, LCV   leuco crystal violet precipitated, no other reaction

Pd^o palladium(0) precipitated

+, Pd^o violet color observed with two bubbles 100% carbon monoxide. Excess precipitated palladium(0).

At other pH values LCV will not dissolve and so no studies were made. Only iodate gave crystal violet as a product of reaction with carbon monoxide. Crystal violet was not produced when mercury(II) was included in the reagent.

After the response of leuco crystal violet, iodate, and $PdCl_4^{2-}$ was observed to be the production of violet colored crystal violet, a series of palladium compounds was qualitatively evaluated. Two bubbles of 100% carbon monoxide were bubbled through about 10 ml of reagent and the absorbance measured. The results are shown in Table VIII.

Table VIII. Effects of Anions on Absorbance

Anion	Absorbance
Acetate	0.17
Nitrate	0.40
Sulfate	0.21
Chloride	0.10
$PdCl_4^{2-}$	0.40
$PdCl_4^{2-}$ + excess NaCl	0.05
$PdCl_4^{2-}$ + NH_4Cl	Pd
$Pd(NO_3)_2$ + EDTA	0.04

Much of the effect of anion can be attributed to the relative solubility of the respective palladium(II) salt. Thus, palladium nitrate and tetrachloropalladate gave higher response due to the higher concentration of palladium. On the other hand, excess chloride reduced the absorbance. This may be due to stronger complexation of the palladium which prevents it from interacting with carbon monoxide. Tetrachloropalladate was selected as the most useful reagent because palladium nitrate was inactive after 24 hours.

Studies were made of the effects of pH, leuco crystal violet concentration, potassium iodate concentration and sodium tetrachloropalladate concentration. The optimum pH (Figure 3) was determined by
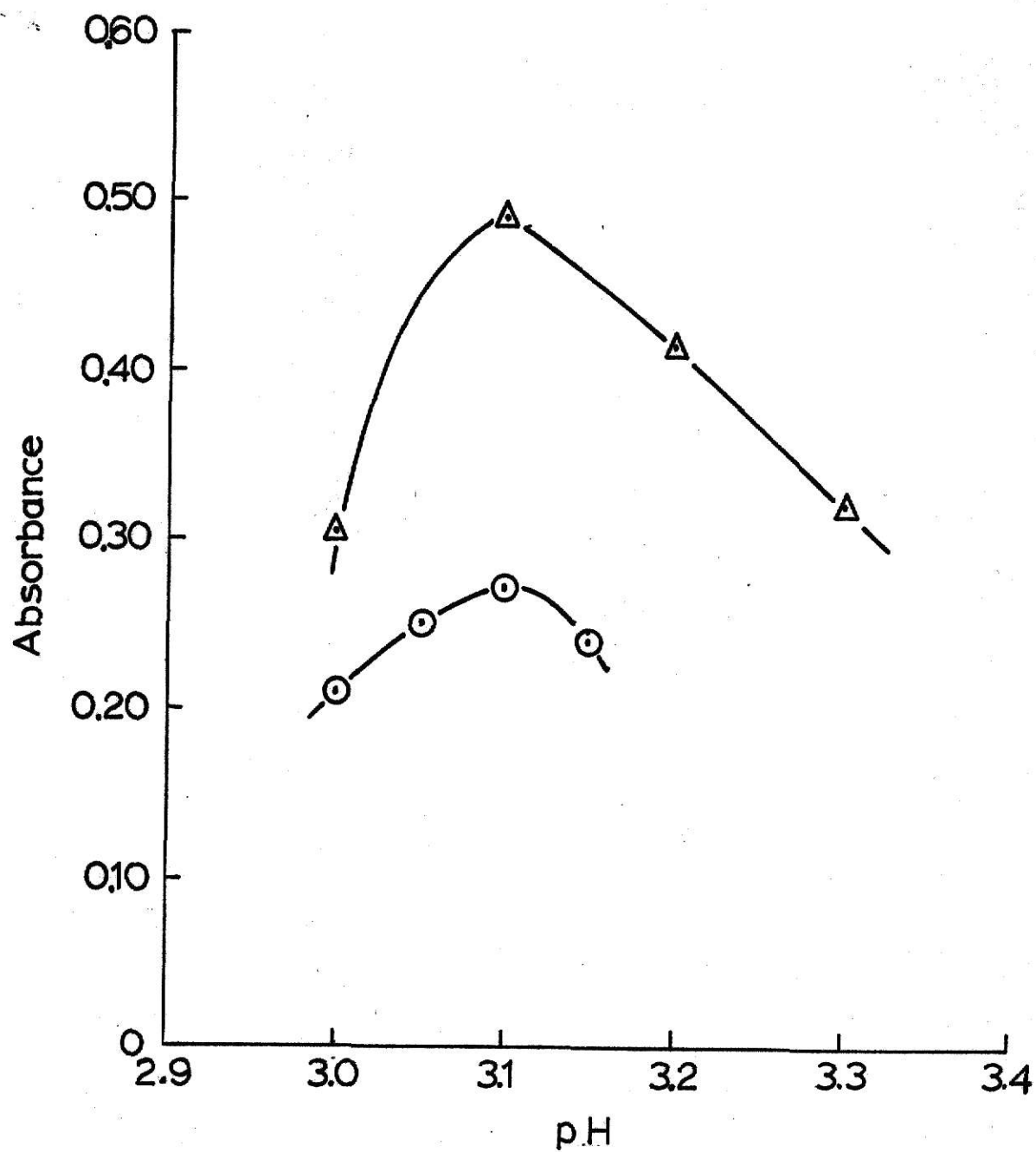
Figure 3. Effect of pH on reagent solution C

