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Part I: Palladium complexes of di-2-thienylketoxime; Part II: Nephelometric determination of palladium with di-2-thienylketoxime.

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I PALLADIUM COMPLEXES OF DI-2-THIENYLKETOXIME

II NEPHELOMETRIC DETERMINATION OF PALLADIUM WITH DI-2-THIENYLKETOXIME

BY
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ABSTRACT

PART I

PALLADIUM COMPLEXES OF DI-2-THIENYLKETOXIME

The reaction between di-2-thienylketoxime and the palladium (II) ion has been studied. The complexes prepared were the complexes dichlorobis(di-2-thienylketoxime-N,N')palladium (II), biaquobis(di-2-thienylketoxime-N,N')palladium (II) half hydrate, and polymeric forms of the chelate bis(di-2-thienylketoxime)palladium (II).

PART II

NEPHELOMETRIC DETERMINATION OF PALLADIUM WITH DI-2-THIENYLKETOXIME

A rapid nephelometric method for the determination of microgram quantities of palladium (II) with di-2-thienylketoxime was developed. A 0.1% solution of di-2-thienylketoxime in ethanol reacts with palladium (II) as chloride in acidic solution to form a colloidal suspension of Pd-di-2-thienylketoxime complex whose turbidity is proportional to the concentration of palladium present. The reagent is highly specific for palladium. Platinum group metals do not interfere in low concentration. Other common cations and anions show no interfer-

ferences except the interference of cyanide ions, which prevent the formation of Pd-di-2-thienylketoxime complex. The method is very sensitive, concentration as low as 1 p.p.m. of palladium can be determined. The degree of turbidity is measured with the Fisher Nefluoro-Photometer. The method has an average error of ±4% over the range of 0.04 mg to 0.25 mg in 50 ml of solution.

ACKNOWLEDGMENTS

The author gratefully acknowledges the able direction of Dr. W. J. Holland, under whose suggestion these studies were undertaken.

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TABLE OF CONTENTS

PART I

PALLADIUM COMPLEXES OF DI-2-THIENYLKETOXIME

Chapter

PART II

NEPHELOMETRIC DETERMINATION OF PALLADIUM WITH DI-2-THIENYLKETOXIME

LIST OF TABLES

PART I

PART II

LIST OF FIGURES

PART I

PART II

PART I

PALLADIUM COMPLEXES
OF
DI-2-THIENYLKETOXIME

CHAPTER I

INTRODUCTION

Many heterocyclic organic compounds derived from furan, pyrole, pyridine, quinoline, etc have been employed as analytical reagents. Thiophene derivatives, which possess strong coordinating ability have drawn the attention of the analysts. A recent investigation of complex formation between bivalent palladium and 2-thienyl-trans-aldoxime has illustrated the utility of a thiophene derivative as an analytical reagent.[1]

A survey of literature reveals a surprising lack of information regarding thiophene derivatives in complex formation with the transition metals. Although thienyltrifluoroacetone has been used for the separation of zirconium and hafnium[2] and the stability constants of metal complexes of 2-thiophene carboxylic acid have been measured[3] no other thiophene derivatives seem to have been studied.

Oximes in general form stable complexes with metals, particularly with those of the transition triads of the periodic table, and are widely used for the detection and estimation of these metals. Examples are salicylaldoxime[4] and benzymethylglyoxime.[5]

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[1] S.G. Trandon and S.C. Bhattacharya, _Anal. Chem._, _32_, 194 (1960).

[2] E.H. Huffman and L.J. Beaufait, _J. Am. Chem. Soc._, _71_, 3179 (1949).

The purpose of the present work was to investigate the complex formation between bivalent palladium and di-2-thienylketoxime with a view of their application to analytical uses.

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[3] P.O. Lumme, Suomen Kemistilehti, 33(2), 85 (1960).

[4] E. Ephriam, Ber., 63, 1930 (1928).

[5] F.P. Dwyer and D.P. Mellor, J. Am. Chem. Soc., 57, 605 (1935).

CHAPTER II

EXPERIMENTAL

The procedure for the synthesis of di-2-thienylketoxime was developed. The reaction between the palladium (II) ion and di-2-thienylketoxime was studied. The complexes dichlorobis(di-2-thienylketoxime-N,N')palladium (II)[6], biaquobis(di-2-thienylketoxime-N,N')palladium (II) half hydrate[7], and polymeric forms of the chelate bis(di-2-thienylketoxime)palladium (II)[8] were prepared and studied. A schematic diagram of the reactions for the preparation of these complexes and their interrelationship is shown in Fig. 1.

Synthesis of Di-2-thienylketoxime

A solution of 11.2 gm of di-2-thienylketone[9], 11.2 gm of hydroxylamine hydrochloride, and 44 gm of potassium hydroxide in 500 ml of alcohol was refluxed for 2 hours. The reaction mixture was poured into 1000 ml of water and made acid to litmus by the addition of hydrochloric acid. The precipitate was filtered under suction and dissolved in alcohol. Water was added until the solution became turbid. On cooling, colorless needles

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[6] This complex was designated as Complex I.

[7] This complex was designated as Complex II.

[8] There were prepared two polymeric forms of the chelate bis(di-2-thienylketoxime)palladium (II) and they were designated as Complex III and Complex IV.

[9] V. Thomas and V. Couderc, Bull. Soc. Chim. France, 23, 288 (1918).

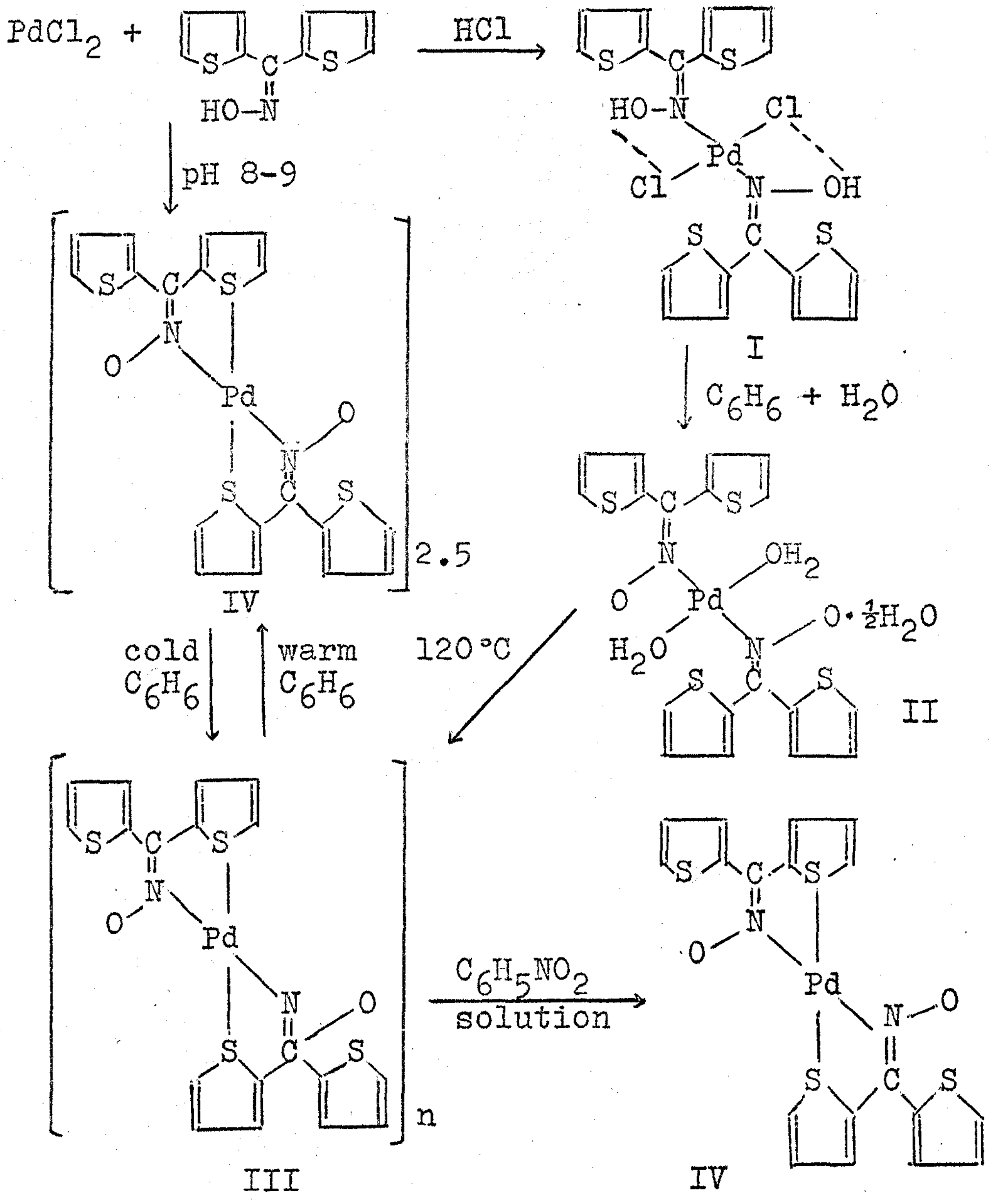

FIGURE 1

A SCHEMATIC DIAGRAM OF THE REACTIONS FOR THE PREPARATION OF THE PALLADIUM-DI-2-THIENYLKETOXIME COMPLEXES AND THEIR INTERRELATIONSHIP

Complex I --- Dichlorobis(di-2-thienylketoxime-N,N') palladium (II)

Complex II -- Biaquobis(di-2-thienylketoxime-N,N') palladium (II) Half Hydrate

Complexes III and IV --- Polymeric forms of the chelate bis(di-2-thienylketoxime)palladium (II) separated which were filtered under suction and air dried. There was obtained 10.3 gm, 86% yield, of white needles, m.p. 134-136°C. Analytical calculation for $C_9H_7NOS_2$: C, 51.63; H, 3.37; N, 6.69. Found:[10] C, 51.56; H, 3.46; N, 6.55.

Preparation and Study of Complex I
Dichlorobis(di-2-thienylketoxime-N,N')palladium (II)

To a 400 ml beaker was added 1.0 gm of di-2-thienylketoxime, 50 ml of alcohol, and 4.2 ml of concentrated hydrochloric acid. A solution of 0.40 gm of anhydrous palladium (II) chloride in 5 ml of concentrated hydrochloric acid was prepared in a 100 ml beaker by warming on a hot plate. To the palladium (II) chloride solution was added 50 ml of water and the pH was adjusted to zero by dropwise addition of a concentrated potassium hydroxide solution. The palladium (II) chloride solution and 100 ml of 1 N hydrochloric acid were added with stirring to the oxime solution. After standing the solution for 1 hour the yellow precipitate was filtered under suction and air dried. There was obtained 1.30 gm, 93% yield, of yellow crystals, m.p. 212-214°C with decomposition. Analytical calculation for $PdC_{18}H_{14}Cl_2N_2O_2S_4$: Pd, 17.85; N, 4.70; Cl, 11.87. Found:* Pd, 17.85; N, 4.58; Cl, 11.85.

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[10] Analysis of C, H, N, Cl were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

* The percentage of palladium in the complex was determined gravimetrically. The crucible containing the complex was put on a hot plate until the complex decomposed. Then all organic matters were got rid of by strongly igniting the crucible. A few drops of formic acid were added to eliminate any palladium (II) oxide formed.

Regeneration of Di-2-thienylketoxime from Complex I

To a 250 ml separatory funnel was added 0.3 gm of complex I, 50 ml of acetone, 50 ml of chloroform, and 50 ml of concentrated hydrochloric acid. On shaking the mixture for three minutes, the solid went into solution and the chloroform layer became colored a pale yellow. The chloroform layer was withdrawn, washed first with a solution of 50 ml of acetone and 50 ml of concentrated hydrochloric acid, then four times with 50 ml portion of water, dried over anhydrous sodium sulfate, and filtered. On evaporation of the chloroform there was obtained a colorless, crystalline residue amounting to 0.22 gm, 100% yield, m.p. 133-136°C. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133-136°C.

Preparation and Study of Complex II
Biaquobis(di-2-thienylketoxime-N,N')palladium (II) Half Hydrate

To a 250 ml separatory funnel were added 1.33 gm of complex I, 50 ml of benzene, 50 ml of acetone, and 50 ml water. The mixture was shaken for 10 minutes, at the end of which time all the solid had gone into solution to give a dark red-brown benzene layer. The benzene layer was washed with seventeen 50 ml portions of water and allowed to stand overnight. The yellow crystalline precipitate was filtered under suction and dried in vacuo over anhydrous calcium sulfate. The residue amounted to 0.80 gm, 63% yield, m.p. 185-188°C with decomposition. Analytical calculation for $PdC_{18}H_{14}N_2O_2S_4 \cdot 2\frac{1}{2}\ H_2O$; Pd, 18.73; H_2O, 7.93. Found: Pd[11],18.77; H_2O,8.06.

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[11] Percentage of palladium was determined gravimetrically.

The above procedure was repeated with 0.7221 gm of complex I. The combined water washings were titrated with 0.102 N NaOH using phenolphthalein as indicator.

Calculation for $PdC_{18}H_{14}Cl_2N_2S_4$: HCl, 12.18. Found: HCl, 12.14.

Regeneration of Di-2-thienylketoxime from Complex II

The procedure used for the regeneration of the ketoxime from complex I was followed with 0.15 gm of complex II. There was obtained 0.11 gm, 93% yield, of a crystalline residue, m.p. 133-136°C. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133-136°C.

Preparation and Study of Complex III
Bis(di-2-thienylketoxime)palladium (II) High Polymer

On heating complex II at 120°C for 3 hours, there was obtained a yellow-brown residue, m.p. 187-190°C with decomposition. Analytical calculation for $PdC_{18}H_{12}N_2O_2S_4$: Pd, 20.35; N, 5.36. Found:[12] Pd, 20.38; N, 5.46.

Ultraviolet absorption measurements for complex III in chloroform were undertaken. The Beckman DU Model Spectrophotometer was employed. In 100 ml of $CHCl_3$ was dissolved 0.0208 gm of complex III. Ten ml of this solution was diluted to 100 ml with $CHCl_3$ and measurements were taken with 0.5 cm cells. Experimental results (Fig. 3 and Table 1) showed that λ_{max} (the maximum wavelength) was 288 mu. $E_{1cm}^{1\%}$ (molar extinction) was calculated to be 547.

Complex III was then treated as follows. Approximately 100 mg of complex III was placed in a 100 ml beaker.

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[12] Percentage of palladium was determined gravimetrically.

TABLE 1

ULTRAVIOLET ABSORPTION MEASUREMENTS OF COMPLEX III IN CHLOROFORM

Wavelength mu	Absorbance	Wavelength mu	Absorbance
245	0.420	295	0.563
250	0.450	300	0.550
260	0.482	305	0.540
265	0.511	310	0.540
270	0.536	315	0.540
275	0.552	320	0.534
278	0.560	325	0.508
280	0.560	330	0.480
282	0.565	340	0.440
284	0.569	350	0.282
286	0.569	360	0.195
288	0.569	370	0.137
290	0.569	380	0.105
292	0.569		

To the beaker was added 20 ml of benzene and the mixture was brought to boil on a hot plate. The solution was filtered and the filtrate evaporated to dryness on top of an oven. A brown residue was obtained. A portion of the residue was used for an ultraviolet absorption measurements. This material in chloroform gave an ultraviolet absorption spectrum identical with that obtained with complex IV: λ_{max} 284 mu; $E^{1\%}_{1cm}$ 509 (Fig.3, Table 2 and 4).

