2,2'-DIMERCAPTODIETHYL SULFIDE

2,2'-DIMERCAPTODIETHYL SULFIDE:
METAL COMPLEXES AND ANALYTICAL APPLICATIONS

By

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SCOPE AND CONTENTS:

This thesis is concerned with 2,2'-dimercaptodiethyl sulfide. In particular, the work reported herein deals with the stability of the reagent in both its pure form and in its solutions; the determination of its acid dissociation constants; its reactivity towards metal ions; the nature of its metal complexes with Co(II), Co(III), Ni(II) and Pd(II); and its application as a potentially useful analytical reagent for the spectrophotometric determination of Ni(II) and Pd(II).

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GENERAL INTRODUCTION

Organic ligands containing sulfur donor atoms have received considerable attention in both coordination and analytical chemistry (e.g., 1, 2, 3, 4, 5, 6, 7). In common with 2,2'-dimercaptodiethyl sulfide, the reagent with which this thesis is concerned, many of these ligands contain thiol groups.

Correlation of a massive amount of data (1) has led to the division of (acceptor) metal ions into two classes: (a) those metal ions which form their most stable complexes with the first ligand atom (e.g., N, O, F) of each of the three groups of ligand atoms in the Periodic Table, and (b) those metal ions which form their most stable metal complexes with the second (e.g., P, S, Cl) or subsequent ligand atoms of each group.

According to this classification, S-donor ligands generally form more stable complexes than the corresponding O-donor ligands with Cu(I), Rh(I), Pd(II), Ag(I), Ir(I), Pt(II), Au(I) and Hg(II)--the most pronounced class (b) acceptors. The relationship between class (b) metals and S-donor ligands has been explained in terms of the polarizability and π-acceptor properties of the S-donor atom, and the π-donor properties of the metals (1, 2, 8). The transition between classes (a) and (b) is gradual, so that the acceptors of pronounced class (b) character are flanked by a fairly extensive borderline region.

Whenever possible, classification of the metals (particularly those in the border region) is made on the basis of quantitative measurements, such as those pertaining to equilibrium constants. Equilibrium data is steadily being accumulated for metal complexes of S-donor ligands (7). (Indeed, in some cases, data is not available for the oxygen analogues.) The amount of data is not large in relation to that accumulated for the N- and O-donor ligands. The reasons for this are: (a) a large number of S-donor ligands (e.g., thiols, dithiols) are prone to air-oxidation (9), (b) many sulfur-metal complexes have exceedingly low solubilities, and (c) the S-donor atom often acts as a bridging atom, resulting in the formation of polynuclear species (10) and rendering invalid any comparison of equilibrium data with data for the corresponding O-ligand system. The possibility of obtaining equilibrium data for metal complexes of 2,2'-dimercaptodiethyl sulfide would, of course, depend on these factors.

Several thiols and dithiols have been applied to chemical analysis. Some outstanding examples are 8-mercaptoquinoline (11), dithio-oxamide (rubeanic acid, 12), quinoxaline-2,3-dithiol (13), and 2,3-dimercaptopropanol (BAL, 14). Only one analytical application of any significance has been reported for 2,2'dimercaptodiethyl sulfide(15).

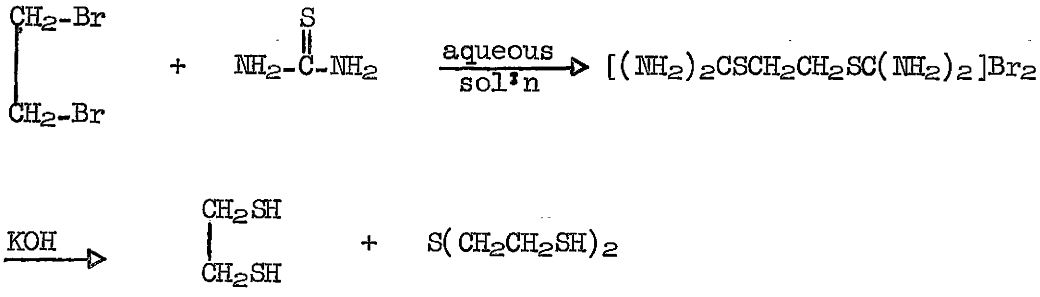
This thesis is concerned with 2,2'-dimercaptodiethyl sulfide; in particular, the stability of this reagent to air-oxidation, its reactivity towards metal ions, the nature of its metal complexes, and its potential use as an analytical reagent.

HISTORICAL INTRODUCTION

Part A 2,2'-Dimercaptodiethyl Sulfide

2,2'-Dimercaptodiethyl sulfide (β,β'-dimercaptodiethyl sulfide; 2,2'-thiodiethanethiol; 2,2'-thiobisethanethiol; bis-(2-mercaptoethyl)-sulfide; bis-(2-mercaptoethyl)-thioether; and, trithiodiglycol) is a colourless liquid that boils at 138°C at 13 mm (16) (135-136°C/10 mm (17)). It has a specific gravity of 1.191 at 20°C (15) ($D_4^0 = 1.2352$, $D_4^{25} = 1.2187$ (17)) and a refractive index of $N_D^{20} = 1.5958$ (15). Its freezing point has been reported as -12.5°C (17) and -11.0°C (16). It is immiscible with water and ethanol but soluble in halogenated organic solvents and dioxane.

2,2'-Dimercaptodiethyl sulfide was first prepared directly by Mathias (16) by the reaction:

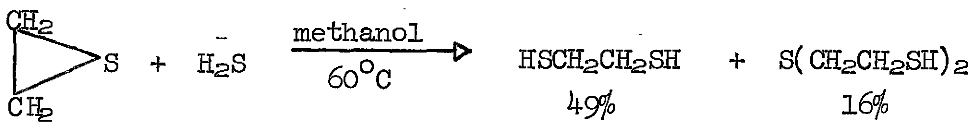


$$\begin{matrix} CH_2\text{-}Br \\ | \\ CH_2\text{-}Br \end{matrix} + NH_2\text{-}\overset{\overset{S}{\|}}{C}\text{-}NH_2 \xrightarrow[\text{sol'n}]{\text{aqueous}} [(NH_2)_2CSCH_2CH_2SC(NH_2)_2]Br_2$$

$$\xrightarrow{KOH} \begin{matrix} CH_2SH \\ | \\ CH_2SH \end{matrix} + S(CH_2CH_2SH)_2$$

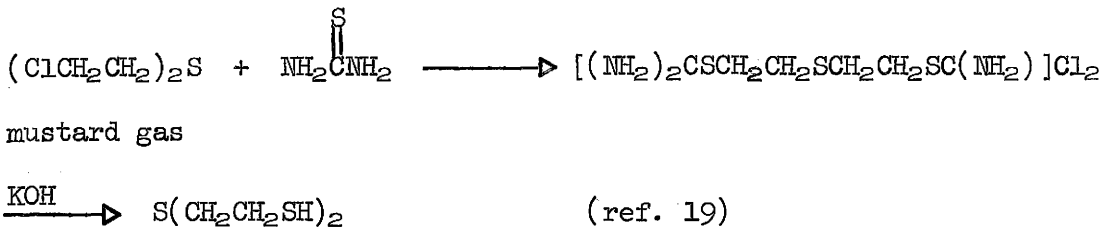
(equal amounts)

Other preparative methods have since been found and are summarized in the following reactions:



$$\begin{matrix} CH_2 \\ CH_2 \end{matrix}\!\!>S + H_2S \xrightarrow[60^\circ C]{\text{methanol}} \underset{49\%}{HSCH_2CH_2SH} + \underset{16\%}{S(CH_2CH_2SH)_2}$$

(ref. 18)



$$(ClCH_2CH_2)_2S + NH_2\overset{\overset{S}{\|}}{C}NH_2 \longrightarrow [(NH_2)_2CSCH_2CH_2SCH_2CH_2SC(NH_2)]Cl_2$$

mustard gas

$$\xrightarrow{KOH} S(CH_2CH_2SH)_2$$

(ref. 19)

Additional references to the dithiol can be found in the literature of synthetic organic chemistry (17, 20-26).

(a) Stability of 2,2'-Dimercaptodiethyl Sulfide

The only reference (15) to the stability of the compound states that the pure reagent, as well as solutions of it in chloroform, could be kept at room temperature in glass-stoppered bottles for 12 months with no change in concentration or any deterioration. This unusually high stability is surprising since thiols characteristically undergo facile air-oxidation to disulfide compounds (27).

In the preparation of metal complexes, particularly for analytical purposes, knowledge of the stability of the reagent in its pure form and in its various solutions is important. Accordingly, further stability studies are reported in this thesis.

(b) Acid-Dissociation Constants

As yet, no quantitative information is available on the acid-dissociation constants of the reagent. Knowledge of the pK_a's of any analytical reagent is important. For example, the pH range of metal-complex formation and of extraction should be known in relation to the pH range of dissociation of the ligand. Furthermore, the pK_a's allow a qualitative estimate of the (equilibrium) stability of metal complexes.

The acid-dissociation constants of 2,2'-dimercaptodiethyl sulfide were determined both spectrophotometrically and potentiometrically in the present study.

Part B Metal Complexes of 2,2'-Dimercaptodiethyl Sulfide

(a) Reactivity of 2,2'-Dimercaptodiethyl Sulfide Towards Metal Ions

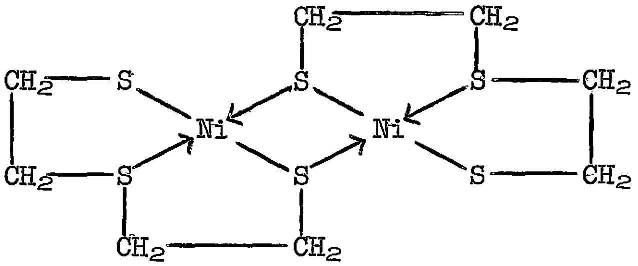
A systematic investigation of the reactivity of the reagent towards the metal ions of the Periodic Table has not yet been made, although a few metal derivatives have been reported. These are the Pb(II) and Hg(II) complexes (16), the Ag(I) complex (17), and the Ni(II), Cu, Cd, Co, Pd, Pt, and Au complexes (the oxidation states, for the most part, are unspecified (19)).

This thesis presents a qualitative survey of the reactivity of the reagent towards certain metal ions. Surveys of this type are important since there is no other way to ascertain the degree of selectivity of a potential analytical reagent.

(b) Solid Metal Complexes

The metal complexes referred to in the previous section have been prepared as solids. All are highly coloured except for the Hg(II) and Ag(I) complexes, which are white. In general, these compounds are not readily soluble in water and organic solvents. The Ni(II)-complex is an exception (19); it is readily soluble in halogenated solvents such as chloroform, yielding deep-red solutions. It also appears to be more crystalline than the other compounds (large garnet-red prisms on recrystallization from chloroform). The Ni(II) compound is stable to alkali but decomposes in mineral acids and potassium cyanide solution. The crystals decompose without melting.

Apart from the Ni(II) compound, no significant data (e.g., analytical data) is available for the metal derivatives. For the red Ni(II)-complex, elemental analysis (19) showed the complex contained one atom of nickel per molecule of dithiol*, but molecular-weight determinations (19) showed that this empirical formula had to be doubled. Very similar red Ni(II)-complexes were obtained (19) with the structurally similar dithiols, $X(CH_2CH_2SH)_2$, where X = MeN and EtN. When X = S $\rightarrow$ O (2,2'-dimercaptodiethyl sulfoxide (19)) and X = O (2,2'-dimercaptodiethyl ether (28)), entirely different, insoluble, yellowish-brown nickel derivatives were formed. Since in the latter two ligands, the central hetero-atom was not expected to be capable of coordination, this was taken as evidence that the hetero atom, when X = S, MeN or EtN, must be coordinated to the metal. The red colour and solubility in halogenated organic solvents suggested that these compounds were non-ionic, square complexes of 4-covalent nickel. On the basis of the above facts, the bridged-structure (I) was assigned to the Ni(II)-complex of 2,2'-dimercaptodiethyl sulfide (19).



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* This is in contrast to the ratio one Ni:two ligand molecules discussed in the following section.

Although the author recognized the possibility of cis-trans isomers (owing to the pyramidal configuration of 3-covalent sulfur), repeated attempts at separation of the isomers failed, suggesting that only one isomer formed.

In this thesis, data on the characterization of the Pd(II), Co(II) and Co(III) complexes is reported, as well as further data on the Ni(II)-complex.

(c) Metal Complexes in Solution

Except for the Ni(II)-complex, no data is available on the solution chemistry of the metal complexes.

In work concerned with the analytical determination of nickel using 2,2'-dimercaptodiethyl sulfide, Segall et al. (15) reported that the formation of the complex in aqueous solution is pH-dependent, with quantitative formation occurring at pH > 10. Furthermore, Job's method of continuous variations indicated that a single complex species is formed in solution and that every nickel atom in the complex is bound to two molecules of the reagent. This latter fact is not consistent with the 1:1 stoichiometry obtained earlier by molecular-weight determinations and elemental analysis (19).

The pH reported for quantitative formation of the complex (15) is unusually high in view of the fact that complexes formed between Ni(II) and ligands with sulfur-donor atoms are appreciably stable (7). Indeed, the situation is even more puzzling in that Fig. 1 of reference (15) more likely represents not complex formation as a function of pH, but percent extraction of the complex as a function of pH. Furthermore, the curve extends over 6 pH units. For a reasonably stable complex and for a large excess of reagent as used by Segall et al. (15), one would expect the extraction curve (or formation curve for that matter) to extend over a much narrower pH range (29), and quantitative extraction (or formation) to occur at pH $\ll$ 10 -- provided equilibrium has been attained.

Because of the above uncertainties, the Ni(II) system was reinvestigated.

Part C Analytical Applications of 2,2'-Dimercaptodiethyl Sulfide

Two analytical applications of 2,2'-dimercaptodiethyl sulfide have been reported to date. One of these involves the formation of the red Ni(II)-complex as a sensitive and specific test for mustard gas (19). The mustard gas is aspirated through a solution of thiourea; the solution is then poured into an ammoniacal nickel sulphate solution and shaken with chloroform. The appearance of a red colour in the chloroform layer constitutes a positive test for the war gas.

The only significant analytical application involves the determination of nickel (15). This method depends on the extraction of the red Ni(II)-complex from ammoniacal solution into chloroform, and measurement of the absorbance at 520 mμ (λ_{max}). The method is apparently suitable for determining nickel in the concentration range 2 to 25 ppm, with an error of one to three percent.

Of importance is the fact that iron (Fe(III)), even when present in relatively large amounts (e.g., in 5-fold excess of nickel), does not interfere. In procedures such as those using dimethylglyoxime (30), α-furildioxime (31), and cyclohexane 1,2-dione dioxime (32), iron interferes and has to be complexed or removed before the determination. Indeed, an examination of reference (33) shows that iron is an interference in most colorimetric determinations of nickel* which, incidentally, are limited to small amounts ($\leq$ 10 ppm) of nickel.

Of 15 common cations and 5 common anions tested, only Cu(II), Co(II) and Pd(II) were found to interfere in the determination of nickel with 2,2'-dimercaptodiethyl sulfide (15); this necessitated their removal by standard methods.

The apparent selectivity and simplicity of the method warranted a closer examination in the present work. This examination led to an improved method for the nickel determination; it also led to a new colorimetric method for the estimation of palladium in the presence of substantial amounts of Fe(III), Ni(II) and Co(II).

Many methods exist for the colorimetric determination of palladium (4, 35). In a recent comprehensive review (4), 65 such methods

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* Quinoxaline-2,3-dithiol appears to be one of the few reagents for nickel in which interference from iron is not encountered. However, this reagent possesses only limited stability (15, 34).

have been listed, making justification of a new method for palladium difficult.

However, a survey of the methods reported in this review shows that nearly all are subject to interferences from common metals such as chromium, iron, cobalt, nickel and copper, and from the noble metals, particularly platinum. In a few cases, common anions such as chloride interfere. Only one method (involving p-nitrosodiphenylamine) seems relatively free of these interferences. About six methods are promising but more restrictive than the first. Another method with promise, not mentioned in the review, is one involving 4,4'-bis-(dimethylamino)-thiobenzophenone as the reagent (36). In view of this, a new method for palladium would be warranted if the method were essentially free of interferences from the ions of the two groups mentioned above(particularly iron and platinum). In addition, despite any lack of obvious advantages, a new method may supply a need in some special application, such as the determination of both palladium and nickel (present simultaneously) with a single reagent.

The colorimetric method for palladium reported in this thesis, as far as investigated, appears relatively free of the above interferences. Furthermore, 2,2'-dimercaptodiethyl sulfide may serve as the reagent in the determination of either nickel or palladium, or both, when these metals occur together.

EXPERIMENTAL AND RESULTS

Apparatus

Calibrated weights and calibrated volumetric ware were used whenever this was appropriate.

Measurements of pH were made with a Radiometer Type PHM 4C pH meter (Radiometer, Copenhagen, Denmark) equipped with Radiometer glass (G202B) and saturated Calomel (K 401) electrodes. The pH meter was standardized each time before use with an appropriate standard buffer solution. Unless otherwise stated, the pH values reported in this work are uncorrected and represent pH meter readings*.

Except when noted, all ultraviolet and visible spectrophotometric measurements reported in Parts A and C** were made using a Hitachi Perkin-Elmer UV-VIS Spectrophotometer, Model 139 (Hitachi, Ltd., through Fisher Scientific Co., Toronto). Spectrophotometric measurements reported in Part B, were made with a Cary Recording Spectrophotometer Model 14 (Applied Physics Corporation, Monrovia, California, U.S.A.). High-quality quartz cells were used for all measurements.

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* The conversion of pH-meter readings into stoichiometric hydrogen-ion concentrations is discussed in (b), Part A, of Experimental and Results.

** For the work in Part C, the cell compartment was kept at constant temperature by installation of a thermal plate (9097-F10, Arthur H. Thomas Company, Philadelphia, U.S.A.), through which was circulated water from a constant-temperature bath (25.0 ± 0.1°C).

Infrared spectra were recorded using a Beckman-IR5 Infrared Spectrophotometer (Beckman Instruments Inc., Fullerton, California, U.S.A.). Liquid samples were examined in potassium bromide cells of equal path lengths (0.5 mm); KBr discs were prepared for solid samples.

The molecular-weight determinations were carried out with a Vapor Pressure Osmometer, Model 301A (Mechrolab Inc., Mountain View California, U.S.A.). Benzil was used for calibration.

Whenever required, constant temperature was attained with a Lo-Temp Bath, Model 882 (Wilkens-Anderson Co., Chicago, Illinois, U.S.A.).

Reagents and Standard Solutions

All common laboratory chemicals were either analyzed grade or of sufficient purity for the purpose intended, and were obtained from reputable suppliers. Unless stated, deionized water (distilled water passed through a mixed-bed ion exchanger) was used in all experiments.

The reagent, 2,2'-dimercaptodiethyl sulfide, was obtained commercially (Aldrich Chemical Company, Inc., Milwaukee 10, Wisconsin, U.S.A.) and was further purified by distillation under reduced pressure (nitrogen gas was passed through the capillary tube). The boiling point was 135-136°C at 10 mm (lit., 135-136°C/10 mm (17); 138°C/13 mm (16)). The purified material was kept under nitrogen gas in glass-stoppered bottles stored in a refrigerator. The nitrogen atmosphere was replaced after every opening. Under these conditions, the 2,2'-dimercaptodiethyl sulfide kept well*.

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* See (a), Part A, of Experimental and Results

1,4-Dioxane (Certified Reagent, Fisher Scientific Co., Toronto) was purified by refluxing over sodium metal, followed by fractional distillation through a four-foot column packed with glass beads (37). The dioxane was collected at 100.4°C (lit., 101.5°/760 mm (37)), and gave a negative peroxide test (38). Unless noted differently, freshly distilled dioxane was used in this work.

The solvent for the molecular-weight determinations was 1,2-dichloroethane (Certified Reagent, Fisher Scientific Co., Toronto) which was redistilled. The fraction used was collected over the range 82.4-83.0°C (lit., 83.5, 83.7°C (39)).

Benzil (British Drug Houses, Toronto) was recrystallized from ethanol: m.p. 93.8-94.5°C (lit., 95°C (40)).

The stock solutions of Ni(II) and Co(II) were prepared from the hydrated perchlorates (G. Frederick Smith Chemical Co., Columbus, Ohio, U.S.A.), and were standardized by accepted EDTA methods (41). The disodium salt of EDTA was initially standardized against a standard Zn(II) solution (42) prepared from zinc metal meeting A.C.S. specifications (Mallinckrodt Chemical Works, Montreal). The concentrations of the Ni(II) and Co(II) stock solutions were $9.78 \pm 0.02 \times 10^{-3}$ M, and $9.85 \pm 0.02 \times 10^{-3}$ M, respectively.

The stock solution of palladium (II) chloride was prepared from anhydrous $PdCl_2$* (Johnson Matthey and Co., Ltd., London, England) and was standardized by precipitation from homogeneous solution as the dimethylglyoximate (43). The biacetyl used in the standardization was

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* The Pd(II) stock solution contained 0.425 g of anhydrous Pd Cl_2, 0.29 g of NaCl and 0.20 ml of 12 M HCl in 250 ml. Heating was necessary for dissolution.

PF/HS - GRADE™ (Burdick and Jackson Laboratories, Muskegon, Michigan, U.S.A.). The stock solution was stable, and had a Pd(II) concentration of 9.489 ± 0.007 x 10^{-3} M.

Part A 2,2'-Dimercaptodiethyl Sulfide

(a) Stability of 2,2'-Dimercaptodiethyl Sulfide

Stability of the pure reagent. Purified 2,2'-dimercaptodiethyl sulfide keeps well when stored under a dry, nitrogen atmosphere in a refrigerator (see above). In the presence of moisture, a white deposit forms after several weeks.

Stability in organic solvents. The ultraviolet spectrum (205-300 mμ) of a petroleum-ether solution of 2,2'-dimercaptodiethyl sulfide showed a shoulder at about 230 mμ ($\varepsilon \sim 480$) and a maximum at 212.5 mμ ($\varepsilon = 1500$). Similar spectra were observed in other solvents such as 1,4-dioxane and chloroform. After a one-to two-week period, the spectra taken in petroleum-ether and chloroform changed only modestly. For example, the absorbance at 250 mμ of a chloroform solution (see below) increased from 0.295 to 0.319 (~8%) in two weeks. The spectrum of dioxane solutions remained essentially unchanged for several days when the solutions were stored under nitrogen gas*. Thus, solutions of the reagent in organic solvents appear to be moderately stable over fairly long periods of time.

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*Dioxane is known to develop peroxides on standing in air (37).

Stability in 50% V/V aqueous dioxane. Since much of the work to be described in later sections was carried out in 50% V/V aqueous dioxane, the ultraviolet spectra of the reagent in this solvent were examined. These spectra were found to be dependent on time and on pH. Since mercaptans are easily oxidized in air (27), the observed changes in the spectra were interpreted as evidence of a process involving oxidation.

Because oxidation of the reagent is a factor to be considered in analytical applications, experiments of a qualitative nature were done to obtain some knowledge of the extent of air-oxidation in 50% V/V aqueous dioxane under laboratory conditions normal for analytical procedures.

Solutions were prepared at room temperature (25 ± 2°C) by diluting a weighed amount of reagent (~ 0.01 g) with dioxane followed by an equal volume (25 ml) of buffer solution or water, and dilution to volume (50 ml) with 50% V/V aqueous dioxane (Table 1). Immediately after the addition of the buffer, the time was noted ($t = 0$). After dilution to volume, the spectra were recorded (220 - 320 mμ) at suitable time intervals. Solutions used as blanks contained appropriate volumes of buffer solution (or water) and dioxane. Between measurements, the solutions were kept in stoppered flasks which were exposed to the light and temperature of the laboratory.

Spectra were obtained at three pH values (Table 1, Fig. 1). The effect of time is illustrated in Figures 2, 3, and 4. By plotting absorbance versus time at a particular wavelength, the absorbance at t = 0 could be obtained by extrapolation (Table 2).

TABLE 1

Ultraviolet Spectra of 2,2'-Dimercaptodiethyl Sulfide
in 50% V/V Aqueous Dioxane

Composition of Buffer Sol'n	pH of Final Sol'n	Absorbance maximum (mμ)	Inflection Point (mμ)	Reagent Molar Absorptivity* (ε)
H_2O	6.0 ± 0.5	-----	-----	365 (235 mμ) 108 (250 mμ)
0.16 M in NH_4Cl, 0.8M in aq. NH_3	9.76 ± 0.02	-----	226	1600 ± 100 (226 mμ) 1500 ± 100 (232.5 mμ) 1400 ± 100 (235 mμ)
0.01 NaOH	13.37 ± 0.02	235	-----	12,420 ± 20 (235 mμ)

From Figures 2, 3 and 4, the following points should be noted: (i) at pH 6.0, the product has a strong absorbance maximum at 250 mμ which develops in about one week; the relative absorbance of the reagent at this wavelength is low; (ii) at pH 9.76, the reagent absorbs strongly at the inflection at 232.5 mμ, while the product displays a

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* Calculated from absorbance at zero time. A 1cm cell was used.

minimum at this wavelength; a maximum at 253 mμ (and a minimum at 233 mμ) develops in a matter of hours; (iii) at pH 13.37, the reagent absorbs strongly at 235 mμ but the absorbance of the oxidation product is relatively weak.

The spectrophotometric data is summarized in Table 2.

TABLE 2

Summary of Spectrophotometric Data for the Air-Oxidation of 2,2'-Dimercaptodiethyl Sulfide

pH	6.0 ± 0.5	9.76 ± 0.02		9.76 ± 0.02		13.37 ± 0.02	
Conc. (M)	1.69 x 10^{-3}	2.98 x 10^{-4}		9.98 x 10^{-4}		1.15 x 10^{-4}	
Temp(°C)	25 ± 2	25 ± 2		25 ± 2		20 ± 2	
Time (hrs)	Absorbance (250 mμ)	Time (hrs)	Absorbance (232.5 mμ)	Time (hrs)	Absorbance (232.5 mμ)	Time (hrs)	Absorbance (235 mμ)
0*	0.182	0	0.477	0	1.42	0	1.43
3.0	0.195	0.83	0.328	0.23	1.20	0.25	1.42
24.5	0.290	1.67	0.178	0.52	1.04	0.62	1.40
46.0	0.375	2.17	0.139	1.03	0.937	1.13	1.40
96.5	0.568	3.50	0.138	1.97	0.837	2.50	1.31
165	0.770			3.95	0.583	45	0.084
1000	0.860			21.25	0.368	120	0.071
				72.58	0.365		

The ultraviolet absorption spectra of disulfides are characterized by a rather broad absorption band in the 250 mμ region (44, 45, 46). At pH 6.0, this is typified by spectrum C, Fig. 2, and at pH 9.76 by

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* Absorbances at zero time were obtained from plots of absorbance versus time (reciprocal absorbance versus time at pH 9.76).

spectrum D, Fig. 3. This is strong evidence for air-oxidation of the dithiol to one or more disulfide species. (Saturated alkyl sulfides normally do not react with oxygen at temperatures below 100°C to form products containing the -SO group (47).) At pH 13.37, the band is not observed because of the low initial concentration of reagent* and the broadness of the band, (spectrum C, Fig. 4), although the strong maximum at 235 mμ due to the reagent is greatly reduced with time.

The data of Table 2 illustrates the changes in absorbance of the reagent (or the product, at pH 6.0) as a function of time at the three pH values investigated. These changes presumably reflect the rates of oxidation of the reagent in the various solutions. A qualitative estimate of the relative reaction rates can be obtained by graphically evaluating the time ($t_{1/2}$) required for the initial absorbance, A_i (i.e., A at t = 0), to decrease to $A_{1/2} = A_i - \left(\frac{A_i - A_f}{2}\right)$ at pH 9.76 and 13.37, and to increase to $A_{1/2} = A_f - \left(\frac{A_f - A_i}{2}\right)$ at pH 6.0. A_f is the last absorbance value recorded in Table 2 for each pH value, and is assumed to be equal to the final absorbance that would be observed if the oxidation were complete. This assumption seems reasonable since at each pH value studied, the absorbance tends to a constant value with time (Table 2). Further support for this assumption is furnished by Fig. 4, in which the initial absorbance of the reagent is reduced to a negligible value by the oxidation process. The estimated

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* The initial concentration was low because the molar absorptivity of the reagent at this pH is very large (Table 1).

values of $t_{1/2}$ were obtained at the corresponding values of $A_{1/2}$ from plots (not shown) made of the data in Table 2. Table 3 contains the necessary data. From the $t_{1/2}$ values, the relative reaction rates at pH 6.0, 13.37 and 9.76 are approximately 1:10:70, in the range of concentration studied.