△ = 83 ppm CO, 20 minutes contact time

⊙ = 83 ppm CO, 15 minutes contact time

preparing reagent solution C and adjusting the pH with 0.1 M phosphoric acid or 0.1 M sodium monohydrogenphosphate. The other effects were determined by preparing reagent solution C except for the component to be studied. The volume of this component was then varied to give Figures 4, 5, and 6.

A sharp pH optimum was observed at 3.10 (Figure 3). The reasons for the sharp optimum are not understood. LCV (Figure 4) and potassium iodate (Figure 5) are required only to be in excess of the amount needed for reaction with carbon monoxide concentrations for optimum reaction conditions to occur.

Sodium tetrachloropalladate(II) concentration has more complicated effects because a concentration peak is reached. Apparently, the amount of carbon monoxide which can react to give crystal violet is limited by alternate reactions which give palladium metal as a product. This is consistent with initial observations (Table VII) that too much carbon monoxide produces palladium metal.

The estimated concentrations of LCV, potassium iodate, and tet-rachloropalladate in reagent solution C and the minimum concentrations required for maximum response are shown in Table IX.

Table IX. Reagent Concentrations in Reagent Solution C.

Reagent	Minimum Concentration[a]	Concentration Used
LCV	5.3×10^{-6} M	5.3×10^{-5} M
KIO_3	5.8×10^{-4} M	3.5×10^{-3} M
H_2PdCl_4	3.3×10^{-4} M	3.3×10^{-4} M

a Concentration required for maximum response to 83 ppm CO. See Figures 4, 5, and 6.