Other properties of the above compounds measured were infrared spectra, molecular weights and dipole moments. The conclusions arrived at from these measurements are given in the discussion.

A cyroscopic molecular weight determination of complex III in nitrobenzene was undertaken. The molecular weight was calculated with the formula: M.W. = $\frac{1000K_f g}{G\Delta T_f}$[13]

The freezing point constant, K_f, was determined experimentally to be 6.94; ΔT_f, the observed depression of freezing point caused by the addition of g gm (0.1141 gm) of complex III to G gm (18.59 gm) of nitrobenzene was 0.08°.

Therefore, the molecular weight

$$= \frac{1000K_f g}{G\Delta T_f}$$

$$= \frac{1000 \times 6.94 \times 0.1141}{18.59 \times 0.08}$$

$$= 533.$$

The calculated value for the monomer of complex IV is 523. Evaporation of the nitrobenzene on a steam bath under an air current gave a dark brown solid residue of complex IV.

A dipole moment measurement of complex III in carbon

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[13] F. Daniels, J.H. Mathews, *et al.*, *Experimental Physical Chemistry*, 5th ed., London: McGraw Hill Company, Inc., (1956) p.65

TABLE 2

ULTRAVIOLET ABSORPTION MEASUREMENTS OF THE RESIDUE FROM THE BENZENE SOLUTION OF COMPLEX III

Wavelength mu	Absorbance	Wavelength mu	Absorbance
250	0.360	284	0.450
255	0.372	286	0.450
260	0.395	288	0.450
265	0.415	290	0.450
270	0.431	295	0.443
275	0.443	300	0.431
278	0.450	310	0.410
280	0.450	320	0.393
282	0.450		

tetrachloride solution was undertaken. The formula of Jensen,[14] $P_m = \frac{900}{C} \left(\frac{\varepsilon \text{ solution} - 1}{\varepsilon \text{ solution} + 2} - \frac{\varepsilon \text{ solvent} - 1}{\varepsilon \text{ solvent} + 2} \right)$, was used for the determination of P_m, the molar polarization, where C was the molar concentration and ε, the value of dielectric constant. The dipole moment, u, was then calculated with the formula, $u = 0.01273\sqrt{P_m T}$ where T was the absolute temperature.

The instrument used was the Sargent Oscillometer. The operation instructions given by Sherrick[15] for oscillometry were followed.The instrument was calibrated with toluene, benzene and carbon tetrachloride. Results are shown in Table 3 and Fig. 2.

A 0.00283 molar solution of complex III in carbon tetrachloride was prepared and the reading of instrument division for this solution determined to be 27,793 at 27°C. A rise of 210 instrument division in Fig. 2 corresponded to a change of 0.0125 dielectric constant unit. A difference of 27793 - 27770 = 23 in instrument division corresponded to a change of 23/210 x 0.0125 = 0.0014 dielectric constant unit. The dielectric constant of the carbon tetrachloride solution of complex III was then 2.226 + 0.0014 = 2.227. Therefore, the molar polarization,

$$P_m = \frac{900}{C} \left(\frac{\varepsilon \text{ solution} - 1}{\varepsilon \text{ solution} + 2} - \frac{\varepsilon \text{ solvent} - 1}{\varepsilon \text{ solvent} + 2} \right)$$

$$= \frac{900}{0.00283} \left(\frac{2.227 - 1}{2.227 + 2} - \frac{2.226 - 1}{2.226 + 2} \right)$$

$$= \frac{900}{0.00283} \times 0.00018 = 57.$$

---

[14] K.A. Jensen, Acta Chem. Scand., 3, 479 (1949).

[15] P.H. Sherrick, G.A. Dawe, et al., Manual of Chemical Oscillometry, Chicago: E.H. Sargent & Co. (1954).

TABLE 3

CALIBRATION OF OSCILLOMETER
(DETERMINATION OF DIPOLE MOMENT OF COMPLEX III)

Solvent	Instrument Division	Dielectric Constant at 27°C
Toluene	30,379	2.377
Benzene	28,583	2.272
Carbon tetrachloride	27,770	2.226

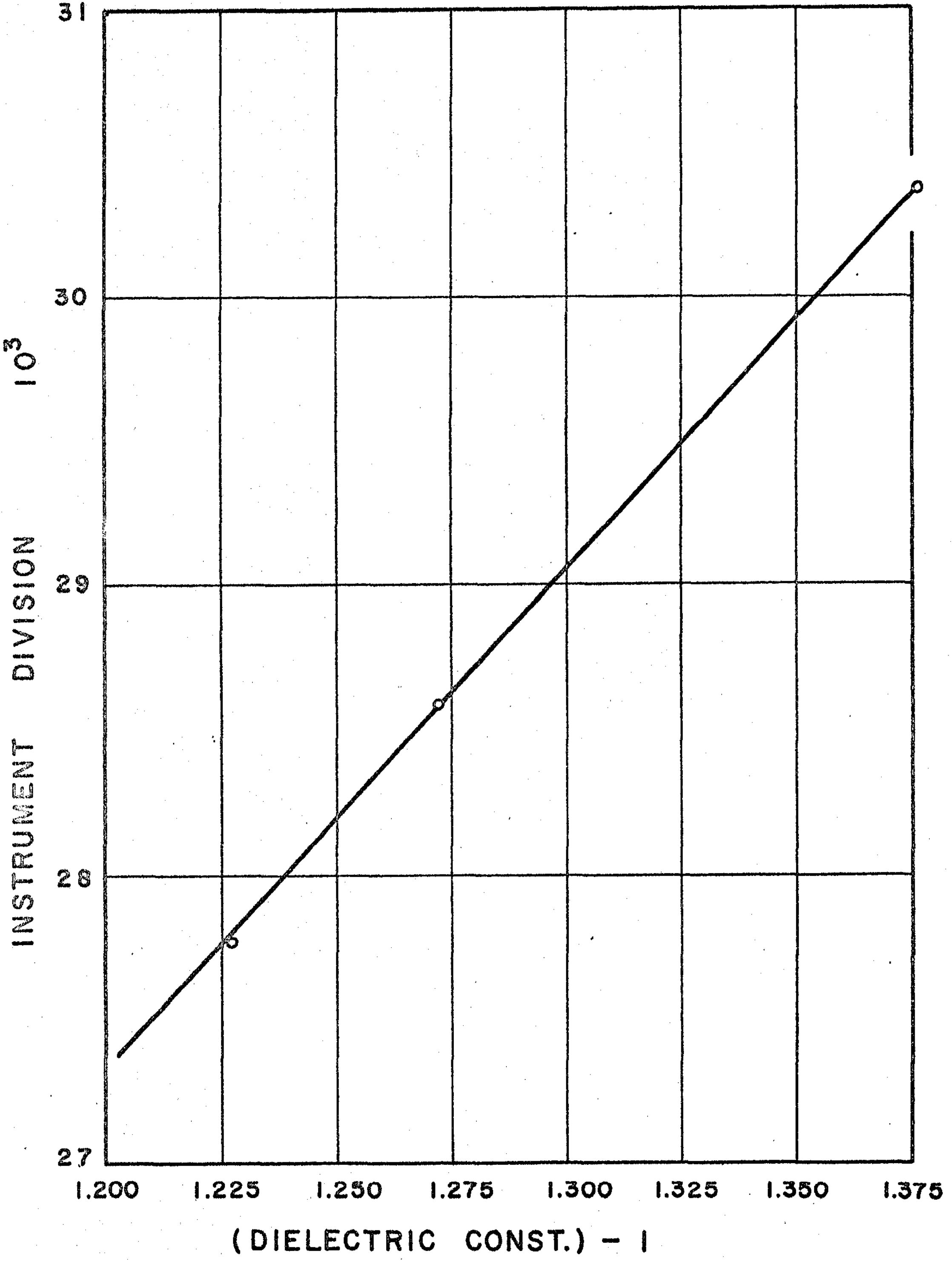

FIG. 2 CALIBRATION OF OSCILLOMETER (DETERMINATION OF DIPOLE MOMENT OF COMPLEX III)

The dielectric constant of complex III was calculated.

$$\begin{aligned} u &= 0.01273\sqrt{P_mT} \\ &= 0.01273\sqrt{57 \times 300} \\ &= 1.67 \text{ D.} \end{aligned}$$

Regeneration of Di-2-thienylketoxime from Complex III

The procedure used for the regeneration of the ketoxime from complex I was followed with 0.15 gm of complex III. There was obtained 0.12 gm; 100% yield, of a crystalline residue, m.p. 133-136°C. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133-136°C.

Preparation and Study of Complex IV
Bis(di-2-thienylketoxime)palladium (II) Low Polymer.

To a beaker was added 1.1 gm of di-2-thienylketoxime, 5 ml of a saturated solution of potassium hydroxide, and 1500 ml of water. The pH of the solution was adjusted to 6.9 by the addition of hydrochloric acid. A solution of 0.4 gm of palladium (II) chloride was prepared in 5 ml of concentrated hydrochloric acid with warming and diluted to 75 ml with water. The pH of the palladium (II) chloride solution was adjusted to 6.2 by the addition of potassium hydroxide solution and the solution diluted to 100 ml. To the boiling ketoxime solution was added alternately 2.0 ml of the palladium (II) chloride solution and 0.70 ml of 0.1024 N sodium hydroxide with vigorous stirring. When all the palladium (II) chloride and a total of 35.0 ml of the sodium hydroxide solution had been added, the reaction mixture was cooled to room temperature. The dark brown precipitate was filtered under suction and air dried. The dried residue was dissolved in benzene and filtered from a small amount of palladium (II) oxide. After evaporation of the benzene the residue was suspended in alcohol overnight to remove any unreacted ketoxime. The suspended chelate was filtered under suction and air dried. There was obtained 0.75 gm of complex IV, m.p. 175-185°C with decomposition. Analytical calculation for $Pd_{18}H_{12}N_2O_2S_4$: Pd, 20.35; N, 5.36. Found: Pd,[16] 20.39; N, 5.44.

Ultraviolet absorption measurements of complex IV in chloroform gave λ_{max} 284 (Fig. 3 and Table 4). The Beckman DU Model Spectrophotometer was employed. In 100 ml of $CHCl_3$ was dissolved 0.0185 gm of complex IV. Ten ml of this solution was diluted to 100 ml with $CHCl_3$ and measurements were taken with 0.5 cm cells. $E^{1\%}_{1cm}$ was calculated to be 509.

A dipole moment measurement of complex IV in carbon tetrachloride was undertaken. The Sargent Oscillometer was used. It was calibrated with toluene, benzene and carbon tetrachloride. Results are shown in Table 5 and Fig. 4. A 0.00352 molar solution of complex IV in carbon tetrachloride was prepared and the reading of instrument division of this solution determined to be 28,160 at 27°C. A rise of 220 instrument divisions in Fig. 4 corresponded to a change of 0.0125 dielectric constant unit. A difference of 28,160 - 28,100 = 60 in instrument divisions corresponded to a change of 60/220 x 0.0125 = 0.0034 dielectric constant unit. The dielectric constant of the carbon tetrachloride solution of complex IV was then 2.226 + 0.0034 = 2.229. The molar polarization, P_m, was calculated in the same manner as for complex III to be 128. Similarly, the dielectric constant of complex IV was calculated: u = 2.5 D.

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[16] Percentage of palladium was determined gravimetrically.

TABLE 4

ULTRAVIOLET ABSORPTION MEASUREMENTS OF COMPLEX IV IN CHLOROFORM

Wavelength mu	Absorbance	Wavelength mu	Absorbance
250	0.385	284	0.473
255	0.398	286	0.473
260	0.420	288	0.473
265	0.439	290	0.473
270	0.452	295	0.470
278	0.468	300	0.458
280	0.473	310	0.440
282	0.473	320	0.420

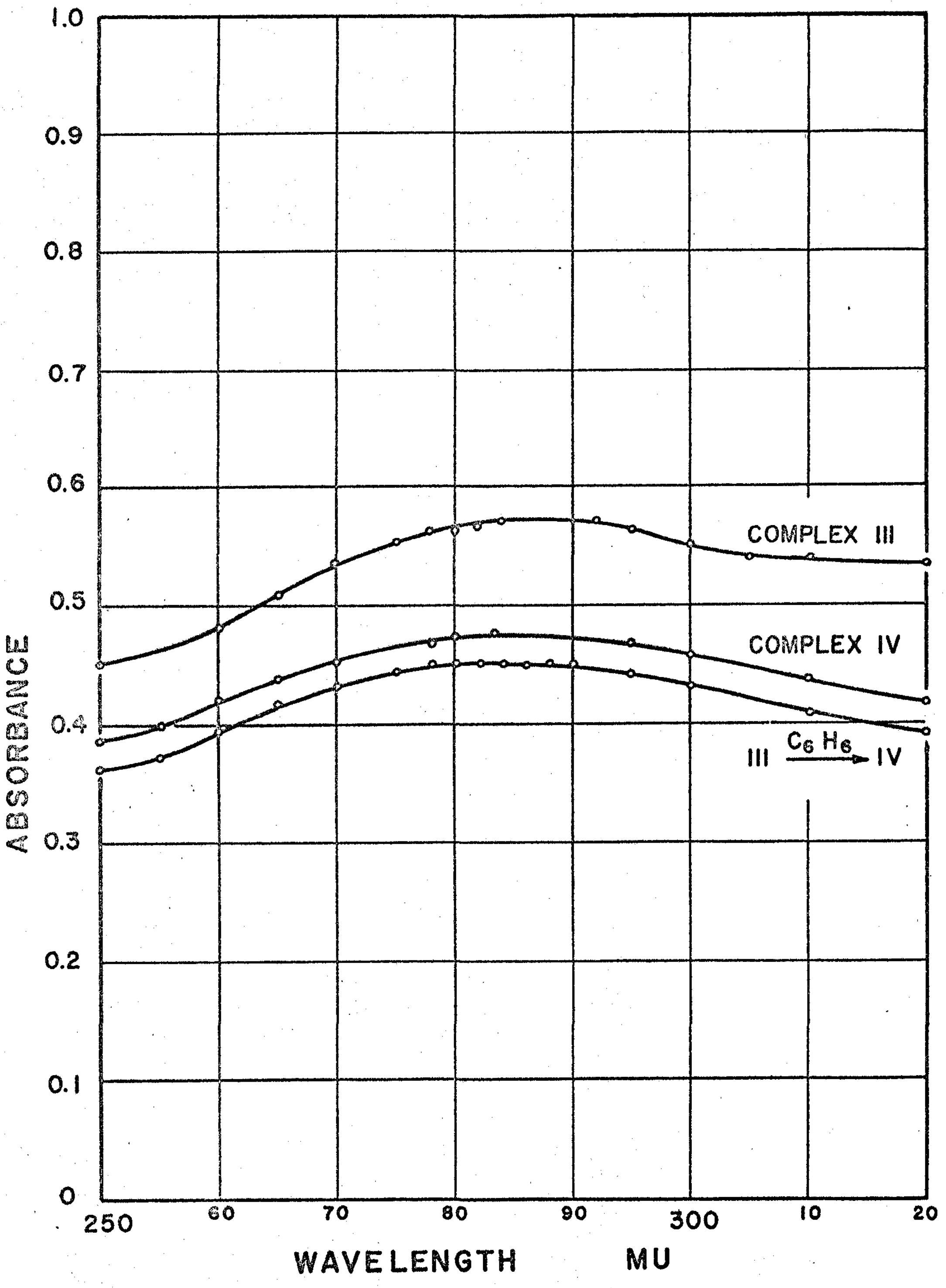

FIG. 3 ULTRAVIOLET SPECTRA OF COMPLEX III, COMPLEX IV, & RESIDUE FROM THE BENZENE SOLUTION OF COMPLEX III

TABLE 5

CALIBRATION OF OSCILLOMETER
(DETERMINATION OF DIPOLE MOMENT OF COMPLEX IV)