TABLE 3

Spectrophotometric Data for Approximate Relative Rates

Conc. (M)	pH	A_i	A_f	$A_{1/2}$	$t_{1/2}$ (hrs)	
1.69×10^{-3}	6.0 ± 0.5	0.182 (250 mμ)	0.860	0.521	84	
2.98×10^{-4}	9.76 ± 0.02	0.477 (232.5 mμ)	0.138	0.307	1.0	1.2
9.98×10^{-4}	9.76 ± 0.02	1.42 (232.5 mμ)	0.365	0.892	1.4	
1.15×10^{-4}	13.37 ± 0.02	1.43 (235 mμ)	0.071	0.750	15	

The effect of dissolved oxygen was demonstrated by the following experiment. Two solutions at pH 13.37 (1.25×10^{-4} M) were prepared as described earlier. These solutions were identical except that measures were taken to exclude dissolved oxygen in one. This was done by passing nitrogen gas through a solution of freshly distilled dioxane and the buffer solution for 30 minutes. In addition, the volumetric flask was flushed with nitrogen before and after preparation of the sample, and whenever a portion of the sample was removed for examination. The data is plotted in Fig. 5. Similar data was not obtained at pH 6.0 and 9.76.

To study the effect of a strong oxidizing agent on 2,2'-dimercaptodiethyl sulfide, oxidation with hydrogen peroxide (30%) in alkaline solution was carried out in 70% V/V aqueous dioxane. A white precipitate formed immediately. The ultraviolet spectrum in 50% aqueous dioxane showed a weak inflection at 250 mμ, indicating the presence of some disulfide linkages.

The infrared spectra of 2,2'-dimercaptodiethyl sulfide in CCl_4 and in dioxane, and of the solid oxidation product (KBr pellet) were recorded in the region 625 - 5000 cm^{-1}. The spectra of both compounds were identical in the regions (5000 - 1110 cm^{-1}, and 1000 - 714 cm^{-1}) in which the various -CH vibrational modes absorb (45, 48). At 2530 cm^{-1}, however, a weak band in dioxane (very weak in CCl_4) corresponding to the -SH stretching frequency was observed for the reagent, but not the oxidation product. A summary of characteristic bands is given in Table 4.

TABLE 4

Characteristic Absorption Frequencies in the Infrared for 2,2'-Dimercaptodiethyl Sulfide and its Oxidation Product

Reagent (cm^{-1})	Oxidation Product (cm^{-1})	Relative Intensity	Assignment*
2530 (CCl_4)	-----	W	-SH str.
-----	1040	M	-S=O str.
680-700 (CCl_4)	-----	broad; M	-C-S-R** str.
694 (dioxane)	-----	M	-C-S-str. (C-S-H)
680 (dioxane)	-----	M	-C-S-str. (C-S-C)
-----	710 †	S	unassigned
-----	670	S	-C-S-str. (C-S-S-)
-----	685	W	unassigned

---

* Based on assignments for related compounds (45, 48)

** This band has no fine structure in CCl_4 (R=H, C)

† Relative band areas at 670 cm^{-1} and 710 cm^{-1} are 2:1. The band area at 685 cm^{-1} is negligible by comparison.

(b) Acid-Dissociation Constants

The Calvin-Wilson (Bjerrum) pH-titration technique (49) was used for the determination of the dissociation constants of 2,2'-dimercaptodiethyl sulfide. Briefly, a 50% V/V aqueous dioxane solution containing known concentrations of the reagent, perchloric acid, and sodium perchlorate (inert electrolyte) was titrated potentiometrically with a standard sodium hydroxide solution.

The following equations relate the degree of protonation ($\bar{n}_H$) and the free hydrogen-ion concentration (expressed as - log [H]) to experimentally determinable quantities.

Let H_2A represent the reagent, $HSCH_2CH_2SCH_2CH_2SH$*. The average number of protons bound to A is:

$$\bar{n}_H = \frac{\text{total conc. of bound protons}}{\text{total conc. of ligand}}$$

$$= \frac{2[H_2A] + [HA]}{C_A} \qquad \text{(i)}$$

where $C_A = [H_2A] + [HA] + [A]$ (ii)

The charge balance is:

$$[Na] + [H] = [OH] + [ClO_4] + [HA] + 2[A] \qquad \text{(iii)}$$

where charges due to the inert electrolyte have been excluded.

Rearrangement of (ii) and (iii) yields:

$$[H_2A] = C_A - [HA] - [A] \qquad \text{(iv)}$$

---

* Charges on the species are omitted; brackets refer to stoichiometric concentrations.

and

$$[HA] = [Na] + [H] - [OH] - [ClO_4] - 2[A] \qquad (v)$$

Substituting (iv) in (i) gives:

$$\bar{n}_H = \frac{2C_A - [HA] - 2[A]}{C_A} \qquad (vi)$$

Substitution of (v) in (vi) gives:

$$\bar{n}_H = \frac{2C_A + [OH] + [ClO_4] - [Na] - [H]}{C_A} \qquad (vii)$$

Equation (vii)requires a knowledge of the hydrogen-ion concentration, [H]. Van Uitert and Haas (50, 51) have shown that the general relation holds:

$$-\log_{10} [H] = B + \log_{10} f + \log_{10} U_H^0 \qquad (viii)$$

where B = pH meter reading

f = activity coefficient of hydrogen ion in the solvent mixture under consideration (at the specified temperature and ionic strength)

U_H^0 = correction at zero ionic strength.

The relation is valid for water and water-dioxane solutions. A plot of $-\log_{10}$ [H] against B, using solutions of known stoichiometric hydrogen-ion concentration (mineral acid at the specified temperature, ionic strength and solvent composition), should be linear and have an intercept equal to $\log_{10} f\, U_H^0$, the correction term which converts B into - $\log_{10}$ [H]*.

A plot of $\bar{n}_H$ versus - $\log_{10}$ [H] (derived from (viii) using $-\log_{10} f\,U_H^0$ = - 0.065**) yields the formation curve. If the two proton formation constants (K_1 and K_2) are poorly separated, the application of Bjerrum's half-$\bar{n}$ rule (at $\bar{n}_H = 0.5$, pH = log K_2; at $\bar{n}_H = 1.5$, pH = log K_1 (52)) to the formation curve will give only approximate values for these constants since, for the rule to apply accurately, a separation of 2.5 - 3.0 log units between successive formation constants is necessary (53).

The slope of the formation curve (Fig. 6) shows that the two constants for 2,2'-dimercaptodiethyl sulfide are not very well separated. The data was therefore treated in the manner described below. The formation constants correspond to the equilibria:

$$^-SCH_2CH_2SCH_2CH_2S^- + H^+ = {}^-SCH_2CH_2SCH_2CH_2SH$$

$$^-SCH_2CH_2SCH_2CH_2SH + H^+ = HSCH_2CH_2SCH_2CH_2SH$$

for which:

$$K_1 = \frac{[^-SCH_2CH_2SCH_2CH_2SH]}{[H^+][^-SCH_2CH_2SCH_2CH_2S^-]} \qquad \text{(ix)}$$

---

* -$\log_{10}$ [H] $\neq$ pH for pH = -log a_{H^+} which is approximately equal to $\frac{E_{obs} - \mathcal{E}}{0.05915}$ (at 25°C) = B,

where $\mathcal{E} = E_{ref} + E_j$ and is assumed constant from one solution to another. -$\log_{10}$ [H] is actually the negative logarithm of the hydrogen-ion concentration which would exist if the solvent were pure water (50).

** This value is for 25.0 ± 0.1°C and ionic strength of 0.08 (private communication, E. J. Billo, McMaster University).

$$K_2 = \frac{[HSCH_2CH_2SCH_2CH_2SH]}{[H^+][^-SCH_2CH_2SCH_2CH_2SH]} . \qquad (x)$$

Thus, $K_{a_2} = 1/K_1$ and $K_{a_1} = 1/K_2$, where K_{a_2} and K_{a_1} are the second and first dissociation constants, respectively. Substitution of (ix) and (x) into (i) gives:

$$\bar{n}_H = \frac{K_1[H] + 2K_1K_2\,[H]^2}{1+K_1[H] + K_1K_2[H]^2} \qquad (xi)$$

Rearrangement of (xi) yields:

$$\bar{n}_H + (\bar{n}_H - 1)K_1[H] + (\bar{n}_H - 2)K_1K_2[H]^2 = 0 \qquad (xii)$$

Division of (xii) by $(\bar{n}_H - 1)\,[H]$ and rearrangement gives

$$\frac{\bar{n}_H}{(\bar{n}_H - 1)[H]} = \frac{(2 - \bar{n}_H)[H]}{(\bar{n}_H - 1)} . K_1K_2 - K_1 \qquad (xiii)$$

A plot of $\dfrac{\bar{n}_H}{(\bar{n}_H-1)[H]}$ (called Y) against $\dfrac{(2-\bar{n}_H)[H]}{(\bar{n}_H-1)}$ (called X) should result in a straight line of slope K_1K_2 and intercept $-K_1$. As $\bar{n}_H$ approaches unity, X and Y each become large. Thus, the experimental points corresponding to values of $\bar{n}_H = 0.95 - 1.05$ are necessarily rejected. In addition, both X and Y vary by several powers of ten in the region of hydrogen-ion concentration usually considered. As a result, X and Y are very sensitive to experimental errors, and it is necessary to treat the data by the least-squares method. The I.B.M. computor on the McMaster campus was used for this.

Titrations were carried out in a 250-ml jacketed titration vessel. Water from a thermostated bath (25.0±0.1°C) was circulated through the jacket. Exact volumes of water (10 ml), dioxane (50 ml), standard perchloric acid solution (50 ml, 10^{-2} M, and adjusted to an ionic strength of 0.20 with $NaClO_4$), and reagent solution (10 ml, 10^{-2}M, dioxane solvent) were pipetted into the titration vessel. The solvent composition of the final solution (ionic strength = 0.08) was 50% V/V aqueous dioxane. Prior to the addition of the reagent solution (added last), the solution in the vessel was de-aerated for 10 minutes with nitrogen gas presaturated with 50% V/V aqueous dioxane. During the titration (10-ml micro-burette) with sodium hydroxide (0.1152 N, carbonate-free), de-aeration was continued and the solution stirred magnetically. For each volume of base added, an equivalent volume of dioxane was also added to maintain the 50% V/V composition. When pH measurements were taken, stirring and nitrogen-bubbling were stopped, although a nitrogen flow was kept above the solution surface. The data from a typical titration is shown in Table 5.

TABLE 5

Typical Data from the Titration of 2,2'-Dimercaptodiethyl Sulfide

Initial Vol. = 119.95 ml
Conc. of NaOH = 0.1152 N
Temp. = 25.0 ± 0.1°C
Ionic strength= 0.08

Moles Reagent = 7.617×10^{-5}
Moles $HClO_4$ = 4.986×10^{-4}

Vol. of NaOH (ml)	$-\log_{10}$ [H]	$\bar{n}_H$	$X=\frac{(2-\bar{n}_H)[H]}{(\bar{n}_H-1)}$ $\times 10^{11}$	$Y=\frac{\bar{n}_H}{(\bar{n}_H-1)[H]}$ $\times 10^{-10}$
4.440	9.65	1.830	4.560	0.9893
4.480	9.78	1.770	5.002	1.376
4.520	9.88	1.709	5.370	1.841
4.560	9.98	1.649	5.620	2.450
4.600	10.08	1.588	5.878	3.217
4.660	10.20	1.497	6.375	4.771
4.720	10.32	1.407	6.918	7.293
4.800	10.49	1.286	8.087	13.90
4.880	10.70	1.165	10.05	35.56
5.000	10.95	0.984*	-70.47	-547.1
5.100	11.15	0.833	-4.964	-70.41
5.200	11.30	0.683	-2.066	43.22
5.300	11.44	0.532	-1.137	-31.42
5.400	11.59	0.382	-0.6794	-23.87
5.500	11.70	0.233	-0.4564	-15.29

---

* Omitted in least squares plot

The proton-formation curve corresponding to the data in Table 5 is shown in Fig. 6. From the plot of least squares, the intercept is -2.813×10^{11} and the slope is 5.786×10^{21}. The values for the dissociation stoichiometric constants (obtained in two titrations) are summarized in in Table 6.

TABLE 6

Potentiometric Acid-Dissociation Constants of 2,2'-Dimercaptodiethyl Sulfide

Temp. = 25°C, $\mu = 0.08$, 50% V/V aqueous dioxane

Moles Reagent	$K_{a_1} = 1/K_2$	pK_{a_1}	$K_{a_2} = 1/K_1$	pK_{a_2}
$7.617\text{x}10^{-5}$	$4.86\text{x}10^{-11}$	10.31	$3.56\text{x}10^{-12}$	11.45
$3.792\text{x}10^{-4}$	$4.81\text{x}10^{-11}$	10.32	$3.91\text{x}10^{-12}$	11.41
Average	$4.84\pm0.03\text{x}10^{-11}$	10.32±0.01	$3.74\pm0.18\text{x}10^{-12}$	11.43±0.02

The first acid-dissociation constant can also be calculated from the spectrophotmetric data at pH 9.76 ((a) Part A) before significant oxidation occurs, if it is assumed that only the neutral and mono-anionic species of the reagent exist in appreciable concentrations at this pH value. This assumption is supported by the pK_a values obtained potentiometrically.

Let ε_1 and ε_2 and ε_3 be the molar absorptivity at 235 mμ of the neutral, mono-anionic and dianionic forms respectively.

Assuming the validity of Beer's law, then at pH 9.76

$$A_{t=o} = \varepsilon_1 C_1 + \varepsilon_2 C_2 \qquad \text{(xiv)}$$

where $C_1 = [S(-CH_2CH_2SH)_2]$, and $C_2 = [HSCH_2CH_2SCH_2CH_2S^-]$ and

$$C_1 + C_2 = C_T \text{ (analytical concentration)} \qquad \text{(xv)}$$

The data at pH 6.0 and 13.37 ((a)A) permit the calculation of ε_1 and ε_3 (235 mμ) on the basis that only neutral and dianionic species are present, respectively. Assuming that $\varepsilon_2 = \varepsilon_3/2$ (e.g., 54) now allows calculation of C_1 and C_2 from equations (xiv) and (xv). The first acid-dissociation constant can then be calculated from

$$K_{a_1} = \frac{C_2\,[H^+]}{C_1} \qquad \text{(xvi)}$$

The data and results are summarized in Table 7.

TABLE 7

Data for the Spectrophotometric Determination of pK_{a_1}

Temp. = 25±2°C, μ* = 0.08,
B = 9.76, $-\log[H^+] = 9.70$ (see above)
$\varepsilon_1 = 365$, $\varepsilon_3 = 12{,}400$ (Table 1),
and $\varepsilon_2 = 6200$

C_T (moles/l)	$A^{**}_{t=o}$ (235 mμ)	$[H^+]$ (moles/l)	C_1 (moles/l)	C_2 (moles/l)	K_{a_1}	pK_{a_1}
9.98×10^{-4}	1.33	2.00×10^{-10}	8.32×10^{-4}	1.66×10^{-4}	3.99×10^{-11}	10.40
2.98×10^{-4}	0.458	2.00×10^{-10}	2.38×10^{-4}	5.98×10^{-5}	5.02×10^{-11}	10.30
				Average:	$4.51\pm0.52\times10^{-11}$	10.35±0.05

* Calculated from the buffer content of the solution
** Obtained by plotting absorbance at 235 mμ and extrapolating to zero time

The value of pK_{a_1} compares well with the potentiometric value (10.32 ± 0.01), thus justifying the assumptions made in its evaluation. Since no spectrophotometric data was obtained in the pH region where only the mono-and di-anions coexist, pK_{a_2} could not be evaluated spectrophotometrically.

Part B Metal Complexes of 2,2'-Dimercaptodiethyl Sulfide

(a) Reactivity of 2,2'-Dimercaptodiethyl Sulfide Towards Metal Ions

Tests for reactivity were made in test-tubes by adding 0.4 ml of metal-ion solution (0.02 M, prepared from metal chlorides, nitrates or perchlorates)* and 0.4 ml of 2,2'-dimercaptodiethyl sulfide solution (0.07 M, dioxane solvent) to 10 ml of buffer solution (Table 8). Each test was compared to a blank containing only the metal ion and buffer solution. The formation of a precipitate or a colour was taken as a positive test for reaction.

TABLE 8

Composition of Buffer Solutions

Buffer	Composition	pH
A	0.005 M H_2SO_4	2.05
B	0.18 M in NaOAc, 0.02 M in HOAc	5.60
C	0.19 M in NH_4OAc, 0.02 M in aq. NH_3	8.45
D	0.16 M in NH_4Cl, 0.80 M in aq. NH_3	10.25

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* A freshly prepared solution of ferrous ammonium sulphate was used for the Fe(II) test.

The following metal ions gave negative tests at all pH values: Mg(II), Sr(II), Y(III), La(III), Ce(III), Th(IV), UO_2^{+2}, Ti(IV), Al(III).* Those metal ions which gave a positive reaction are listed in Table 9, together with the pH conditions necessary for reaction and the colour of the precipitates or soluble complexes that formed.

TABLE 9

Summary of Positive Tests Between Metal Ions
and 2,2'-Dimercaptodiethyl Sulfide

(Positive test indicated by +, negative by -; blank signifies test not tried)

Metal		Buffer Sol'n			
Ion	A	B	C	D	Colour
Cr(III)	-	-	-	+	light green
Mn(II)	-	-	-	+	off-white
Fe(III)	-	+	+	+	green
Fe(II)	-	+	+	+	green
Co(II)	-	+	+	+	greenish-brown
Ni(II)	-	+	+	+	red
**Cu(II)	+	+	+	+	white
Zn(II)	-	+	+	-	white
***Rh(III)		+	+		orange
Pd(II)	+	+	+		orange
Pt(IV)	+				light brown
Ag(I)	+	+	+	+	white
Cd(II)	+	+	+	+	white
Hg(II)	+				white
Tl(I)		-	+		yellow
Pb(II)	-	+	+	+	yellow
Bi(III)		+			yellow

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* In buffer solution C, the reagent showed a tendency to be absorbed onto the gelatinous hydrous-oxide precipitates formed by the lanthanide and rare-earth metal-ions.

** With copper in excess, a mauve precipitate formed (buffer sol'n B).

*** Heating (steambath) was necessary for reaction with Rh(III) at both pH values tested.

The source of platinum for the spot test was platinic acid, $H_2PtCl_6 \cdot 6H_2O$, dissolved in 0.01 M HCl. One ml of the metal-and 0.5 ml of the reagent solutions were used. Reaction at room temperature was slow, requiring about 5-10 minutes before a precipitate* (light brown) formed. When heat was applied to a test solution, a yellow-green precipitate** resulted.

(b) Solid Metal Complexes

<u>Preparation</u>. Tris(2,2'-dimercaptodiethyl sulfide)dicobalt(III). This complex was prepared from hexamminecobalt(III)trichloride*** by the reaction:

$$2[Co(NH_3)_6]Cl_3 + 3\ S(CH_2CH_2SH)_2 + H_2O \xrightarrow[\text{dioxane, }70^{\circ}C]{\text{aqueous}}$$

$$Co_2(SCH_2CH_2SCH_2CH_2S)_3 \cdot H_2O + 6NH_3 + 6NH_4Cl$$

1.25 g (4.67×10^{-3} moles) of hexamminecobalt(III) trichloride (dried at 110°C for one hour) was dissolved in 50 ml of water. Unpurified (not distilled, see section on reagents) dioxane was then added until precipitation just occurred. Twenty ml of water and 1.59 g (1.03×10^{-2} moles) of 2,2'-dimercaptodiethyl sulfide in 10 ml of dioxane were then added with stirring. The flask was then placed in a water-bath at 70°C. Precipitation occurred. The reaction mixture was kept at 70°C for 30 min to complete the precipitation. After cooling to 5°C in an ice-bath, the mixture was filtered by suction. The bluish-black crystalline

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* Extractable into benzyl alcohol as pale brown

** Not extractable into benzyl alcohol

*** The preparation of the hexamminecobalt(III) trichloride is well-known (55). The crystalline orange compound was identified by its infrared spectrum (56).

material was washed with dioxane, and then with water; it was dried overnight at 60°C, and finally for one hour at 110°C. The yield was 1.16 g (83.9%). Attempts at recrystallization from chloroform were not successful because of the low solubility of the complex.

Bis(2,2'-dimercaptodiethyl sulfide)dinickel(II). The complex was prepared essentially as described by Harley-Mason (19). To a solution of 1.19 g (3.13×10^{-3} moles) of $NiCl_2 \cdot 6\ H_2O$ in 130 ml of water was added 20 ml of concentrated aqueous ammonia with stirring. The blue-violet solution was filtered to remove insoluble impurities, and was then stirred magnetically while 0.60 g (3.90×10^{-3} moles) of 2,2'-dimercaptodiethyl sulfide (dissolved in 10 ml of dioxane) was added dropwise from a burette. Precipitation occurred immediately. Stirring was continued for 40 minutes. The maroon crystals were washed by decantation with several portions of 2M aqueous ammonia, and were then filtered by suction. The crystals were washed first with a small volume of 2M aqueous ammonia and then, in succession with hot water, cold water, ethanol and ether. The product was dried in vacuo for one hour at 25°C. A quantitative yield (0.66 g) was obtained. The compound was recrystallized from chloroform-petroleum ether (3:1) solution. The compound did not melt sharply but decomposed over a wide temperature range, beginning at about 200°C. At about 270°C, a condensate of the reagent was observed in the capillary tube.

Bis(2,2'-dimercaptodiethyl sulfide)dipalladium(II). 0.288 g (1.62×10^{-3} moles) of $PdCl_2$ was dissolved with heat and stirring in 100 ml of water containing 0.30 g (5.20×10^{-3} moles) of sodium chloride. (The addition of a few drops of concentrated HCl aided dissolution.) The brownish-red solution was then cooled and filtered to remove traces of undissolved material.

2,2'-Dimercaptodiethyl sulfide (2.48 g) was dissolved in a solution containing 10 ml of 0.25 M $HClO_4$, 40 ml of water and 150 ml of dioxane (not purified). To this solution was added the palladium chloride solution in small portions (with stirring) over a period of 20 minutes. An orange precipitate formed almost immediately. Stirring was continued for an additional 30 minutes. The compound was washed with 50% V/V aqueous dioxane by decantation, filtered by suction and then washed with small amounts of chilled 50% V/V aqueous dioxane, ethanol and ether in succession. The compound was dried overnight in vacuo at 55°C. The yield was 0.216 g (51.6%). (Large mechanical losses prevented a higher yield.) No suitable solvent could be found from which to recrystallize the product.

Complex derived from Co(II) and 2,2'-dimercaptodiethyl sulfide. To a solution containing 75 ml of a hydroxylamine buffer solution*, 120 ml of dioxane (not purified)and 2.15 g (1.40×10^{-2} moles) of 2,2'-dimercaptodiethyl sulfide, 1.44 g (6.05×10^{-3} moles) of $CoCl_2 \cdot 6\,H_2O$ dissolved in 10 ml of water was added dropwise with stirring. Precipitation occurred immediately. Stirring was continued for 30 minutes, and the solution was then cooled to 5°C in an ice-bath. The greenish-

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* 17.4 g of $NH_2OH \cdot HCl$ and 5.2 g of NaOH dissolved in 250 ml of water (pH = 6.0).

black precipitate was filtered by suction and washed extensively with unpurified dioxane. The precipitate was dried overnight in an oven at 60°C. The yield was 1.59 g. Because of its low solubility, the complex could not be recrystallized, although it dissolved sufficiently in both water and polar organic solvents to render them deep brown. The compound did not melt sharply. Softening started at about 90°C, which resulted in a deeply coloured viscous liquid by 190°C.

Elemental analyses. The metal complexes were analyzed for C, H, S, metal and O where water was thought to be present. The analyses were performed by the Alfred Bernhardt Microanalytical Laboratories, Mülheim, Germany. The samples were prepared as just described. Prior to each elemental determination, the Ni(II)-complex and that derived from Co(II) were dried in vacuo (2 mm) at 60°C; the Pd(II)- and Co(III)-complexes were similarly dried prior to only the carbon, hydrogen, and oxygen determinations. The data is compiled in Table 10 together with the empirical formula most consistent with each analysis.

TABLE 10

Summary of Analytical Data on Metal Complexes

Metal Complex	Ni(II)		Co(III)		Derived from Co(II)	Pd(II)	
Empirical Formula	$NiC_4H_8S_3$		$Co_2(C_4H_8S_3)_3 \cdot H_2O$		-----	$PdC_4H_8S_3$	
Element	Calc. %	Exp. %	Calc. %	Exp. %	Exp. %	Calc. %	Exp. %
C	22.77	22.96	24.31	24.54	22.81	18.57	18.43
H	3.82	4.01	4.42	4.51	3.98	3.12	3.15
S	45.58	45.42	48.68	48.56	41.43	37.18	37.00
O	-----	-----	2.70	2.61	6.89	-----	-----
Metal	27.83	27.80	19.88	20.13	20.02	41.13	40.26*
Cl	-----	-----	-----	-----	2.63		
% Total	100.00	100.19	99.99	100.35	97.76	100.00	98.84

The empirical formula suggested for the Ni(II)-, Pd(II)- and Co(III)-complexes fit the analytical data particularly well. Molecular weight determinations are required, however, in order to obtain the molecular formulas.

The analytical data for the complex derived from Co(II) does not fit the simple empirical formula $CoC_4H_8S_3$, or other simple formulas such as $Na_2Co(C_4H_8S_3)_2$. As will be discussed later, oxidation of Co(II) appears to occur. This could lead to the isolation of complicated

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* A note from the Bernhardt Laboratories suggested the possibility of volatilization during fuming with H_2SO_4 and HNO_3 and ignition of the sample in the palladium determination. (The palladium was weighed as the metal.) This likely explains the low palladium result.

mixtures of compounds containing cobalt in either the +2 or +3 oxidation state, or both. A flame test for sodium was very strong, suggesting its presence in the substance, but a quantitative determination was not made. See DISCUSSION for further comments.

Molecular-weight determinations. The vapour phase osmometer was calibrated with solutions of benzil of known concentrations in freshly distilled 1,2-dichloroethane (see Reagents and Standard Solutions). All ΔR values given below, including those for the metal complexes, are the average of four or five two-minute readings.

During this work, it was found that solutions of benzil in 1,2-dichloroethane were sensitive to daylight. The change in molarity (as measured by the osmometer) that occurred over a period of five days is illustrated by A, Fig. 7. A comparison was made with an identical solution protected from daylight by storage in a dark cupboard (B, Fig. 7). The slight increase in concentration exhibited in B is likely due to the small, but unavoidable, amount of exposure to daylight during measurements. The data is summarized in Table 11.

TABLE 11

Decomposition of Benzil

Time	Sol'n Exposed to Daylight		Sol'n Protected from Daylight	
(days)	△ R (ohms)	Observed Conc.(M x 10^3)	△ R (ohms)	Observed Conc. (M x 10^3)
0	1.50±0.01	3.84†	1.50±0.01	3.84†
1	1.71±0.02	4.52	1.51±0.01	3.90
$3\frac{1}{3}$	2.05±0.02	5.60	1.55±0.02	4.00
5	2.23±0.01	6.15	1.53±0.01	3.97

† 3.84 x 10^{-3}M is both the stoichiometric and observed concentration.

The calibration curves were determined with freshly prepared benzil solutions* to minimize the effect of photolysis. In Fig. 8, two calibration curves are shown. Curve B was determined two months after Curve A. Thus the characteristics of the instrument appear to be a function of time. However, periodic checks of calibration Curve B during a period of two weeks (the time curve B was employed) revealed good reproducibility. The calibration data is summarized in Table 12 and 13.

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* Solutions of known concentrations were prepared by suitable dilution of measured quantities of a stock solution of benzil. The stock solution was prepared by dissolving a known weight of benzil in an exact volume of solvent. All dilutions were made at room temperature (23° ± 1°C).