Increased contact time caused a linear response increase (Figure 7). Although contact times of 0.5 hours were used for these experiments, greater sensitivity can be acheived by using contact times of two hours.
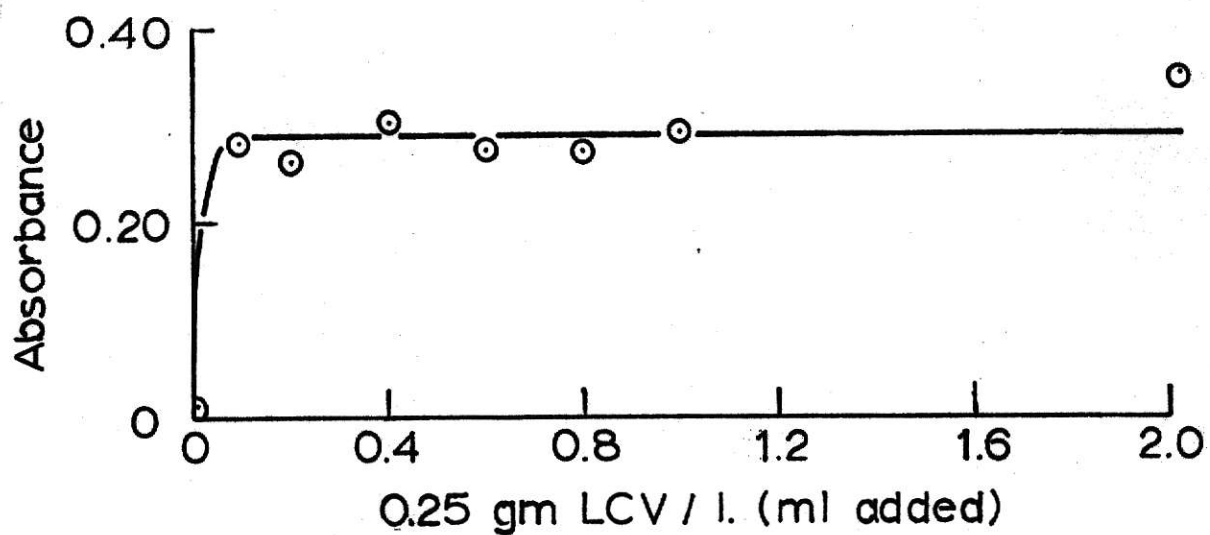
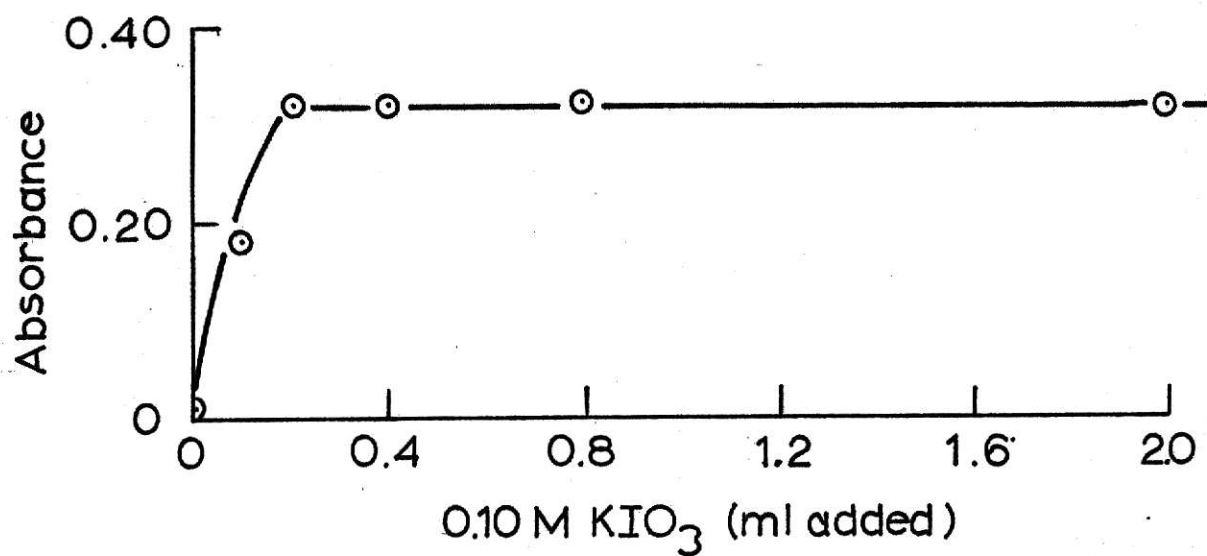Figure 4. Effect of LCV on reagent solution C (83 ppm CO)

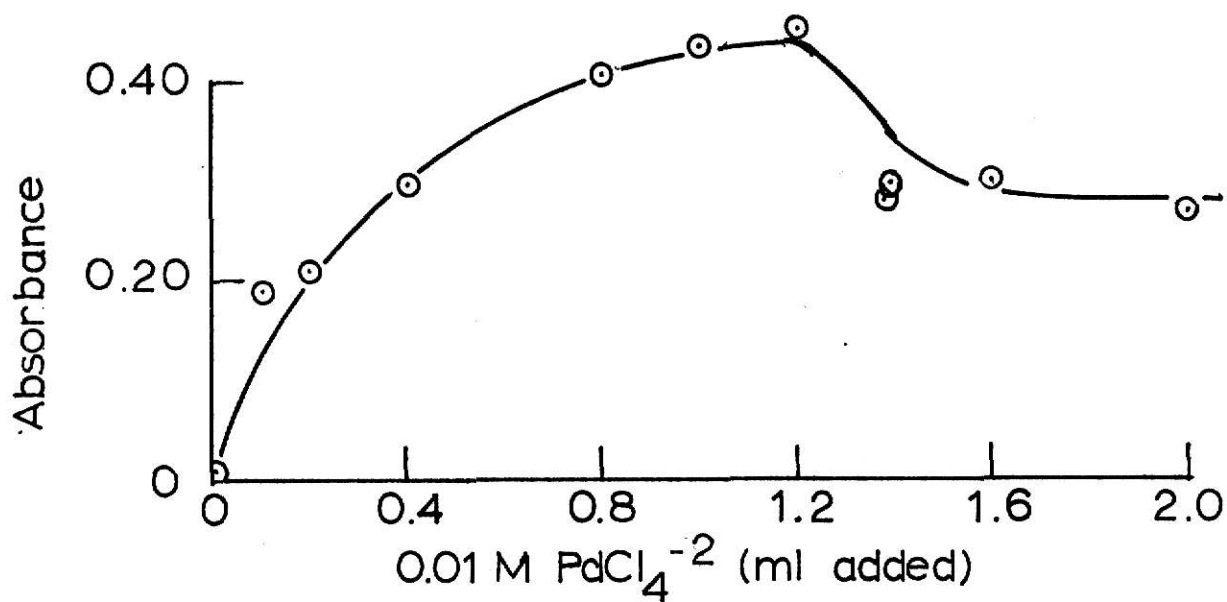Figure 5. Effect of iodate on reagent solution C (83 ppm CO)