Solvent	Instrument Division	Dielectric Constant at 27°C
Toluene	30,833	2.377
Benzene	29,020	2.272
Carbon tetrachloride	28,100	2.226

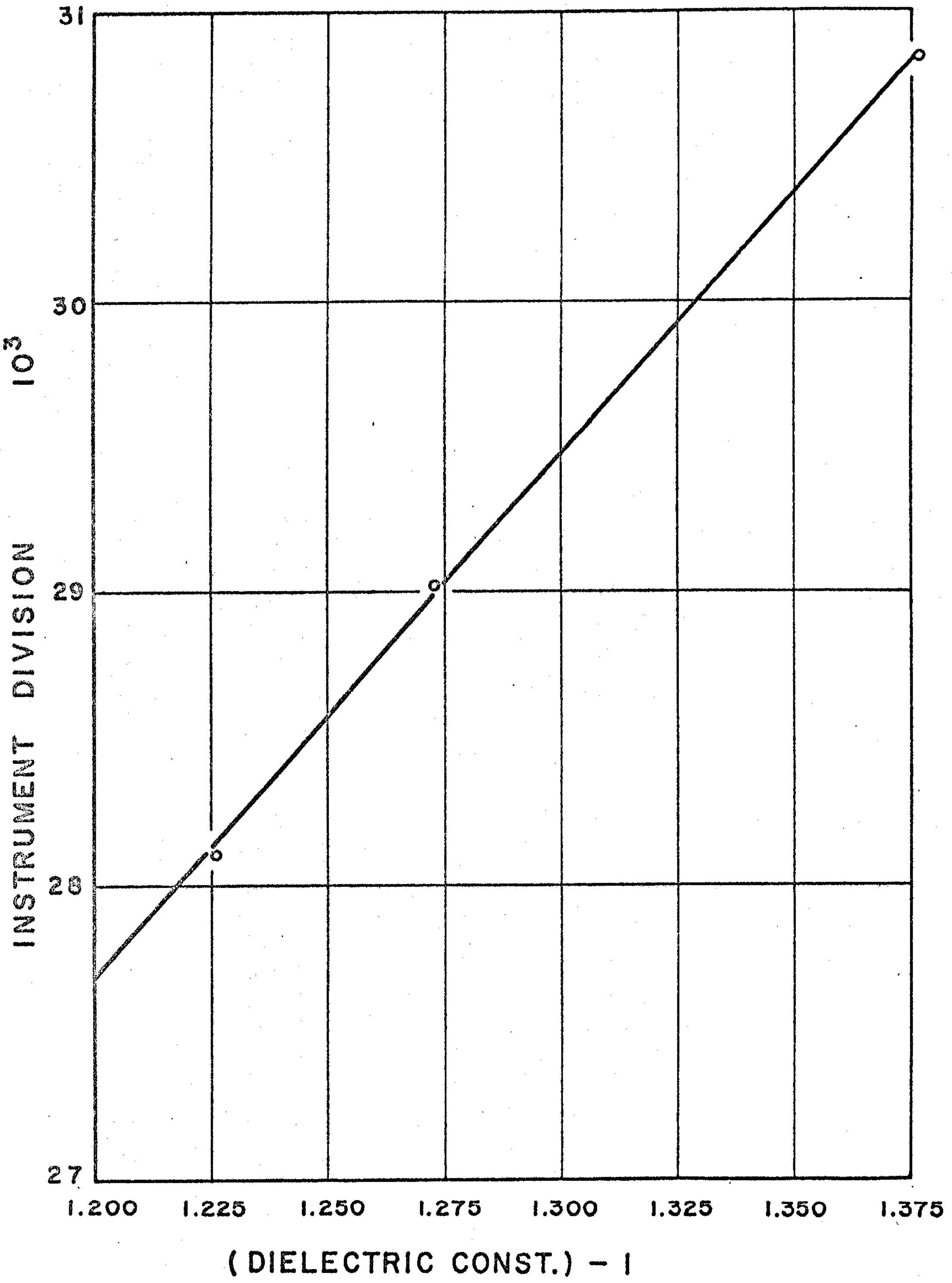

FIG. 4 CALIBRATION OF OSCILLOMETER (DETERMINATION OF DIPOLE MOMENT OF COMPLEX IV)

A cyroscopic molecular weight determination of complex IV in nitrobenzene was undertaken. A depression of freezing point of 0.48° was observed when 0.6934 gm of complex IV was dissolved in 19.27 gm of nitrobenzene. The molecular weight of complex IV in nitrobenzene was calculated in the same manner as for complex III to be 519.

The calculated value for the monomer is 523. A similar determination in benzene gave a value of 1290. On standing, the cold benzene solution deposited yellow crystals of complex III, m.p. 185-190°C with decomposition. The value 1290 corresponds to an average degree of polymerization of 2.5 for complex IV.

Regeneration of Di-2-thienylketoxime from Complex IV

The procedure used for the regeneration of the ketoxime from complex I was followed with 0.15 gm of complex IV. There was obtained 0.07 gm, 60% yield, of a crystalline residue, m.p. 133-136°C. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133-136°C.

CHAPTER III

DISCUSSION

In the present work di-2-thienylketoxime was found to form either a complex or a chelate with bivalent palladium, depending on the pH of the reaction medium. In 2 N hydrochloric acid a small amount of the complex (I) formed and the major part of the reagent was recovered. In 1 N acid solution an almost quantitative yield of the complex (I) was obtained, while in neutral or slightly basic solution there was a good yield of the chelate IV. In moderately acid solution in the pH range 1 to 6, mixture of I and IV formed. A schematic diagram of the reactions for the preparation of the Pd-di-2-thienylketoxime complexes and their interrelationship is shown in Fig. 1.

The complex (I) is a pale yellow crystalline solid insoluble in water and slightly soluble in benzene and chloroform, while the chelate (IV) is a dark brown solid insoluble in water and very soluble in benzene and chloroform, giving dark red-brown solutions.

When the complex (I) was treated with a mixture of benzene and water, hydrogen chloride was eliminated quantitatively as was shown by titration of the water layer with standard base. On standing, the benzene layer deposited a yellow crystalline solid which at 120°C lost $2\frac{1}{2}$ moles of water to give a light brown solid of complex (III), insoluble in water and slightly soluble in benzene and chloroform.

In alcoholic silver nitrate solution complex (I) gave no immediate precipitate, but on standing, the solution became turbid and silver chloride began to precipitate. This indicates that the chlorine atoms are bound covalently to the palladium. Analysis of complex(I) showed that two molecules of the ketoxime and two atoms of chlorine are associated with each palladium atom. Palladium therefore has a coordination number of four. This is to be expected since the existence of palladium (II) compounds with a coordination number greater than four has never been convincingly demonstrated.[17] Although there is no experimental evidence to indicate whether coordination is with the nitrogen of the oxime group rather than with the sulphur of the thiophene ring, nevertheless the coordinating ability of the oxime group and the very strong donor properties of the oxime nitrogen are very well known.[18] Further, one would expect the donor ability of the sulphur to be decreased because of resonance with the unsaturated ring.

Magnetic susceptibility[19] measurements showed complexes(I)and(II)to be diamagnetic. The complex(I) therefore is considered to be planar rather than tetrahedral. This is in accord with the fact that no tetrahedral structure for palladium (II) complexes has yet been identified positively, unless, of course, it is sterically impossible for the compound to assume a planar configuration. Also coordination theory predicts a planar configuration for ions such as bivalent palladium which have one d-orbital available for bond formation. In such a situation dsp^2 hybridization occurs and a square planar structure results.

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[17] A. Martell and M. Calvin, Chemistry of the Metal Chelate Compounds, New Jersey: Prentice Hall Inc., (1959).

[18] J.C. Bailar, Chemistry of Coordination Compounds, New York: Reinhold Publishing Corp., (1956).

[19] Magnetic susceptibility measurements were carried out by Graduate School of Wayne State University, (Chemistry), Detroit, Michigan.

The postulated hydrogen bonding for complex (I) eliminated the possibility of cis-trans isomerism. Such bonding would give rise to a more stable structure, since it has long been observed that an increase in the number of rings within a particular complex structure results in greater stability.[20] Such a postulated bonding has precedent in the literature. For example, Brady and Muers[21] proposed such bonding in their study of the nickel derivatives of biacetyl dioxime. That the complex (I) exists in the trans form is borne out by the facile elimination of hydrogen chloride. The ease of such elimination indicates that the hydrogen and chlorine atoms are adjacent to each other, whereas a cis configuration would place them on opposite sides of the molecule. Further, molecular models reveal that a cis configuration would be more strained than a trans configuration. Infrared spectra of complex (I) indicate hydrogen bonding. Such spectra reveal no hydroxyl band present in the region 3400-3700 cm^{-1}, but do show a very broad band at 3100 cm^{-1}. Thus, the hydroxyl group band has been shifted considerably to a lower frequency. Such a shift is considered evidence for strong intramolecular bonding.

The structure shown for the hydrate (II) is based on the analysis and the course of the reaction used in its preparation. Thus, on shaking complex (I) in a mixture of benzene and water the benzene layer becomes colored a dark red-brown and hydrogen chloride is produced in the water layer. The color of the benzene layer indicates that a chelate has formed. On standing, the color disappears

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20 M. Calvin and R.H. Bailes, <u>J. Am. Chem. Soc.</u>, <u>68</u>, 949 (1946).

21. O.L. Brady and M.M. Muers, <u>J. Chem. Soc.</u>, (1930) 1599.

and a yellow crystalline precipitate forms. This is interpreted as being due to a displacement of the palladium-sulphur bond in the chelate with formation of a complex in which water molecules are coordinately bonded to palladium. Molecular models reveal that the two water molecules must be trans since a cis configuration would impart a large strain. The remaining one-half water molecule is considered to be involved in crystal formation.

The structure assigned to complex (III) is based on the analysis and on molecular weight determinations of complexes(III)and(IV).Thus complex (IV) in freezing benzene gave a molecular weight corresponding to that of a low polymer of complex(IV),the average degree of polymerization being 2.5. On standing, the cold benzene solution deposited a yellow-brown solid with the same melting point as III. Thus IV is converted to III from cold benzene solution. This indicates that III is a polymer of IV. No direct molecular weight determination of complex(III)could be carried out in benzene owing to its insolubility in this solvent. On suspending complex(III)in boiling benzene and allowing the solvent to evaporate at 50°C complex(IV) was obtained. Thus in hot benzene complex(III)is reconverted to complex (IV). In freezing nitrobenzene complex (III) gave a molecular weight corresponding to that of a monomer of complex (IV). On evaporation of the nitrobenzene a dark brown residue of complex (IV) was obtained. Substance (III) is thus converted to a low polymer of complex (IV) from warm nitrobenzene.

The analyses of complexes (III) and (IV) showed these sustances to be isomeric. That III and IV are not simply dimorphic is borne out by an examination of their ultraviolet absorption spectra in chloroform solution. Small, but definite, differences in their spectra were found. (Fig. 3)

The possibility of complexes (III) and (IV) being cis-trans isomers was eliminated by dipole moment measurements in carbon tetrachloride solution. The moments of complexes (III) and (IV) were 1.8 and 2.6 D respectively. If complex (IV) were a cis isomer the dipole moment would be expected to be much higher. Also a cis configuration for complex (IV) would mean that the two negatively charged oxygens of the nitrone groups would be adjacent to one another. It is highly unlikely that such a separation of like charges would take place since the resulting compound would be highly unstable.

The assignment of the chelate structure to IV is based on the analysis and on its solubility in benzene or chloroform to give highly colored solutions. Molecular weight determination in benzene indicates that complex(IV) is a low polymer of the structure shown. Similar determination in nitrobenzene reveals complex (IV) as the monomer in this solvent. That the structure contains two nitrone groups is inferred by reference to the studies made by Pfeiffer[22] on the nickel dimethylglyoxime chelate. In this case the author showed that a covalent linkage exists between nitrogen and the metal rather than between oxygen and the metal.

Finally, that the ketoxime reagent undergoes no change in structure is shown by the fact that it could be readily regenerated in high yield from each of complexes (I), (II), (III), and (IV) by treatment with strong hydrochloric acid solution.

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[22] P. Pfeiffer, Ber., 63, 1811(1930).

PART II

NEPHELOMETRIC DETERMINATION OF PALLADIUM (II)
WITH
DI-2-THIENYLKETOXIME

CHAPTER I

INTRODUCTION

The investigation of the complex formation between the palladium (II) ion and di-2-thienylketoxime was described in Part I of this paper. Further investigation of the complex formation between bivalent palladium and di-2-thienylketoxime showed the possibility of its application as an analytical reagent. The purpose of the present work was to develop a rapid nephelometric method for the determination of microgram quantities of palladium (II) with di-2-thienylketoxime.

Of the several methods generally recommended for the determination of microgram quantities of palladium, as indicated by Beamish and McBryde,[23] the most sensitive colorimetric reagent is *p*-nitrosodiphenylaniline. Yoe and Kirkland[24] described a method in which palladium was determined with *p*-nitrosodiphenylamine after the separation of the palladium from most of the platinum group metals by extraction of the diethyldithiocarbamate salts of these metals.

Reed and Banks[25] used α-furildioxime and Trandon Bhattacharya[26] used 2-thienyl-trans-aldoxime for the

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[23] F.E. Beamish and W.A.E. McBryde, *Anal. Chim. Acta*, *9*, 349 (1953).

[24] J.H. Yoe and J.M. Kirkland, *Anal. Chem.*, *26*, 1335 (1954).

[25] S.A. Reed and C.V. Banks, *Proc. Iowa Acad. Sci.*, *55*, 267 (1948).

[26] S.G.Trandon and S.C. Bhattacharya, *Anal. Chem.*, *32*, 194 (1960).

gravimetric estimation of palladium while Meins and Rains[27] applied α-furildioxime colorimetrically. However, it was thought desirable to attempt to develop a rapid photometric procedure for palladium which could compare favorably in accuracy with the more complicated and time-consuming gravimetric and volummetric procedures and also be simpler than the usual colorimetric procedures which require separations of the complexes formed into an organic phase before determination.

Di-2-thienylketoxime in ethanol solution reacts with microgram quantities of palladium (II) as chloride in acidic solution to form a slightly yellowish colloidal dispersion showing that the reagent can be applied for nephelometric determination of microgram quantities of palladium (II). The reagent is stable to heat, light and air and can be preserved indefinitely either as such or in ethanol solution. The reaction between the palladium (II) ion and di-2-thienylketoxime in ethanol solution was then investigated to determine such factors as optimum concentration of reagents, effect of time of standing, pH, temperature, stabilizing reagents and effects of various concentration of other ions on the reaction.