TABLE 12

Calibration Data for Curve A

Stoich. Conc. (M x 10^3)	Δ R (ohms)
1.44	0.90 ± 0.01
2.88	1.41 ± 0.02
4.32	1.92 ± 0.02
7.20	2.95 ± 0.02
10.80	3.96 ± 0.02

TABLE 13

Calibration Data for Curve B

Stoich. Conc. (M x 10^3)	Δ R (ohms)
0.55	0.28 ± 0.00
1.10	0.51 ± 0.01
1.64	0.71 ± 0.02
2.20	0.92 ± 0.02
3.84	1.50 ± 0.01
5.49	2.01 ± 0.02
6.66	2.38 ± 0.02

Solutions for the molecular-weight determinations of the metal complexes were prepared in the manner described below. Known weights of the complexes (prepared and dried as described earlier) were placed in either about 8 or 22 ml of 1,2-dichloroethane at room temperature (23 ± 1°C). Dissolution was never complete; in particular the complex derived from Co(II)* and the Pd(II)-complex were only sparingly soluble. After equilibration, the undissolved residue was filtered, dried and weighed. Next, the filtrate was carefully transferred to the appropriate volumetric flask, and diluted to exactly 10.0 or 25.0 ml. The Δ R value was then measured.

The data is summarized in Tables 14 and 15. The poor precision in the results for the "Co(II)" and Pd(II)-complexes is partly due to the error associated with determining the weight of the small amounts of these complexes that dissolved. Uncertainties of 5 to 10 percent could easily result from this factor. The use of a balance with a reproducibility of ± 0.01 mg is recommended. Another source of error is the precision of the Δ R values. Because of the low concentrations of the solutions (about a factor of 10 lower than recommended by Mechrolab Inc.), the Δ R values are low, with a precision of 5 to 10 percent. Therefore, the total error in the determination of the molecular weights of these two complexes is 10 percent (at best) to 20 percent(at worse). The situation is much more favourable with the Ni(II)-complex, of course.

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* Hereafter, also referred to as the "Co(II)"-complex.

TABLE 14

Data for Molecular-Weight Determinations

Metal Complex	Weight of Metal Complex Dissolved (mg)	Final Vol. (ml)	△ R (ohms)	Observed Conc. (M)	Observed Molecular Weight
Ni(II)	22.4	10.0	1.93±0.01	5.20	431
	41.6	25.0	1.79±0.03	3.98	418†
				$(\times 10^{-3})$	
Complex	2.0	10.0	0.16±0.01	3.3±0.2	610±60
Derived from	3.2	10.0	0.32±0.02	4.9±0.4	650±70
Co(II)	3.2	10.0	0.26±0.02	5.3±0.4	600±60
				$(\times 10^{-4})$	
Pd(II)	1.9	10.0	0.18±0.01	3.7±0.2	510±50
	2.7	10.0	0.24±0.02	5.0±0.4	540±50
				$(\times 10^{-4})$	

† Calibration curve A, Fig. 8 was used. For all remaining determinations, Curve B was employed.

TABLE 15

Molecular Formula of Metal Complexes Based on Molecular Weights and Analytical Data

Empirical Formula†	Observed Molecular Weight	Precision (Approx.) %	Suggested Molecular Formula	Formula Molecular Weight
$NiC_4H_8S_3$	425 ± 7	± 2	$Ni_2(C_4H_8S_3)_2$	422.0
$PdC_4H_8S_3$	530 ± 50	±10	$Pd_2(C_4H_8S_3)_2$	517.4
"Co(II)" complex	620 ± 70	±10	-----	-----

†See Table 10

The molecular weight determinations are sufficiently good to show that the Ni(II)- and Pd(II)-complexes are dimeric. See DISCUSSION for the interpretation of the data for the "Co(II)"-complex. The molecular weight for the Co(III)-complex was not determined. Magnetic susceptibility measurements should shed further light on these complexes.

Magnetic susceptibilities. The magnetic measurements were made by the Gouy method (e.g., 57) on powdered samples of the metal complexes prepared and dried as described earlier. The magnetic susceptibility was calculated from the formula:

$$10^6\chi = \frac{\alpha + \beta F^1}{\omega}$$

where χ = the magnetic susceptibility per gram in c.g.s. units

α = a constant (in mg.) allowing for the displaced air and is equal to 0.029 x specimen volume

β = the tube-calibration constant

$F^1 = F - \delta$ = the force exerted by the specimen (mg)

F = the observed force (mg)

δ = the force exerted by the tube alone (mg)

ω = the weight of the specimen (g)

Mercury(II)tetrathiocyanatocobaltate*, $Hg[Co(CNS)_4]$, was used to evaluate the tube-calibration constant, β (58, 59). After preparation (58), it was dried for one hour at 110°C. The tube used was

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* The accepted magnetic susceptibility per gram for this standard is 16.44×10^{-6} (± 0.5%) at 20°C (58, 59).

flat-bottomed and had an inside diameter of 4 mm. The volume calibration was carried out for two lengths of the tube (each level was marked by a permanent etching on the outside of the tube). The volumes were calculated from the weight and the density of water. Thus, two possible sample volumes could be used in the magnetic measurements.

Table 16 summarizes the constants which characterize the Gouy tube. Except in the case of δ, the data represents the average of two determinations; δ is the average of six determinations.

TABLE 16

Gouy-Tube Constants

Length of Specimen (cm)	Vol. of Specimen (ml)	α (mg)	δ (mg)	β (mg)
3.07	0.388±0.000	0.011	-2.97±0.07	0.152±0.001
5.07	0.631±0.001	0.018	-2.97±0.07	0.234±0.004

The magnetic data is summarized in Table 17. The molar susceptibilities (χ_M) of the Pd(II)- and Ni(II)-complexes were calculated on the basis of the molecular formula assigned above (Table 15); and that for the Co(III)-complex on the basis of its formula in Table 10. The susceptibilities were not determined as a function of temperature.

TABLE 17

Molar Susceptibilities of Metal Complexes

Metal Complex	Sample Length (cm)	Specific Susc. $10^6\chi$ (cgs)	Molar Susc. $10^6\chi_M$ (cgs)	Temp. $^{\circ}K$	No. of Det'ns
Ni(II)	3.07	-0.457±0.012	-193±5	292	2
Pd(II)	3.07	-0.27±0.08	-140±40	293	2
Co(III)	3.07	-0.22±0.02	-130±10	293	2
"Co(II)"	3.07	1.51±0.02	-----	293	3
"Co(II)"	5.07	1.51±0.02	-----	293	1

The Pd(II)-, Ni(II)- and Co(III)-complexes are diamagnetic. The "Co(II)"-complex exhibits appreciable paramagnetism, which will be interpreted in the DISCUSSION.

(c) Metal Complexes in Solution

Metal-complex formation as a function of pH. The formation of the Ni(II)-, "Co(II)-" and Pd(II)-complexes was examined as a function of pH. These are dealt with in turn.

Ni(II)-complex. The solutions were prepared by pipetting the components below into 50-ml volumetric flasks in the following order: buffer solution (Table 18), aqueous sodium perchlorate solution (0.49 M)*,

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* The ionic strength of the final solution was 0.10 M. The volume of $NaClO_4$ solution required was calculated after taking into account the ionic strength and volume of buffer and nickel perchlorate solutions.

and water to yield a combined volume of 20.0 ml; 2.00 ml of a 2,2'-dimercaptodiethyl sulfide solution (0.0820 M, dioxane as solvent); 23.0 ml of dioxane*; and 5.00 ml of an aqueous nickel (II) perchlorate solution (5.87×10^{-3}M). The solutions at room temperature (24 ± 2°C) were then diluted to volume with 50% V/V aqueous dioxane solution. Next, the visible spectrum of each solution was recorded in the range 300 to 600 mμ and lastly, the pH (Table 18) was measured.

TABLE 18

Composition and Volume of Buffer Solutions;

pH of Final Solution

Sol'n No.	Comp. of Buffer Sol'n	Vol. of Buffer Sol'n (ml)	pH of Final Sol'n**
1	0.025 M H_2SO_4	10.0	2.34
2	0.025 M H_2SO_4 0.85 M in HOAc, 0.15 M in NaOAc	11.1 1.0	2.43
3	0.025 M H_2SO_4 0.85 M in HOAc, 0.15 M in NaOAc	10.3 2.0	2.86
4	0.025 M H_2SO_4 0.85 M in HOAc, 0.15 M in NaOAc	9.8 2.5	3.12
5	0.025 M H_2SO_4 0.85 M in HOAc, 0.15 M in NaOAc	9.4 3.0	3.45
6	0.025 M H_2SO_4 0.85 M in HOAc, 0.15 in NaOAc	7.7 5.0	4.75
7	0.85 M in HOAc, 0.15 M in NaOAc	10.0	5.18
8	0.02 M in HOAc, 0.15 M in NaOAc	10.0	6.58
9	0.02 M in aq.NH_3, 0.15 M in NH_4Cl	10.0	7.28
10	0.85 M in aq.NH_3, 0.15 M in NH_4Cl	10.0	9.43
11	0.05 M NaOH	10.0	12.36

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* The choice of 50% V/V aqueous dioxane as solvent was necessitated by the very low solubilities of the metal complexes in water.

** Corrected pH values (see (b), Part A).

Curve B (Fig. 9) is representative of the spectra at pH values up to and including pH 7.28 (the solutions are red). The absorbance at λ_{max} = 505 mμ (Table 19) was plotted against pH (up to pH 7.28) to give the pH-formation curve (C, Fig. 10). Complex formation appears to be complete at about pH4 (constant absorbance at pH $\gtrsim$ 4).

Much different spectra are observed at high pH values (e.g., C, Fig. 9, pH = 12.36). The colour of the solution is now yellow-orange. At pH 9.43, the spectrum (not shown) is intermediate in appearance to B and C in Fig. 9. On standing overnight, the yellow-orange solutions turn red and the spectra change accordingly (those solutions which were red originally remained so*). The characteristic features of the spectra are summarized in Table 19.

TABLE 19

Features of Visible Spectra of Ni(II)-Complex

pH Range	Reagent to Metal Molar Ratio	Colour of Sol'n	λ_{max} (mμ)	$\lambda_{shoulder}$ (mμ)
†2.9 - 7.3	5.6	red	378, 505 (ε=1310, ε=1060)	414 (ε=1160)
9.4 - 12.4	5.6	yellow-orange	463 (ε=740)	-----

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† A sol'n prepared by dissolving the solid nickel complex in 50% V/V aqueous dioxane gave an identical spectrum.

* This applies to solutions at pH 7.28 and 6.58 only. At pH $\lesssim$ 5.18, a white flocculent precipitate forms overnight and some loss of the red colour occurs. This precipitate forms also in the absence of metal ion in solutions containing acetic-acid buffer and/or sulphuric acid. It does not occur in hydrochloric or perchloric acid solutions.

"Co(II)"-complex. The procedure was essentially that described for the Ni(II)-complex except that $NaClO_4$, which caused precipitation, was not added to adjust the ionic strength. The quantities pipetted were: buffer solution (Table 20) and water to total 20.0 ml; 1.00 ml of the 2,2'-dimercaptodiethyl sulfide solution, 24.0 ml of dioxane and 5.00 ml of an aqueous cobalt(II) perchlorate solution (9.84×10^{-4} M). Final adjustment to 50.0 ml (at room temperature) was made with 50% V/V aqueous dioxane.

TABLE 20

Composition and Volume of Buffer Solutions; pH of Final Solution

Sol'n No.	Comp. of Buffer Sol'n	Vol. of Buffer Sol'n (ml)	pH of Final Sol'n
1	0.01 M HCl	11.0	2.69
2	0.01 M HCl	5.0	2.99
3	0.01 M HCl	1.0	3.50
4	0.02 M in HCl, 0.15 M in KH phthalate	2.0	4.29
5	0.01 M HCl 0.15 M KH phthalate	3.0 1.0	4.65
6	0.85 M in HoAc, 0.15 M in NaOAc	2.0	5.56
7	0.02 M in HoAc, 0.15 M in NaOAc	2.0	6.99
8	0.02 M in aq.NH_3, 0.15 M in NH_4Cl	2.0	7.42
9	0.85 M in aq.NH_3, 0.15 M in NH_4Cl	2.0	9.55
10	0.05 M NaOH	2.0	11.67
11	0.85 M in HoAc, 0.15 M in NaOAc	1.0	5.52
12, 13	0.02 M in HoAc, 0.15 M in NaOAc	2.0	7.12

The spectrum of each solution was recorded (300-600 mμ) 20 to 40 minutes after preparation. Representative spectra (for sol'ns 1-8 in Table 20) are C and B in Figures 11 and 12 respectively, each with shoulders at ~ 325 mμ ($\mathcal{E}$=8740) and ~ 385 mμ ($\mathcal{E}$=6690). At pH 9.55 (sol'n 9), only a shoulder at 375 mμ is observed; at pH 11.69 (sol'n 10), this shoulder is very weak. The formation of the metal complex as a function of pH is shown in B, Fig. 10 where the absorbance at the shoulder (385 mμ) is plotted against pH.

Changes in spectra of solutions 6-10 were followed with time for a period of one day. Solutions were kept at room temperature in volumetric flasks, and small aliquots were removed periodically to record the spectrum. Curves C, C' and C", Fig. 11, illustrate the changes in the spectrum at pH 7.42 (sol'n 8), recorded 36 min, 110 min and one day, respectively, after preparation. Similar changes were observed at pH 5.56 (sol'n 6) and pH 6.99 (sol'n 7). In contrast, the rate of change in absorbance was much faster at pH 9.55 (sol'n 9). This is demonstrated by B, Fig. 11, which was recorded one day after preparation. The rate at pH 11.69 (sol'n 10), expected to be even greater, was in fact the slowest.

In addition to changes in absorbance, λ_{max} also shifted to higher wavelengths with time (followed for 24 hours). The higher the pH, the lower was the final λ_{max} (Table 22, sol'ns 6-10). For purpose of comparison, the spectrum of the solid "Co(II)" complex (A, λ_{max} = 402 mμ, shoulder at $\lambda \doteq$ 330 mμ) freshly dissolved in 50% V/V aqueous dioxane (2.0 mg in 40 ml) has been included in Fig. 11. Its resemblance to other spectra in Fig. 11 is striking.

The spectra were also found to be dependent on the length of time the dioxane was stored in air (i.e., storage time) after distillation*. This effect was studied in solutions 11-13. The solutions were prepared as outlined above, although the volumes and concentrations of the various components differed (for details, see Table 21). Dioxane of various storage times was used. The time was noted directly after the addition of the Co(II) solution. After dilution to volume, the spectrum was taken at appropriate intervals during a one-day period. Spectra B and B' (Fig. 12) correspond to solution 13 at 20 minutes and 1 day, respectively, after its preparation; curve C corresponds to solution 12 at 20 minutes. Thus, the time required for an absorbance maximum to develop is much less than 24 hours when stored dioxane is used. In addition, there is no further shift of λ_{max} (sol'ns 11 and 12, Table 22) to higher wavelengths during the remainder of the one-day period -- although the absorbance continues to increase slowly.

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* It is appropriate to repeat (see section on reagents) that freshly distilled dioxane was used in this work unless stated otherwise.

TABLE 21

Composition of Solutions 11-13

Sol'n No.	Vol. of Buffer Sol'n* (ml)	Vol. of Water (ml)	Vol. of Co(II) Sol'n (ml)	Conc. of Co(II) Sol'n (M)	Vol. of Reagent Sol'n** (ml)	Conc. of Reagent Sol'n (M)	Vol. of Dioxane† (ml)
11	1.0	22.5	2.50	1.97x10^{-3}	1.0	0.0820	24.0
12	2.0	18.0	5.00	9.84x10^{-4}	2.0	0.0253	23.0
13	2.0	18.0	5.00	9.84x10^{-4}	2.0	0.0253	23.0

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* For composition of buffer solutions, see Table 20, solutions 11-13.

** Prepared with freshly distilled dioxane

† For storage time of dioxane, see Table 22, solutions 11-13.

TABLE 22

Changes in λ_{max} with pH, Time and Storage Time of Dioxane

Sol'n No.	pH of Sol'n	Final λ_{max} (mμ)	Time for Transition λ_{385}(shoulder)→ final λ_{max} (hrs)	Storage Time of Dioxane
6	5.56	416	24	freshly distilled
7	6.99	414	24	freshly distilled
8	7.42	409	24	freshly distilled
9	9.55	405	24	freshly distilled
10†	11.69	----	----	freshly distilled
11	5.52	421	0.9	3 days
12	7.12	420	0.3	7 days
13	7.12	420	24	freshly distilled

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† The spectrum of solution 10 did not change significantly in 24hrs. The shoulder at 375 mμ did not shift, but only grew in intensity.

All solutions prepared with freshly distilled dioxane were yellow-brown. Solutions prepared with dioxane that had been standing (e.g. sol'n 12) were darker.

Co(III)-complex. The formation of the Co(III)-complex as a function of pH was not studied since the Co(III) ion is not stable in aqueous solution in the absence of suitable complexing agents. However, the spectrum of dissolved tris(2,2'-dimercaptodiethyl sulfide) dicobalt(III) in chloroform aids in the interpretation of the data just presented for the Co(II) system. A solution of freshly dissolved Co(III)-complex in $CHCl_3$ (~1.5 mg/ 25 ml, reddish-brown sol'n) yielded spectrum B, Figure 13. The same solution after 3 days (kept stoppered at room temperature) gave spectrum A, Fig. 13. Spectrum C, Fig. 13, is that of a freshly dissolved sample of the "Co(II)"-complex in $CHCl_3$ (~0.7 mg/40 ml), which did not change with time. Spectra A and C are very similar*, and the corresponding solutions are yellow-brown.

Pd(II)-complex. The procedure described for the Ni(II)-complex was followed except that 0.50 ml of the reagent solution and 24.50 ml of dioxane were added. The solution of palladium(II)chloride was 9.480×10^{-4} M**. The composition of the buffer solutions, the volumes used and the (corrected) pH of the final solutions are listed in Table 23.

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* A, λ_{max} = 397 mμ; B, λ(shoulder) = 495, 430 mμ; C, λ_{max} = 404 mμ; λ(shoulder) = 325 mμ.

** This solution was unstable; palladium was deposited after several days. It was prepared by dilution of the Pd(II) stock solution (see section on standard solutions).

TABLE 23

Composition and Volume of Buffer Solutions;
pH of Final Solution

Sol'n No.	Comp. of Buffer Sol'n.	Vol. of Buffer Sol'n (ml)	pH of Final Sol'n
1	2.5 M HCl	20.0	0(calc)
2	2.5 M HCl	10.0	0.3(calc)
3	0.25 M HCl	20.0	1.0(calc)
4	0.25 M HCl	6.0	1.67
5	0.25 M HCl	2.0	2.18
6	0.02 M in HCl, 0.15 M in KH phthalate	2.0	4.14
7	0.02 M in HOAc, 0.15 M in NaOAc	10.0	6.91
8	0.02 M in aq.NH_3, 0.15 M in NH_4Cl	10.0	7.75
9	0.85 M in aq.NH_3, 0.15 M in NH_4Cl	10.0	9.64
10	0.05 M NaOH	10.0	12.45

Spectrum B, Fig. 14, is typical for the pH range 1.0-7.8 (i.e. sol'ns 3-8). For strongly acid (sol'ns 1 and 2) and basic (sol'ns 9 and 10) solutions, the spectra are different; for example, see spectra A (pH = 0) and C (pH region 9.6-12.5) in Fig. 14. The spectrum of palladium (II) chloride in water at pH 2.08, at the same Pd(II) concentration as in the above solutions, is also shown in Fig. 14 (E). The characteristic features of the various spectra are summarized in Table 24, including the colours of the corresponding solutions.

Curve A, Fig. 10, illustrates the dependence of the formation of the Pd(II)-complex on pH. The absorbance at 340 mμ (λ_{max}, in the pH range 1.0-7.0, sol'ns 1-7, Table 23) is plotted against pH.

TABLE 24

Features of Visible Spectra of Pd(II)-Complex

Sample	pH	Colour	λ_{max} (mμ)	λ(shoulder) (mμ)	Molar Absorptivity ε
Pd(II) complex*	0	deep yellow	----	310	7810
"	0.30	deep yellow	----	325	7070
"	1.0-7.0	yellow(pH=1.0) to greenish-yellow (pH=7.0)	340	----	7380
"	9.6-12.5	(pale) greenish-yellow	335	410 (broad)	5830;570
$PdCl_2$	2.08	Yellow	(weak)424	307	237;980

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* Reagent to metal ratio is 8.6. For comments on the stability of these solutions see below.

Solvent extraction as a function of pH. The extraction of the Ni(II)-, Pd(II)- and "Co(II)"- complexes are dealt with in turn.

Ni(II)-complex. The extraction of the Ni(II)-complex from aqueous solution into 1,2-dichloroethane was studied as a function of the pH of the aqueous phase. 1,2-Dichloroethane was chosen as the solvent because firstly, the molecular-weight determination indicated that the complex was appreciably soluble in this solvent, and secondly, the solvent is stable and is easily purified.

Water and buffer solution (Table 25) (to a total volume of 37.0 ml) and 3.00 ml of nickel(II)perchlorate solution (9.78×10^{-3} M) were placed in a 100-ml separatory funnel. The Ni(II)-complex was then extracted with three 10-ml portions of 1,2-dichloroethane which was 2.04×10^{-2} M in 2,2'-dimercaptodiethyl sulfide. Shaking for one to two minutes with each 10-ml aliquot proved to be sufficient. The aqueous phase was then washed with one 5-ml portion of pure 1,2-dichloroethane and the pH of the extracted aqueous phase was measured. The organic phases were collected and transferred to a 50-ml volumetric flask, and were diluted to the mark at room temperature (23 ± 1°C) with additional solvent. The spectrum was then recorded in the range 300-600 mμ using solvent as the blank. Spectrum A, Fig. 9, is typical of the extracted species (λ_{max} = 389, 512 mμ, red extract)* The dependence of the extraction on pH is illustrated by curve B, Fig. 15, where the

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* A spectrum of the solid Ni(II)-complex dissolved in 1,2-dichloroethane was identical (λ_{max} = 388, 512 mμ).

absorbance at 512 mμ is plotted against the pH of the aqueous phase.

At pH 10.25 the aqueous phase was yellow after extraction with the three 10-ml portions of the solvent containing the reagent. Repeated washing of the aqueous phase with pure solvent removed the yellow colour imparting a pink colour (due to low concentration) to the organic phase. At all lower pH values, the aqueous phase was colourless after extraction and the single washing with pure solvent.

TABLE 25

Buffer Composition

Comp. of Buffer Sol'n	Vol. of Buffer Sol'n (ml)	pH of Extracted Aq. Phase
0.25 M $HClO_4$	1.8	2.10
0.15 M KH phthalate	3.0	4.01
0.1 M in HOAc, 0.1 M in NaOAc	5.0	4.50
0.02 M in HOAc, 0.15 M in NaOAc	10.0	5.60
0.02 M in NH_4OH, 0.15 M in NH_4Cl	10.0	7.78
0.04 M aqueous NH_3	10.0	9.50
dilute NH_4OH	10.0	10.25

For analytical purposes described later in Part C (Analytical Applications), the extraction of the nickel complex into benzyl alcohol was also examined. The experimental procedure was essentially that described above. The Ni(II)-complex was successively extracted with a 20-ml and a 10-ml portion of reagent solution (1.93×10^{-2} M), followed by washing with 10 ml of pure benzyl alcohol. After dilution of the combined portions to 50 ml, the spectrum was recorded, using a solvent blank. The spectrum of the extracted species had maxima at 308 and 508 mμ, and a shoulder at 413 mμ. Curve A, Fig. 15 shows the absorbance at 508 mμ plotted against the pH of the extracted aqueous phase.

Pd(II)-Complex. Attempts to extract the palladium into 1,2-dichloroethane failed. Shaking with the organic phase (i.e., reagent solution) produced a deep yellow aqueous phase containing a precipitate. Only partial extraction occurred. The extracted species was greenish-yellow. Its spectrum is given by D, Fig. 14. The extractions were attempted in the pH range 1.5-5.6.

Benzyl alcohol proved to be an effective solvent for extracting the Pd(II)-complex. No precipitation in the aqueous phase occurred, although the yellow, extractable species again formed. Extractions were done in 50-ml separatory funnels at pH 1.50 and pH 2.10. At pH 1.50, the aqueous phase contained 5.0 ml of 0.25 M $HClO_4$, 30 ml of water, and 5.00 ml of a 4.74×10^{-4} M palladium(II)chloride solution prepared in dilute $HClO_4$ (see below). At pH 2.10, the aqueous phase consisted of 1.7 ml of 0.25 M $HClO_4$, 33.5 ml of water and 5.00 ml of the palladium(II)chloride solution. Two extractions with benzyl alcohol (0.0193 M in reagent; 20-ml and 10-ml portions), followed by washing (one 10-ml portion) with pure benzyl alcohol were required. In both cases, the organic phases were greenish-yellow. After dilution to 50 ml (23 ± 1°C), the extracts yielded spectra of identical shape and absorbance. The equivalent extractions suggest quantitative extraction of Pd(II) at both pH values. The spectra of the extracted species were identical to that recorded previously for the Pd(II)- complex formed in 50% V/V aqueous dioxane (B, Fig. 14, λ_{max} = 340 mμ).

"Co(II)"-complex. The extraction of the "Co(II)"-complex was not studied in detail. Since both the Ni(II)-and "Co(II)"-complexes form over similar ranges of pH (Fig. 10), it is likely that the extractions also occur over similar pH ranges. Both ions extract simultaneously when present together in the aqueous phase* (15).

Stoichiometry. The ligand-to-metal ratio of the Ni(II)-, Co(II)- and Pd(II)-complexes was determined spectrophotometrically by the mole-ratio method (60, 61), in which the concentration of the metal ion is kept constant while the concentration of 2,2'-dimercaptodiethyl sulfide is varied.

A 1:1 and 2:1 stoichiometry have been reported for the Ni(II)-complex (see HISTORICAL INTRODUCTION). To shed further light on this apparent conflict, the ligand-to-metal ratio was determined at two widely different pH values.

At the lower pH value (6.75 ± 0.03, μ = 0.1), the solutions were prepared in 50 ml flasks by pipetting in the following order: 10.0 ml of buffer solution (0.02 M in HOAc and 0.15 M in NaOAc); 7.0 ml of 0.49 M $NaClO_4$; 3.0 ml of water; (25.0 - x) ml of dioxane; x ml (Table 26) of 2.53×10^{-2} M 2,2'-dimercaptodiethyl sulfide solution**

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* (b), Part C of EXPERIMENTAL AND RESULTS.

** Pipetted at 25.0 ± 0.1°C.

(dioxane solvent); and 5.00 ml of 5.87×10^{-3} of Ni(II) perchlorate solution*. Each solution was then diluted to the mark at room temperature (23 ± 1°C) with 50% V/V aqueous dioxane. The spectrum (e.g., B, Fig. 9) of each solution was recorded in the range 300 - 600 mμ and the absorbance measured at 505 mμ (λ_{max}). The absorbance due to the reagent and uncomplexed Ni(II) ion is negligible at this wavelength. A plot of the molar ratio of reagent to metal (R/M) yields a sharp break at 1.08, indicative of a 1:1 stoichiometry (Curve A, Fig. 16).

TABLE 26

Data from Mole-Ratio Method for Ni(II)-Complex (pH 6.75)

Vol. of Reagent Sol'n* x (ml)	R/M Mole Ratio	Absorbance at 505 mμ
0.29	0.25	0.135
0.58	0.50	0.286
0.87	0.75	0.414
1.16	1.00	0.578
1.45	1.25	0.621
2.32	2.00	0.622
4.64	4.00	0.620

A similar procedure was used to determine the stoichiometry at pH 12.14. The solution components were pipetted in the following order: 5.0 ml of 0.050 M NaOH; 9.5 ml of 0.49 M $NaClO_4$; 7.5 ml of water;

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* Pipetted at 25.0 ± 0.1°C

(25.0 - x) ml of dioxane; x ml (Table 27) of 2.53×10^{-2} M reagent solution; and 3.00 ml of 9.78×10^{-3} M nickel(II) perchlorate solution*. The solutions were diluted to the mark and the spectra recorded as before. The pH values and the spectra were not the same for all solutions. For solutions (red) with R/M values in the range 0.28 - 2.25, the pH was 12.14 ± 0.02 and the spectra were identical to B, Fig. 9. The mole-ratio plot yielded a R/M ratio of 1.05 (B, Fig. 16). Solutions (yellow-red) with R/M values of 4.00 and 6.00, had spectra initially identical to C, Fig. 9, and the pH was 11.44 ± 0.02; these spectra changed overnight to those observed at the lower R/M values. Correspondingly, the pH value changed to 12.19 ± 0.02. These observations are dealt with in the DISCUSSION.