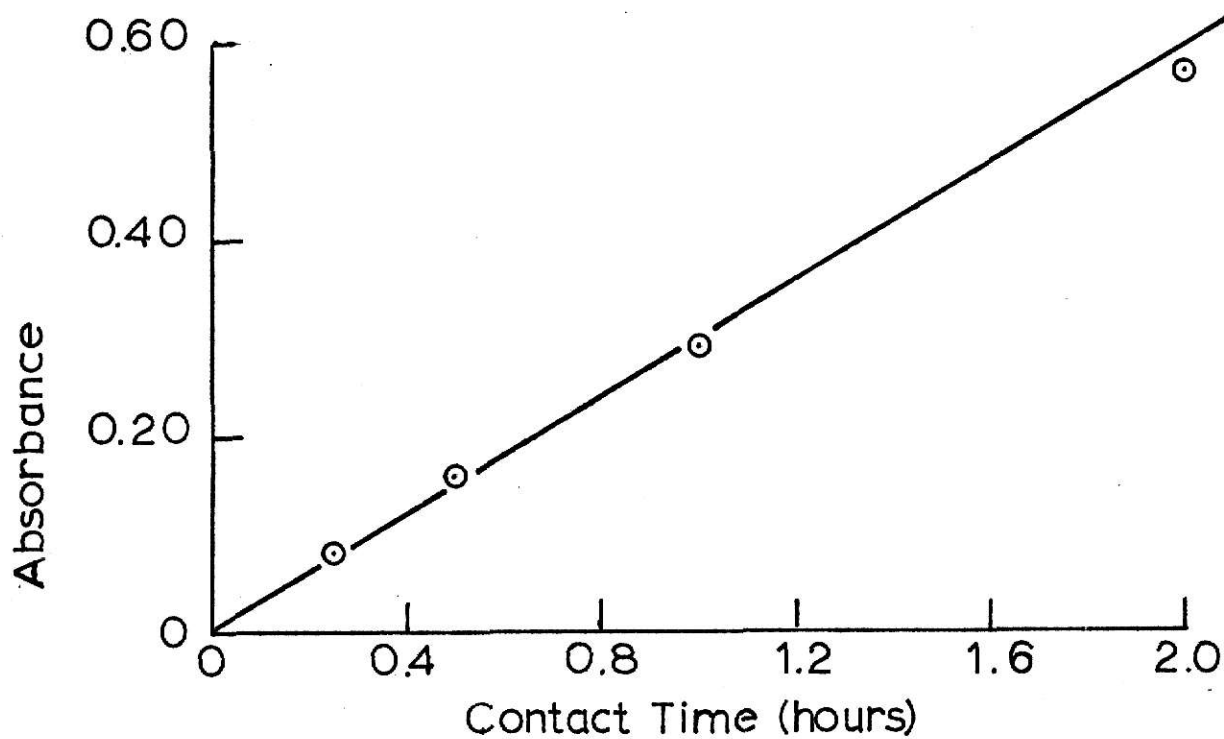Figure 6. Effect of palladium(II) on reagent solution C (83 ppm CO)

Figure 7. Effect of contact time on reagent solution C (42 ppm CO)

Reagent solution C was used to prepare a calibration curve. Five determinations were done for four concentrations of carbon monoxide. Standard deviation was calculated according to the equation

$$s = \sqrt{\frac{\sum (A_i - \bar{A})^2}{N - 1}}$$

where s is standard deviation, A_i is each absorbance measurement, $\bar{A}$ is the average of the absorbance measurements, and N is the number of A_i. The results are given in Table X and Figure 8.

Table X. Absorbance and Standard Deviations for a Calibration Curve for Reagent Solution C

(30 minutes contact time, 25 ml reagent)

Concentration of CO (ppm)	Absorbance and Standard Deviation
20.9	0.208 $\pm$ .016
41.9	0.390 $\pm$ .033
62.7	0.55 $\pm$ .026
101.2	0.90 $\pm$ .024

Blanks were found to be relatively stable. Table XI shows the steady rise in absorbance which did occur. Since experiments