Experimental investigations were carried out with a Fisher Nefluoro-Photometer using suitable filters. A standard nephelometric procedure was consequently developed for the determination of palladium (II) of concentration over the range from 0.04 to 0.25 mg in a 50 ml solution.

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[27] O. Menis and T.C. Rains, Anal. Chem., 27, 1932 (1955).

CHAPTER II

THEORY

Nephelometry and turbidimetry as quantitative evaluating techniques are over a hundred years old. The oldest method of measuring turbidity was by means of extinction criterion. This method is an obvious outgrowth of the simple observation of objects beneath the surface of the sea, sticking a platinum wire into a piece of wood and lowering it into sewage until it vanished. This method has become now a standard method of water analysis. Smokes much over 100γ per liter coagulate rapidly. Direct weighing is too time-consuming and tidious. Optical effect of smokes was first noted by M. Faraday[28] and studied by J. Tyndall,[29] yielding a rapid and sensitive measure of the concentration of the colloidal system.

The earliest procedure involved making direct visual comparison between two specimens or between a specimen and a standard material. Developments in instrumentation and elimination of systematic errors made it possible to achieve high precision for analytical purposes. 30,31,32,33,34,35,36,37,38.

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[28] M. Faraday, <u>Proc. Roy. Soc. (London)</u>, <u>6</u>, 356 (1857).

[29] J. Tyndall, <u>Phil. Mag.</u>, <u>4</u>, 37,384 (1869).

[30] J.H. Yoe, <u>Photometric Chemical Anaylsis, Vol. II</u>, <u>Nephelometry</u>, New York: John Wiley and Son (1929).

[31] P.V. Wells, <u>Chem. Reviews</u>, <u>3</u>, 331-381 (1927).

[32] R.H. Muller, <u>Ind. Eng.Chem.</u>, <u>Anal. Ed.</u>, <u>11</u>, 1 (1939).

In turbidimetry and nephelometry, the substances to be determined are converted to insoluble compounds or complexes which are uniformly dispersed through the solution, i.e., a suspension having suitably reproducible optical properties. The transmission of light through fluid media is effected not only by light-absorbing (colored) material but also by light scattering or light obstructing particles such as suspended particles of insoluble substances. The light emergent from a turbid medium is less intense than the incident light because of two effects, the absorption of and subsequent transformation into heat of light rays by the suspended particles and reflection and refraction of the light in all direction by the suspended particles. Analytical procedures have been devised which employ measurements of the intensity of the transmitted light or of the scattered (Tyndall) light. Turbidimetric measurements are usually made by measuring the light absorbed or transmitted. In nephelometry, the light reflected or scattered by the particles in the illuminated suspension is compared with that reflected or scattered by a standard suspension similarly prepared and illuminated.

The instruments in these procedures are given names which indicate how the measurements are made.

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[33] M.G. Tsyurupa and V.M. Peshkava, *Vestnik Moskov. Univ., Ser. Mat., Mekh., Astron., Fiz., Khim.*, *13(6)*, 165-170 (1958).

[34] R.B. Barnes and C.R. Stock, *Anal. Chem.*, *21*, 181 (1949).

[35] J.E. Land, *J. Chem. Ed.*, *34*, 38 (1957).

[36] Shigeo Moriyo, (Research Inst. Japan, Tokyo.) *Tanken*, *9*, 226-232 (1958).

[37] H.E. Rose, *J. Soc. Chem. Ind. (London)*, *69*, 266-272 (1950).

[38] J.H.T. Ledrut, *Pharm.France*, *4*, 95-100 (1957-1958).

Tyndallmeters are used to measure the Tyndall ratio; or ratio of the intensity of the Tyndall light to the intensity of the incident light. Nephelometers are used in procedures where the intensity of the scattered light from a sample solution is compared directly with that from a solution of known concentration. In both of these the measurements are made on the light scattered at right angles to the incident light. Turbidimeters measure the intensity of the emergent light in the direction of the incident light. One type of turbidimeters measures the ratio of the intensity of the emergent light as compared with the intensity of the incident light. Another measures the depth of turbid fluid necessary to cause a target to disappear (extinction effect). For measurements at very low turbidity, the method making use of the Tyndall ratio are most sensitive. The transmission effect is most commonly used for intermediate turbidities, and the extinction effect is most satisfactory for work on liquids with the greatest turbidities.

The theory of the scattering of light of very small particles was given by Lord Rayleigh[39] who showed that the intensity of the scattered light varies inversely as the fourth power of the wavelength. For particles which are not small as compared with the wavelength and when the medium is densely filled with particles, the secondary scattering becomes of importance and has to be taken into consideration.

One of the difficult aspects of nephelometry and turbidimetry is that of obtaining reproducible particle size in the dispersions. Careful investigations of the procedures must be made to determine the correct techniques used in any nephelometric and turbidimetric

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[39] J.W. Strutt (Lord Rayleigh), Phil. Mag., 41, 107 (1871).

procedure. Extreme care must be exercised in following prescribed conditions and work must be methodically carried out so that suspensions are prepared under identical conditions.

In order to have reproducible suspensions, the precipitates should be very fine so that they do not settle rapidly. Several conditions must be carefully controlled in order to obtain suspensions of uniform nature. These include concentrations of reacting ions, ratio of concentration in the solutions which are mixed, time of mixing, manner and order of mixing, amount of other salts or protective colloids present, pH, and the temperature. The concentration of the substances being determined should be about 0.1 gm per liter. The precipitate should be amorphous since crystalline substances may settle rapidly. Protective colloids may be used to prevent coagulation and rapid settling of precipitates. Some of the protective colloids used are starch, gelatin, gum arabic, or gum tragacanth. According to Wells,[40] the ratio of the turbidities to be compared in nephelometric and turbidimetric procedures should not be greater than 1;4. Over a wide range of concentration, there may be a rather wide deviation from the Beer's Law, especially at higher concentration where secondary scattering effects become more pronounced.

In spite of all the adverse factors, nephelometry and turbidimetry present real possibility in analytical work. Once the limitations of such optical methods are understood, their application may be appreciated at their true work. The breadth of the field of application of these methods is suggested by the fact that in biochemistry, they are used in the analysis of blood, spinal fluid,

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[40] P.V. Wells, Chem. Reviews, 3, 331-381 (1927).

urine and proteins, in the standization of vaccines and in bacteria counting.[41] Such substances as phosphorus, ammonia, sulfates,[42] chlorine,[43,44,45,46,47] calcium,[48] nickel,[49] sodium,[50] fluorine,[51] tantalum,[52] fats, oils, acetone, amylase, mustard gas, nuclei acids, β-oxybutyric acid, purine, bases and trypen are among those listed by Yoe and Kleinmann[53] for which this type of determination can be made.

Usually, several choices of geometry can be made for measuring the light scattered by a material.

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[41] P.B. Hawk, B.L. Oser and W.H. Summerson, Practical Physiological Chemistry, 13th ed., New York: McGraw Hill Book Company, Inc., (1954) p.595.

[42] J.F. Boyd and J.W. Sommerville, J. Clin. Path., 13(1), 85-86 (1960).

[43] P. Litrinenko and M. Rozivskii, Gigiena i Sanit, (1954) No.1, 52-53.

[44] Y.Y. Lure and Z.V. Nikolaeva, Zavodskaya Lab., 12, 161 (1946).

[45] R.K. McAlpine, J. Am. Chem. Soc., 51, 1065 (1929).

[46] T.W. Richards, R.C. Wells, J. Am. Chem. Soc., 31, 235 (1904)

[47] R.C. Wells, J. Am. Chem. Soc., 35, 99 (1906).

[48] A. Saifer and F.D. Clark, Ind. Eng. Chem., Anal. Ed., 8, 248 (1936).

[49] R. Juza and R. Langheim, Angew Chem., 50, 255 (1937).

[50] F.K. Lindsay and D.G. Braithwaite and J.S. D'Aminco, Ind. Eng. Chem., Anal. Ed., 18, 101 (1946).

[51] R.E. Stevens, Ind. Eng. Chem., Anal Ed., 8, 248 (1936).

[52] R. Saint-James and T. Lecomte, Anal. Chim. Acta, 24, 155-160 (1961).

[53] J.H. Yoe, Photometric Chemical Analysis, Vol. II, Nephelometry, New York: John Wiley & Son, (1929).

Some designs involve reverse scattered light;[54] some scattering at right angles to incidence;[55,56,57] some at selected angles.[58,59,60,61]

In the present work, the scattering of light is measured at right angle to the incidence using the Fisher Nefluoro-Photometer. The transmittance of the Pd-di-2-thienylketoxime suspensions of known concentrations are determined and a calibration curve is constructed by plotting scale reading against concentration on regular graph paper. Then the transmittance of the unknown sample is measured and the concentration of the unknown sample read from the graph.

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[54] A.S.T.M., Committee 20, Subcommittee IV Report, Feb.17 (1942).

[55] H.P. Kortschak, Anal. Chem., 19, 692 (1947).

[56] A.J. Stamm and T. Svedberg, J. Am. Chem. Soc., 47, 1582(1925)

[57] N. Underwood and A.H. Doermann, Rev. Sci. Instruments, 18, 665 (1947).

[58] P.P. Debye, J. Applied Phys., 17, 392-398 (1946)

[59] B.M. Axilrod and G.M. Kline, J. Research Natl. Bur. Standards, 19, 356-400 (1937), Research Paper 1031.

[60] R.L. Libby, J. Immunol, 34, 401-71 (1938).

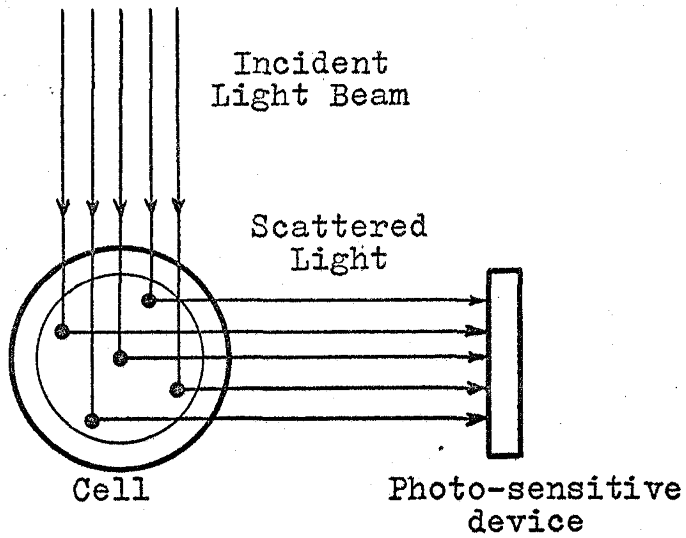
[61] L.A. Wagner, Proc. Am. Soc., Testing Materials Part II, 33, 553 (1933).

CHAPTER III

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

Apparatus

The apparatus used in the present work was the Fisher Nefluoro-Photometer.[62] The particles in suspension scatter the light of an incident beam by reflection and diffraction. The amount of light scattered is a function of the concentration of the particles. The scattered light is measured at right angles to the incident beam as illustrated in the diagram below.



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[62] Instruction Manual for Fisher Nefluoro-Photometer, New York: Fisher Scientific Co.

A schematic diagram of the optical system of the instrument is shown in Fig. 5.

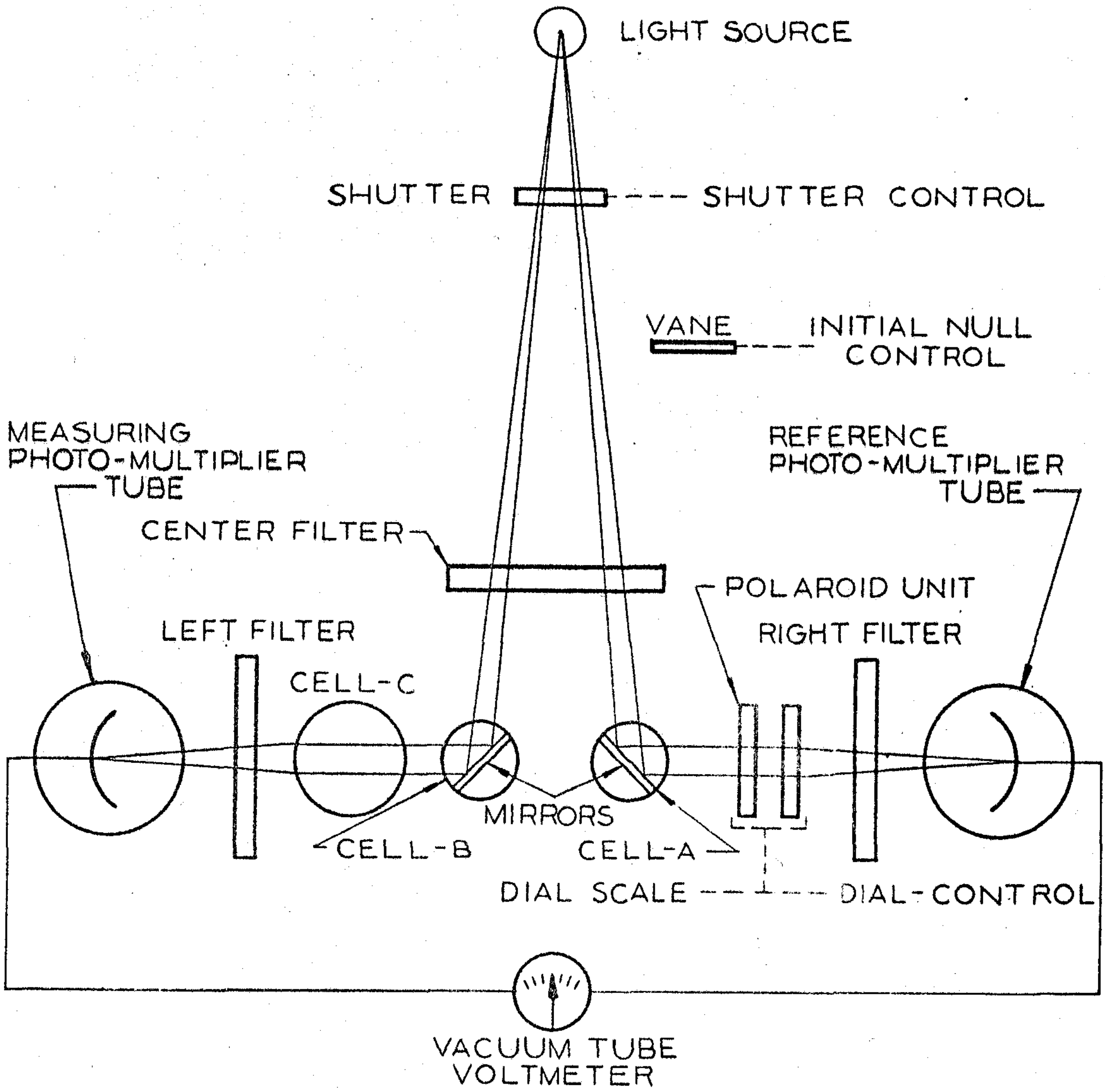

FIGURE 5

A SCHEMATIC DIAGRAM OF FISHER NEFLUORO-PHOTOMETER

The Nefluoro-Photometer is a null-reading instrument that employs two photosensitive detectors. The dashed lines in Fig.5 indicate mechanical connections between the components in the optical system and controls on the front panel. Incident light from the source is divided into two beams which pass through the shutter, the centre filter and then into cell A and cell B. In Fig. 5, mirrors are shown reflecting the light beams at right angles to their incident directions. The left beam passes through cell C, the left filter and strikes the measuring phototube. The right beam passes through the Polaroid Unit, the right filter and strikes the reference phototube. The electrical outputs of the two phototubes are compared in the electronic portion of the instrument and the difference is indicated on the meter on the front panel. The shutter is operated from the front panel and affords a means of interrupting the light beams.