TABLE 27

Data from Mole-Ratio Method for Ni(II)-Complex

(pH 12.14)

Vol. of Reagent Sol'n**, x (ml)	R/M Mole Ratio	Absorbance At 505 mμ
0.32	0.28	0.161
0.87	0.75	0.425
1.45	1.25	0.602
1.74	1.50	0.604
2.03	1.75	0.606
2.61	2.25	0.608
4.64	4.00	-----
6.96	6.00	-----

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* Pipetted at 25.0 ± 0.1°C.

** added from 10-ml micro-burette

"Co(II)"-complex. The experimental procedure differed little from that used for nickel. The following volumes were pipetted into 50-ml volumetric flasks in the order stated: 10.0 ml of buffer solution (0.12 M in $NH_2OH \cdot HCl$ and 0.04 M in NaOH); 10.0 ml of water; (25.0 - X) ml of dioxane; X ml (Table 28) of reagent solution* (2.53 x 10^{-2} M) and 5.00 ml of Cobalt(II)perchlorate solution* (9.84 x 10^{-4} M). Dilution to volume followed. In each case, the spectra were recorded in the range 300 - 600 mµ, 30 - 40 minutes after the solutions were prepared. The pH of the solutions was then measured immediately (5.80 ± 0.05). All spectra looked alike (broad shoulder around 393 mµ) and were intermediate in appearance to C and C', Fig. 11. Transition to spectrum C^{8} and then to C'' occurs on standing.

TABLE 28

Data from Mole-Ratio Method for "Co(II)"-Complex

(pH 5.80)

Vol. of Reagent Sol'n**, X (ml)	R/M Mole Ratio	Absorbance at 393 mµ
0.05	0.26	0.046
0.15	0.77	0.203
0.25	1.28	0.359
0.30	1.54	0.452
0.35	1.80	0.527
0.45	2.31	0.610
1.00	5.13	0.608

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* Pipetted at 25.0 ± 0.1°C

** Added from a 10-ml micro-burette

Since in the Co(II) system, oxidation is a complicating factor (see above), the break at R/M = 2.05 (Fig. 17) does not necessarily indicate a 2:1 stoichiometry. The reagent and uncomplexed Co(II) ion do not absorb appreciably at 393 mμ.

Pd(II)-Complex. The stoichiometry of the Pd(II)-complex was studied at pH 2. This value was chosen because it is in an analytically useful pH range (see Part C, Analytical Applications).

The following volumes were pipetted into 50-ml volumetric flasks in the order stated: 2.0 ml of $HClO_4$ (0.25 M); 18.0 ml of water; (25.0 - X) ml of dioxane; X ml (Table 29) of reagent solution (7.97×10^{-3} M); and 5.00 ml* of palladium(II)chloride solution (4.74×10^{-4} M)**. The solutions were diluted to volume as before ($23 \pm 1^{o}C$), and the spectra were recorded in the range 300 - 600 mμ. The pH of the final solutions was 2.31 ± 0.02.

The spectrum varied with the R/M ratio (Fig. 18). At R/M values < 1 the spectra had maxima at 340 and 410 mμ, while for R/M > 1 only the maximum at 340 m) occurred. The data is collected in Table 29.

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* Pipetted at $25.0 \pm 0.1^{o}C$

** This solution was prepared by diluting 5.00 ml of palladium(II) stock solution (see section on standard solutions) and 2.0 ml of 0.25 M $HClO_4$ to 100.0 ml. It decomposed slowly.

TABLE 29

Data from Mole-Ratio Method for Pd(II)-Complex
(pH 2.31)

Vol.* of Reagent Sol'n, X (ml)	R/M Mole Ratio	Absorbance at 340 mμ	Absorbance at 410 mμ
0.15	0.50	0.242	0.222
0.23	0.77	0.300	0.272
0.30	1.01	0.321	0.254
0.45	1.51	0.337	0.222
0.53	1.78	0.340	0.210
0.68	2.28	0.344	0.195
0.90	3.02	0.347	0.178
1.50	5.04	0.346	0.147
3.00	10.08	0.348	0.132

The absorbance at 340 mμ increases with R/M and is constant when R/M ~ 3. Furthermore, the absorbance at 410 mμ attains a maximum value at R/M ~ 0.8, and then decreases regularly with increasing R/M values. This behaviour suggests the presence of two distinct species in solution. The dependence of the absorbance at 340 and 410 mμ on the R/M ratio is given by A and B respectively, Fig. 19. The reagent does not absorb at 340 or 410 mμ, while the absorbance due to uncomplexed Pd(II) is negligible**. Extrapolation of the linear segments of curve A yields a R/M ratio of 1.0. Curve B has a sudden break at a R/M ratio of 0.7 - 0.9, suggesting for the species absorbing at 410 mμ

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* added from a 10-ml micro-burette

** Curve E, Fig. 14 is the spectrum of palladium(II)chloride at pH 2.08 (in water) at twice the concentration of palladium used above.

a formula in which the ligand-to-metal ratio is somewhat less than unity (see DISCUSSION).

The spectra of solutions with R/M ratios < 0.5 could not be recorded because of the formation of a black suspension (in time, a black solid precipitated). The same behaviour is observed for palladium(II) chloride solutions in 50% V/V aqueous dioxane. It appears that Pd(II) is reduced to Pd metal, either by dioxane or by impurities in the dioxane which are difficult to remove.

A systematic change in colour occurs with increasing R/M values. At low R/M ratios, the solutions are deep yellow (maximum intensity at R/M ~ 0.8). At R/M values $\gtrsim 5$, the solutions are pale yellow-green.

Turbidity was observed in solutions where R/M$\lesssim 2.3$. This turbidity was slight at the time the spectra were recorded, but overnight an orange-yellow deposit was obtained*. The extent of precipitation increased as the intensity of the yellow colour increased.

Filtration through a fine-porosity, glass-sintered Büchner funnel removed the turbidity and yielded filtrates varying from colourless (R/M < 0.8) to pale yellow-green (R/M > 1.0). The spectra of the filtrates resembled C, Fig. 18 (or B, Fig. 14) and provided no evidence for the presence of the species that, before filtration, absorbed strongly at 410 mμ (e.g., A, Fig. 18). It is apparent that the deep-yellow species (which has maxima at 410 and 340 mμ) is removed by filtration, while the

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* All solutions, except those where R/M = 5.04 and 10.08 developed a precipitate overnight. The turbidity was more serious at higher absolute concentrations of palladium and reagent for a particular R/M value. Also, the turbidity increased in the presence of $NaClO_4$.

yellow-green species (which has a maximum at 340 mμ only) remains in the filtrate. The more insoluble species, therefore, predominates at ligand-to-metal ratios of less than one; as this ratio is increased, the more soluble species predominates.

Palladium(II)perchlorate. Since the standard palladium stock solution* contained a high concentration of chloride ion ($Cl^-/Pd(II) \sim 5$), it is possible that the formation of the deep-yellow species is dependent on the chloride-ion concentration. To test this possibility, a chloride-free Pd(II) solution was prepared and the mole-ratio method repeated.

A silica crucible containing palladium(II)chloride (~75 mg) was brought to a red heat over a Meker burner and allowed to cool to about 70°C. The palladium oxide formed was then wafted with a strip of filter paper soaked in methanol to produce Pd metal, 0.0267 g of which was placed in 17 ml of concentrated HNO_3. The mixture was left on a hot plate at low heat overnight. All but a few particles dissolved. Additional heating and acid did not effect dissolution. The solution was filtered through a glass-sintered Büchner funnel. The small amount of residue appeared to be undecomposed palladium(II)chloride. Perchloric acid (70%, 4.5 ml) was then added and the solution evaporated to fumes. Following dilution to 4.0 ml (with 70% $HClO_4$), the reddish-brown liquid was transferred to a 50-ml volumetric flask and diluted to volume with distilled** water at 25.0 ± 0.1°C. The solution was then standardized***

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* See section on reagents.

** Distilled water was used to avoid possible contamination, and reduction of Pd(II), by minute resin particles sometimes present in the deionized water.

*** See (a) Part C, of EXPERIMENTAL AND RESULTS. The expected concentration calculated from the weight of Pd metal taken is 5.02×10^{-3}M.

immediately and found to have a concentration of 4.75×10^{-3}M. This solution contained a trace amount of chloride-ion carried in the distilled water. This amount is negligible, however, compared to the much larger concentration of chloride-ion previously present. The solution decomposed slowly.

Aliquot volumes of this stock solution (9.99 ml) were diluted to 100 ml with distilled water and immediately used for the mole-ratio study. Solutions for the mole-ratio graph were prepared as before, although it was not necessary to add additional $HClO_4$ (Table 30). The pH of the solutions was 2.20 ± 0.02.

TABLE 30

Data from Mole-Ratio Method for Pd(II)-Complex in Absence of Chloride Ion
(pH 2.20)

Vol*, of Reagent Sol'n X (ml)	R/M** Ratio	Absorbance at 340 mμ	Absorbance at 410 mμ
1.50	0.57	0.275	0.250
2.00	0.76	0.303	0.280
2.50	0.95	0.321	0.266
3.00	1.14	0.330	0.234
3.50	1.33	0.332	0.216
4.00	1.52	0.335	0.196
4.50	1.72	0.340	0.194
5.00	1.91	0.341	0.179
5.50	2.10	0.340	0.171
1.50	5.72	0.349	0.131
2.00	7.62	0.350	0.121
2.50	9.53	0.350	0.117
4.00	15.2	0.351	0.117
9.99	38.1	0.350	0.117
14.99	57.1	0.350	0.117

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* Added from a 10-ml micro-burette or calibrated pipettes

** The concentration of the reagent solution was 9.05×10^{-4} and 9.05×10^{-3} M for R/M ranges of 0.57 - 2.10 and 5.72 - 57.1, respectively.

As previously, the absorption maxima occurred at 340 and 410 mμ. The variation of absorbance at 410 mμ with R/M is shown by C, Fig. 19. The similarity of C to curve B indicates that the exclusion of chloride-ion has only a minor effect. The break occurs in the R/M region 0.7 - 0.9, as before. A plot of the data at 340 mμ (intersection at R/M = 1.0) is not shown because of its very close resemblance to A, Fig. 19.

Potentiometric titrations. The number of protons released per metal ion complexed is a measure of the ligand-to-metal ratio in the metal complex formed. For example, the formation of a 1:1 complex of 2,2'-dimercaptodiethyl sulfide is accompanied by the release of two protons per metal ion:

$LH_2 + M \rightleftharpoons ML + 2H$

(LH_2 is the ligand; charges are ignored.)

Ni(II)-complex. The titrations were carried out at 25.0 ± 0.1°C in the titration vessel already described ((b), Part A). The following quantities were pipetted in the order stated into the titration vessel: exactly 50 ml of 9.975×10^{-3}M $HClO_4$, 10 ml of water, 50 ml of dioxane and, 10 ml (9.99) of reagent solution (7.620×10^{-3} M, dioxane solvent). Prior to the addition of the reagent solution, nitrogen gas presaturated with 50% V/V aqueous dioxane was bubbled through the titration mixture for about ten minutes. The solution was titrated with 0.1152 M NaOH, which was added from a 10-ml micro-burette. An equivalent volume of dioxane for each aliquot of base was added. The titration curve is shown in A, Fig. 20.

The titration was repeated, but now 5.00 ml of 9.780×10^{-3}M Ni(II) perchlorate was substituted for an equivalent volume of water. Curve B, Fig. 20 is the titration curve in the presence of Ni(II). The Ni(II)-complex began to form at about pH2.5 (first traces of red). No precipitation occurred during the titration. The volume of base, ΔV, consumed by the protons released on chelation was evaluated at pH 7.00 as indicated in Fig. 20. The data is summarized in Table 31.

"Co(II)"-complex. 3.84×10^{-4} Moles of reagent were titrated, as above, in the absence and presence of 4.93×10^{-5} moles of cobalt (II) perchlorate. The titrations were repeated with 5.26×10^{-4} moles of reagent and 4.93×10^{-5} moles of cobalt(II) perchlorate. ΔV was evaluated as before. A typical titration curve with Co(II) present is A, Fig. 21. The first trace of colour (yellowish-brown) appeared at about pH 2.4 and precipitation occurred at about pH 2.8. The data is summarized in Table 31.

Pd(II)-complex. 3.79×10^{-4} Moles of reagent were titrated in the absence and presence of 4.75×10^{-5} moles of palladium(II) chloride. The Pd(II) solution used was the stock solution described in the section on reagents, which contained HCl. This was an additional source of mineral acid in the titration of Pd(II). To compensate for this in the titration of the reagent alone, dilute $HClO_4$ equivalent to that contained in the volume (5.00 ml) of Pd(II) solution titrated was added. The acid content of the Pd(II) stock solution was calculated from its pH value (= 2.28).

Precipitation occurred as soon as the Pd(II) solution was added to the titration vessel. The orange precipitate dissolved as the pH increased during the titration to give a greenish-yellow solution. Dissolution was practically complete at ~pH 8.7, although a slight turbidity persisted till the end of the titration. The titration curve is given by B, Fig. 21. The data is compiled in Table 31.

TABLE 31

Data from the Potentiometric Titration of the Metal Ion-Reagent Systems

Metal Ion	Moles of Metal Titrated x 10^5	R/M Ratio	ΔV (ml)	Moles H^+ Released x 10^5	Proton/ Metal Ratio
Ni(II)	4.89	1.56	0.86	9.91	2.03
Co(II)	4.93	7.77	0.78	8.99	1.82
Co(II)	4.93	10.67	0.76	8.76	1.78
Pd(II)	4.75	7.98	0.94	10.83	2.28
			1.37*	15.79	3.32

Two protons are released per Ni(II) ion in the formation of the nickel complex. This is consistent with the stoichiometry, elemental analysis and molecular weight discussed earlier.

It appears that two protons per Pd(II) ion are also released on formation of the palladium complex. This is in keeping with the data on the Pd(II)-complex discussed in previous sections. The high value, 2.28, obtained for the proton-to-metal ratio is not unreasonable because

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* Corresponds to weak inflection between pH 8 - 9 in Curve B, Fig. 21.

the acid content of the Pd(II) stock solution was estimated (see above).

It is interesting that the inflection in B, Fig. 21 coincides with a proton-to-metal ratio of 3.32, corresponding to the release of an additional proton per Pd(II) ion (3.32 - 2.28 = 1.04). The evaluation of ΔV from a differential plot ($\frac{\Delta pH}{\Delta V}$ versus volume) confirmed this.

From the data in Table 31, it appears that two protons are released per Co(II) ion. The titration was done at two R/M ratios, yielding an average value of 1.80 ± 0.02 for the proton-to-metal ratio. Hence, this value appears to be significant. The spectrum of a portion of the final titration mixture had a broad shoulder in the range 380 - 410 mμ and was intermediate in appearance to Spectra C and C' in Fig. 11. See DISCUSSION for the interpretation.

Part C Analytical Applications of 2,2'-Dimercaptodiethyl Sulfide

(a) Determination of Palladium

The data on the formation of the Pd(II), Ni(II) and "Co(II)" complexes suggest that at low pH values, and at suitable concentrations of excess reagent, the quantitative determination of Pd(II) in the presence of Ni(II) and Co(II) should be possible. For example, Fig. 10 shows that in 50% V/V aqueous dioxane, the formation of the Pd(II)-complex is complete at least by pH 1.60, while the Ni(II) and "Co(II)" complexes only begin to form at a pH $\gtrsim$ 2.3. Thus, adjustment of the pH to fall in the range 1.7 - 2.0 would permit the determination of Pd(II) without interference from Ni(II) and Co(II).

The absorbance of the Pd(II)-complex was found to obey Beer's Law by the following experiment. Quantities of 0.06 M HCl and 25.0 ml of reagent solution (1.93×10^{-2}M) in dioxane were pipetted into 50-ml flasks. Appropriate volumes of Pd(II) solution* (1.898×10^{-4}M) were then added accompanied by swirling to avoid precipitate formation due to local excesses. The solutions were diluted to volume with 50% V/V aqueous dioxane at $25.0 \pm 0.1^{\circ}$C. The absorbance was measured at 340 mμ using a solvent blank. Pertinent data is summarized in Table 32.

TABLE 32

Data for Beer's Law Behaviour of Pd(II)-Complex.

Vol.**of 0.06 M HCl (ml)	Vol.***of Pd(II) Sol'n (ml)	Conc. of Pd(II) (M x 10^5)	pH of Final Sol'n	Absorbance (340 mμ)	Absorbance after 15 hrs.
20.0	5.00	1.90	1.68	0.140	0.140
15.0	9.99	3.79	1.66	0.278	0.279
10.0	14.99	5.69	1.67	0.420	0.420
5.0	19.97	7.58	1.68	0.561	0.561

In Fig. 22, the absorbance at 340 mμ is plotted against the Pd(II) concentration. The plot is linear and passes through the origin. Points obtained in other experiments (Table 33) have been included in Fig. 22 to illustrate the reproducibility. The colour is very stable once formed.

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* Unless stated otherwise, the Pd(II) solutions used throughout Part C were prepared in the following way: 5.00 ml of the Pd(II) stock solution (see section on standard solutions) and 1.25 ml of 12 M HCl were diluted to 250.0 ml at $25.0 \pm 0.1^{\circ}$C. The solution was thus 0.06 M in HCl. The Pd(II) concentration diminished slowly on standing a few days.

** 0.06 M $HClO_4$ can also be used

*** calibrated pipettes were used.

TABLE 33

Data from Beer's Law Behaviour of Pd(II)-Complex
(Taken from (c), Part B)

Conc'n of Pd(II) ($M \times 10^5$)	Absorbance (340 mμ)	R/M Mole Ratio	pH of Final Sol'n
4.75	0.350	9	2.24
9.48	0.700	10	2.25
9.85*	0.721	95	----

The above method was applied to a solution of palladium(II) chloride of unknown concentration. The unknown solution was diluted 50-fold. 19.97 ml of this diluted solution was then pipetted with swirling into a 50-ml volumetric flask containing 25.0 ml of reagent solution (1.88×10^{-2} M) and 5.0 ml of 0.06 M $HClO_4$. The contents were mixed, and after dilution to volume (25.0 ± 0.1°C), the absorbance was measured at 340 mμ (solvent blank). Four determinations were done. The concentration of the Pd(II) in the unknown was calculated by reference to the calibration curve. The results are listed in Table 34.

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* This solution was prepared by adding, in order, to a 50-ml volumetric flask the following: 10.0 ml of dioxane; 12.0 ml of 0.06 N $HClO_4$; 15.0 ml of reagent solution (3.13×10^{-2} M); and 12.99 ml of Pd(II) sol'n (3.792×10^{-4} M).

TABLE 34

Application of Spectrophotometric Method to Unknown

Det'n	Conc. of Pd Found in Unknown (mg/ml)
1	1.00
2	0.999
3	1.00
4	1.00
AV.	1.00 ± 0.01

Standardization of the same unknown Pd(II) solution by the established procedure of homogeneous precipitation as the palladium(II) dimethylglyoximate (43) gave 1.01 ± 0.00 mg Pd/ml*. The agreement between the results obtained by the spectrophotometric and gravimetric methods is excellent.

The effect of foreign ions, particularly Ni(II), Co(II) and Fe(III), was investigated in the following experiment. The quantities** below were pipetted, in order, into a 50-ml volumetric flask: (6-0.24 x)

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* These results were obtained through private communication with O. E. Hileman, Jr., McMaster University.

** The final solution is 0.03 M in acid. Since the Pd(II) solution is 0.06 M in HCl and the $HClO_4$ solution is 0.25 M, (6-0.24 x) ml of 0.25 M $HClO_4$ need to be added (where x is the ml of Pd(II) solution added). If y ml of foreign metal-ion solution is added, 25-(6-0.24x + x + y) = (19-0.76x - y) ml of water need to be added. For example, the following applies to the first solution in Table 35.

(cont'd)

ml of 0.25 N $HClO_4$; (19 - 0.76 x - y) ml of water; y ml of the solution(s)* of foreign metal ion; 25.0 ml of reagent solution (10^{-2}M, dioxane solvent); and x ml of palladium(II)chloride solution (1.898×10^{-4}M), added with swirling. This combination of components gave a final solvent composition of 50% V/V aqueous dioxane and a pH of 1.67 ± 0.03. After shaking, the solution was diluted to volume** at 25.0 ± 0.1°C with 50% V/V aqueous dioxane, and the absorbance measured at 340 mμ (solvent blank). A summary of the data is in Table 35. The palladium found was calculated by reference to Fig. 22.

** (cont'd)

Volume of Component (ml)		Component
x	(14.99)	Pd(II) solution
6-0.24x	(2.4)	0.25 M $HClO_4$
y	(2.00)	Ni(II) solution
19-0.76x - y	(5.6)	water
25.0	(25.0)	

* Ni(II) perchlorate, 9.78×10^{-3} M; Co(II)perchlorate, 9.85×10^{-3} M; Fe(III)chloride, 5.05×10^{-3} M.

** The volumetric flasks were not calibrated, but should be for greater accuracy and precision.

TABLE 35

Effect of Foreign Ions in Pd(II) Determination

Pd(II) Taken* ug/ml	Pd(II) Found ug/ml	Percent Deviation %	Foreign Ion(s) Present	Conc'n of Foreign Ions ug/ml	Foreign Ion to Pd(II) Molar Ratio	Reagent to Pd(II) Molar Ratio
6.05	6.06	+0.17	Ni(II)	23.0	6.9	87
6.05	6.01	-0.66	"	23.0	6.9	40
8.05	8.22	+2.11	"	34.5	7.8	30
3.94	3.96	+0.51	"	57.5	26.4	135
6.05	6.05	0	Co(II)	23.2	6.9	87
5.91	6.05	+2.36	"	23.2	7.1	90
3.94	4.11	+4.31	"	58.0	26.6	135
6.05	6.05	0	Fe(III)	16.9	5.3	87
3.94	3.89	-1.27	"	67.6	32.8	135
3.93	3.96	+0.76	Ni(II)	11.5	5.3	104
			Co(II)	11.6	5.3	
3.93	3.93	0	Ni(II)	11.5	5.3	104
			Fe(III)	11.3	5.5	
3.93	4.13	+5.09	Co(II)	11.6	5.3	104
			Fe(III)	11.3	5.5	
3.94	4.17	+5.84	Co(II)	11.6	5.3	122
			Fe(III)	11.3	5.5	
3.93	4.13	+5.09	Ni(II)	11.5	5.3	104
			Co(II)	11.6	5.3	
			Fe(III)	11.3	5.5	
5.91	6.31	+6.77	Ni(II)	23.0	7.0	90
			Co(II)	23.2	7.1	
			Fe(III)	16.9	5.5	
6.05	6.49	+7.27	Ni(II)	23.0	6.9	87
			Co(II)	23.2	6.9	
			Fe(III)	16.9	5.3	

* Calculated from volume of palladium(II) chloride solution taken.

The data in Table 35 illustrates that Pd(II) may be determined at about pH 1.7 (or in a 0.03 M acid solution*) in 50% V/V aqueous dioxane in the presence of substantial amounts of Ni(II), Co(II) or Fe(III). When only one foreign ion is present, the largest error occurs when large amounts of Co(II) are present. The determination can be made when the foreign ions are present in any combination, although errors of about 5-7% occur when Co(II) and Fe(III) are present together. For all solutions, except those containing Co(II), the absorbance remained constant overnight. Solutions containing Co(II), in the absence of Fe(III), were stable for four to five hours after which, the absorbance increased slowly. In the presence of Fe(III), solutions containing Co(II) become slightly turbid (eventually a precipitate forms) shortly after their preparation. The absorbance of such solutions, therefore, must be measured immediately after preparation. The possible effect of other ions is dealt with in the DISCUSSION.

The data in (c), Part B, on the extraction of the Pd(II) complex suggests an alternative way for determining Pd(II) in the presence of Ni(II) and Co(II). The method would involve the extraction of the Pd(II)-complex at low pH into benzyl alcohol, followed by measurement of its absorbance. This method was tried at pH 2 and a calibration curve was constructed. Beer's Law was obeyed, but the data lacked precision. This was traced to impurities in the benzyl alcohol which are difficult to remove and which absorb at 340 mμ (λ_{max}). This method was abandoned

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* Total HCl or HCl plus $HClO_4$ content

for the quantitative determination of Pd(II) but as shown below, benzyl alcohol is useful for removing Pd(II) as the 2,2'-dimercaptodiethyl sulfide complex from a solution in which Ni(II) is to be determined quantitatively.

(b) Determination of Nickel

The lower pH limit for the quantitative extraction of the Ni(II)-complex with 1,2-dichloroethane is about pH 5.6 (B, Fig. 15; (c), Part B). Also, at pH $\geq$ 9.5, repeated washings of the extracted aqueous phase with pure solvent are necessary to effect complete extraction ((c), Part B; also reference (15)). Thus, the pH range 6-9 would be suitable for quantitative extraction. A buffer solution of about pH 8 (0.02 M in aqueous ammonia and 0.15 M in NH_4Cl) was used in the work that follows.

The extractions were carried out in 100-ml separatory funnels with glass-wool plugs inserted in the stems to trap water droplets during drainage of the organic phase. Quantities (Table 36) of nickel (II) perchlorate solution (9.77×10^{-4}M)* were pipetted into separatory funnels containing 10 ml of buffer solution and sufficient water to bring the aqueous phase to 50 ml. The Ni(II) was then extracted with three 10-ml portions of a 1, 2-dichloroethane solution of the reagent (2.53×10^{-2}M). Each portion was shaken with the aqueous phase for 1 - 2 minutes, and then drained through the glass-wool plug. Next, the residual aqueous phase was washed with one 10-ml portion of pure solvent.

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* Prepared by dilution of the stock solution (see section on standard solutions)

The organic phases were collected in a 50-ml volumetric flask and diluted to the mark at 25.0 ± 0.1°C. The absorbance was then measured at 512 mμ ((c), Part B) using pure solvent as a blank. The pH of the residual phase, which varied slightly with the amount of Ni(II) extracted, was 7.6 ± 0.2.

Table 36 summarizes the data, and Fig. 23 shows the variation in absorbance at 512 mμ with Ni(II) concentration. Beer's Law is obeyed at least over an eight fold concentration range. The absorbance was re-measured after the solutions had been kept in a bath at 25.0 ± 0.1°C for 40 hours. The colour is very stable, although a slight decrease in absorbance occurred in the two most concentrated solutions.

TABLE 36

Data for Beer's Law Behaviour of Ni(II)-complex

Vol. of Ni(II) Sol'n (ml)	Conc'n of Ni(II) ($M \times 10^4$)	Absorbance at 512 mμ	Absorbance After 40 hrs.
5.00	0.977	0.111	0.111
9.99	1.95	0.221	0.224
19.97	3.90	0.441	0.441
24.99	4.88	0.553	0.558
29.96	5.86	0.662	0.650
39.94	7.80	0.879	0.863

Because the Pd(II)-complex is extracted into 1,2-dichloroethane ((c), Part B), it would extract with the Ni(II)-complex and contribute to the absorbance at 512 mμ. Since the Pd(II)-complex, but not the

Ni(II)-complex, is extracted into benzyl alcohol at about pH 2.0 ((c), Part B), a separation of Pd(II) from Ni(II) ought to be possible. This separation was used in the determination of Ni(II). Fe(III) was added to some solutions as well, but it was not expected to interfere (15).

The volumes of nickel(II)perchlorate (9.77×10^{-4} M), palladium (II)chloride (1.898×10^{-4} M), iron(III) chloride (5.05×10^{-3} M), and $HClO_4$ (0.25 M) listed in table 37 were pipetted into a 100-ml separatory funnel. The Pd(II) was extracted with two 10-ml portions (shaking for 1 - 2 minutes) of a benzyl alcohol solution of the reagent (10^{-2} M). The aqueous phase was then washed with two 5-ml portions of pure benzyl alcohol, followed by a 10-ml portion of 1,2-dichloroethane to remove any residual benzyl alcohol. Next, the stem of the funnel was cleaned and dried with tissue, and a glass-wool plug inserted. Aqueous ammonia (1:1) was added to precipitate Fe(III) as the hydroxide and, with the pH at about 8, 10 ml of the aqueous NH_3/NH_4Cl buffer solution was added. The nickel was extracted as before, and the absorbance measured at 512 mμ. The pH of the residual aqueous phase was 8.4 ± 0.3.

