ASPECTS OF SUBSTOICHIOMETRY:

PALLADIUM

A thesis presented

for the Degree of

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Summary

A detailed study has been carried out of the solvent extraction of the complexes formed by palladium with diethyldithiocarbamic acid and dithizone under substoichiometric conditions. The results of this study have been applied to the development of methods for the determination of palladium by neutron activation analysis and isotope dilution analysis.

Under substoichiometric conditions, that is, where the metal is in excess of the chelating agent, palladium was found to form three complexes with diethyldithiocarbamic acid (HDDC); the normal complex, palladium diethyldithiocarbamate [$Pd(DDC)_2$], and two ternary complexes, palladium chloride diethyldithiocarbamate [Pd.Cl(DDC)] and palladium hydroxide diethyldithiocarbamate [Pd.OH(DDC)]. With dithizone (H_2Dz) three complexes were also formed; primary palladium dithizonate [$Pd(HDz)_2$], secondary palladium dithizonate [Pd.Dz] and palladium chloride dithizonate [Pd.Cl(HDz)]. The formulae of these complexes have been verified by analysis and their ultra-violet spectra examined. The extraction of palladium diethyldithiocarbamate, palladium chloride diethyldithiocarbamate, primary palladium dithizonate and palladium chloride dithizonate into chloroform and carbon tetrachloride has been studied under a variety of conditions, using radioactive tracer techniques, and the partition coefficients and solubilities in both solvents have been measured. The extraction constants of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate into chloroform have been determined by competition with ethylenediaminetetraacetic acid and potassium cyanide and hence the stability constants calculated. The stability constants of the cyanopalladate ion [$Pd(CN)_4^{2-}$] and the protonated ethylenediaminetetraacetic acid complex [H_2PdY] have also been determined.

Two highly selective, radiochemical separation procedures have been developed and applied to the determination of traces of palladium in rocks, biological material and platinum. The first involves the extraction of palladium diethyldithiocarbamate from a medium of 5N hydrochloric acid using a substoichiometric amount of cupric diethyldithiocarbamate in chloroform. Using this separation, amounts of palladium down to 10^{-8} g have been determined by neutron activation analysis. The second involves the extraction of primary palladium dithizonate from a medium of 0.1N sulphuric acid and less than 0.01N chloride ion concentration using a substoichiometric amount of dithizone in carbon tetrachloride. Using this separation, amounts of palladium down to 3×10^{-9} g have been determined by isotope dilution analysis.

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CHAPTER 1

Introduction.

I. The Use of Substoichiometry in Radiochemical Analysis.

The technique of substoichiometry, introduced by Ruzicka and Stary in 1961[1-4], can be applied to both the analysis of radioactive materials and the analysis of non-radioactive materials by the use of radioactive tracers. The former includes radiochemical analysis of fission products and analysis of radioactive preparations. The latter includes the important trace analysis techniques of neutron activation analysis and isotope dilution analysis. Neutron activation analysis is one of the most important methods for trace analysis because of its high sensitivity (sensitivities for the elements have been listed by Yule[5]). Isotope dilution has only been suitable for fairly large traces up till now, due to the limits imposed by the necessity of determining the chemical yield by physico-chemical methods, but the greater selectivity obtainable by the use of substoichiometry and the elimination of the chemical yield determination, enables this technique to be as sensitive, or even in certain cases to be more sensitive, than neutron activation analysis, and hence, because no irradiation is necessary, it can be more useful than neutron activation analysis in some cases. Substoichiometric chemical separations have been developed for a large number of elements[6-20] and the purpose of this work was to develope separations suitable for neutron activation analysis and isotope dilution analysis of traces of palladium, and to investigate the chemistry involved in such separations.

1. The Application of Substoichiometry to Neutron Activation Analysis.

Activation analysis involves the formation of radioactive nuclides by irradiation with nuclear particles, usually thermal neutrons. For thermal neutrons, the activity, A, produced in any element is given by the expression:

$$A = N.F.\sigma.\Theta(1 - e^{-\lambda t}), \qquad (1.1)$$

where N = number of atoms of element present,

F = thermal neutron flux in neutrons.cm^{-2}.sec^{-1},

σ = activation cross section in cm^2,

Θ = isotopic abundance of isotope being activated,

λ = decay constant of radioactive isotope produced,

t = time of irradiation.

If the time of irradiation is such that the expression λt is large, the expression in parentheses approaches unity. This occurs when the time of irradiation, t, is about six times the half-life, $t_{\frac{1}{2}}$, of the isotope produced, $t_{\frac{1}{2}}$ being given by

$$t_{\frac{1}{2}} = \frac{0.693}{\lambda} . \qquad (1.2)$$

When this condition is achieved, the activity produced does not change with the time of irradiation, and the element is said to be irradiated to saturation.

If all the quantities in equation 1.1 are known, it is possible to calculate the number of atoms of the element present, N, from the activity produced, A. However, some of these quantities, especially the neutron flux, are difficult to determine accurately, and absolute measurements of activity are also difficult, and so this method is rarely used in practice. The most usual method is to irradiate a standard containing a known amount of the element to be determined simultaneously with the sample and compare the activities produced. If the weight of the element in the sample is x g and in the standard is x_sg, and the activities produced in sample and standard are A and A_s respectively, then from equation 1.1 it can be seen that

$$A/A_s = x/x_s . \qquad (1.3)$$

Of course, most of the elements in the sample will become radioactive to a greater or lesser extent, and the activities of the trace elements will usually be swamped by the activities of the main constituents. Hence direct measurement of the activity of a particular element by gamma-ray spectrometry has limited sensitivity, and