The vane in the right beam is operated by the Initial Null Control. It is used to attenuate the light in the right beam so that an initial balance can be achieved at the start of the analysis.

The Polaroid Unit is a precision photometering device that attenuates the light in the right beam, so that the intensity of the light in the right beam can be made equal to the intensity of the light in the left beam which is scattered by the samples being measured. The Polaroid Unit is operated by the Dial Control. The control is also connected mechanically to the Dial Scale which indicates directly the scattering of light by the sample being measured.

The electronic portion of the instrument consists of the two photosensitive detectors, a vacumn tube voltmeter, and a regulated power supply. The two detectors are multiplier phototubes, capable of self-amplifications of the electric currents that are generated when their photosensitive surface are irradiated. The amount that the photoelectric current is amplified by a multiplier phototube can be controlled in this instrument, and therefore, the sensitivity of the multiplier phototubes as light detectors can be varied over a wide range by the operator.

The regulated power supply is compensated for variations in line voltage from 95-125 volts. It contains a constant voltage transformer that will operate on 60 cycle A.C. power only.

In the present work, the light source is a mercury arc lamp having its principle emission in the near ultraviolet range.

Filter arrangement:
Left filter - # 430+
Center filter - # 425
Right filter - # 430+

Reagents

Di-2-thienylketoxime

This reagent was synthesized according to the procedure in Part I of our studies. (Page 4)

Di-2-thienylketoxime Ethanol Solution

A 0.1% di-2-thienylketoxime solution in ethanol was prepared with 95% ethanol. This reagent is stable at room temperature and there is no chemical reaction between ethanol and di-2-thienylketoxime.

Palladium Standard Solution

A standard palladium (II) stock solution was prepared by dissolving a known amount of palladium (II) chloride in concentrated hydrochloric acid on a hot plate and then diluted to the corresponding volume with distilled water. Purified reagent grade palladium chloride from Fisher Scientific Company was used. This material was analysed gravimetrically by precipitation with dimethylglyoxime following the standard procedure. It was found that the reagent was 100% anhydrous palladium (II) chloride. The palladium content of the stock solution was established to contain 0.1 mg of palladium per ml. The other palladium standard solutions, which were used in this work, were prepared by appropriate dilution of aliquots of this stock solution with a buffer of pH 3.2.

Solutions of Diverse Ions

Reagent grade salts were employed in the preparation of solutions of inorganic ions. All interfering cations were added as chlorides. Sodium salts were used for anion studies.

Stabilizing Reagent

A 1% gelatin solution was used as stabilizing reagent. To 5 gm of granular gelatin were added 200 ml of distilled water and the mixture was heated on a steam bath with occasional stirring until dissolved and then diluted with distilled water to 500 ml to make a 1% solution. If the solution congeals on cooling, it should be warmed slightly until fluid. A fresh solution should be made every few days.

Experimental

Generator Solution

The function of the generating solution is to act as a source of light for the right beam in the instrument. The turbidity of the generating solution must be stable and constant, otherwise different readings will be resulted for solutions having the same turbidity but measured at different times. The generating solution used in the present work was prepared from pyrex glass following the procedure given by Fikhman.[63,64,65]

A glass stoppered pyrex reagent bottle of 1 litre capacity was filled to about one fourth its capacity with fragments of clean pyrex glass. Distilled water was poured over the glass fragments and the mixture was agitated vigorously on a mechanical shaker until a milky suspension was produced. (Eight to twenty hours is ordinarily sufficient.) The suspended glass was decanted into a 1000 ml cylinder and diluted to the mark with distilled water. The mixture was then shaken and allowed to stand for 14 days. The upper 500 ml was decanted to use as a stock standard.

Standard reference solutions used for comparison of relative turbidity in later part of the present work were also prepared by diluting this stock solution with distilled water to give the required appropriate turbidity.

Another alternative method was also employed.

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63 P.B. Hawk, P.B. Oser and W.H. Summerson, Practical Physiological Chemistry, 13th ed., New York: McGraw Hill Book Company, Inc., (1954) p.595

64 B.A. Fikhman, Lab. Delo, 4.(2), 53-55(1958).

65 B.A. Fikhman, USSR, 115,987, Nov22, (1958).

Finely divided silica powder of homogeneous particle size of 150 Å was obtained from Cabot Corporation, Boston, Mass., U.S.A. The finely divided silica powder was used instead of fragments of pyrex glass and the above procedure was followed.

The glass stock suspension used as generator solution was checked for its stability against a diluted glass suspension which was used as a reference standard. The following experimental procedure was followed.

The operating instructions for nephelometric analysis in the instruction manual[66] for Fisher Nefluoro-Photometer were followed. The stock suspension used as generator solution was introduced into cell A; and the diluted glass suspension used as a reference standard was introduced into cell B. The transmittance reading was at first adjusted to read 70%. (Since it was used for comparison, it was not necessary to have it adjusted to read 100%). Further readings were taken at appropriate time intervals. There was obtained a constant reading of transmittance for at least 5 hours time interval (Table 6) showing that the glass suspensions were stable.

Protective Colloids

One of the limitations of nephelometric determination is that the precipitates should be very fine and must not settle rapidly or coagulate. Protective colloids such as starch, gelatin and glycerine are generally used to prevent coagulation and rapid settling of precipitates.

Starch, glycerine and gelatin were tested for their stabilizing effect. A 1% gelatin solution (5 ml

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[66] Instruction Manual for Fisher Nefluoro-Photometer, New York: Fisher Scientific Co.

TABLE 6

TEST OF STABILITY OF GLASS SOLUTION

Time Interval	Percent Transmittance
15 mins.	70.0
30 mins.	70.0
45 mins.	70.0
1 hr.	70.0
2 hrs.	70.0
3 hrs.	70.0
4 hrs.	70.0
5 hrs.	70.0

for 50 ml volume) gave the best results. A constant reading was observed for at least one hour time interval. Starch (5 ml of 1%) and glycerine (2 ml of 50%) were found to be unsatisfactory. Coagulation of precipitates was observed and colloidal suspensions were not obtained. The 1% gelatin solution was prepared according to the procedure given on Page 40. The following experimental procedure was followed to test the stabilizing effect of the gelatin solution.

A volume of 25 ml of palladium standard solution containing 0.15 mg of palladium (II) prepared by diluting the palladium stock solution with distilled water was pipetted into a 50 ml volummetric flask. Five ml of 0.1% ethanolic di-2-thienylketoxime solution was added to the flask while the flask was shaken gently. A colloidal dispersion was observed. After standing the solution for 1 to 1½ hours for complete reaction, 5 ml of 1% gelation solution was introduced. The mixture was diluted to mark with distilled water and was then shaken vigorously for 2 minutes. A homogeneous colloidal suspension was obtained and it was ready for determination. Glass suspension was used as generator solution. Transmittance reading was taken one minute after the introduction of the suspensions into the cells so that all air bubbles would have escaped from the suspensions. The starting instrument reading of transmittance was adjusted to read 70% for comparison. Further readings were taken at various time intervals. If the suspension was not introduced into the cell for determination immediately after the 2 minutes vigorous agitation, a 30 seconds agitation was necessary again before its introduction into the cell. Results (Table 7) showed that a constant reading of transmittance was obtained for at least one hour proving that the gelatin solution served the purpose as a good stabilizing reagent. When the gelatin solution was added to the palladium solution before the

TABLE 7

STUDY OF EFFECT OF GELATIN SOLUTION AS STABILIZING REAGENT

Time after Introduction	Percent Transmittance
1 min.	70.0
2 mins.	70.0
3 mins.	70.0
4 mins.	70.0
5 mins.	70.0
6 mins.	70.0
7 mins.	70.0
8 mins.	70.0
9 mins.	70.0
10 mins.	70.0
20 mins.	70.0
30 mins. *	70.0
40 mins. *	70.0
60 mins. *	70.0

* A 30 seconds agitation was again necessary upon a long time of standing after the 2 minutes vigorous agitation.

addition of the ethanolic di-2-thienylketoxime solution, no turbidity was obtained. This was interpreted as being due to the fact that the gelatin molecules prevented the reaction of the palladium ions and di-2-thienylketoxime.

Study of Variation of Acidity

As is well known, chemical reactions and reaction rates are greatly dependent upon the electrolyte concentration of the solution. The amount of turbidity and stability of a colloidal suspension are greatly affected by the variation of the acidity of the solution.

Di-2-thienylketoxime was found to form either a complex or a chelate with bivalent palladium depending on the pH of the reaction medium. In a low pH, a small amount of complex of dichlorobis(di-2-thienylketoxime-N, N')palladium (II) was formed. In a higher pH solution, a quantitative yield of the complex was obtained. The following investigation was carried out to determine the effect of varying the acidity on the turbidity of a solution having a constant palladium content.

Standard palladium solutions having the same palladium content (0.15 mg of palladium per 25 ml) were adjusted to have different pH values with 0.1 N HCl and 0.1 N NaOH solutions. (Sodium ions were found not to form a complex or develop turbidity with ethanolic di-2-thienylketoxime solution. See section of Effect of Diverse Ions.) Suspensions were prepared from these solutions following the same procedure as described in last section. The glass suspension was used as generator solution and a diluted glass suspension was used as a reference standard. The latter was adjusted so that it was slightly more turbid than the most turbid suspension prepared. It was made to give a 100% transmittance and the transmittance of the suspensions prepared were measured accordingly. There was found that solutions with pH 1.5 to 2.5 gave the most

TABLE 8

EFFECT OF VARIATION OF PH OF PALLADIUM SOLUTION

Palladium Content mg	pH of Solution	Scale Reading Percent Transmittance
0.15	1.2	2.0
0.15	1.4	8.0
0.15	1.6	65.0
0.15	1,8	86.0
0.15	1.9	88.0
0.15	2.1	59.0
0.15	2.2	58.0
0.15	2.5	42.0
0.15	2.7	38.0
0.15	2.8	31.0
0.15	3.0	30.5
0.15	3.2	31.0
0.15	3.4	30.0
0.15	3.5	31.0
0.15	3.6	31.0
0.15	3.8	31.5
0.15	4.0	31.0
0.15	4.1	31.0
0.15	4.3	31.0
0.15	4.6	15.0
0.15	4.8	9.0
0.15	5.2	7.0
0.15	6.8	0.0
0.15	10.0	0.0

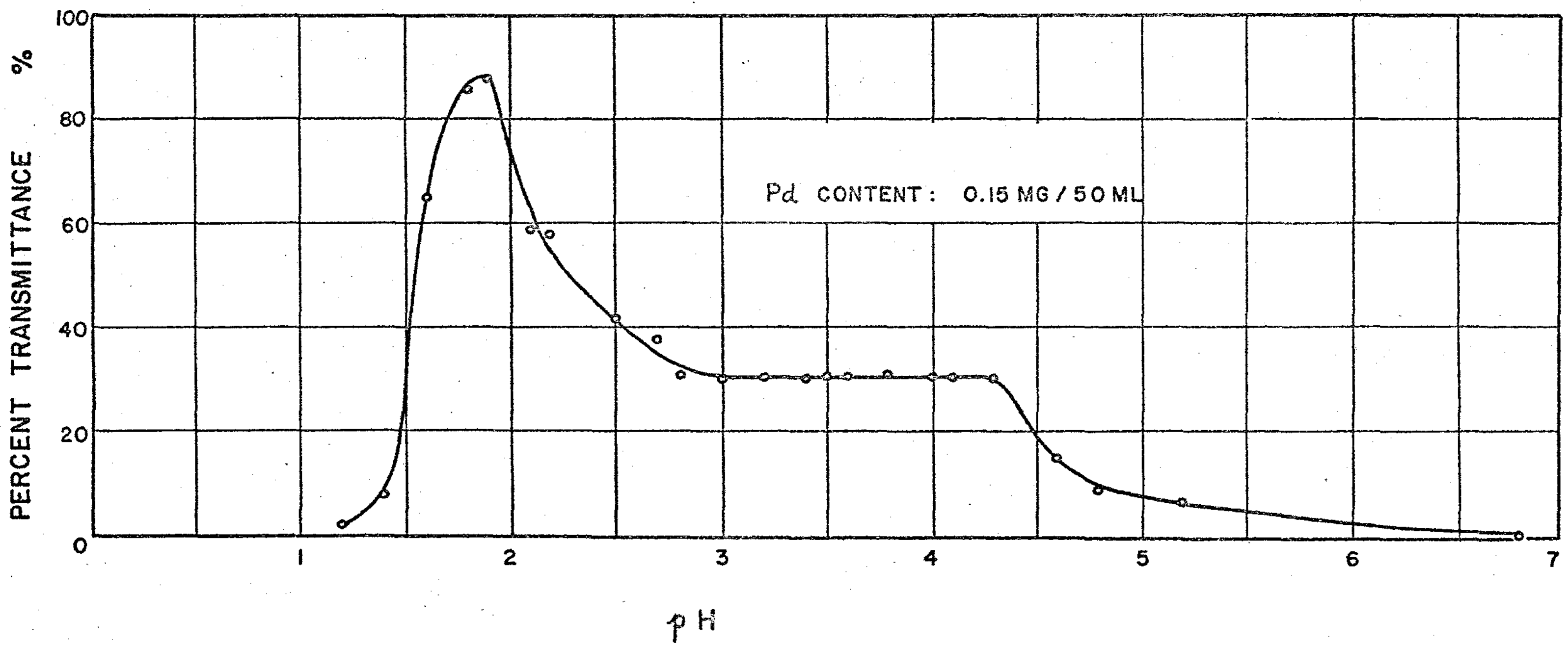

FIG. 6 EFFECT OF VARIATION OF pH OF Pd SOLUTION

turbid suspensions while solutions with pH lower than 1.2 and higher than 4.5 gave very little turbidity. Solutions having pH values between 2.8 and 4.2 had almost a constant transmittance reading. A pH value of 3.2 was then chosen as the optimum pH value for determination. A buffer was employed for the purpose of pH control. Results of effect of variation of pH of the palladium solution are shown in Table 8 and Fig. 6.

Buffer Solution - pH 3.2

To prepare the palladium solution at the optimum pH of 3.2, a buffer solution was made following the procedure of Clark and Lubs.[67] A volume of 147.0 ml of 0.1 N HCl was added to 500 ml of 0.1 N potassium acid phthalate and diluted to 1000 ml.(It was checked that potassium acid phthalate did not form a complex or develop turbidity with ethanolic di-2-thienylketoxime solution.) The effect of the buffer was tested for reproducibility of results. The following experimental procedure was undertaken.