TABLE 37

Solution Components for Ni(II) Determination

Vol. of Ni(II) Sol'n (ml)	Vol. of Pd(II) Sol'n (ml)	Vol. of Fe(III) Sol'n (ml)	Vol. of 0.25 M $HClO_4$ (ml)
5.00	24.99	5.00	5.0
19.97	19.97	----	4.0
29.96	5.00	----	5.0

The extraction of Pd(II) and of Ni(II) are without complications, although the presence of ferric hydroxide in the Ni(II) extraction requires a little additional care during the separation of the two phases. The data (Table 38) illustrates the potential of the determination. The nickel found was calculated by reference to the calibration curve, Fig. 23.

TABLE 38

Effect of Foreign Ions in Ni(II) Determination

Total Ni(II) Taken (mg)	Total Ni(II) Found (mg)	% Deviation	Pd(II) Present (mg)	Fe(III) Present (mg)
0.29	0.29	0	0.50	1.41
1.15	1.14	-0.87	0.40	----
1.72	1.71	-0.58	0.10	----

Co(II) is known to interfere in the Ni(II)-determination (15). In the present work, an attempt was made to salt out quantitatively the "Co(II)" species in the aqueous phase, with the idea of back-extracting with water whatever amount of the "Co(II)"-complex extracted with the Ni(II)-complex into the organic phase. This procedure was only partially successful. As a result, the Co(II) must be removed from the system before the extraction of the Ni(II)-complex, perhaps by the method already suggested (15). The possible effect of other ions is considered in the DISCUSSION.

DISCUSSION

Part A 2,2'-Dimercaptodiethyl Sulfide

(a) Stability of 2,2'-Dimercaptodiethyl Sulfide

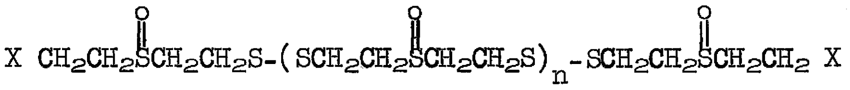
Although 2,2'-dimercaptodiethyl sulfide is considerably more stable than other analytical reagents containing the mercapto group, it does not possess, in either pure or solution form, the unusually high stability attributed to it by Segall et al (15). The pure reagent does keep well when stored under dry nitrogen in a refrigerator, but in the presence of moisture forms a white deposit after several weeks. Solutions of it in organic solvents are only moderately stable, but the rate of decomposition is such that in most cases, these solutions can be kept for periods of up to two weeks.

In 50% V/V aqueous dioxane, the deterioration of solutions is arrested if air is excluded (Fig. 5). Air-oxidation results in the formation of a product that contains disulfide linkages, as characterized by the broad absorption maximum at about 250 mμ (C, Fig. 2; D, Fig. 3). Because of the presence of the terminal mercapto groups in the reagent, a polymeric oxidation product is likely, although at low concentration of the reagent, formation of some cyclic disulfide (seven-membered ring) would also be expected. If the product formed is a polymer, its molecular weight is likely low (see below), since no precipitate formed at any pH value.

The stability of solutions of the reagent in 50% V/V aqueous dioxane is pH dependent. Oxidation in neutral solution is very slow, with a half-life of about 80 hours (Table 3). The rate of oxidation increases considerably as the pH is increased, and the half-life is reduced to one hour at about pH 10. Surprisingly, the half-life is considerably larger in very basic solution--approximately 15 hours at pH 13.4. The pH dependence of the rate of oxidation of mercaptans is complex and not well understood, although an inverse relationship with hydrogen ion concentration appears established (27).

In summary, 2,2'-dimercaptodiethyl sulfide may be used in 50% V/V aqueous dioxane in neutral solution (and presumably in acid solution) without special precautions against air-oxidation. Even in very basic solution, the process of oxidation is sufficiently slow to allow use of solutions for a few hours without application of precautionary measures. In contrast, the rate of deterioration of solutions at about pH 10 is fast, and air must be excluded as described in the EXPERIMENTAL AND RESULTS.

The product of mild oxidation of a mercaptan is usually the corresponding disulfide, while vigorous conditions convert the disulfide into more highly oxidized products leading finally to the sulfonic acid (27). Oxidation of 2,2'-dimercaptodiethyl sulfide with 30% hydrogen peroxide yields a white insoluble substance, the infrared data for which (Table 4) shows no evidence of free mercapto, sulfonic acid, or sulfone groups, but which identifies the sulfoxide and disulfide groupings. The broad absorption in the 250 mμ region in the ultraviolet is further evidence for the disulfide linkage. On the basis of the above spectral data, a polymeric structure such as proposed below is reasonable:



$$X\ CH_2CH_2\overset{\overset{O}{\|}}{S}CH_2CH_2S\text{-}(SCH_2CH_2\overset{\overset{O}{\|}}{S}CH_2CH_2S)_n\text{-}SCH_2CH_2\overset{\overset{O}{\|}}{S}CH_2CH_2\ X$$

where X could be $-SO_3H$, but in too low a concentration to be detected by infrared analysis. It is interesting that other workers could not isolate 2,2'-dimercaptodiethyl sulfone and sulfoxide because of rapid conversion to a white amorphous polymeric material(19).

(b) Acid-Dissociation Constants

2,2'-Dimercaptodiethyl sulfide is a weak acid and its proton dissociation constants are separated by one log unit. The values $pK_{a_1} = 10.32$ and $pK_{a_2} = 11.43$ conform to those reported for related compounds (7). As explained in the HISTORICAL INTRODUCTION, a knowledge of the acid dissociation constants of an analytical reagent is very useful, particularly in the interpretation of experimental data.

Part B Metal Complexes of 2,2'Dimercaptodiethyl Sulfide

(a) Reactivity of 2,2'-Dimercaptodiethyl Sulfide Towards Metal Ions

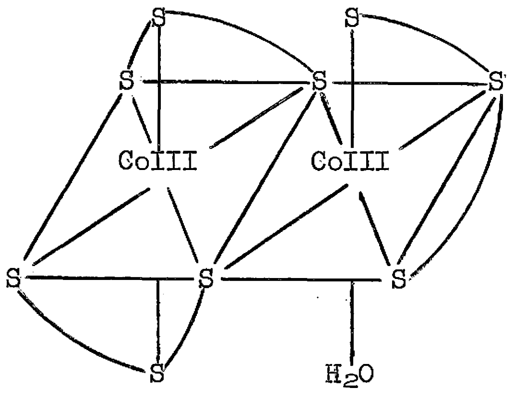
2,2'-Dimercaptodiethyl sulfide reacts with metal ions (Table 9) as expected for a ligand containing easily polarizable donor groups. Hence, there is no reaction with class (a) acceptors (see GENERAL INTRODUCTION) such as Mg(II), Sr(II), Al(III), Th(IV), and the rare-earth metal ions. Reaction occurs only at higher pH values with borderline acceptors (e.g., Mn(II), Cr(III)), and at low pH values with class

(b) acceptors (e.g., Pd(II), Ag(I), Cd(II), Hg(II)). Ions with a d^{10} configuration, Ag(I), Cd(II), Hg(II) and Zn(II), form white insoluble complexes. The complex derived from Cu(II) when the reagent is in excess is likely a Cu(I) derivative because it forms in strongly acid solution, is colourless like the other d^{10} complexes, and oxidation of mercaptans by Cu(II) is well known (e.g., 62). The ligand can be either the disulfide or unoxidized dithiol. The mauve complex that forms when Cu(II) is in excess may be a Cu(II) derivative of the disulfide. Iron(II) and (III) react similarly with the reagent to give a green complex. Presumably, this is an Fe(II) complex since Fe(III) is known to oxidize mercaptans to their respective disulfides (e.g., 6, 27).

In summary, 2,2'-dimercaptodiethyl sulfide forms metal complexes with numerous metal ions, and possesses no apparent specificity.

(b) Solid Metal Complexes

Co(III)-complex. The assigned formula, $(\mathrm{CoIII})_2\mathrm{L}_3\cdot\mathrm{H_2O}$ (Table 10), fits the analytical data well. The complex is diamagnetic, as are essentially all Co(III)-complexes in an octahedral field (e.g., 63, 64). The following structure, involving bridging S atoms, is suggested. Several other geometric isomers are possible, some of which are less important.



Ni(II)-complex. The analytical data (Table 10) and molecular weight (Table 15) confirm the formula $(NiL)_2$ suggested by Harley-Mason (19). In addition, the diamagnetism of the complex (Table 17) is consistent with the square-planar configuration* around the Ni(II) ion assigned by this worker (see HISTORICAL INTRODUCTION). Structures such as I shown on page 6 of this thesis have been established for related compounds (3).

Pd(II)-complex. This complex appears to be identical to the Ni(II)-complex. The analytical data, molecular weight and diamagnetism suggest a dimeric species with the Pd(II) in a square planar environment (e.g., structure I, page 6). Similar dimeric palladium(II)-complexes have been found with related ligands such as methyl-2,2'-dimercaptodiethylamine (3, 10).

"Co(II)"-complex. The interpretation of the data on the solid "Co(II)"-complex (EXPERIMENTAL AND RESULTS, (b), Part B) will be considered later in connection with the solution data found in (c), Part B.

Before completing this section, it is worthwhile commenting on the molecular-weight determinations made with the Mechrolab Osmometer, a relatively new instrument which has not yet been fully tested. Firstly, benzil is commonly used as the calibration standard. Solutions of benzil in 1,2-dichloroethane are sensitive to light as evidenced by the increasing molarity (i.e., increasing number of particles in solution) with time

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* Magnetic measurements do not distinguish between square planar, square pyramid and trigonal bipyramid configurations, although the latter two configurations are less common.

(Fig. 7). Thus, standard solutions of benzil should be freshly prepared or protected from light if they are to be used at a later time. No attempt was made to identify the products of the photolytic reaction.

Secondly, it is important to emphasize that the characteristics of the osmometer change with time. This is illustrated by the two calibration curves in Fig. 8. Thus, the determination should be made as soon as possible after completion of the calibration and, if the work extends over a period of time, frequent calibration checks should be made. Contamination of the sample thermistor bead may explain this phenomenon.

Lastly, it is significant that the osmometer can by used to determine approximate molecular weights of sparingly soluble complexes by the technique used in this work. The data is certainly adequate to distinguish between monomeric and dimeric species.

(c) Metal Complexes in Solution

Ni(II)-complex. Complex formation in solution (C, Fig. 10) is complete at about pH 4. Correspondingly, the extraction of Ni(II) with 2,2'-dimercaptodiethyl sulfide into 1,2-dichloroethane (B, Fig. 15) and into benzyl alcohol (A, Fig. 15) is quantitative at about pH 5.5 and 5, respectively. Thus, both formation and extraction of the Ni(II)-complex are complete at a much lower pH value than previously reported (about pH 10 (15), HISTORICAL INTRODUCTION).

The stoichiometry at pH 6.8 is 1:1 (50% V/V aqueous dioxane) and only one species exists in solution at all R/M values (0.25 - 4) investigated (A, Fig. 16; Table 26). The fact that two protons per Ni(II) ion are released in the potentiometric titration (Fig. 20, Table 31) is consistent with this ligand-metal-ratio. Since the Ni(II)-complex exists as a dimeric species in 1,2-dichloroethane (molecular-weight determination), it probably is dimeric in other solvents such as 50% V/V aqueous dioxane. Also, it very likely is a dimer in the solid. In support of this, the spectrum of the solid complex dissolved in 1,2-dichloroethane is identical to that of the species extracted into 1,2-dichloroethane from an aqueous phase (e.g., A, Fig. 9). Furthermore, the Ni(II)-complex is 1:1 in the solid as well as in solution.

The visible spectra of solutions (yellow-orange) at $pH \geq 10$ with R/M ratios $\gg 2$ indicate the formation of another complex (C, Fig. 9; Table 19). At pH 12.1, the red 1:1 species formed up to R/M ratios of 2.25 (B, Fig. 16) and the yellow-orange one at $R/M > 2.25$ (Table 27). This dependence on the pH and R/M ratio is what is expected if another ligand molecule were to add. Thus, the new species probably has a ligand-to-metal ratio > 1. The addition of another ligand molecule was not detected in the potentiometric titration. However, it might be obscured since it would occur in the pH region where the excess reagent is being titrated (Figs. 6, 20). The yellow-orange complex still extracts as the red species into the organic phase, although repeated washing with pure solvent is necessary ((15); EXPERIMENTAL AND RESULTS, (c), Part B).

The formation of the yellow-orange complex may account for the reported 2:1 stoichiometry (15). If the previous work had been done in alkaline solution (the pH is not reported), then the Job method, which was used for establishing the stoichiometry, would yield erroneous results, since more than one species would have been present in solution.

The observation that solutions initially yellow-orange became red on standing overnight must be the result of lowering of the R/M ratio through oxidation of the reagent. Appreciable oxidation of the reagent would be expected in the pH region (9.4 - 12.4) for which this phenomenon was observed, since the half-lives at pH 9.8 and 13.4 are about one and 15 hours (Table 3), respectively. Thus, as the reagent is oxidized, the yellow-orange complex would convert to the red 1:1 complex.

Pd(II)-complex. Formation of the Pd(II)-complex appears to be complete at about pH 1.5 (A, Fig. 10). Extraction into benzyl alcohol is also quantitative at this pH value. The stoichiometry of the complex in solution is 1:1 (A, Fig. 19) and, like the Ni(II)-complex, exists as a dimer in solution (molecular-weight determination) and quite likely in the solid. The visible spectrum depends on the pH value (Fig. 14, Table 24) and the R/M ratio (Fig. 18, Table 29). The 1:1 species absorbs at 340 mμ and exists in the pH region 1 - 7 (B, Fig. 14, Table 24). At pH$<$1.0 (A, Fig. 14), there is probably a breakdown of the 1:1 complex because the competition of protons for the reagent becomes too great. The colour of the solution is deep yellow, which is characteristic of the Pd(II) species with a ligand-to-metal ratio of less than 1:1 (see below). At the higher pH values (e.g. ~ 10), the spectrum changes substantially (C, Fig. 14) and two possibilities exist for its explanation. At high pH values, the addition of hydroxyl ion (equivalent to acid-dissociation of aquated water) to the Pd(II)-complex may occur in the same fashion as is observed with Pd(II)-EDTA complexes (65). The other possibility is the addition of another reagent molecule to the complex.

The potentiometric titration shows that initially, two protons are released per Pd(II) ion (Table 31) and is therefore consistent with the 1:1 stoichiometry in acid solution. The inflection in the titration curve at about pH 9 (B, Fig. 21) corresponds to the release of one additional proton per Pd(II) ion. At this point in the titration, the precipitate that had formed earlier redissolved. Furthermore, the change in the spectrum (C, Fig. 14) is noticeable at this pH value. Hence, either one hydroxyl group is added per Pd(II) ion to give $[Pd_2L_2(OH)_2]^=$, or one ligand molecule adds to form $[Pd_2L_3]^=$. Since Pd(II) is a class (b) acceptor, the addition of another reagent molecule seems the more probable. Several examples of six-coordinate Pd(II)-complexes can be found (e.g., 64, 66).

The dependence of the spectrum of the Pd(II)-complex on the R/M ratio (Fig. 18) may be understood in terms of the formation of a complex species that has a stoichiometry$<$1:1. This species is characterized by an absorbance maximum at 410 mμ (Fig. 18) and a deep yellow colour. It is quite insoluble in 50% V/V aqueous dioxane and may be readily removed by filtration, suggesting it to be a polymeric substance. On the other hand, the dimeric 1:1 complex (340 mμ) is more soluble and remains in the filtrate. Even in the absence of chloride ion, both species again form and have the same dependence on the R/M ratio (Fig. 19). Thus, chloride ion does not play a major role in the formation and structure of the species absorbing at 410 mμ.

On the basis of this evidence, reactions of the type below are plausible in acid solution at $R/M < 1$:

$$PdCl_4^{=} + LH_2 = 2H^+ + PdClL^- + 3\,Cl^-$$

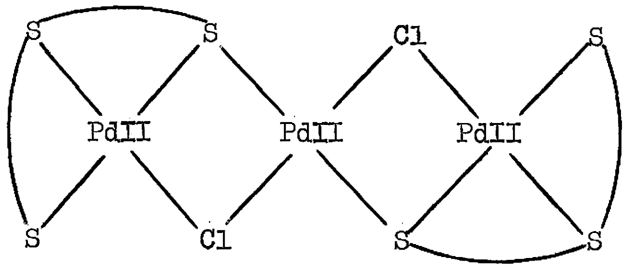
$$2PdClL^- + PdCl_4^{=} = Pd_3L_2Cl_2 + 4Cl^-\text{, etc.}$$

Also, $nPdClL^- + PdCl_4^{=} = [Pd(PdClL)n(Cl)_{4-n}]^{-2} + nCl^-$

where $n = 1$ --- 4.

As the R/M ratio is increased above one, species like $Pd_3L_2Cl_2$ are converted to the 1:1 dimeric species (see changes in absorbance at 340 and 410 mμ in Fig. 19). Similar reactions may be written by substituting water for chloride, when chloride ion is absent.

Busch (3) has reported bridged Pd(II)-complexes of the type suggested above. A logical structure for $Pd_3L_2Cl_2$ would be:



A plausible structure for $[Pd(PdClL)_n(Cl)_{4-n}]^{-2}$ (say, for n = 4) would be to have four square-planar units (each containing one ligand molecule and one chloride) share one of its sulfur atoms with a centrally located Pd(II) ion to form a fifth square planar unit in the centre.

"Co(II)"-Complex. The cobalt-2,2'-dimercaptodiethyl sulfide system is much more complicated compared to the metal-complex systems discussed above, and exact interpretation is difficult. It can perhaps be better understood in terms of several facts established for cobalt complexes. Firstly, in aqueous media containing complexing ligands such as ammonia (64) and mercaptans (67, 68), Co(III) is stabilized and oxidation of Co(II) to Co(III) occurs readily. Secondly, peroxy-bridged binuclear complexes are often intermediates in the oxidation of Co(II) (e.g., 69, 70). For example, in the oxidation of ammoniacal cobalt(II) nitrate solution by atmospheric oxygen, the intermediate is $[(NH_3)_5\ Co^{III}-O-]_2\ (NO_3)_4\cdot 2H_2O$ (69). In acid or weakly basic solution, such peroxy complexes undergo rapid hydrolysis to aquo Co(III)-complexes (e.g., 70). The overall reaction is

$$4CoL^{+2} + O_2 + 2H_2O \rightarrow 4\ CoL^{+3} + 4OH^-$$

where L is an uncharged ligand (68).

Lastly, in systems where the complexing agent is also oxidized readily, such as mercaptans (27, 68), a competing reaction occurs:

$$4RSH + O_2 \rightarrow 2\ RSSR + 2H_2O$$

The relative extent of this oxidation depends on such conditions as pH and concentration. Thus, in the Co(II)-cysteine system (68), the oxidation of the reagent predominates at low pH (~ 5) and low absolute concentrations of Co(II) and cysteine, the Co(II) probably serving as a catalyst.

In view of this discussion, it is likely that oxidation occurs in the Co(II)-2,2'-dimercaptodiethyl sulfide system. The effect of using dioxane that had been stored in air substantiates this assumption (Table 22, Fig. 12).

Curve B, Fig. 10, shows that the formation of the Co(II)-2,2'-dimercaptodiethyl sulfide complex (before the occurrence of significant oxidation) is complete at about pH 4. The spectrum obtained from these solutions is represented by C, Fig. 11, with shoulders at about 325 and 385 mμ. Note that on standing, the spectrum gradually changes (yellow-brown solutions; C', C", Fig. 11). The isosbestic point at about 378 mμ indicates the existence of two species in solution.

The spectrum of the freshly prepared Co(III)-complex, dissolved in chloroform, displays shoulders at 430 and 495 mμ (brown solution; B, Fig. 13). After the solution has stood for three days, the spectrum changes to A. Spectrum A is similar to spectrum C, which was obtained by dissolving the "Co(II)"-complex in chloroform. Note the similarity of spectra A and C, Fig. 13, to spectra A and C", Fig. 11. This data suggests quite strongly that a new complex is formed, regardless of whether the Co(II) or Co(III) complex is present initially. The absorbance of this new species is considerably more intense in the 400 mμ region than either the Co(II) or Co(III) complex. A reasonable guess on the nature of this species is that it is binuclear and contains both Co(II) and Co(III). Binuclear complexes that contain central ions in different oxidation states are reported to have intense charge-transfer absorption bands in the ultraviolet-visible region (71).

The following process is suggested for the formation of the complex that absorbs strongly in the 400 mμ region. Initially, a true Co(II)-complex is formed. The potentiometric titration suggests a 1:1 stoichiometry because two protons (actually, 1.8) are released per Co(II) ion(Table 31). In analogy with the Ni(II)- and Pd(II)-complexes, this species could be dimeric. Oxidation of the Co(II)-complex then occurs. Since molecular oxygen (or peroxides when "stored" dioxane is used) is the oxidant, a peroxy-bridged species probably forms. This would then hydrolyze rapidly in acid and weakly basic solutions, and much more slowly in strongly basic solutions. Interestingly, the formation of the new species is slowest at pH 11.7 (sol'n 10, Table 22), with no development of the maximum in the 400 mμ region. Since Co(III) has a strong affinity for ammonia (64, 69), it is not surprising that the new species forms most rapidly in ammoniacal solution (sol'n 9, Table 22; B, Fig. 11).

After hydrolysis to an aquo Co(III) species, combination with unoxidized Co(II)-complex may occur. Since the supply of oxygen is limited in the systems studied, binuclear species containing only Co(III) would not be expected to form in high concentration.

The pH dependence of λ_{max} of the final product (Table 22) may be due to its hydrolysis,* or to the addition of a further ligand to it as the pH increases.

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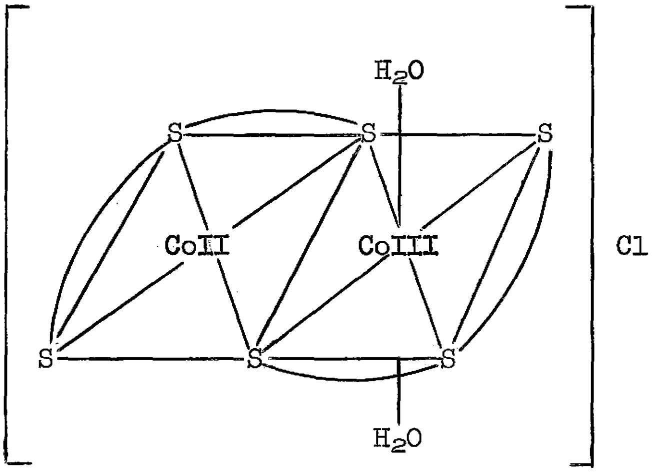
* Aquocobalt(III) species are acidic in nature (e.g. 69, 70)

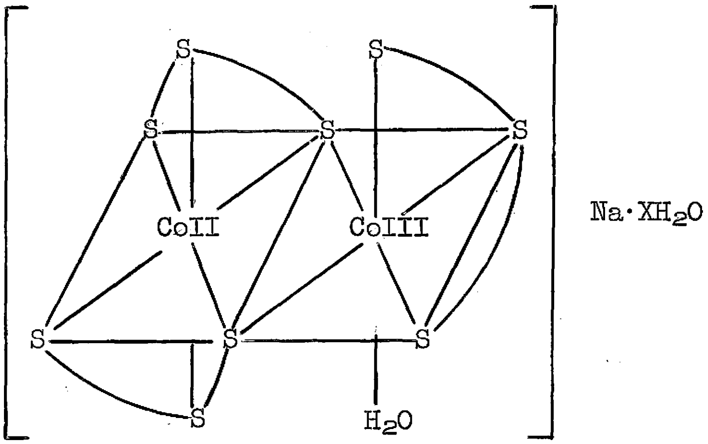
The spectrum of the titration mixture showed that some formation of the new complex occurred during the potentiometric titration. In this may lie the explanation of the 1.8 protons (rather than 2.0) released per Co(II) ion, since the oxidation process consumes protons.

The molar- ratio data (Table 28, Fig. 17) suggests a 2:1 stoichiometry. However, this may be fortuitous since the experiment was done at relatively low pH (5.8) and a low concentration of the reagent. At pH 5.8, cobalt-catalyzed oxidation of the reagent may predominate over oxidation of the Co(II)-complex, just as in the cobalt-cysteine system (68). It is interesting that at pH 5.8, cysteine, like 2,2'-dimercaptodiethyl sulfide ((a), Part A), undergoes very slow oxidation. In the presence of Co(II), however, the oxidation to cystine is extremely fast -- especially in dilute solutions. Co(II) is thought to catalyze the oxidation. It is reasonably to suppose 2,2'-dimercaptodiethyl sulfide to behave similarly. If catalytic oxidation of 2,2'-dimercaptodiethyl sulfide does occur, the R/M ratio plotted in Fig. 17 would be too large and the 2:1 stoichiometry would be erroneous.

The presence of both chlorine and sodium in the solid "Co(II)"-complex (Table 10) suggests that this complex is a mixture of charged species. This is consistent with the appreciable solubility of the complex in water, and with the fact thatno simple formula fits the analytical data. Presumably, the isolated "Co(II)"-complex is a mixture of species such as $(Co^{II}L)_2$, $Co_2^{III}L_3 \cdot H_2O$, $[Co^{II}Co^{III}L_3 \cdot H_2O]Na \cdot XH_2O$ and $[Co^{II}Co^{III}L_2 \cdot 2H_2O]Cl$. The experimental molecular weight is 620 ± 70 and does not distinguish between the possibilities.

The paramagnetism of the "Co(II)"-complex (Table 17) could result from the presence of unoxidized Co(II)-complex and/or complexes containing both Co(II) and Co(III) as suggested above. The proposal of binuclear complexes with central ions having different oxidation states is consistent with the interpretation of the solution behaviour just discussed. The paramagnetism corresponds roughly to one unpaired electron per molecular unit, based on structures such as shown below.





Part C Analytical Applications of 2,2'-Dimercaptodiethyl Sulfide

(a) Determination of Palladium

Although only a small amount of data was obtained, the spectrophotometric determination of Pd(II) with 2,2'-dimercaptodiethyl sulfide appears to be accurate and precise, and is considerably less laborious than the gravimetric procedure involving homogeneous precipitation as the Pd(II)-dimethylglyoximate (Table 34).

It also has definite advantages over existing spectrophotometric methods (4) for palladium. Unlike most other reagents for palladium, 2,2'-dimercaptodiethyl sulfide does not absorb in the visible region. Also, Fe(III) and Ni(II), which are common interferences (see HISTORICAL INTRODUCTION), do not interfere even when present in relatively large amounts (Table 35). Furthermore, Co(II) which also commonly interferes, may be present, at least up to a Co/Pd ratio of seven. It is only when the molar ratio is large (e.g., Co/Pd = 27) that the error becomes appreciable (4.3%) -- but, this might be fortuitous since only one result was obtained. However, since the amount of palladium taken for the determination is about 4-6 ppm, this error even if real appears tolerable. Except when Co(II) and Fe(III) occur together, only small errors are produced when combinations of Ni(II), Co(II) and Fe(III) are present with Pd(II). The simultaneous presence of Co(II) and Fe(III) leads to positive errors of about 5 to 7 percent. Larger errors are incurred if the absorbance measurements are not made promptly after preparation of the solution. When Co(II) is present in the absence of Fe(III), the solutions are stable (i.e., the absorbance is constant) for at least three to four hours. Thus, the interference due to (Co(II) is apparently catalyzed by Fe(III), and is dependent on time. It is likely due to oxidation of Co(II) and the subsequent formation of absorbing cobalt complexes of the type discussed above (Part B).

The fact that the determination of Pd(II) with 2,2'-dimercaptodiethyl sulfide is comparatively free from interferences due to Ni(II), Co(II) and Fe(III) is a matter of the relative equilibrium stabilities (i.e., the relative magnitudes of the equilibrium constants) of the metal complexes in solution. Since ligands with S-donor atoms react more strongly with class (b) metals such as Pd(II) than with metals belonging to class (a) or to the borderline region (e.g., Fe(III), Co(II), Ni(II)), a difference in equilibrium stabilities is expected. This is reflected by the fact that the Pd(II)-complex forms quantitatively at an appreciably lower pH value than the other metal complexes (Fig. 10), thus allowing the determination of Pd(II) without interference.