Table XI. Increase of Blank Absorbance with Time

Time (hour)	Absorbance of Blank
0	0.02
$\frac{1}{2}$	0.04
2	0.07
3	0.12
6	0.21
9	0.26
14	0.30

required only half hour contact times and blanks were taken from each lot of freshly prepared reagent, this increase was not considered to be a serious defect.
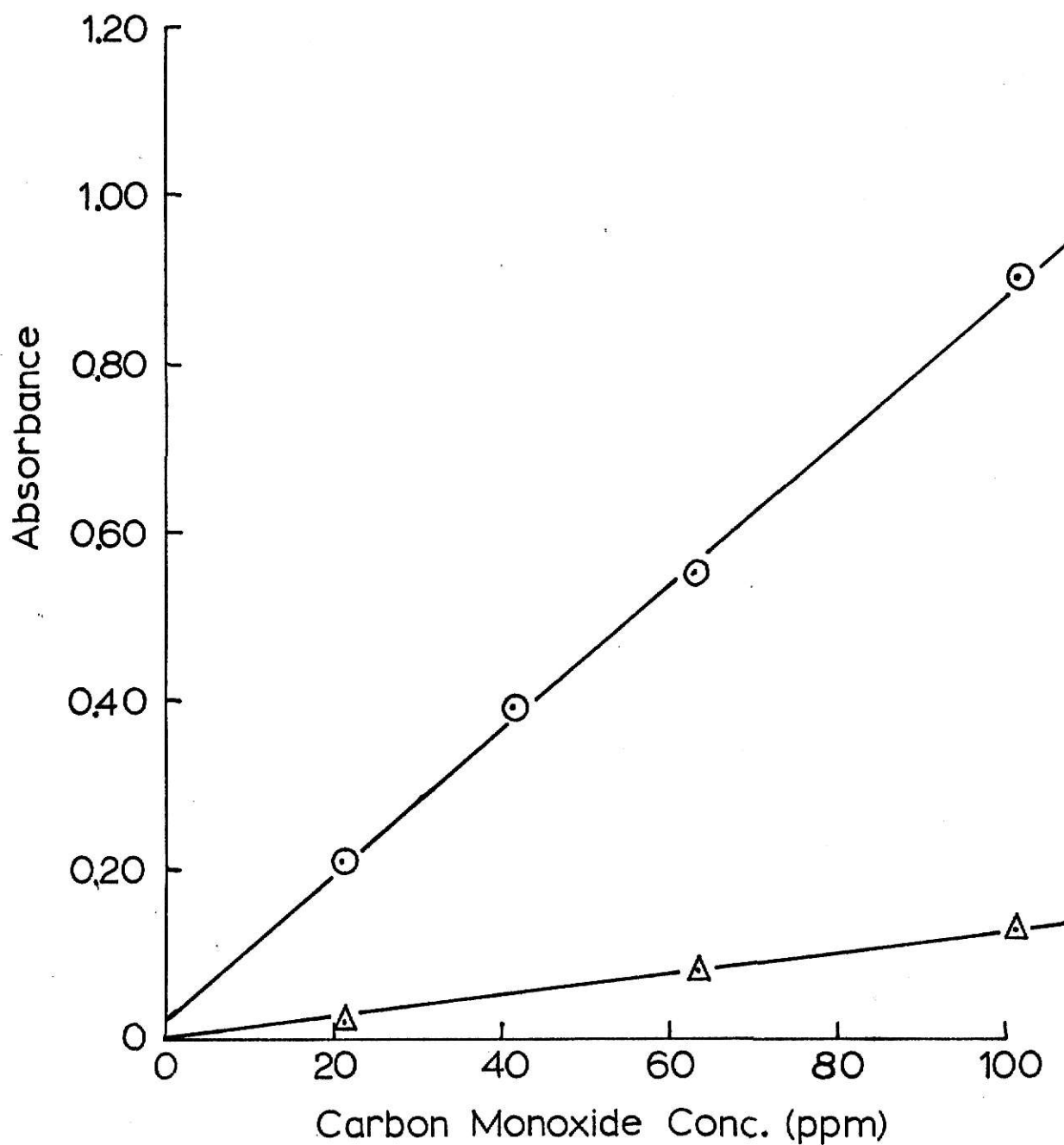
Figure 8. Absorbance versus carbon monoxide concentration
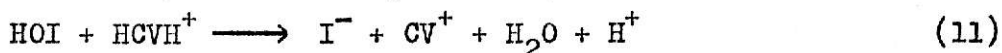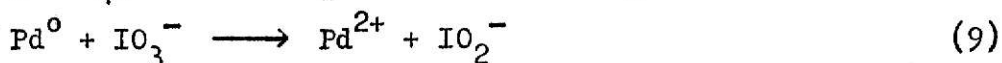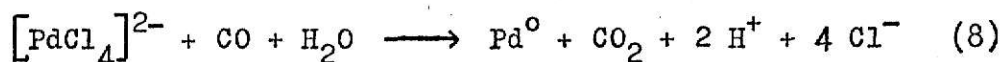
⊙ = reagent solution C

△ = silver p-sulfaminobenzoate reagent

The slope and intercept of Figure 8 was obtained by using a least-squares calculation on a Digital Equipment PDP-8 minicomputer. The slope was $0.00858 \pm .0012$ ppm^{-1} and the intercept as $0.0256 \pm .079$.