A standard palladium solution was prepared by diluting aliquots of the palladium stock solution with the buffer. A volume of 25 ml of this solution was pipetted into a 50 ml volummetric flask. To the flask was added 5 ml of 0.1% ethanolic di-2-thienylketoxime solution while the flask was shaken gently. After 1 to 1½ hours of standing, 5 ml of 1% gelatin solution was introduced and the mixture diluted to mark with distilled water. The suspension was ready to be determined after 2 minutes vigorous agitation. Nine suspensions were prepared in the same way from standard palladium solutions (buffered) having the

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[67] N.A. Lange, Handbook of Chemistry, 8th ed., Sandusky, Ohio: Handbook Publishers, Inc., (1952) p.938.

TABLE 9

EFFECT OF BUFFER SOLUTION

Preparation No.	Pd Content mg.	pH	Percent Trans-mittance	Percent Recovery
1	0.15	3.2	70.0	100.0
2	0.15	3.2	69.0	99.7
3	0.15	3.2	70.5	100.7
4	0.15	3.2	70.2	100.3
5	0.15	3.2	71.0	101.4
6	0.15	3.2	69.0	98.6
7	0.15	3.2	69.5	99.3
8	0.15	3.2	70.5	100.7
9	0.15	3.2	71.0	101.4
10	0.15	3.2	69.5	99.3

Average percent recovery: 99.8

Greatest deviation from 100% recovery: ±1.4%

Average deviation from 100% recovery: ±0.8%

same palladium content. The glass stock suspension was used as generator solution and a selected suspension prepared was made to read 70% transmittance for comparison. The transmittance of the other suspensions were measured accordingly. Experimental results (Table 9) showed a high reproducibility for nephelometric work.

Effect of Time of Standing

It is important to determine the time required for complete reaction to take place. The following work was carried out to determine the effect of variation of time of standing. Suspensions were prepared with palladium solutions having the same palladium content following the same procedure given in the section of Buffer Solution except that the time of standing the solution after the addition of the reagent and before the addition of the gelatin solution varied. It was found in the previous work that no turbidity was observed when the gelatin solution was added to the palladium solution before the addition of the reagent. This fact was made use of and it was assumed that the reaction was stopped upon the addition of the gelatin solution.

Experimental results (Fig. 7 and Tables 10,11 & 12) showed that constant readings were obtained after a standing period of 1 hour. A period of time of 1 to 1½ hours was then chosen as the appropriate time of standing for complete reaction, i.e., for maximum turbidity to occur.

Reagent Concentration

The following investigations were undertaken to determine the effect of varying the concentration of

TABLE 10

EFFECT OF VARIATION OF TIME OF STANDING
(Pd Content: 0.10 mg)

Time of Standing	Percent Transmittance
15 mins.	25.0
30 mins.	25.0
45 mins.	25.8
1 hr.	29.0
2 hrs.	29.0
1½ hrs.	29.0
3 hrs.	28.5
4 hrs.	30.0
5 hrs.	29.0
8 hrs.	29.5
10 hrs.	29.5
12 hrs.	30.0

TABLE 11

EFFECT OF VARIATION OF TIME OF STANDING
(Pd Content: 0.15 mg)

Time of Standing	Percent Transmittance
15 mins.	33.8
30 mins.	36.0
45 mins.	44.0
1 hr.	43.5
1¼ hrs.	44.0
1½ hrs.	44.0
2 hrs.	43.5
3 hrs.	44.5
4 hrs.	44.0
5 hrs.	44.5

TABLE 12

EFFECT OF VARIATION OF TIME OF STANDING.
(Pd Content: 0.20 mg)

Time of Standing	Percent Transmittance
15 mins.	55.0
30 mins.	58.0
45 mins.	61.0
1 hr.	60.0
1½ hrs.	60.0
2 hrs.	60.5
3 hrs.	60.0
4 hrs.	61.0
4½ hrs.	60.5

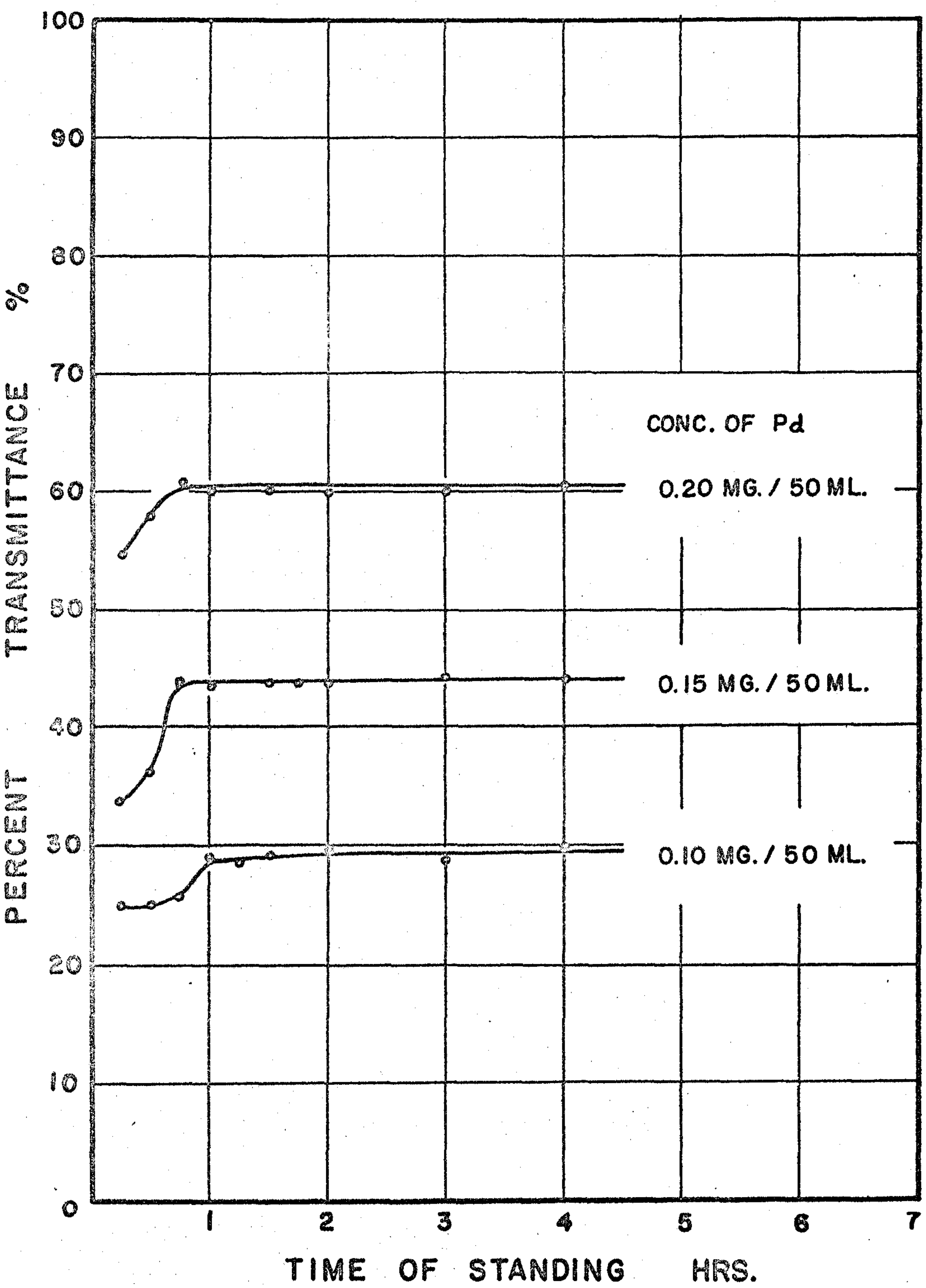

FIG. 7 EFFECT OF VARIATION OF TIME OF STANDING

di-2-thienylketoxime in ethanol and of varying the amount of ethanol in the solution on the turbidity of a solution having a constant palladium content.

Effect of Variation of Concentration of Di-2-thienylketoxime in Ethanol.

Suspensions were prepared as before with palladium solutions having the same palladium content following the same procedure except that the concentration of the reagent employed varied. (Volumes of 5 ml of 0.05%, 0.1%, 0.2%, 0.3%, 0.4% and 0.5% of the reagent in ethanol were used.) The glass stock suspension was used as generator solution and the turbidities of the suspensions prepared were compared with that of a diluted glass suspension which was adjusted to give 100% transmittance.

Experimental results (Table 13) showed that the 0.1% ethanolic di-2-thienylketoxime was the most suitable for use as constant readings were obtainable at that range. (Fig.8) Results also showed that, when 0.4% and 0.5% solutions were used, high readings of transmittance were obtained. It was found, however, this was due to the fact that some of the reagent was recovered in the solution when the mixture was diluted to mark and then vigorously agitated. This was proved by the following work. To a 50 ml volummetric flask with 25 ml of distilled water was added 5 ml of 0.5% ethanolic di-2-thienylketoxime solution. Five ml of 1% gelatin solution was then introduced and the mixture diluted to mark with distilled water. Colorless needles were observed when the mixture was agitated vigorously. The crystalline residue was filtered and air dried. Its melting point was found to be 133-136°C, that of di-2-thienylketoxime. A mixture melting point determination with an authentic sample of di-2-thienylketoxime showed no depression; mixture m.p. 133-136°C.

TABLE 13

EFFECT OF VARIATION OF CONCENTRATION OF DI-2-THIENYLKETOXIME IN ETHANOL SOLUTION

Pd Content mg	Concentration of Di-2-thienylketoxime in Ethanol	Volume Added ml	Percent Transmittance
0.15	0.05	5	7.0
"	0.1	"	44.0
"	0.2	"	44.0
"	0.3	"	72.0
"	0.4	"	Over 100
"	0.5	"	Over 100

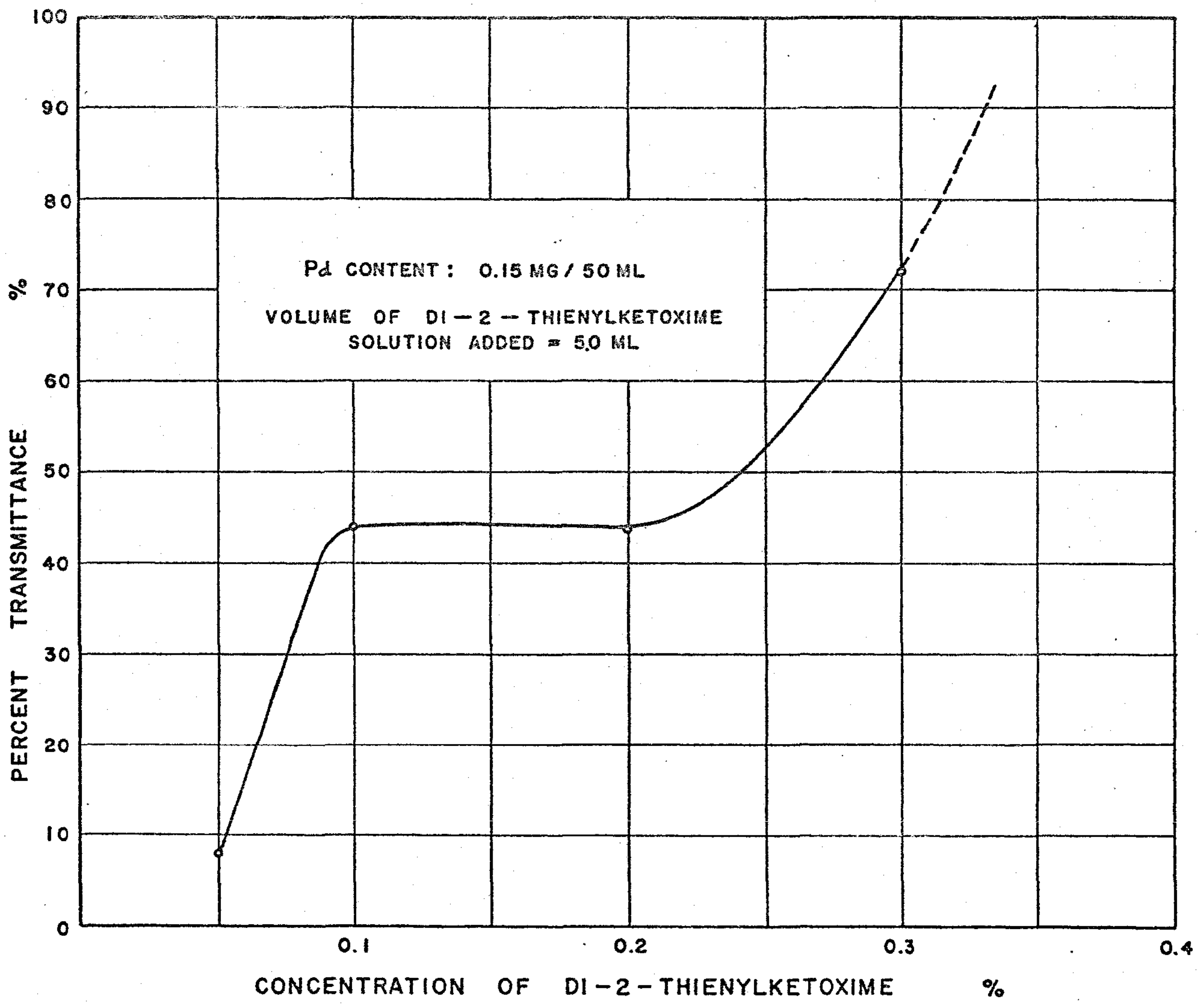

FIG. 8 EFFECT OF VARIATION OF CONCENTRATION OF DI-2-THIENYLKETOXIME IN ETHANOL

Effect of Variation of Total Amount of Ethanol in Solution.

The Pd-di-2-thienylketoxime complex was found to be slightly soluble in ethanol. The effect of variation of amount of ethanol present in solution (50 ml volume) on the turbidity of a solution having a constant palladium content was investigated.

The same procedure was employed for the preparation of suspensions from palladium standard solutions having the same palladium content,except that the amount of ethanol present in the solutions varied. The amount of di-2-thienylketoxime added was constant while the total volume of ethanol present in the solution varied. A volume of 1 ml of 0.5% ethanolic di-2-thienylketoxime solution was employed and it was in turn diluted to a total volume of 2,3,4,5,6 ml etc before its addition to the palladium solution. The turbidities of the suspensions were compared with that of a diluted glass suspension which had been adjusted to give 100% transmittance for comparison.

Experimental results (Table 14) showed that a volume of 5 ml of ethanol present in solution was most appropriate as constant readings were obtained in that range.(Fig,9). The presence of a large volume of ethanol in solution tended to , as it was expected, dissolve some of the complex formed, thus decreasing the turbidity and hence the transmittance reading.

Effect of Variation of Temperature

Since temperature is an important factor which generally affects a chemical reaction, the effect of variation of temperature on the turbidity of a solution having the same palladium content was studied.

Suspensions were prepared as before from palladium standard solutions having the same content, except that temperatures for the reaction were carefully controlled.