An examination of the data in Table 9 permits speculation on the effect of other foreign ions. Since Cr(III), Mn(II), Fe(II), Zn(II), Pb(II) and Tl(I) do not react with 2,2'-dimercaptodiethyl sulfide at pH 2, they should not interfere in the Pd(II) determination -- provided that the respective aquated ions do not absorb significantly at 340 mμ. Ions of definite class (a) behaviour such as the alkali metals, alkaline earths, Al(III), the lanthanides and actinides do not react with the reagent and as a result, should not interfere.

The metals that normally interfere most seriously in palladium determinations are typically class (b) such as Pt, Ir, Au, Rh, Ag and Hg ((4), the oxidation states are not specified, but see GENERAL INTRODUCTION). The reaction of Pt(IV) and Rh(III) with 2,2'-dimercaptodiethyl sulfide is slow at pH 2 and room temperature and may permit the Pd(II) determination in their presence. Ag(I) and Hg(II), which are d^{10} ions, form insoluble white compounds in strongly acid solution. Possibly, these precipitates can be removed by filtration prior to the dilution to volume with 50% V/V aqueous dioxane. Other d^{10} ions (class (b)) such as Cu(I) (from the reduction of Cu(II) by the reagent) and Cd(II) behave similarly to yield white precipitates in acid solution. Thus, interference from class (b) ions can be avoided, perhaps, by a combination of favourable rate and solubility effects.

The potential of 2,2'-dimercaptodiethyl sulfide as a reagent for the spectrophotometric determination of palladium cannot be fully realized until the above possibilities have been investigated. It appears, however, that the criterion of a good reagent for palladium -- little interference from first-row transition and noble metals (4) -- may be fulfilled.

(b) Determination of Nickel

The investigation of the solution properties of the Ni(II)-complex resulted in an analytical procedure somewhat improved over that reported by Segall et al (15). For example, the extraction of Ni(II) is best carried out in the pH range 6 - 9, because this circumvents the formation of the yellow-orange species that is soluble in the aqueous phase and rather difficult to extract. Also, the interference from Pd(II) is easily overcome by extracting the ion (even in large amount) from strongly acid solution into benzyl alcohol with 2,2'-dimercaptodiethyl sulfide. This extraction is done prior to the nickel determination. The use of one reagent for both the removal of Pd(II) and for the Ni(II) determination is convenient.

Segall et al. (15) did not investigate the effect of class (b) metal ions on the nickel determination. Since these ions react strongly with the reagent (Table 9), they would be expected to interfere. However, an investigation of the data related to Table 9 reveals two interesting possibilities. Firstly, the Pt(IV) complex (although it forms slowly at room temperature) can likely be extracted from acid solution into benzyl alcohol together with the Pd(II). Secondly, the white complexes of Cu(I), Zn(II) and Hg(II) are insoluble* in 1,2-dichloroethane (and even in benzyl alcohol), and should not extract with the Ni(II)-complex. Similarly, the white complexes formed with other d^{10} ions referred to earlier are not likely to extract. Even if the white complexes were to extract, they would not absorb at 512 mμ. It would be necessary, of course, to use large excesses of reagent in the organic phase if several ions that react with the ligand were present.

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* Not reported in EXPERIMENTAL AND RESULTS

Interference from Fe(III) can be avoided by adjusting the pH of the aqueous phase to about 8, after extraction of Pd(II) from acid solution. The Fe(III) is not extracted into 1,2-dichloroethane and remains in the aqueous phase as the hydroxide.

In addition to the ions discussed above, Segall et al (15) found that the following cations and anions do not interfere: alkali metals, alkaline earths, Pb(II), Sn(II), Mn(II), Sb(III), Cr(III), Al(III), Cl^-, NO_3^-, CH_3COO^-, SO_4^{-2}, and PO_4^{-3}. The improved procedure presented in this work should not alter the effect of these ions.

Co(II) appears to be the only ion tested that interferes in the nickel determination. It must therefore be removed, perhaps by the method suggested (15).

Finally, 2,2'-dimercaptodiethyl sulfide shows considerable promise as an analytical reagent for nickel. In addition to its simplicity, the method is accurate and precise over the concentration range studied (6 - 35 ppm, with respect to the aqueous phase). Future investigations are necessary to assess the high degree of selectivity suggested above. This potential selectivity is a result of not only limited reactivity of 2,2'-dimercaptodiethyl sulfide toward metal ions, but also of differences in the properties of the metal complexes formed.

SUMMARY

1. The stability of pure 2,2'-dimercaptodiethyl sulfide and of its solutions, particularly in 50% V/V aqueous dioxane, have been investigated under conditions normal to analytical procedures.
2. The acid-dissociation constants of the reagent have been determined in 50% V/V aqueous dioxane at 25°C and ionic strength of 0.08.
3. The reactivity of the reagent towards representative metal ions of class (a), class (b) and the borderline region has been determined.
4. Complexes derived from Co(II), Co(III), Ni(II) and Pd(II) have been prepared and characterized by elemental analysis, magnetic measurements and molecular-weight determinations (the latter was not done for the Co(III)-complex).
5. Complexes derived from Co(II), Ni(II) and Pd(II) were prepared in solution and studied with respect to their stoichiometry, and their formation and extraction as a function of pH.
6. The potential of 2,2'-dimercaptodiethyl sulfide as an analytical reagent for Ni(II) and Pd(II) has been demonstrated. Its selectivity in the determination of palladium and nickel can be attributed to its behaviour towards class (a), class (b) and borderline metal ions; to favourable properties of the metal complexes such as solubility, colour, and pH of formation or extraction; and perhaps, to favourable rates of formation.

APPENDIX

Figures

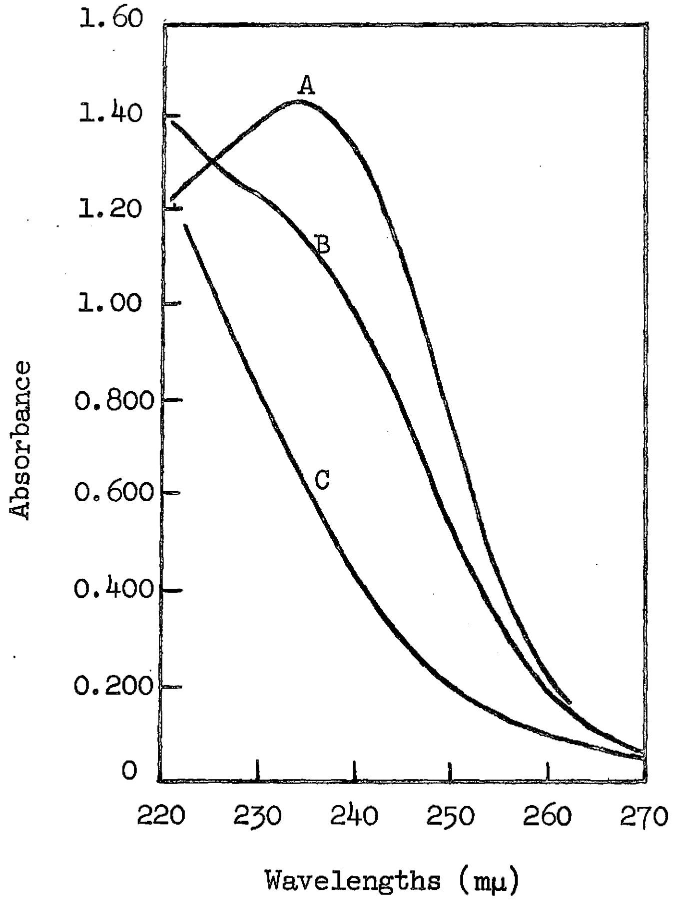


Figure 1

Ultraviolet Spectra of 2,2'-Dimercaptodiethyl Sulfide in 50% V/V Aqueous Dioxane

A, pH = 13.4 (1.15×10^{-4}M, t = 0.25 hrs)
B, pH = 9.8 (9.98×10^{-4}M, t = 0.25 hrs)
C, pH = 6.0 (1.69×10^{-3}M, t = 3 hrs)

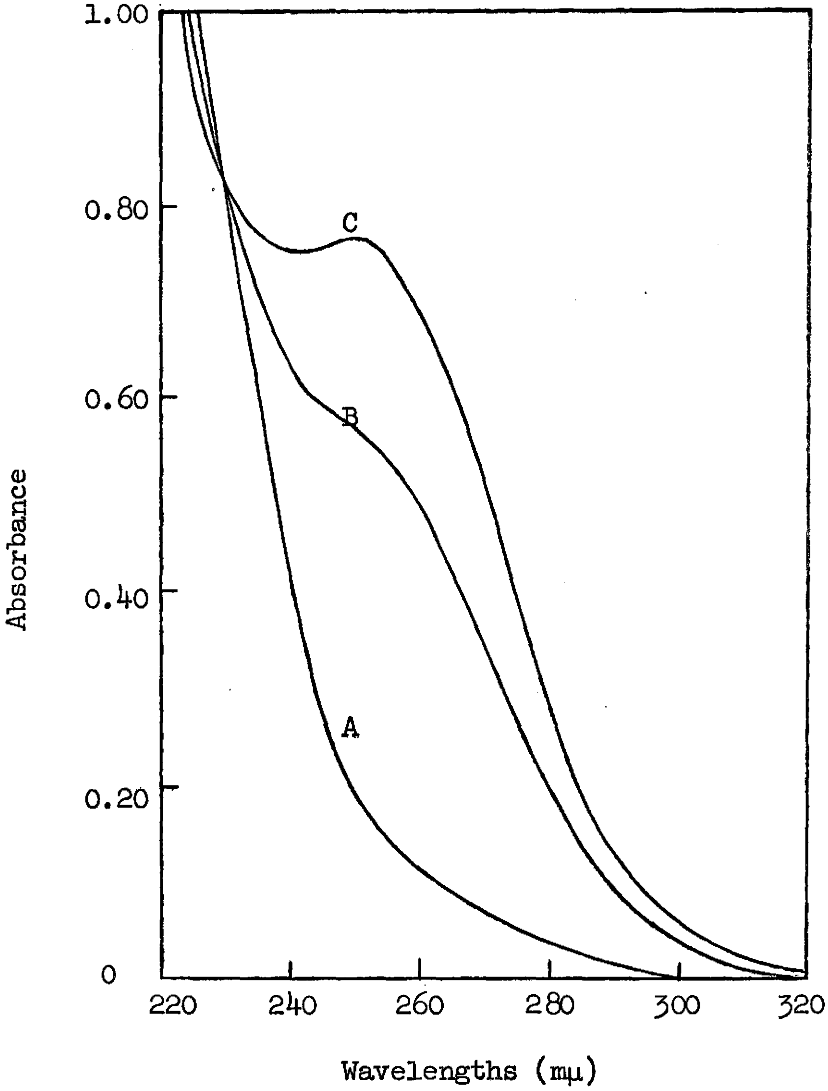


Figure 2

Changes in Spectrum of 2,2'-Dimercaptodiethyl Sulfide with Time at pH 6.0

A, t = 3 hrs; B, t = 97 hrs

C, t = 165 hrs

1.69×10^{-3} M

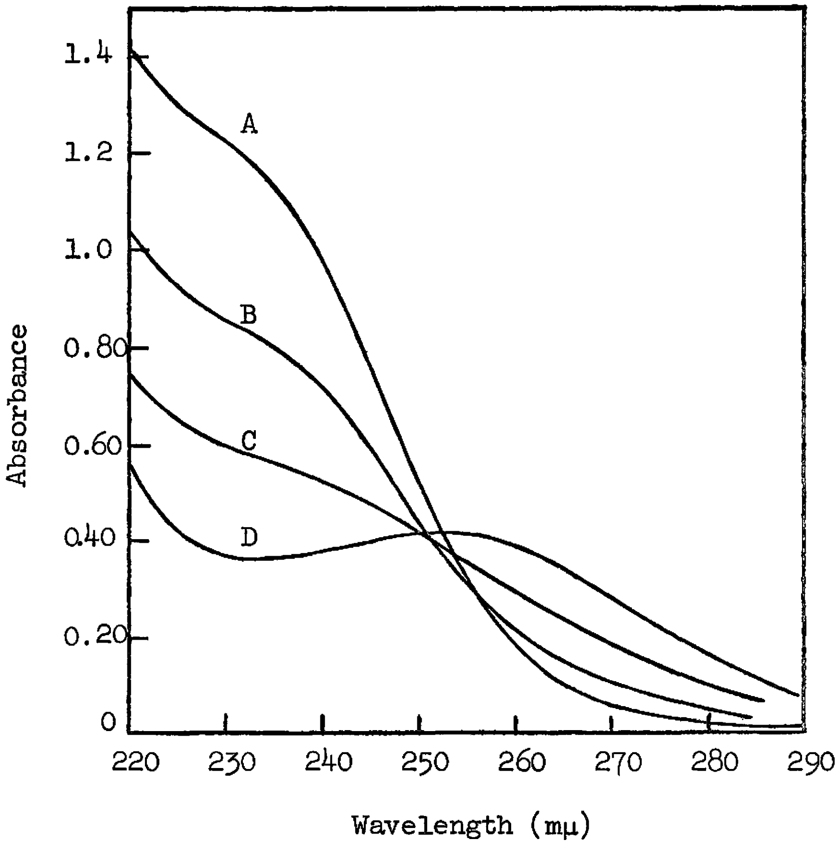


Figure 3

Changes in Spectrum of 2,2'-Dimercaptodiethyl Sulfide
with Time at pH 9.8

A, t = 0.25 hrs; B, t = 2.0 hrs
C, t = 4.0 hrs; D, t = 21 hrs.
9.98×10^{-4}M

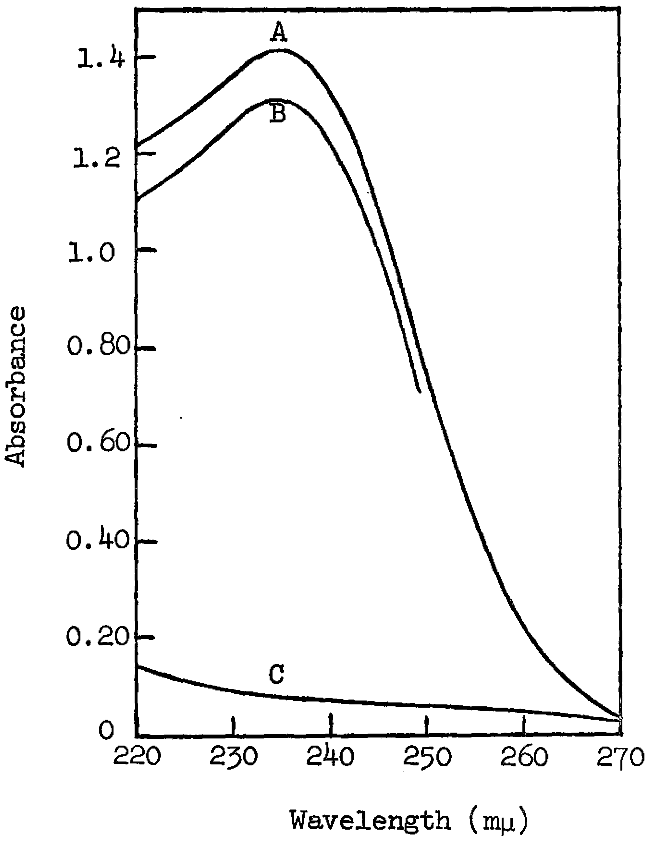


Figure 4

Changes in Spectrum of 2,2'-Dimercaptodiethyl Sulfide with Time at pH 13.4

A, t = 0.25 hrs; B, t = 2.5 hrs
C, t = 45 hrs

1.15×10^{-4}M

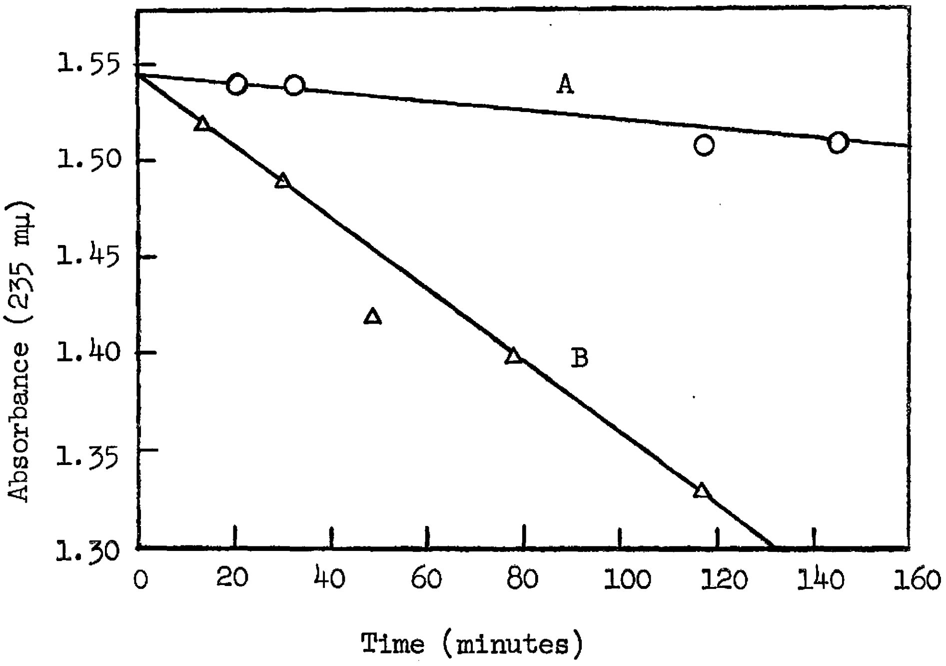


Figure 5

Effect of Dissolved Oxygen on the Oxidation of the Reagent at pH 13.4

A, oxygen excluded; B, oxygen not excluded

1.25×10^{-4}M

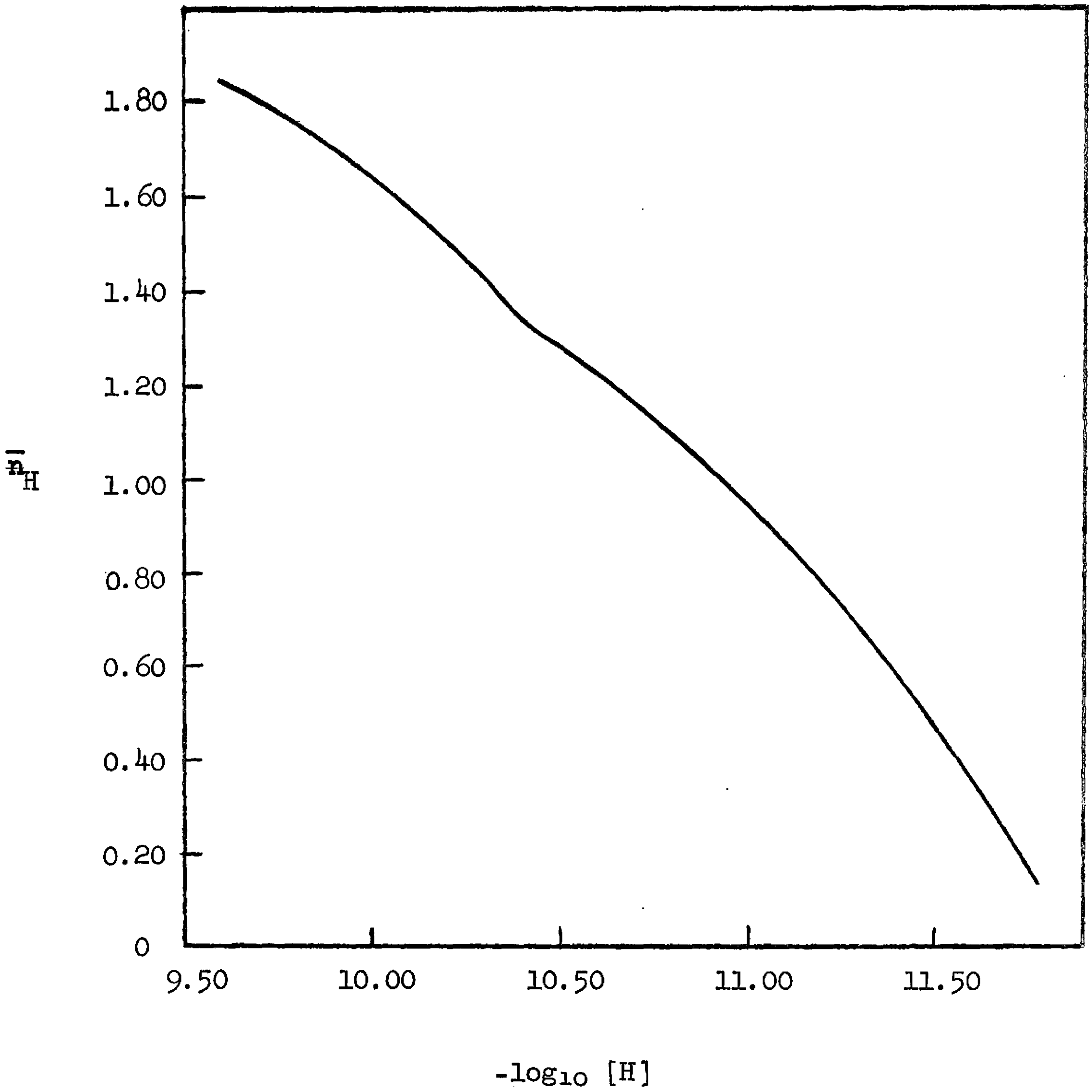


Figure 6

Experimental Proton-Formation Curve
for 2,2'-Dimercaptodiethyl Sulfide

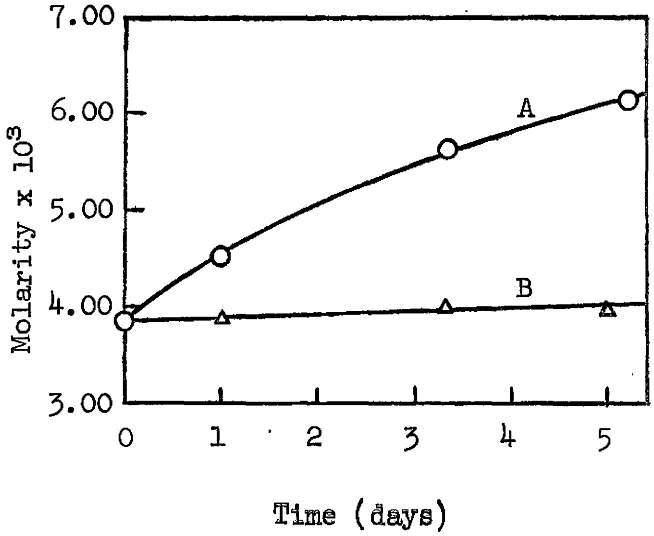


Figure 7

Decomposition of Benzil

A, solution exposed to light

B, solution protected from light

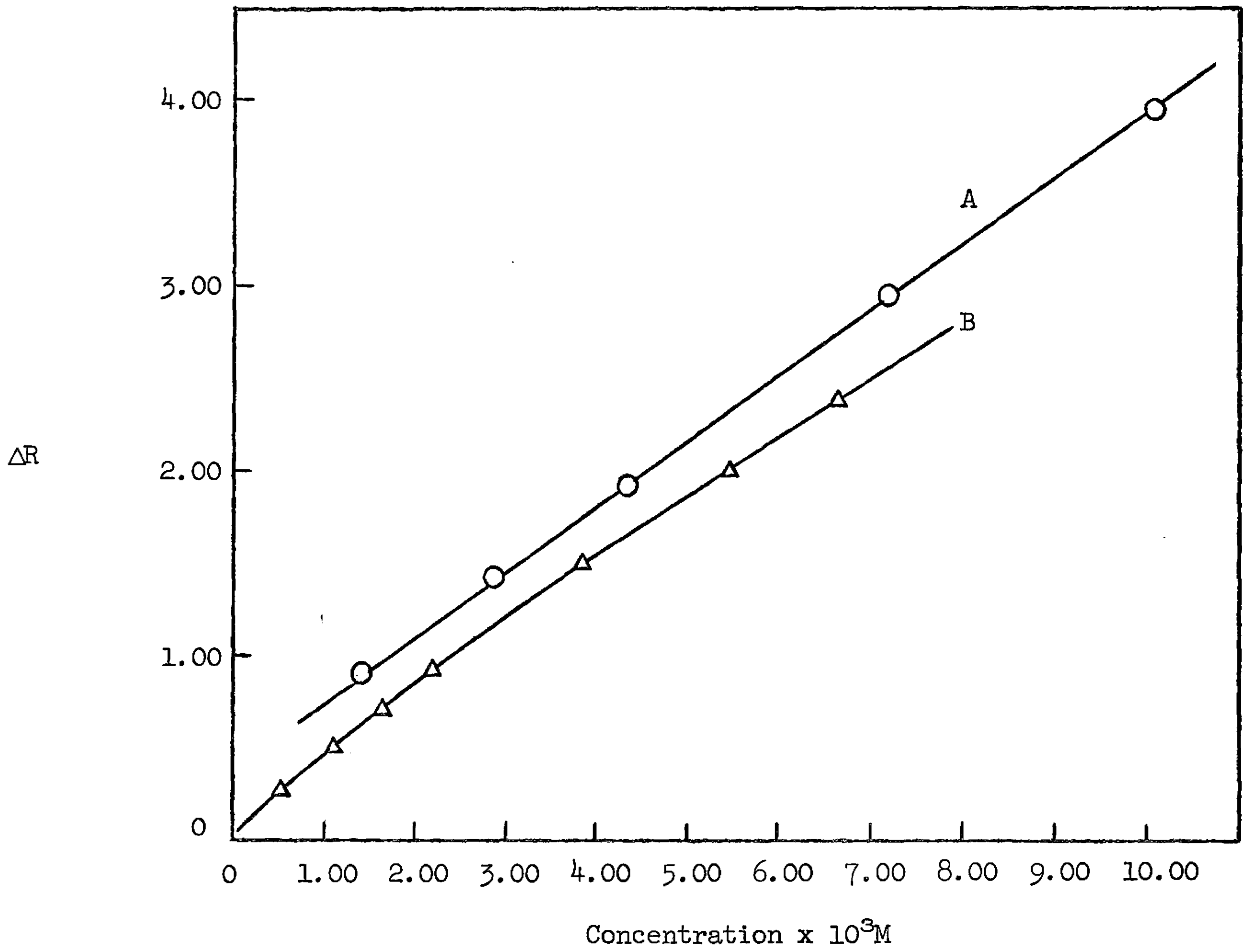


Figure 8

Calibration Curves for Molecular Weight Determinations
(Benzil in 1,2-Dichloroethane)