The interference of nitrogen dioxide, hydrogen sulfide and sulphur dioxide with this method was studied (Figure 9). Nitrogen dioxide and hydrogen sulfide were found to be inert, but 42 ppm sulphur dioxide gave about 30% high results for 42 ppm carbon monoxide. One ppm sulphur dioxide had negligible effects on reagent response.

Discussion

Leuco crystal violet is selectively oxidized by hypoiodous acid, HOI (Equation 11). In this method, the reaction of iodate and LCV (or HCVH$^+$) is induced by carbon monoxide (Equations 8, 9, 10, and 11). A cyclic continuation is catalyzed by iodide (Equations 11, 12, and 13).

$$[PdCl_4]^{2-} + CO + H_2O \longrightarrow Pd^o + CO_2 + 2\,H^+ + 4\,Cl^- \quad (8)$$

$$Pd^o + IO_3^- \longrightarrow Pd^{2+} + IO_2^- \quad (9)$$

$$2\,IO_2^- \longrightarrow IO^- + IO_3^- \quad (10)$$

$$HOI + HCVH^+ \longrightarrow I^- + CV^+ + H_2O + H^+ \quad (11)$$

$$2\,IO_3^- + I^- \longrightarrow 3\,IO_2^- \quad (12)$$

$$3\,IO_2^- \longrightarrow \tfrac{3}{2}\,IO^- + \tfrac{3}{2}\,IO_3^- \quad (13)$$

The proposed reaction sequence is supported by the observation that mercury(II) slowed down color development (Table VII). The formation of the mercury(II) iodide complex, HgI$^+$, with the iodide produced in Equation 11 would effectively interfere with the chain reaction described by Equations 11, 12, and 13.

The sensitivity and speed of reaction will allow this method to be used at the part per million range for carbon monoxide detection and determination. The equipment required is easily available and the techniques used are not difficult. All that is required to test an
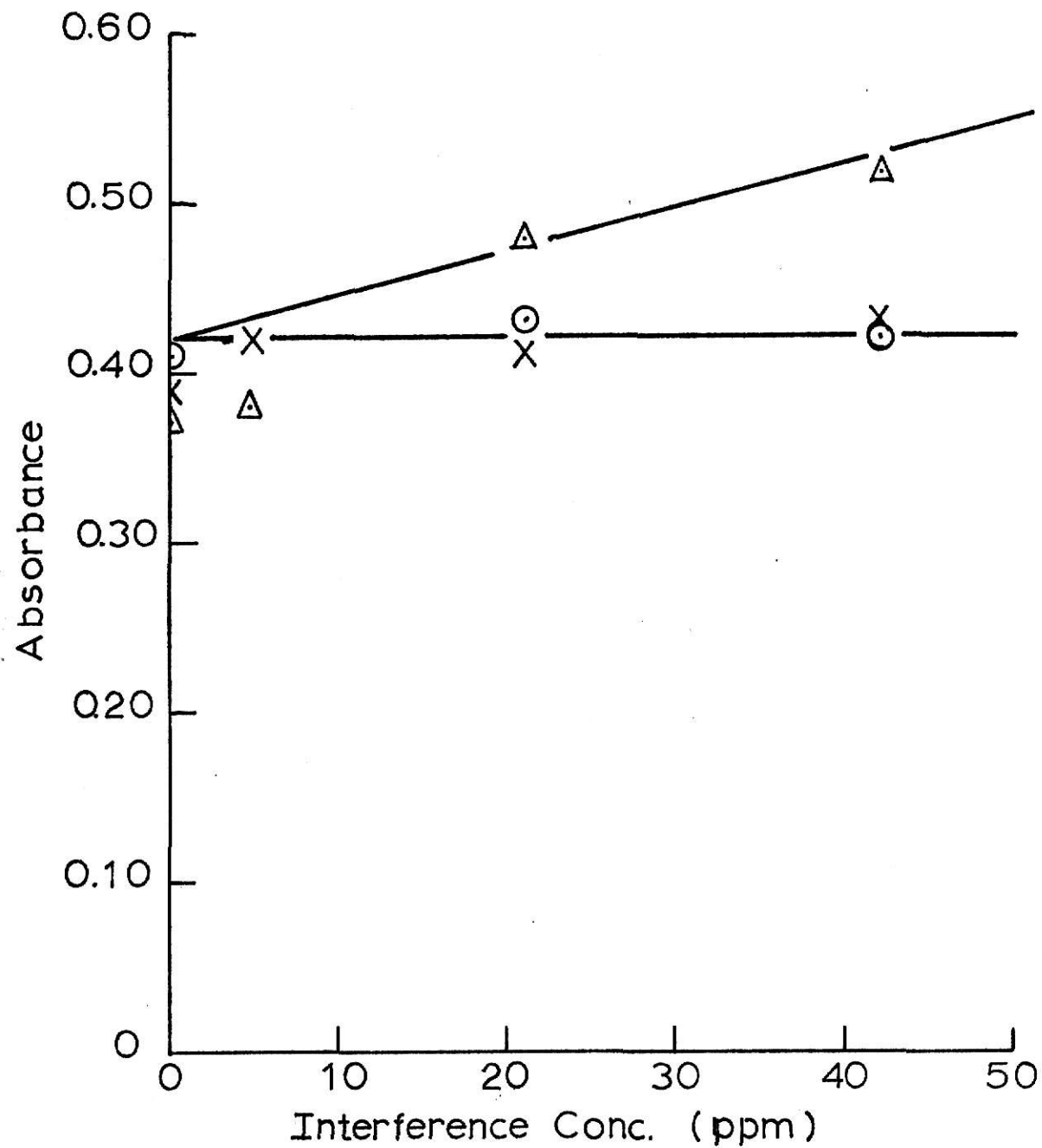
Figure 9.   Interference effects on reagent solution C
            (42 ppm CO, $\frac{1}{2}$ hour contact time)