TABLE 14

EFFECT OF VARIATION OF TOTAL VOLUME OF ETHANOL PRESENT IN SOLUTION

Pd Content (mg)	0.5% Ethanolic Di-2-thienylketoxime Solution Used in ml	Ethanol Added (ml)	Total Volume of Ethanol (ml)	Percent Transmittance
0.15	1	0	1	53.0
0.15	1	1	2	59.0
0.15	1	2	3	55.0
0.15	1	3	4	44.0
0.15	1	4	5	43.5
0.15	1	5	6	43.5
0.15	1	6	7	37.0
0.15	1	7	8	33.0
0.15	1	9	10	31.0
0.15	1	14	15	19.0
0.15	1	19	20	8.0

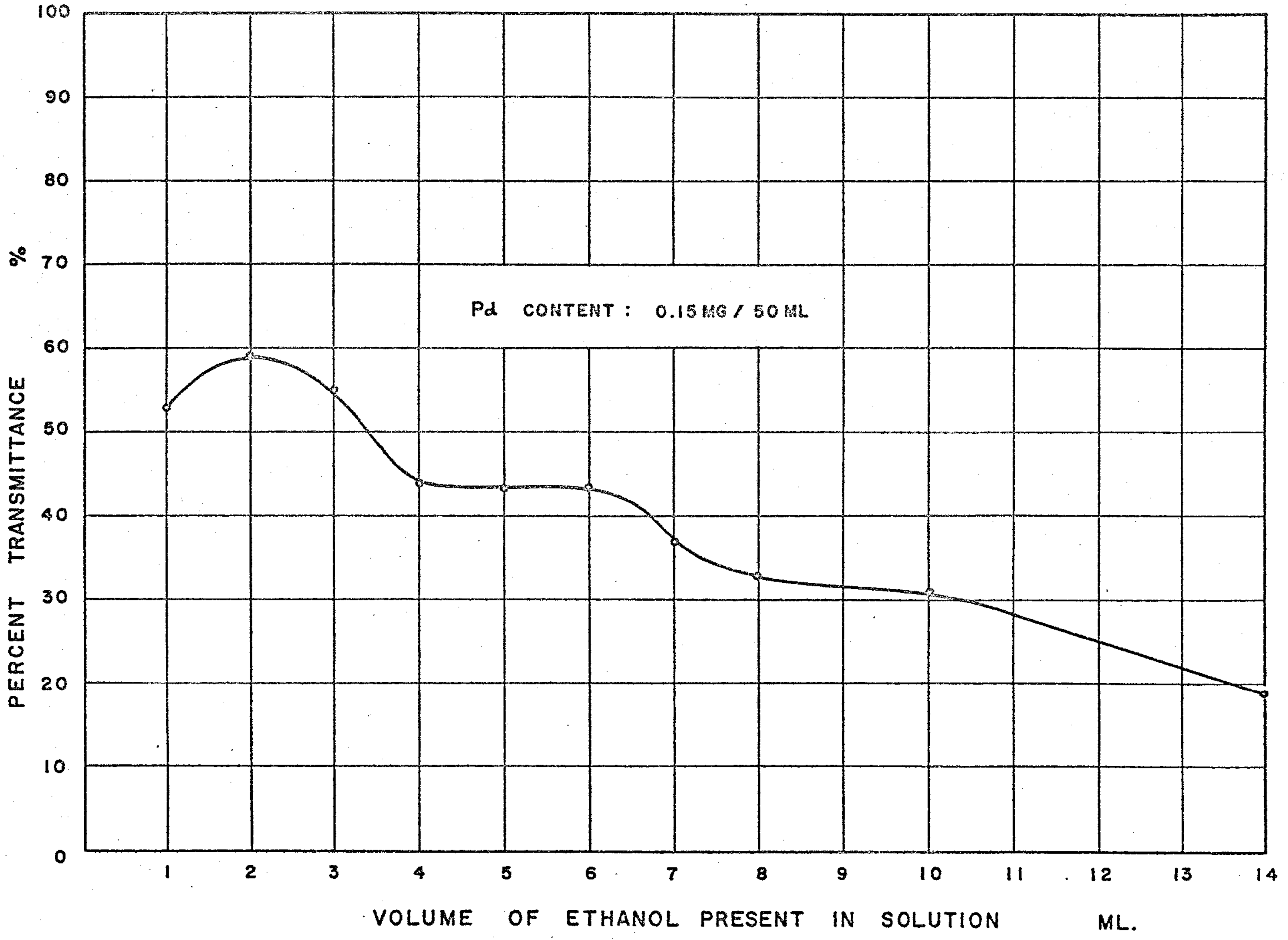

FIG. 9 EFFECT OF VARIATION OF TOTAL VOLUME OF ETHANOL IN SOLUTION

To a 50 ml volummetric flask was added exactly 25 ml of palladium standard solution. The flask was placed in a water bath maintained at a certain temperature of the temperatures shown in Fig.10. After 30 minutes time interval, 5 ml of 0.1% ethanolic di-2-thienylketoxime solution which had been brought to the same temperature was added to the flask. The mixture was then placed in a water bath maintained at that temperature for 1 to 1½ hours. At the end of that time, 5 ml of 1% gelatin solution was added and the mixture diluted to the mark with distilled water. The transmittance of the suspension was measured after 2 minutes vigorous agitation. Other suspensions were prepared in the same way at different temperatures and their transmittance measured accordingly. The glass stock suspension was used as generator solution and a diluted glass suspension of appropriate turbidity was made to give 100% transmittance as a reference standard.

Experimental results (Fig.10 and Table 15) showed that the temperature had little or no effect between 20-28°C. Beyond this range a mark decrease in transmittance values was observed, these values decreasing with the temperature. While control of the temperature is not essential for routine analysis, more consistent values had been obtained by maintaining the temperature at about 25°C or at room temperature.

Effect of Diverse Ions

To the extent that the effects of other ions were examined (Tables 16,17,18,19), no serious interferences were observed.

The solutions of inorganic ions required for testing the specificity of the reagent against different ions for quantitative analysis were prepared from reagent

TABLE 15

EFFECT OF VARIATION OF TEMPERATURE

Palladium Content mg	Temperature °C	Percent Transmittance
0.15	20	43.5
0.15	25	44.0
0.15	28	43.5
0.15	30	38.0
0.15	38	35.0
0.20	20	60.0
0.20	25	60.0
0.20	28	58.0
0.20	30	52.0
0.20	38	49.0

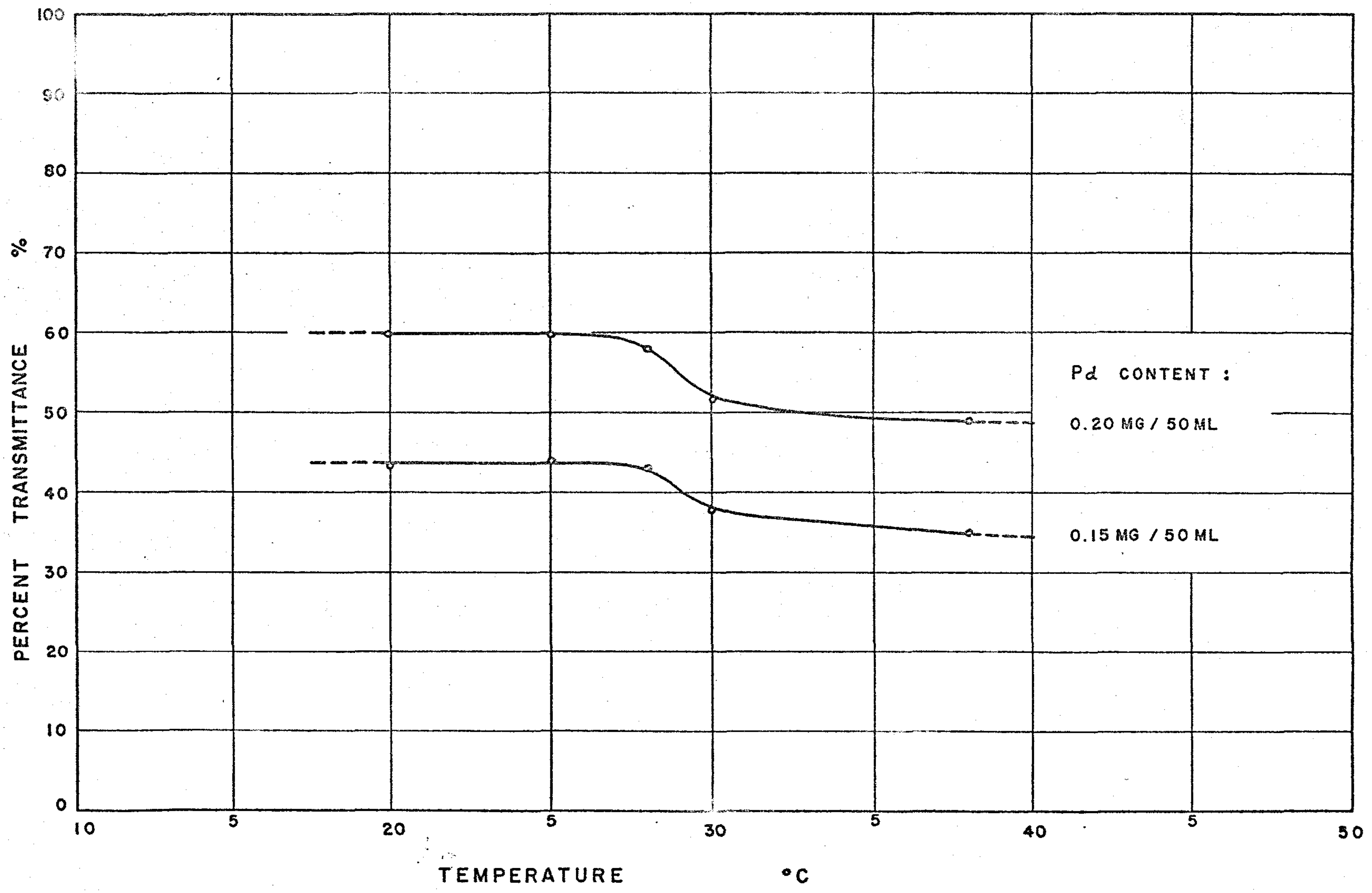

FIG. 10 EFFECT OF VARIATION OF TEMPERATURE

grade salts. Alkali salts were used for the solutions of the anions and chlorides for the solutions of the cations. The concentration of the solutions were adjusted to give about 5 mg per ml of the ion in question. The experimental procedure employed was basically the procedure of West.[68]

One milliliter of the solution containing 5 mg of the ion in question was introduced into a 50 ml volummetric flask and diluted to a volume of 25 ml with the buffer solution. To the flask was added 5 ml of 0.1% ethanolic di-2-thienylketoxime solution and the mixture was allowed to stand for 5 hours and then 5 ml of 1% gelatin solution was added. The mixture was checked to see if any turbidity was developed. If no turbidity was observed meaning that the ion did not form a complex with di-2-thienylketoxime, the ion was further tested for negative interference.[68]

Suspensions were prepared from solutions having the same palladium content and various amount of other ions. The same procedure for the preparation of suspensions described in the section of Buffer Solution had been followed. The values of transmittance of these suspensions were determined and compared with that of the suspension prepared from a solution which had the same palladium content but no other ions.

Experimental results (Table 16) showed that the platinum group metals (Pt, Rh, Ir, Ru, Os) did not form complexes or develop turbidity with the reagent after 5 hours standing. Gold formed turbidity with the reagent after standing for 1 hour. When present in low concentration, (1 mg of Au present when determined with 0.15 mg of Pd), Au gave no change to the transmittance value as the turbidity formed due to the presence of Au was

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68 P.W. West, J. Chem. Ed., 18, 528 (1941).

negligible in comparison to that due to the palladium ion. The following common cations were also tested:- Na^+, Co^{++}, Mn^{++}, Mg^{++}, Hg^{++}, Cd^{++}, Cr^{+++}, K^+, Cu^{++}, F^{+++}: None of these ions formed a complex or developed turbidity with the reagent. When present as chloride, Fe^{+++}formed turbidity with the buffer solution. If $Fe^{+++}$is present, the analysis can be done without using the buffer solution but to adjust the pH of the solutions to be determined to 3.2 with 0.1 N HCl and 0.1 N NaOH.

The chlorides of iridium, ruthenium, nickel, chromium did, however, form deeply colored solutions, and in their presence in high concentration, (5 mg of the ion present when determined with 0.15 mg of Pd.), the transmittance value was decreased. No serious interferences were observed , however, when they were present in low concentration. (1-2 mg of the ion present when determined with 0.15 mg of Pd.) (Table 18)

The anions studied were the following:- HPO_4^{2-}, Ac^-, CO_3^{2-}, CN^-, SO_4^{2-}, NO_3^- and F^-. None of these ions formed a complex or developed turbidity with the reagent. (Table 17) The presence of 5 mg of these ions when determined with 0.15 mg of palladium did not interfere with the transmittance value except CN^-, which prevented the formation of the Pd-di-2-thienylketoxime.(Table 19)

Determination of Calibration Curve and Determination of Unknown Sample

Theoretically speaking, nephelometric analyses are supposed to obey Beer's Law. When the medium is densely filled with particles, however, secondary scattering becomes of importance and causes deviation from the Beer's Law. Therefore, in most nephelometric determinations, a calibrated curve must be constructed.

TABLE 16

DETERMINATION OF INTERFERENCE OF CERTAIN CATIONS

Foreign Ions	Amount Taken mg	Ethanolic Di-2-thienylketoxime Solution (0.1%) Used ml	Appearance of Solution After 5 Hrs. Standing
Pt^{++}	5	5	Not turbid
Ir^{+++}	"	"	"
Rh^{+++}	"	"	"
Ru^{+++}	"	"	"
Os^{++++}	"	"	"
Au^{+++}	"	"	Slightly turbid
Na^{+}	"	"	Not turbid
Co^{++}	"	"	"
Ni^{++}	"	"	"
Mn^{++}	"	"	"
Mg^{++}	"	"	"
Hg^{++}	"	"	"
Cd^{++}	"	"	"
Cr^{+++}	"	"	"
Fe^{+++}	"	"	"
Cu^{++}	"	"	"
K^{+}	"	"	"

TABLE 17

DETERMINATION OF INTERFERENCE OF CERTAIN ANIONS

Foreign Ions	Amount Taken mg	Ethanolic Di-2-thienylketoxime Solution (0.1%) Used ml	Appearance of Solution After 5 Hrs. Standing
HPO_4^{2-}	5	5	Not turbid
Ac^-	"	"	"
CO_3^{2-}	"	"	"
CN^-	"	"	"
SO_4^{2-}	"	"	"
NO_3^-	"	"	"
F^-	"	"	"

TABLE 18

EFFECT OF CERTAIN CATIONS ON DETERMINATION OF PD

Foreign Ions	Amount Taken mg	Pd Taken mg	Percent Transmittance
--	--	0.15	70.0
Pt^{++}	2	0.15	70.0
"	5	0.15	70.0
Ir^{+++}	2	0.15	70.0
"	5	0.15	65.0
Rh^{+++}	2	0.15	69.0
"	5	0.15	70.0
Ru^{+++}	1	0.15	69.0
"	5	0.15	62.0
Os^{++++}	1	0.15	68.0
"	5	0.15	54.0
Au^{+++}	1	0.15	69.0
"	5	0.15	62.0
Na^{+}	2	0.15	70.0
"	5	0.15	71.0
Co^{++}	2	0.15	71.0
"	5	0.15	70.0
Ni^{++}	2	0.15	70.0
"	5	0.15	60.0
Mn^{++}	2	0.15	71.0
"	5	0.15	72.0
Hg^{++}	2	0.15	69.0
"	5	0.15	70.0
Cd^{++}	2	0.15	70.0
"	5	0.15	53.0

TABLE 18
(continued)

EFFECT OF CERTAIN CATIONS ON DETERMINATION OF PD

Foreign Ions	Amount Taken mg	Pd Taken mg	Percent Transmittance
Cr^{+++}	2	0.15	71.0
"	5	0.15	52.0
K^{+}	2	0.15	69.0
"	5	0.15	70.0
Cu^{++}	2	0.15	70.0
"	5	0.15	72.0

TABLE 19

EFFECT OF CERTAIN ANIONS ON DETERMINATION OF PD

Foreign Ions	Amount Taken mg	Pd Taken mg	Percent Transmittance
HPO_4^{2-}	2	0.15	69.0
"	5	0.15	70.5
Ac^-	2	0.15	70.0
"	5	0.15	72.0
CO_3^{2-}	2	0.15	70.0
"	5	0.15	70.5
CN^-	2	0.15	No turbidity
"	5	0.15	"
SO_4^{2-}	2	0.15	71.0
"	5	0.15	70.5
NO_3^-	2	0.15	71.0
"	5	0.15	69.0
F^-	2	0.15	69.0
"	5	0.15	70.0
---	---	0.15	70.0

Standard buffered palladium solution of various concentrations (0.05 mg to 0.25 mg of Pd per 25 ml of solution) were prepared by pipetting aliquots of palladium stock solution (0.1 mg of Pd per ml) into 100 ml volummetric flasks and then diluted to mark with the buffer solution. Exactly 25 ml of these solutions were pipetted into 50 ml volummetric flasks. To each flask was added 5 ml of 0.1% ethanolic di-2-thienylketoxime solution while the flask was shaken gently. After standing the solution for 1 to 1½ hours, 5 ml of 1% gelatin solution was introduced. The mixture was then diluted to mark with distilled water. After 2 minutes vigorous agitation, the suspension prepared with the most concentrated palladium solution was made to give 100% transmittance and the transmittance of the other suspensions measured accordingly. The glass stock suspension was used as generator solution and readings of transmittance were taken one minute after the suspensions were introduced into the cell so that any air bubble would have escaped from the suspension in the cell. If the suspension was not determined immediately after the 2 minutes vigorous agitation, a 30 seconds agitation was again necessary before its introduction into the cell.