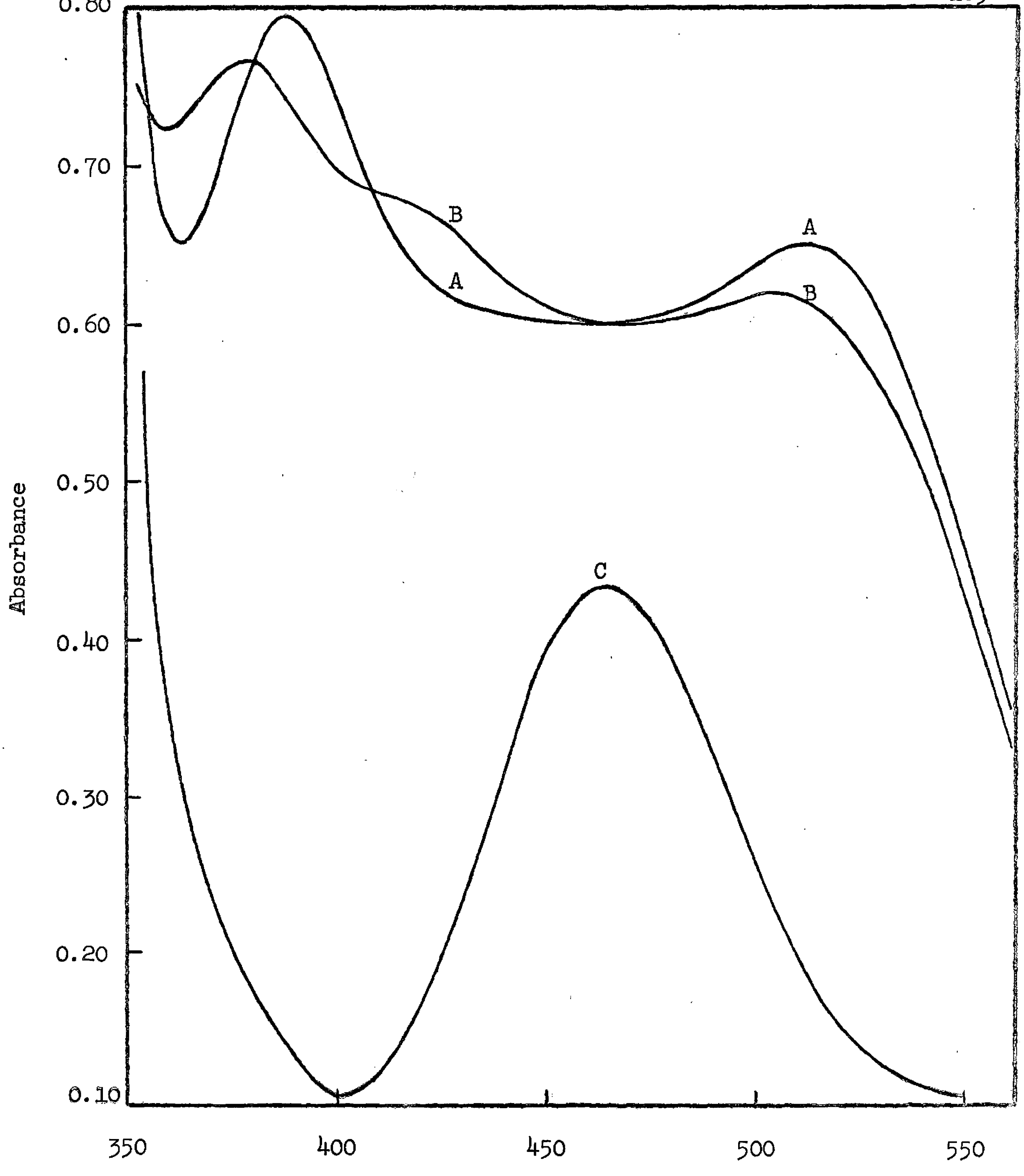


Figure 9

Visible Spectra of Ni(II)-Reagent System

A, extracted into 1,2-dichloroethane from aqueous phase (pH 9.5)
B, 50% V/V aqueous dioxane, pH = 6.6
C, 50% V/V aqueous dioxane, pH = 12.4

Ni(II) concentration: 5.87×10^{-4}M

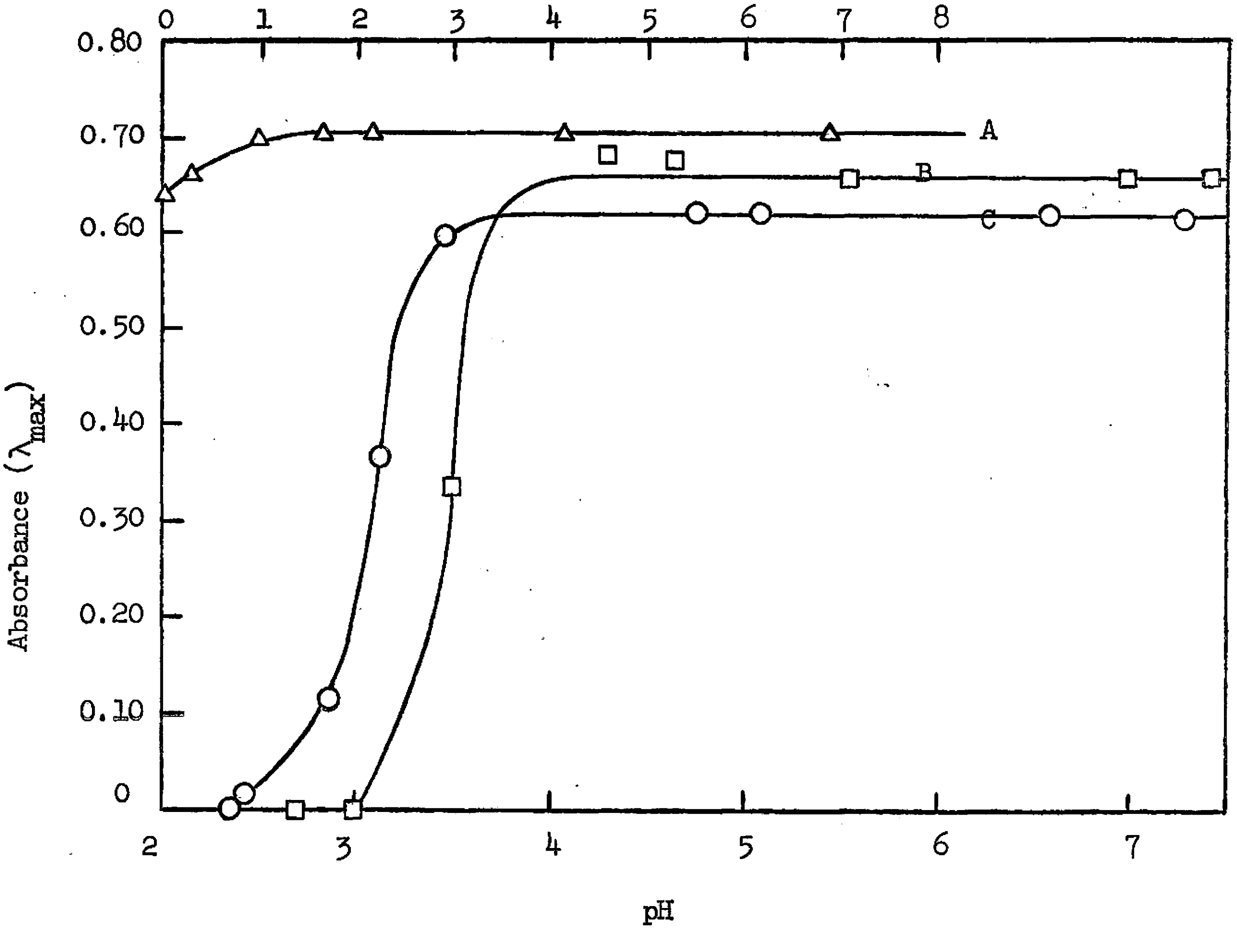


Figure 10

Complex Formation as a Function of pH

Curve A, Pd(II)-complex, λ_{max} = 340 mμ, upper pH scale

Curve B, Co(II)-complex, λ(shoulder) = 385 mμ, lower pH scale

Curve C, Ni(II)-complex, λ_{max} = 505 mμ, lower pH scale

(50% V/V aqueous dioxane)

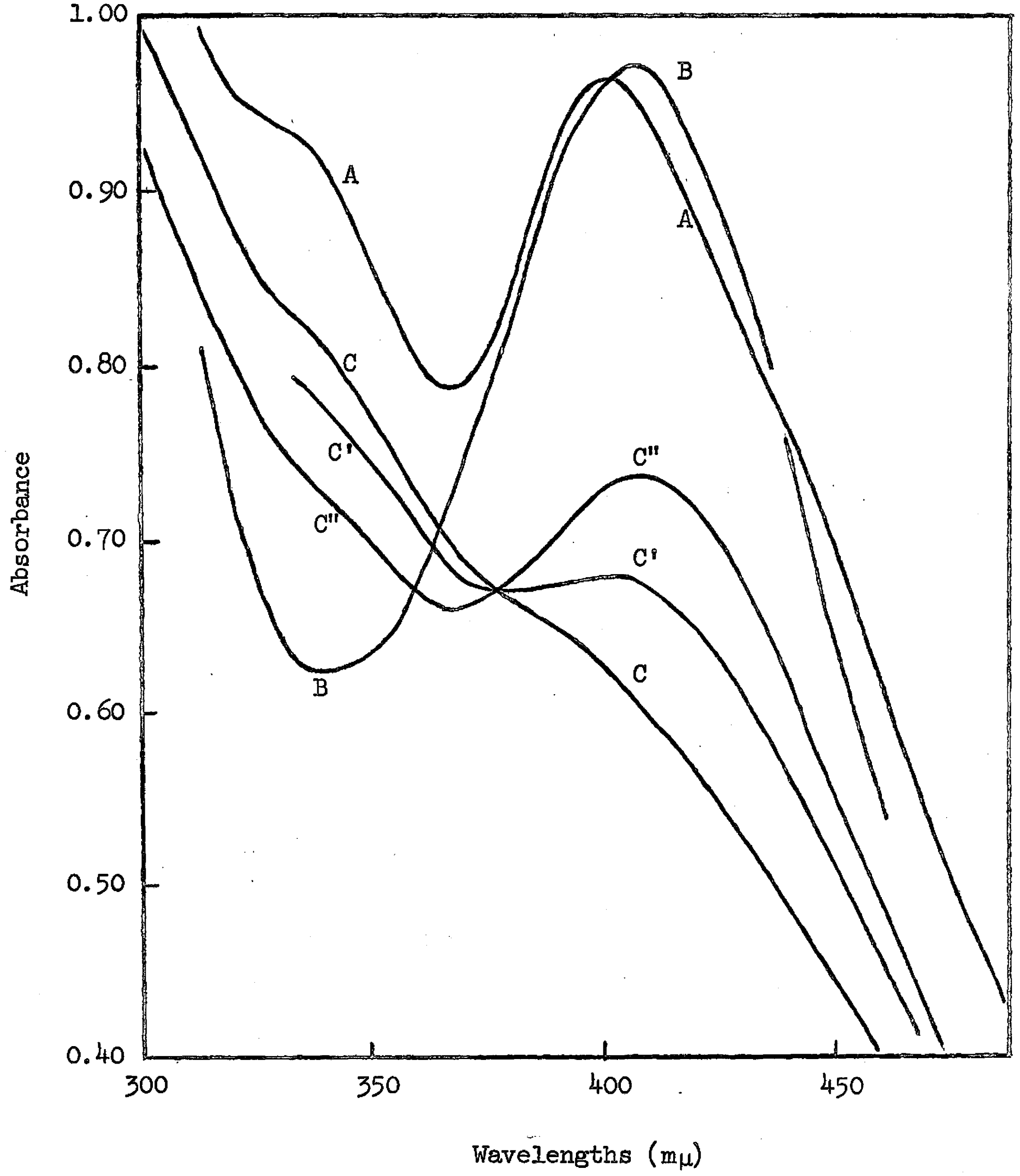


Figure 11

Visible Spectra for Co(II)-2,2'-Dimercaptodiethyl Sulfide System in 50% V/V Aqueous Dioxane

A - "Co(II)"-complex (dissolved solid)
B - pH 9.6, t = 24 hrs, 9.84×10^{-5}M in Co(II)
C - pH 7.4, t = 1/2 hrs, 9.84×10^{-5}M in Co(II)

C' - C at t = 2 hrs
C" - C at t = 24 hrs

t = time recorded after preparation

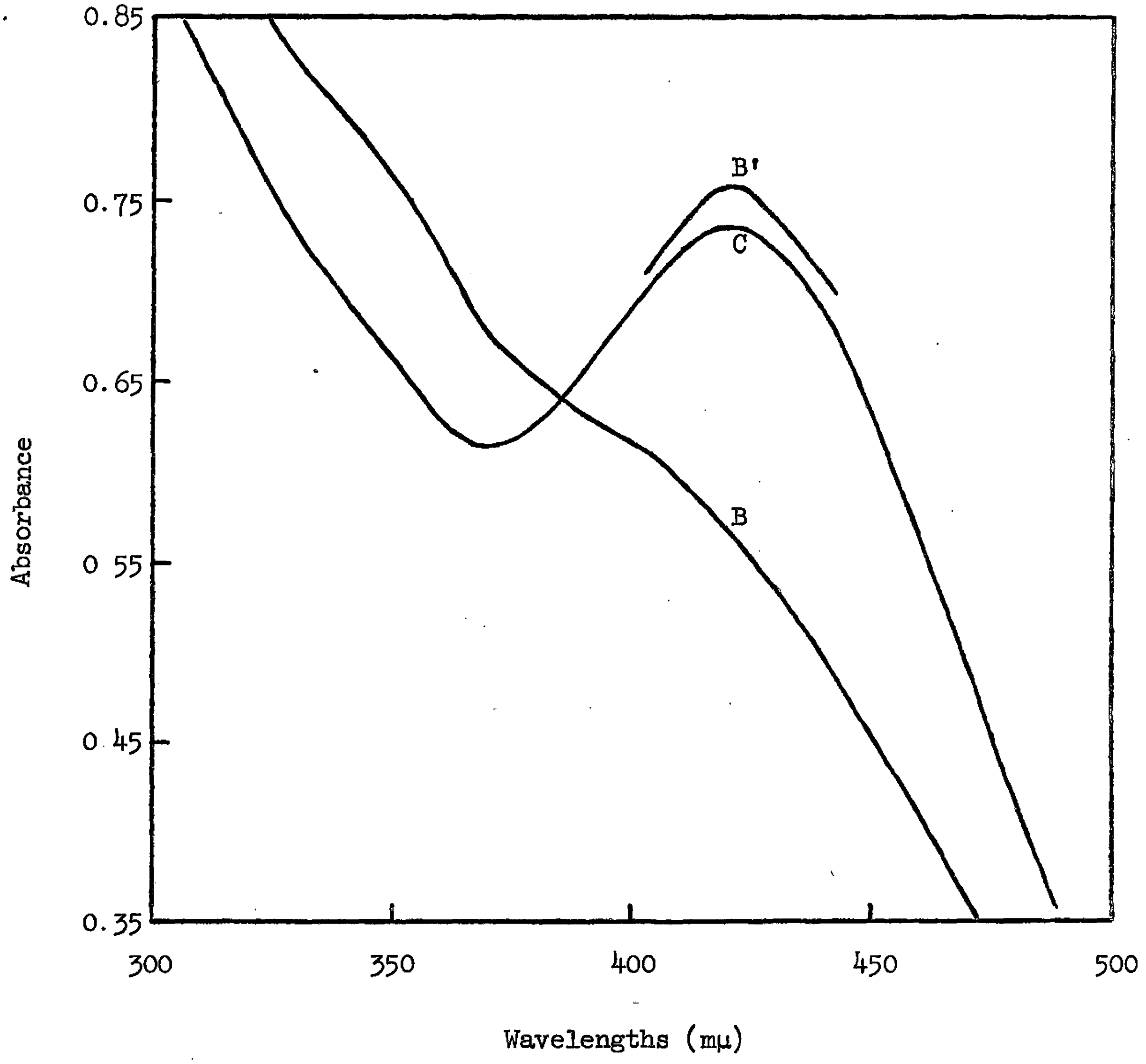


Figure 12

Effect of "Stored" Dioxane on Co(II)-2,2'-Dimercaptodiethyl Sulfide System

B - pH 7.1, freshly distilled dioxane, t = 1/3 hrs, 9.84 x 10^{-5}M in Co(II)

B' - B at t = 24 hrs

C - pH 7.1, dioxane stored in air for one week, t = 1/3 hrs, 9.84 x 10^{-5}M in Co(II)

t = time recorded after preparation

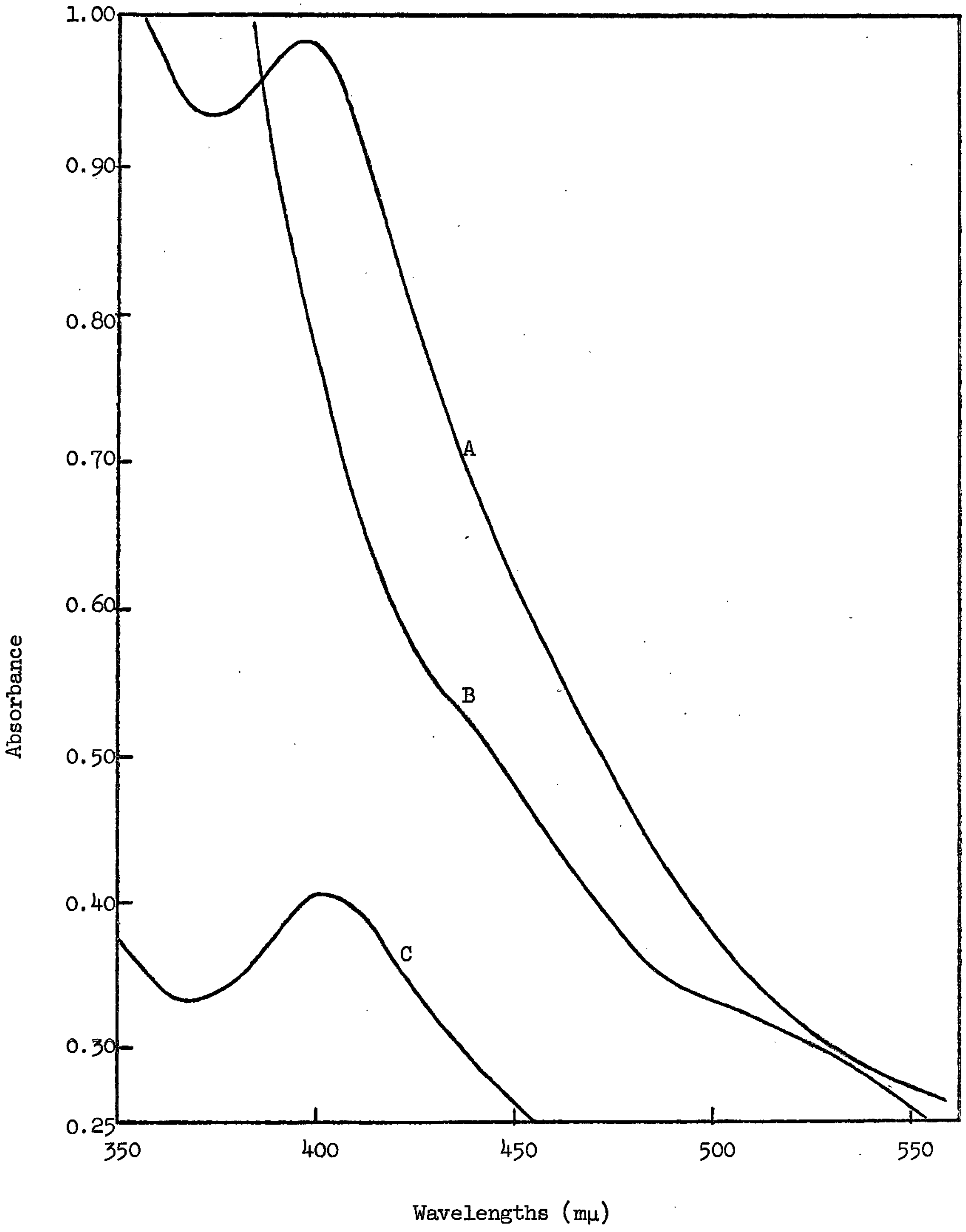


Figure 13

Visible Spectra of the Solid Co(III)-and "Co(II)"-Complexes in Chloroform
A, Co(III) solution after three days
B, freshly prepared Co(III) solution

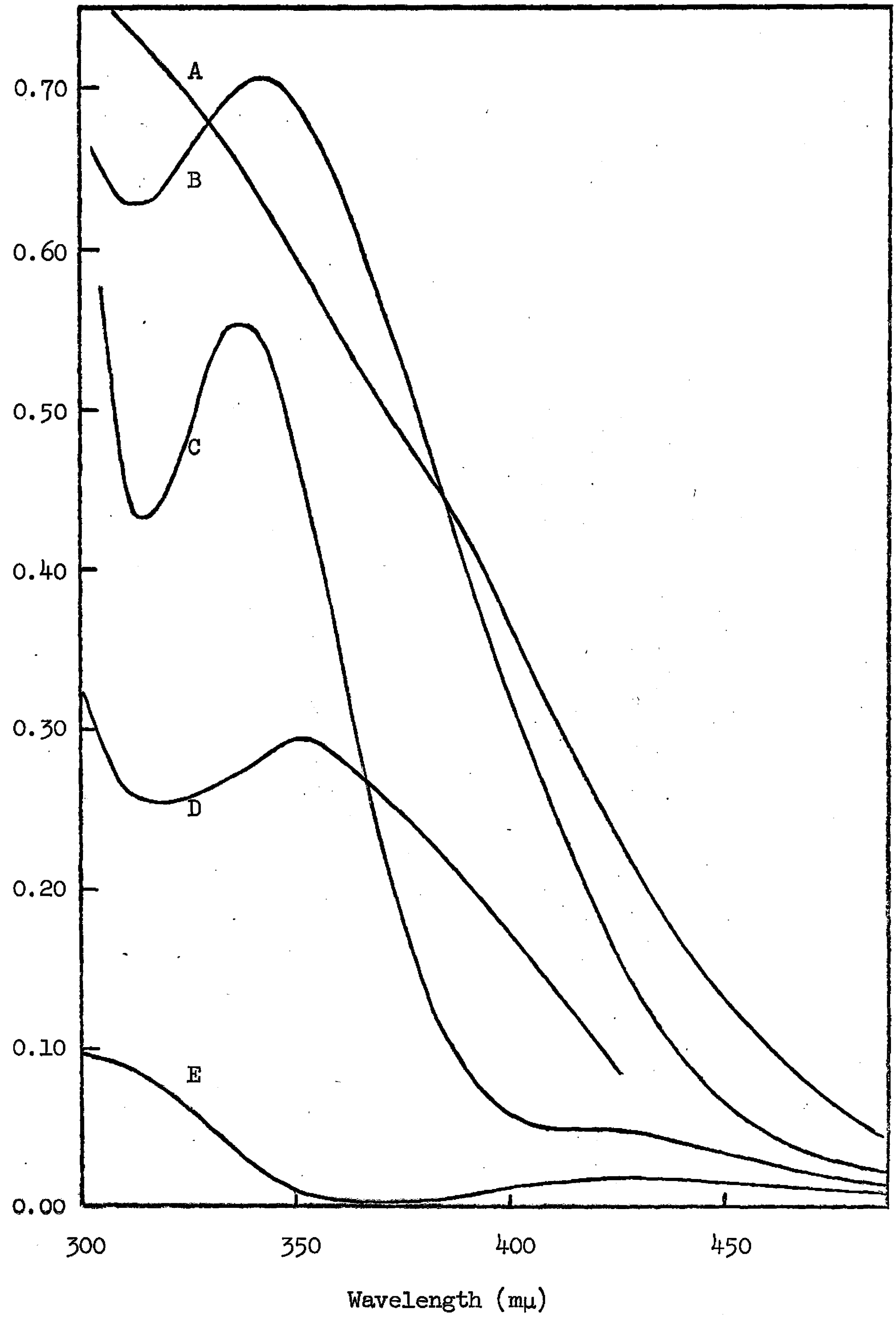


Figure 14

Visible Spectra of Pd(II)-Reagent System

A - pH = 0
B - pH = 2.2
C - pH = 12.4
} 50% V/V aqueous dioxane, 9.48×10^{-5}M in Pd(II)

D - Pd(II)-complex extracted into 1,2-dichloroethane

E - $PdCl_2$ solution (pH = 2.1, 9.48×10^{-5}M)

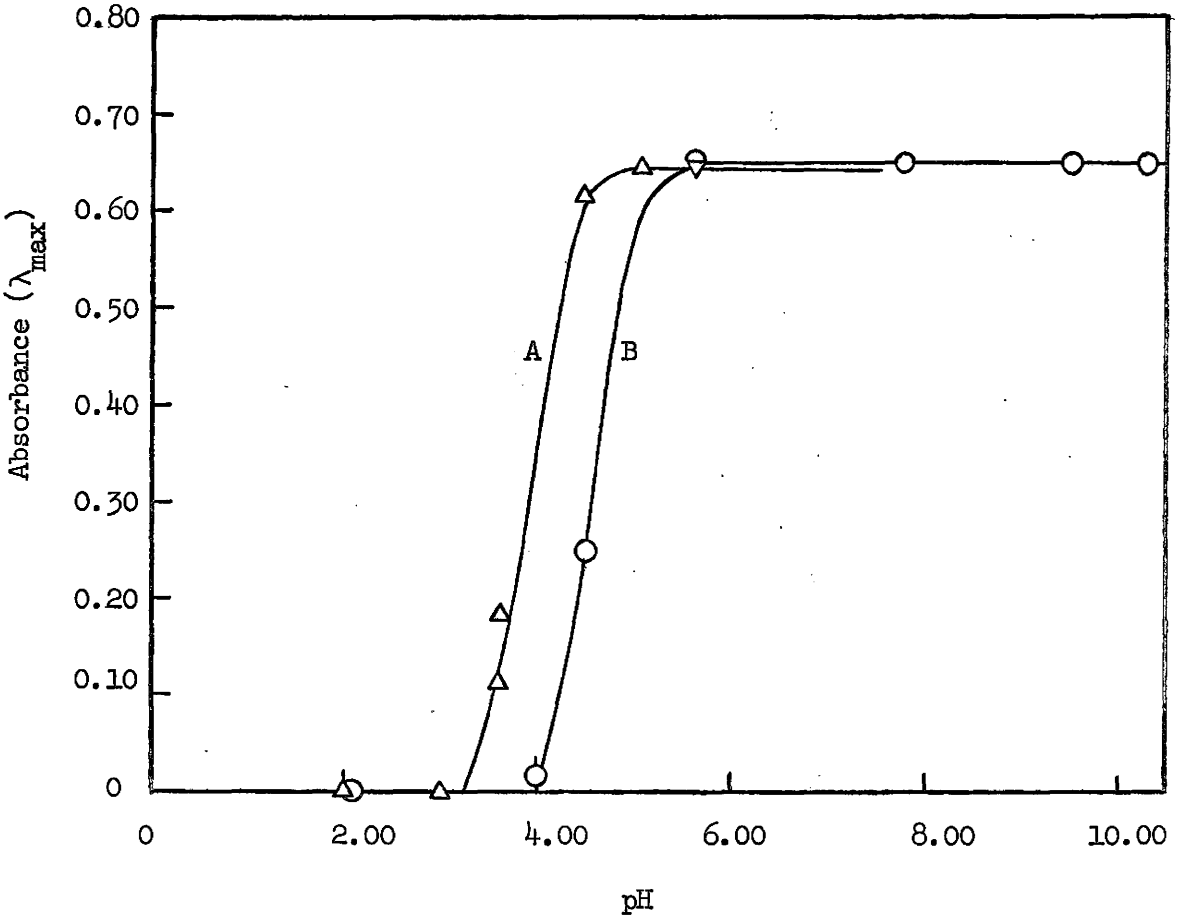
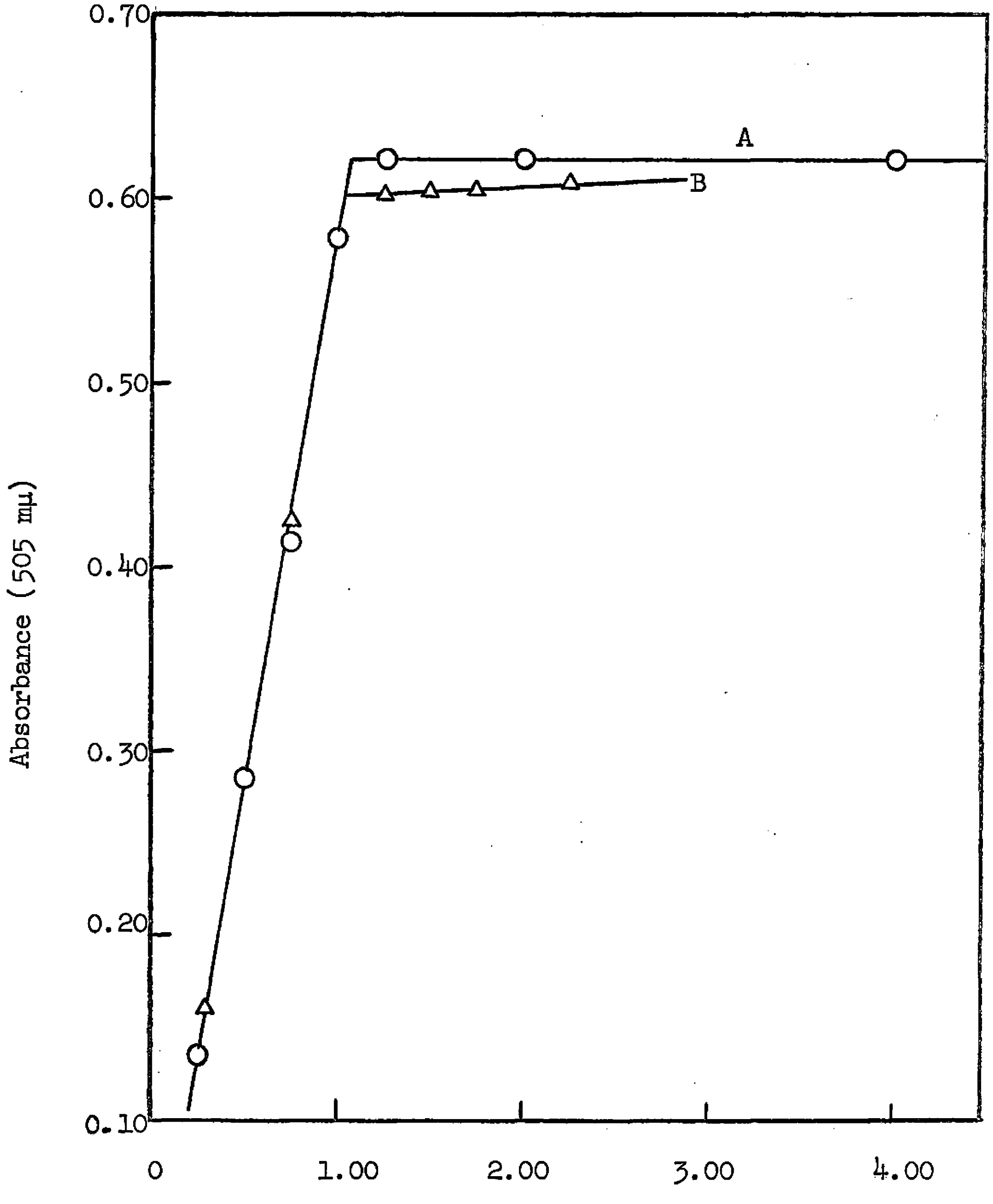