    ⊙   =   Nitrogen Dioxide
    X   =   Hydrogen Sulfide
    △   =   Sulphur Dioxide

atmosphere is an evacuated flask containing reagent, a wrist action shaker and a visible range spectrophotometer. The flask is opened to the test atmosphere, shaken, and the absorbance of the solution is compared to a calibration curve.

The method was compared with the tentative Intersociety colorimetric method using silver(I) and p-sulfaminobenzoate reagent.[21] Experimental conditions were modified to be identical with those used to determine the calibration curve in Figure 8. It is apparent that the new reagent is more sensitive. In addition, alkaline solutions are not required and a sol is avoided.

Several problems were encountered. First, the reagent response is pH sensitive. Other buffer systems could be studied for better pH adjustment. Second, sulphur dioxide was an interference. Passing air samples over ascarite or other suitable absorbing agents would selectively absorb the sulphur dioxide when its concentration is known to be greater than 10 ppm. Difficulty was also encountered with the stability of the tetrachloropalladate(II) solution. More work can be done to optimize the chloride concentration and pH of this solution. In addition, the palladium(II) concentration in reagent solution C should be studied further to determine the best compromise between faster reactions and the formation of palladium(0) at higher palladium(II) concentrations.

In conclusion, a new sensitive reagent for carbon monoxide has been developed. The oxidation of leuco crystal violet by hypoiodous acid is the final step in the production of crystal violet by the oxidation of carbon monoxide.

CHAPTER VI

EXTENSIONS AND CONTINUATIONS

Further studies of the tetrazolium compounds can be undertaken to try to increase absorbtivity coefficients and eliminate the light sensitivity of the formazans.

The crystal violet method has been studied, but further characterization needs to be done. The reaction mechanism is not completely understood and mechanism studies may be undertaken. Temperature effects on this method are not known. Hatch[44] found that the response of an LCV-containing reagent for iodide was enhanced by increased temperature. Since a catalytic mechanism is proposed for the carbon monoxide reagent, increased response with increased temperature would also be expected for reagent solution C. Palladium(II) concentration was found to have a large effect on the rate of reaction. More work needs to be done to find the best complexing agent and its optimum concentration.

The interference found for sulphur dioxide needs to be eliminated. It is believed that drawing the test atmosphere across a bed of ascarite will reduce the concentration of sulphur dioxide significantly.

A solid reagent may be developed from Reagent Solution C. Initial attempts to use paper as a support were not successful, but the value of sensitive, inexpensive indicators for carbon monoxide would encourage further studies of this possibility.