By plotting the scale reading of percent transmittance against concentration of palladium on ordinary graph paper, a straight line was obtained.over the range from 0.05 mg to 0.20 mg of palladium (II). A straight line was also obtained over the range from 0.05 to 0.25 mg. When the concentrations are higher, points obtained are scattered. The palladium concentration of an unknown samples can then be read off from the curve when its transmittance has been determined.

Determination of Known Samples

Palladium solutions of known contents were prepared. The palladium content of known samples were determined

TABLE 20

DETERMINATION OF CALIBRATION CURVE

Concentration of Pd Solution mg per 25 ml	Percent Transmittance*
0.20	100.0
0.15	72.0
0.10	44.0
0.05	17.0

* Average result of duplicate samples.

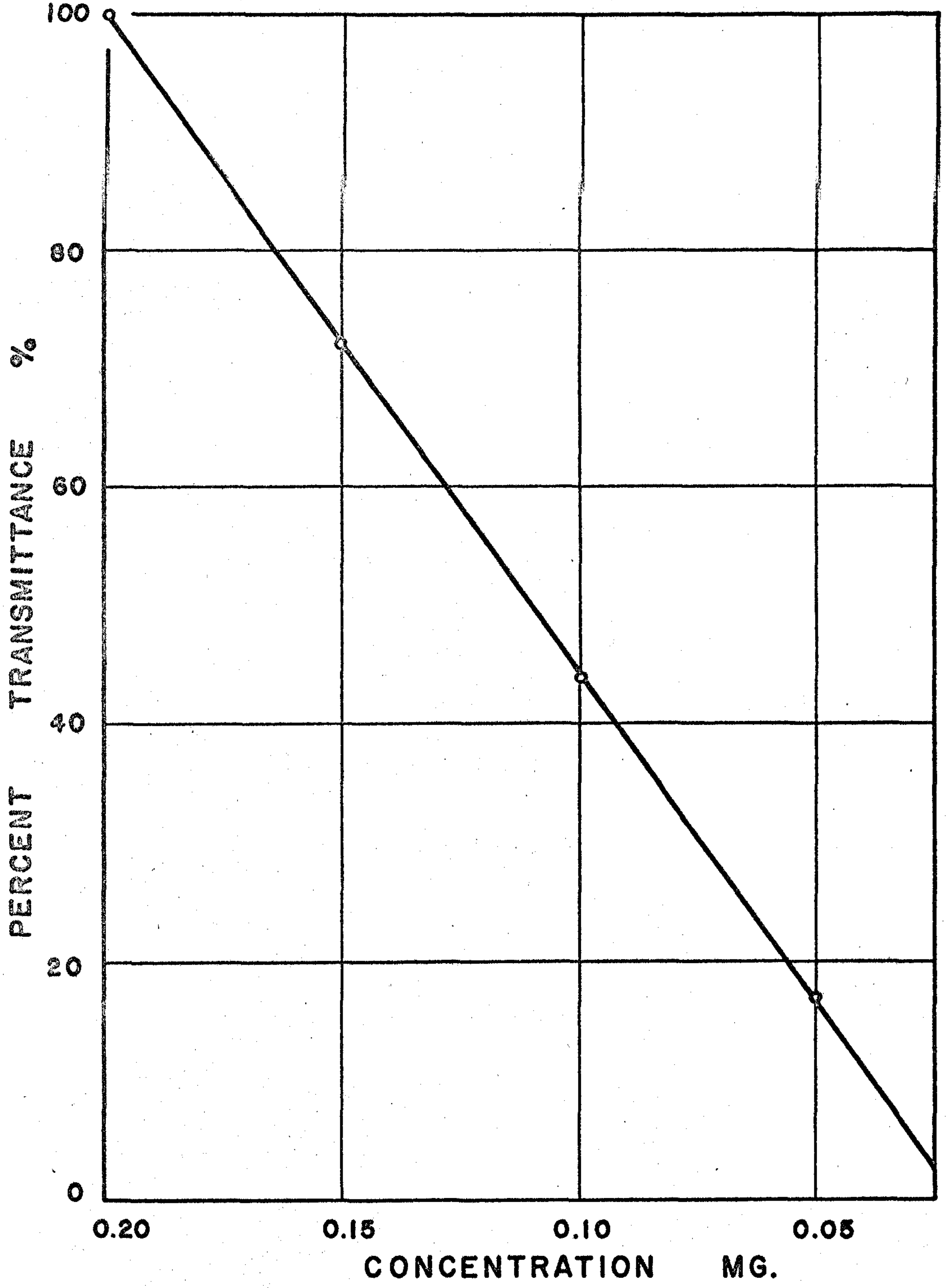

FIG. 11 DETERMINATION OF CALIBRATION CURVE

mined in duplicate as unknown samples following the procedure given in the previous section and the results are shown in Table 21.

TABLE 21

DETERMINATION OF KNOWN SAMPLES

Sample	Pd Present mg	Pd Found mg	Deviation* %
1	0.175	0.180	+2.8
2	0.150	0.145	-3.3
3	0.100	0.095	-5.0
4	0.075	0.079	+5.3
5	0.040	0.044	+10.0

* Average result of duplicate samples.

CHAPTER IV

DISCUSSION

In the present work, the application of di-2-thienylketoxime to nephelometric determination of microgram quantities of palladium (II) was investigated. The reaction between palladium (II) ions and di-2-thienylketoxime was studied to determine such factors as stabilizing reagents, effect of pH, time of standing, optimum concentration of reagents, temperature and effects of various concentrations of other ions on the reaction.

Experimental investigations were carried out with the Fisher Nefluoro-Photometer and a pyrex glass suspension was prepared and employed as generator solution. A 1% gelatin solution was found to be a good stabilizing reagent and 5 ml was used for a volume of 50 ml solution. A homogeneous colloidal suspension was then obtained and a constant transmittance was observed for at least one hour time interval. Investigation showed that the transmittance values varied with the pH values of the palladium solution and determinations had to be carried out at a controlled pH. The transmittance values remained constant for solutions from pH 2.8 to 4.0. A pH value of 3.2 was employed as the optimun pH for determination and a HCl-potassium acid phthalate buffer of 3.2 was used for the purpose of pH control. Stable transmittance values were obtained after 1 hour standing and a standing period of 1 to 1½ hours was chosen for complete reaction to take place. A 0.1% di-2-thienylketoxime in ethanol was found to be the optimum concentration of the reagent in ethanol and the optimum volume of ethanol present in a 50 ml solution was found to be 5 ml. The variation of temperature from 20-28°C did not affect the transmittance value and these transmittance values remained constant at room temperature. The degree of turbidity was consequently found to be proportional to the concentration of palladium present over the range of 0.04 to 2.5 mg in a 50 ml solution. The average error is ± 4%.

Most of the common ions, including the platinum group metals, had little or no effect on the reaction, except the interference of cyanide ions, which prevented the formation of the palladium di-2-thienylketoxime complex.

The method is found to be particularly useful for carrying out large numbers of determinations, as in routine or control analysis of palladium samples and where great accuracy is not the prime consideration.

BIBLIOGRAPHY

1. *A.S.T.M.*, Committee 20, Subcommittee IV Report, *Feb. 17* (1942).

2. Axilrod, B.M. and Kline, G.M., *J. Research Natl. Bur. Standards*, *19*,356-400 (1937); *Research Paper 1031.*

3. Bailer, J.C., *Chemistry of Coordination Compounds*, New York: *Reinhold Publishing Corp., (1956).*

4. Barnes, R.B. and Stock C.R., *Anal. Chem.*, *21*,181 (1949).

5. Batalin, A.K.H., *Zavodskaya Lab.*, *16*, 1411-16 (1950).

6. Beamish, F.E., McBryde,W.A.E., *Anal. Chim. Acta*, *9*, 349 (1953).

7. Boyd, J.F. and Sommerville, J.W., *J. Clin. Path.*, *13(1)*, 85-86 (1960).

8. Brady, O.L. and Muers, M.M., *J. Chem. Soc.*, (1930) 1599.

9. Calvin, M. and Bailes, R.H., *J. Am. Chem. Soc.*, *68*, 949 (1946).

10. Daniels, F., Mathews J.H., *et al.*, *Experimental Physical Chemistry*, 5th ed., *London: McGraw Hill Book Company, Inc.*, (1956) p.65.

11. Debye, P.P., *J. Applied Phys.*, *17*, 392-398 (1946).

12. Dwyer, F.P. and Mellor, D.P., *J. Am. Chem. Soc.*, *57*, 605 (1935).

13. Ephriam, E., *Ber.*, *63*, 1930 (1928).

14. Faraday, M., *Proc. Roy. Soc.*,(London), *6*, 356 (1857).

15. Fikhman, B.A., *Lab. Delo*, *4(2)*, 53-55 (1958).

16. Fikhman, B.A., *USSR*, *115,987*, Nov. 22 (1958).

17. Hawk, P.B., Oser, B.L. and Summerson, W.H., *Practical Physiological Chemistry*, 13th ed., New York: *McGraw Hill Book Co.,Inc., (1954)* p.595.

18. Huffman, E.H. and Beaufait, L.J., J. Am. Chem. Soc., 71, 3179 (1949).

19. Instruction Manual for Fisher Nefluoro-Photometer, New York: Fisher Scientific Co.

20. Jensen, K. A., Acta Chem. Scand., 3, 479 (1949).

21. Juza, R. and Langheim, R., Angew.Chem., 50, 255 (1937).

22. Kortschak, H.P., Anal. Chem., 19, 692 (1947).

23. Land, J.E., J. Chem. Ed., 34, 38 (1957).

24. Lange, N.A., Handbook of Chemistry, 8th ed., Sandesky, Ohio: Handbook Publishers, Inc., (1952) p.938.

25. Ledrut, J.H.T., Pharm. France, 4, 95-100 (1957/8).

26. Libby, R.L., J. Immunol, 34, 401, 71 (1938)

27. Lindsay, F.K., Braithwaite, D.E. and D'Aminco, J.S., Ind.Eng. Chem., Anal. Ed., 18, 101 (1946).

28. Litrinenko, P. and Rozivshii, M., Gigiena i Sanit, (1954), No. 1, 52-53.

29. Lumme, P.O., Suomen Kemistilehti, 33, No.2, 85 (1960).

30. Lure, Y.Y. and Nikolaeva, Z.V., Zavodshaya Lab., 12, 161 (1946).

31. Martell, A. and Calvin, M., Chemistry of the Metal Chelate Compounds, New Jersey: Prentice Hall Inc., (1959).

32. McAlpine, R.K., J. Am. Chem. Soc., 51, 1065 (1929).

33. Meins, O. and Rains, T.C., Anal. Chem., 27, 1932 (1955).

34. Miqull, y P.L., Afinidad, 21, 458-71, 565-16, (1944).

35. Moriyo Shigeo, (Research Inst. Japan, Tokyo.), Tanken, 9, 226-232 (1958).

36. Muller, R.H., Ind. Eng. Chem., Anal. Ed., 11, 1 (1939).

37. Petrov, A.M., Trudy Khim. i Khim. Tekhnol., 1, 603-4 (1958).

38. Pfeiffer, P., Ber., 63, 1811 (1930).

39. Reed, S.A. and Banks, C.V., Proc. Iowa Acad. Sci., 55, 267 (1948).

40. Richards, T.W. and Wells, R.C., J. Am. Chem. Soc., 31, 235 (1904).

41. Rose, H.E., J. Soc. Chem. Ind. (London), 69, 266-272 (1950).

42. Saifer, A. and Clark, F.D., Ind. Eng. Chem., Anal. Ed., 8, 248 (1936).

43. Saint-James, R. and Lecomte, T., Anal. Chim. Acta, 24, 155-160 (1961).

44. Sherrick, P.H., Dawe, G.A., et al., Manual of Chemical Oscillometry, Chicago: E.H. Sargent & Co., (1954).

45. Stamm, A.J. and Svedberg, T., J. Am. Chem. Soc., 47, 1582 (1925).

46. Stevens, R.E., Ind. Eng. Chem., Anal. Ed., 8, 248 (1936).

47. Strutt, J.W. (Lord Rayleigh), Phil. Mag., 41, 107 (1871).

48. Thomas, V. and Couderc, V., Bull. Soc. Chim. France, 23, 288 (1918).

49. Trandon, S.G. and Bhattacharya, S.C., Anal. Chem., 32, 194 (1960).

50. Tsyurupa, M.G. and Peshkava, V.M., Vestnik Moskov. Univ., Ser. Mat., Mekhi, Astron., Fiz., Khim., 13, No. 6, 165-170 (1958).

51. Tyndall, J., Phil. Mag., 4, 37, 384 (1869).

52. Underwood, N. and Doermann, A.H., Rev. Sci. Instruments, 18, 665 (1947).

53. Wagner, L.A., Proc. Am. Soc., Testing Materials, 33, Part II, 553 (1933).

54. Wells, P.V., Chem. Reviews, 3, 331-81 (1927).

55. Wells, R.C., J. Am. Chem. Soc., 35, 99 (1906).

56. West, P.W., J. Chem. Ed., 18, 528 (1941).

57. Yoe, J.H., Photometric Chemical Analysis, Vol. II, Nephelometry, New York: John Wiley & Son, (1929).

58. Yoe, J.H. and Kirkland, J.M., Anal. Chem., 26, 1335 (1954).

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