Figure 15

Extraction of the Ni(II)-Complex as a Function of pH

A - benzyl alcohol solvent, λ_{max} = 508 mμ

B - 1,2-dichloroethane solvent, λ_{max} = 512 mμ



Reagent/Metal (Molar Ratio)

Figure 16

Mole Ratio Plots for Ni(II)-Complex

A - pH 6.8

B - pH 12.1

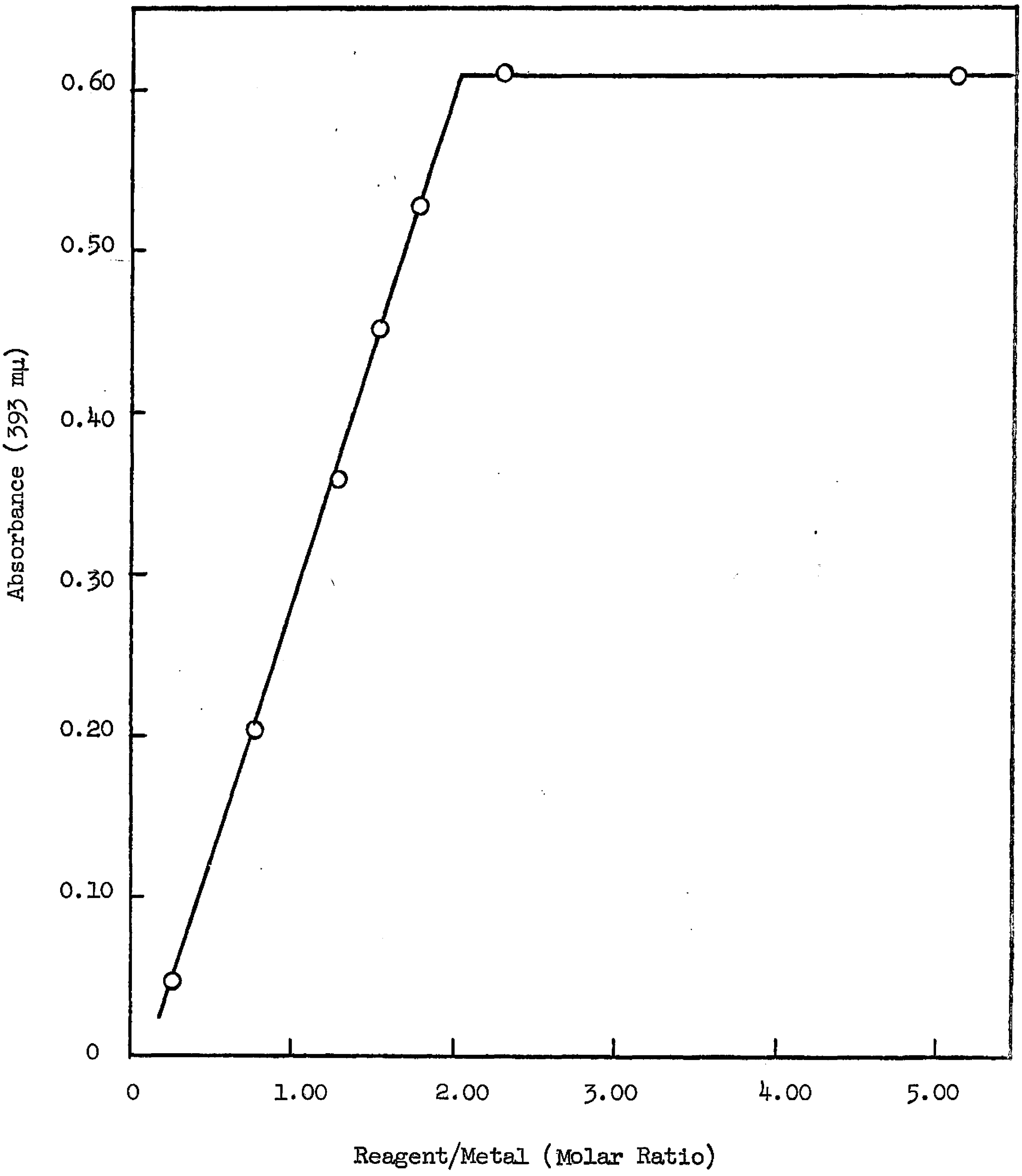


Figure 17

Mole Ratio Plot for Co(II)-Reagent System

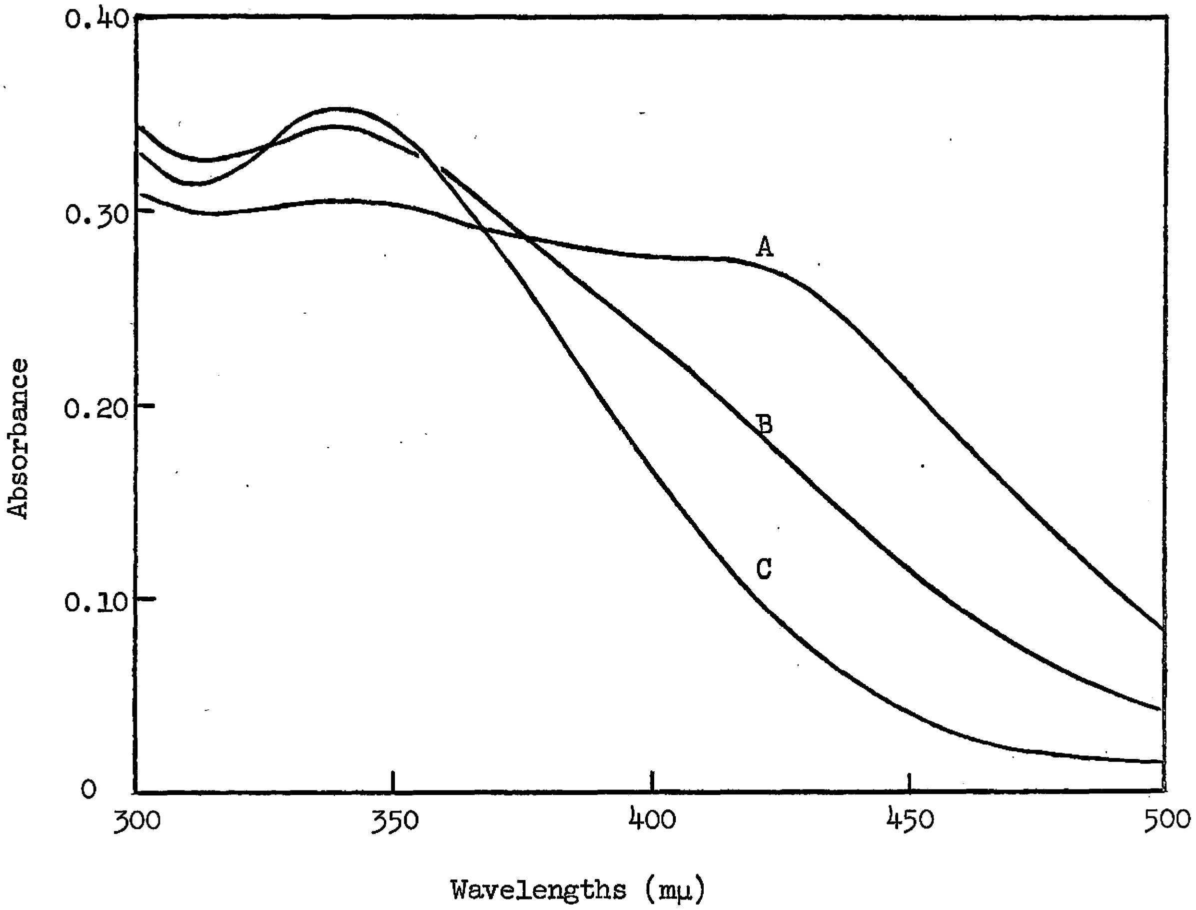


Figure 18

Spectra of Pd(II) Solutions at Various R/M Values

A - R/M = 0.77
B - R/M = 1.78
C - R/M = 10.1

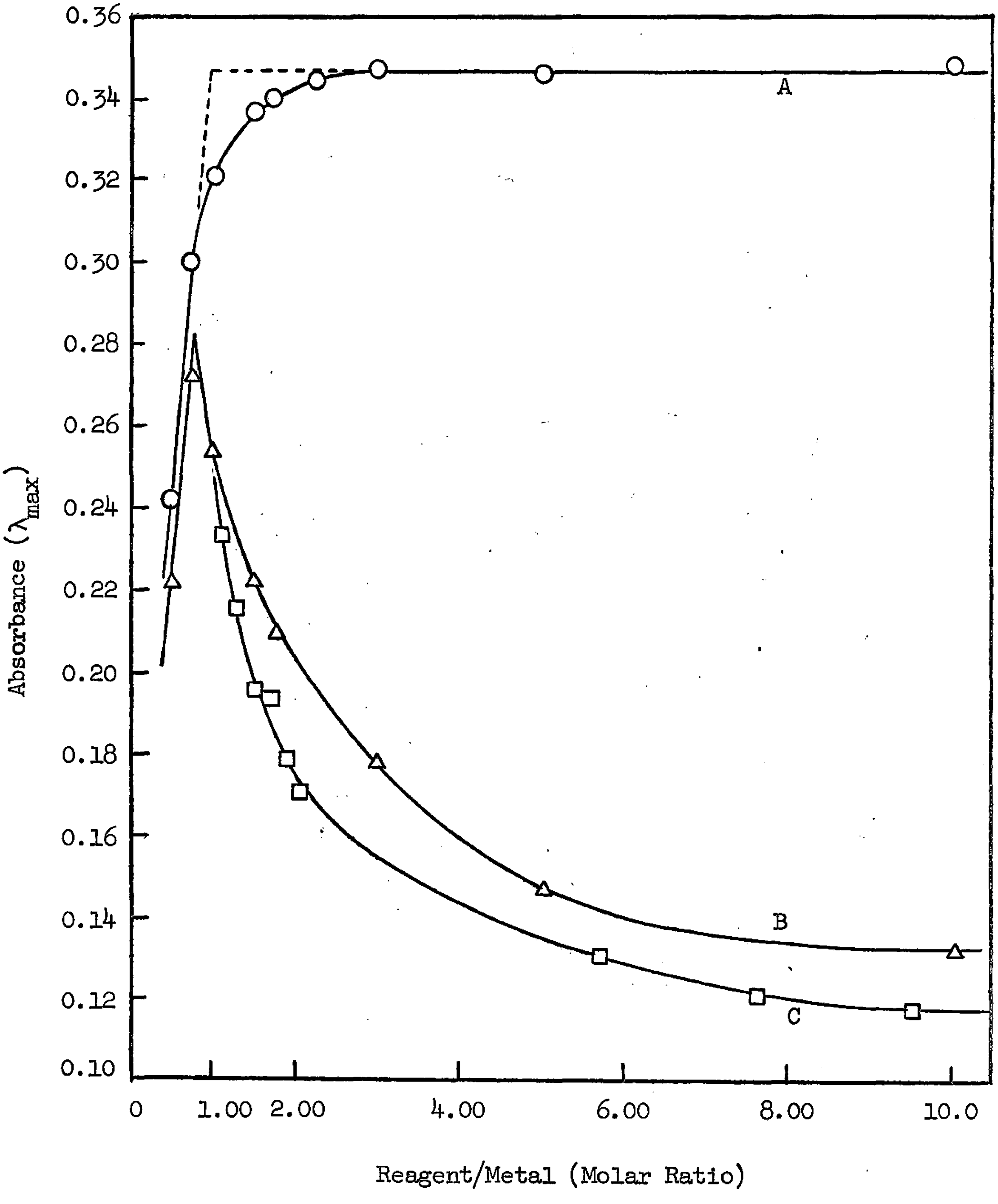


Figure 19

Mole Ratio Plots for Pd(II)-Reagent System

A, λ_{max} = 340 mμ (chloride present)
B, λ_{max} = 410 mμ (chloride present)
C, λ_{max} = 410 mμ (chloride absent)

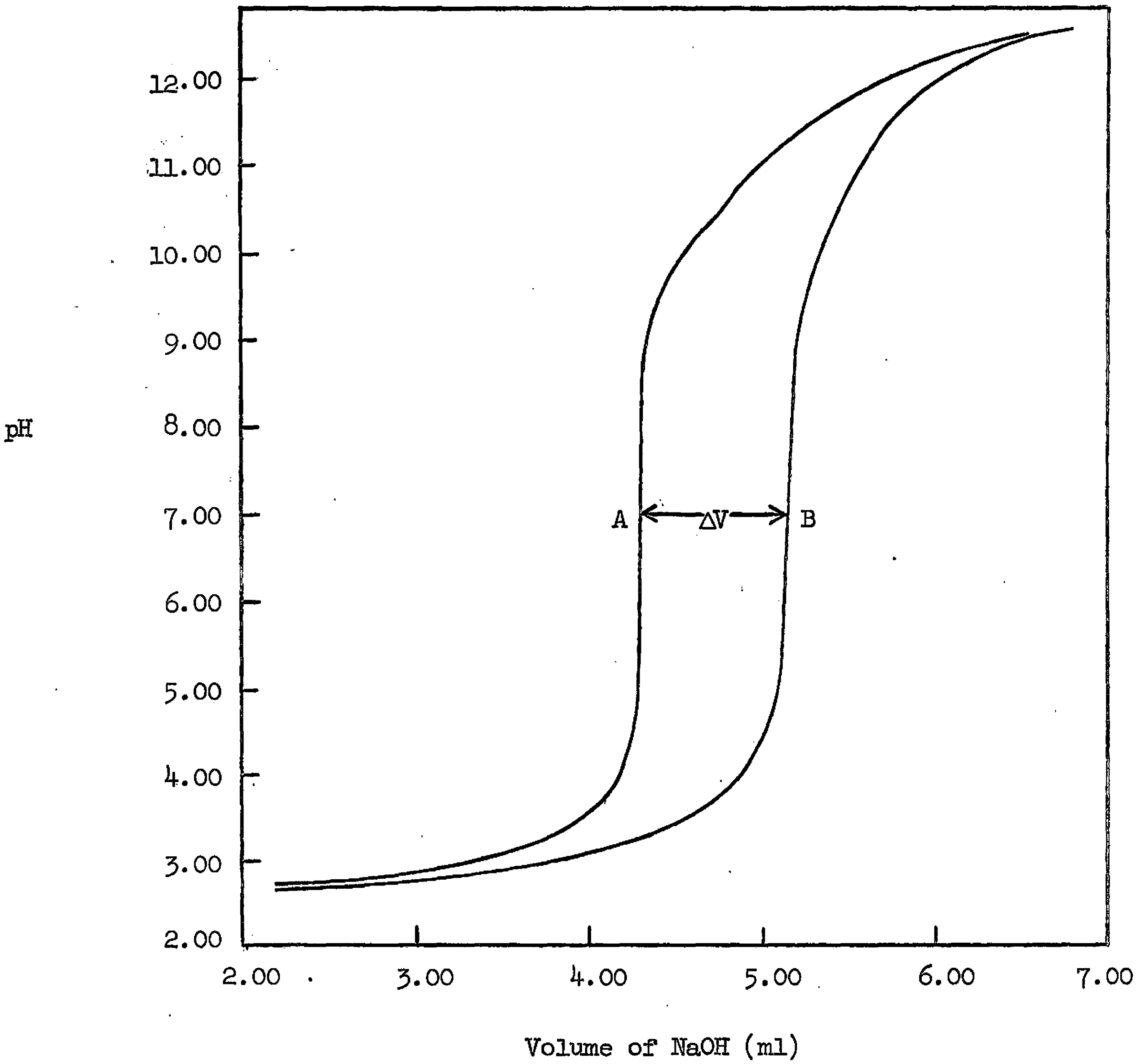


Figure 20

Potentiometric Titration of the Ni(II)-2,2'-Dimercaptodiethyl Sulfide System

A, Reagent alone (7.63×10^{-5} moles)

B, Reagent (7.63×10^{-5}moles)+Ni(II) (4.89×10^{-5}moles)

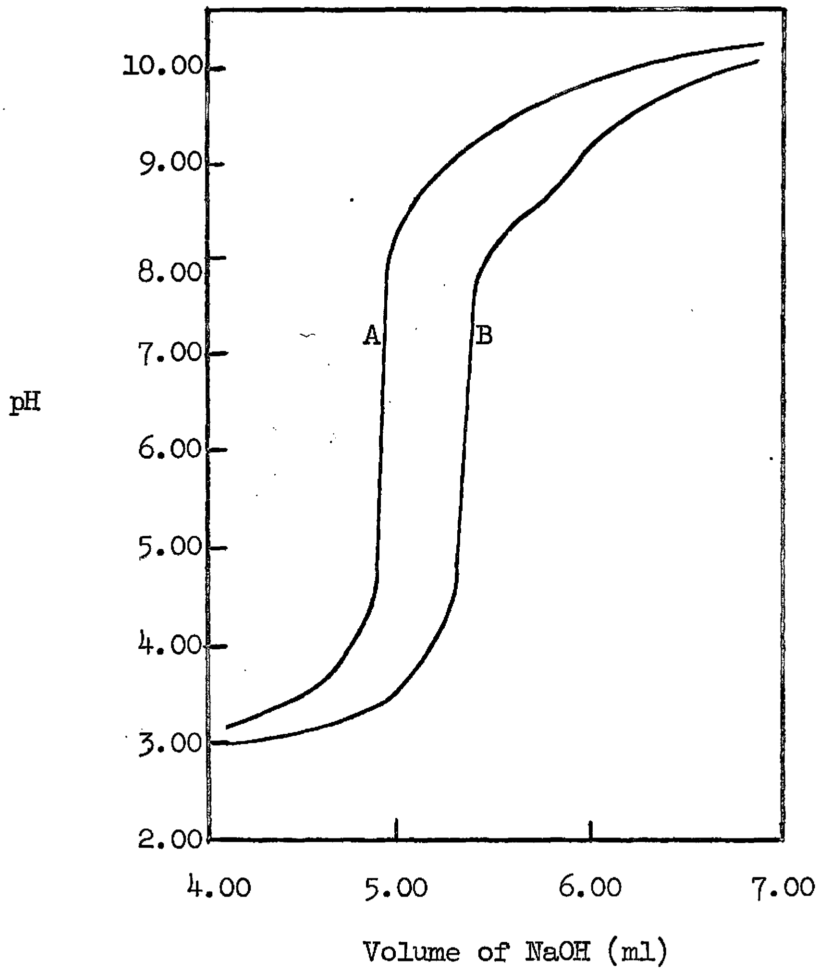


Figure 21

Potentiometric Titrations of the Co(II)- and Pd(II)- 2,2'-Dimercaptodiethyl Sulfide Systems

A, Reagent (3.84×10^{-4}moles)+Co(II) (4.93×10^{-5}moles)
B, Reagent (3.79×10^{-4}moles)+Pd(II) (4.75×10^{-5}moles)

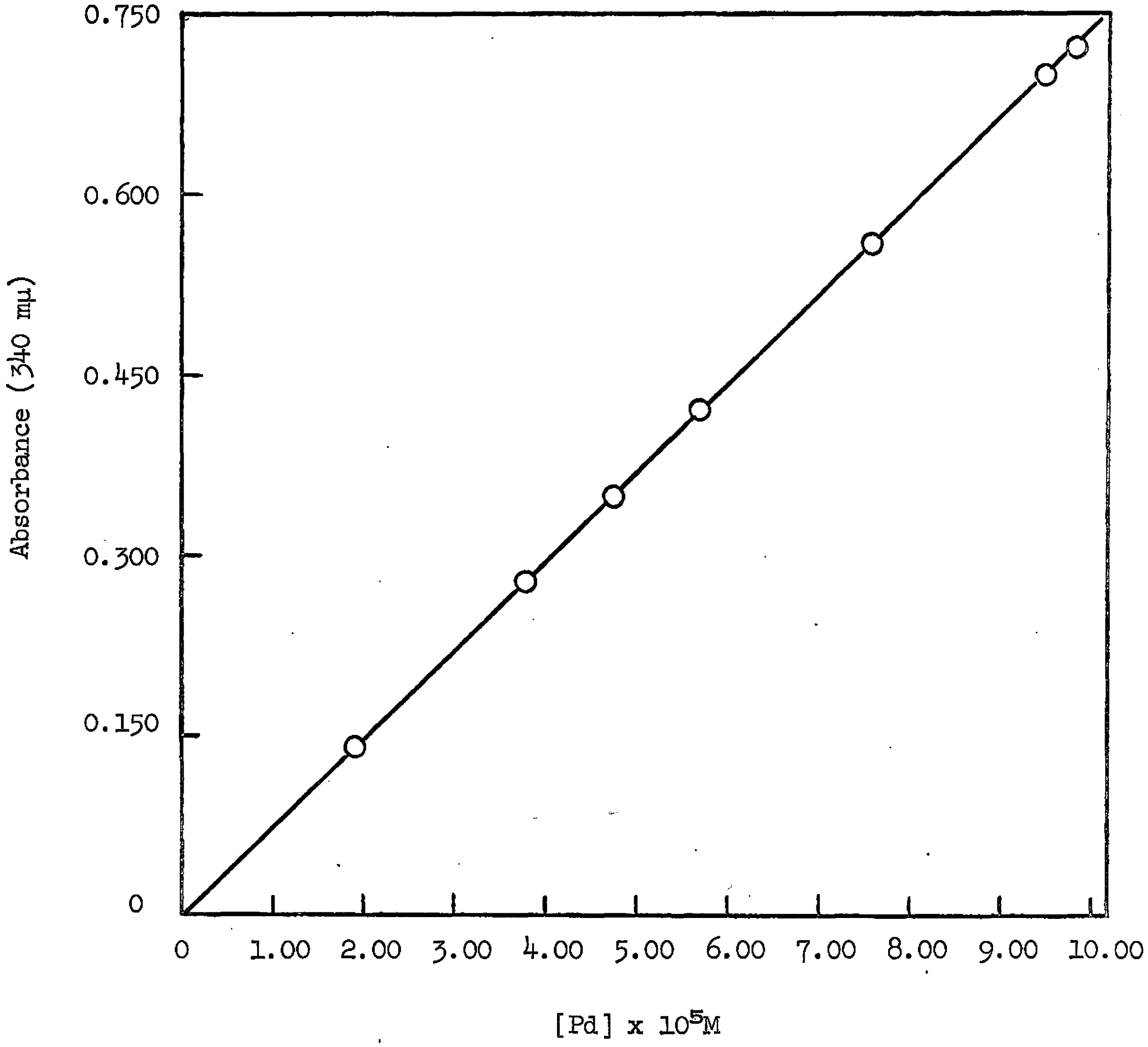


Figure 22

Absorbance of Pd(II)-Complex (340mμ);

Beer's Law Calibration Plot

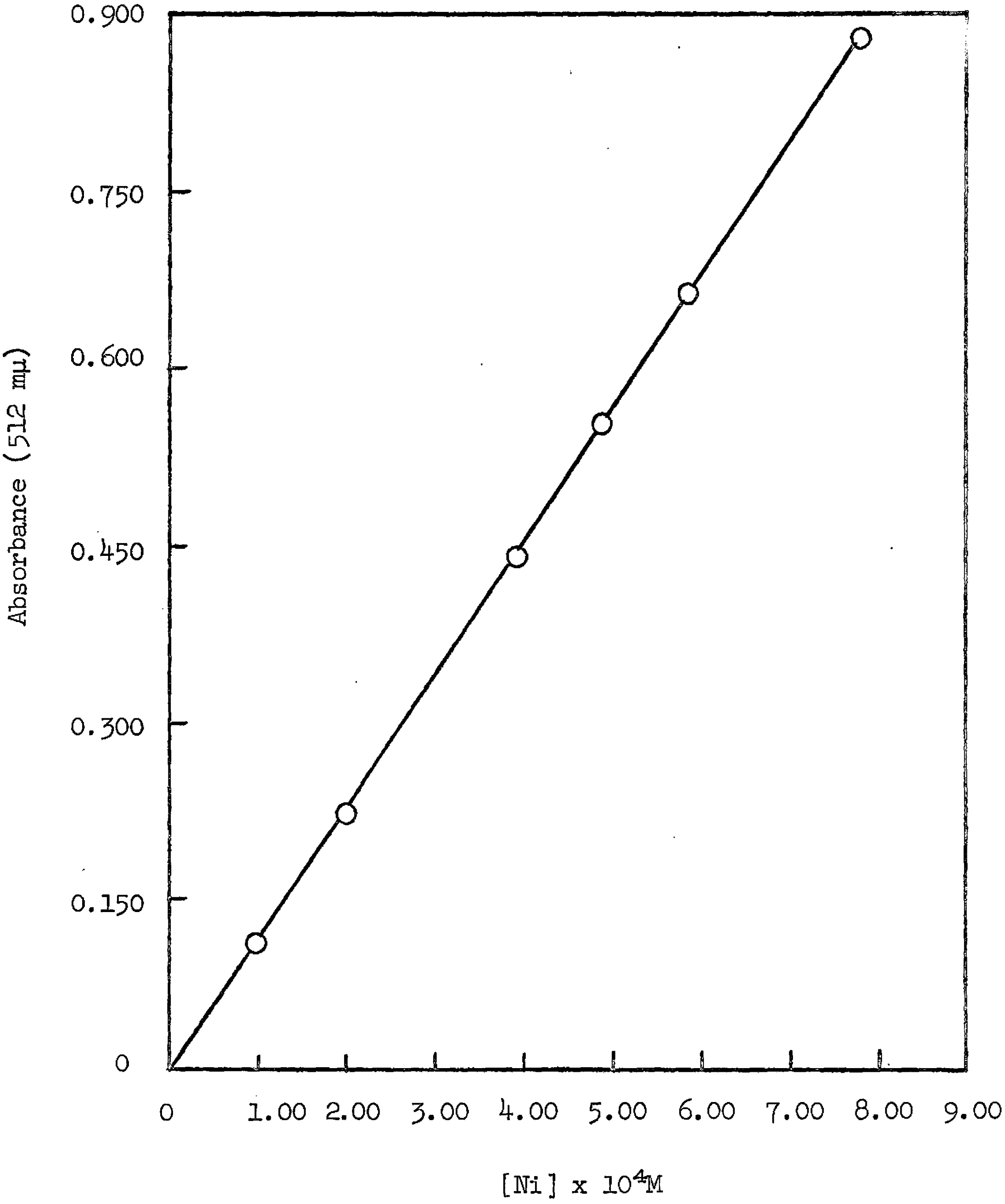


Figure 23

Absorbance of Ni(II)-Complex (512 mμ);

Beer's Law Calibration Plot

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