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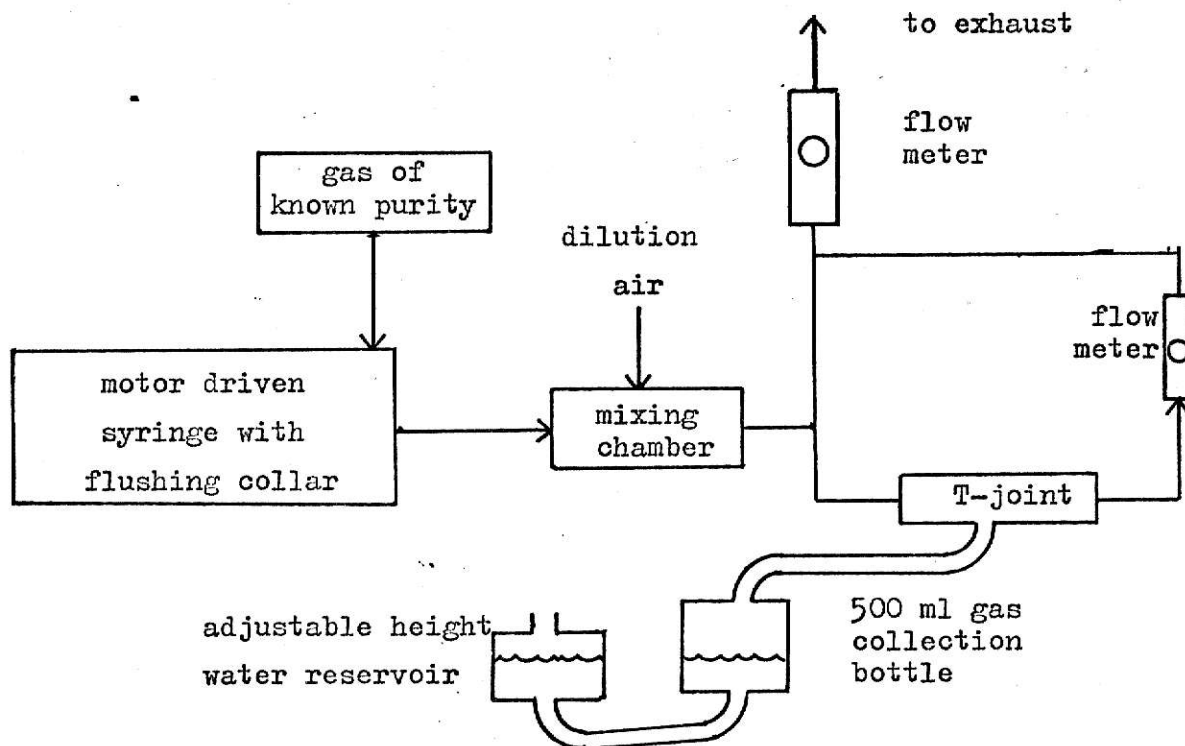
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APPENDIX

Schematic diagram of the gas dilution apparatus. The motor driven syringe was capable of delivering: 19.4, 9.7, 3.88, 1.94, 0.97, 0.388, 0.194, 0.097, 0.0388. 0.0194, 0.0097, or 0.00388 ml per minute. Total flow could be controlled between 250 ml per minute and 12,000 ml per minute. Flow through the reagent could be controlled between 20 ml per minute and 800 ml per minute. The system was all glass, except for valves which were either glass or teflon.

A 500 ml gas collection bottle was connected to the reagent branch with a glass T-joint. An adjustable height reservoir was used to fill the bottle with water and the dilution system adjusted to the desired concentration. Water was then allowed to flow back to the reservoir over a period of about 30 minutes. The gas bottle was thus filled with an atmosphere containing a desired concentration of carbon monoxide.

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VITA

Robert Elmer Wiens was born March 8, 1947 in Hutchinson, Kansas and lived in Inman, Kansas till he graduated from Inman Rural High School in 1965. He is the eldest of five sons born to Elmer P. and O. Ruth Wiens. Bethel College awarded him the B. A. degree in Chemistry in 1969. He married Dorothy Ann Nachtigal on August 17, 1969. After being drafted he served two years in a Topeka, Kansas hospital as a Conscientious Objector. In the fall of 1971, he entered Kansas State University as a full time graduate student.

COLORIMETRIC METHODS FOR THE DETERMINATION

OF CARBON MONOXIDE IN AIR

by

ROBERT ELMER WIENS

B. A., Bethel College, 1969

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KANSAS STATE UNIVERSITY
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Colorimetric methods for carbon monoxide are described. A previously known reagent utilizing a palladium-carbon monoxide complex to reduce iron(III) EDTA to iron(II) EDTA was studied. A ligand exchange of EDTA for 1,10-phenanthroline(L) produced $Fe(L)_3^{2+}$ which was measured spectrophotometrically.

Attempts are described to utilize the reducing character of CO. Alkaline silver solution catalyzes the reduction of tetrazolium salts to pink formazans which are measured spectrophotometrically.

A sensitive, new, colorimetric reagent for carbon monoxide is described. The supposed reaction sequence involves CO attack on a palladium(II) complex which reduces iodate(V) to hypoiodous acid (HOI). HOI selectively oxidizes leuco crystal violet (4,4',4"-methylidynetris(N,N-dimethylaniline) or LCV) to crystal violet which is measured spectrophotometrically. Iodide produced in the reaction reacts with iodate to produce more HOI catalytically and thus increases the reagent sensitivity. Maximum sensitivity is found at pH 3.10. The reagent is more sensitive than the tentative manual colorimetric reagent of the Intersociety Committee.