therefore in order to measure the activity, A, it is necessary to carry out a chemical separation. To facilitate this, an inactive carrier for the element being determined is added, usually milligram quantities of the same element. Suppose yg. of carrier is added to the sample and y_sg. to the standard, then mg. separated from the sample and m_sg. from the standard, and the measured activities of these separated fractions are a and a_s c.p.s. Then for the sample

$$A = \frac{a.y}{m} \qquad (1.4)$$

assuming x is insignificant with respect to y, and similarly

$$A_s = \frac{a_s.y_s}{m_s}. \qquad (1.5)$$

Hence by substitution into equation 1.3 and rearrangement it can be seen that

$$x = x_s.\frac{a.y.m_s}{a_s.y_s.m}. \qquad (1.6)$$

However, if it can be arranged that $y = y_s$ and $m = m_s$ then equation 1.6 can be simplified to

$$x = x_s.\frac{a}{a_s}. \qquad (1.7)$$

The first condition is easy to fulfil by adding equal aliquots of a carrier solution to sample and standard, but the second is more difficult as most chemical separations isolate all, or a variable percentage of the element being determined. It can be achieved, however, by adding less reagent than is necessary to separate all of y, that is less than the amount required to combine stoicheiometrically with y. This not only eliminates the necessity for determining the chemical yield, m, of the radiochemical separation, but increases the selectivity of the separation to such an extent that in some cases only one separation step is necessary. For this technique to work the reagent used must react quantitatively and the complex formed must be easily separated from the unreacted element, for example by solvent

extraction or ion exchange. Precipitation reactions are less useful because of co-precipitation.

2. The Application of Substoichiometry to Isotope Dilution Analysis.

The main advantage of conventional isotope dilution analysis is that not all the element to be determined need be separated. The principle of the method involves measuring the change of specific activity brought about by mixing active and inactive isotopes of the element and allowing them to equilibrate. Suppose a sample, containing x g. of this element is mixed with a known amount, x_s g. of the element, specific activity A_s c.p.s. The specific activity will be lowered to A c.p.s., and as the total activity is unchanged,

$$x_s.A_s = A(x + x_s). \qquad (1.8)$$

By rearranging

$$x = (A_s/A - 1)x_s. \qquad (1.9)$$

The specific activities A and A_s are given by the expressions $A = a/m$ and $A_s = a_s/m_s$ where a and a_s are the activities of the separated amounts m and m_s, from sample and standard respectively. As m and m_s must be determined, usually gravimetrically, the difficulty is obvious where m is very small, but if it is possible to separate, from sample and standard, exactly equal amounts of the element to be determined, by the use of substoichiometry, the need to determine m can be eliminated, as

$$x = (a_s/a - 1)x_s. \qquad (1.10)$$

Also, the greater selectivity of substoichiometry makes the task of separating very small quantities of an element, in the presence of large excesses of many other elements, less formidable than it would be if conventional separations were used. Substoichiometric separations using solvent extraction or ion exchange techniques can be suitable for the determination of quantities down to 10^{-6} g. or less.

3. Substoichiometric Solvent Extraction.

Consider a metal, M, valency N, in an aqueous solution which reacts with an acid, HA, in an immiscible organic solvent, to form a complex, MA_N, which is soluble in the organic solvent. The reaction can be represented by the following equation:

$$M_{aq} + N(HA)_{org} \rightleftharpoons MA_{N\,org} + NH \qquad (1.11)$$

where the subscripts aq and org indicate that the species is in the aqueous or the organic phase respectively and the signs have been omitted for convenience. The constant, K, for this reaction will be given by the equation:

$$K = \frac{[MA_N]_{org}.[H]^N_{aq}}{[HA]^N_{org}.[M]_{aq}} . \qquad (1.12)$$

For a substoichiometric separation, it is necessary that, for a given initial concentration of the acid, HA, the final concentration of the complex, MA_N, in the organic phase must be constant for any initial concentration of the metal, M, as long as there is insufficient acid to combine with all of the metal. This condition is known as substoichiometric reproducibility. To achieve this condition with reasonable precision, at least 99.9% of the acid, HA, must be consumed. From equation 1.12 it is possible to calculate the pH range over which this occur by substitution of the required reagent concentrations and the value of the extraction constant, K, (if known). The higher the value of this constant, the higher the maximum hydrogen ion concentration permissible for any given concentration of metal. It is also desirable that at least 99.9% of the complex, MA_N, is in the organic phase. If the partition coefficient of the complex is not sufficiently high, this condition can be achieved by extraction with successive portions of the organic solvent. Finally, it is important that the metal, M, forms only one complex with the acid, HA, as if more than one complex is formed, the concentration of the metal in the organic phase will depend on the initial concentration of the metal in the aqueous phase.

In order to demonstrate the increased selectivity of substoichiometric solvent extraction, consider a system in which there are two metals present, M and M', which both form extractable complexes with the acid, HA. If the valencies of the two metals, N and N', are equal, then from equation 1.12

$$\frac{[MA_N]_{org}}{[M'A_N]_{org}} = \frac{K}{K'} \cdot \frac{[M]_{aq}}{[M']_{aq}} . \qquad (1.13)$$

If the reagent concentration is greater than that necessary to react completely with the two metals, and the initial concentrations of the metals are equal, then for the ratio of the concentrations of the two complexes, $[MA_N]/[M'A_N]$, to be greater than 100, and hence the final ratio of the metal ion concentrations in the aqueous phase, $[M']/[M]$, to be also greater than 100, the ratio of the extraction constants, K/K', must be greater than 10^4. However, if a sufficient quantity of the acid, HA, is present to separate only 50% of the metal, M, then the final ratio of the metal ion concentrations, $[M']/[M]$, will be 2. Hence, from equation (1.13), the ratio of the extraction constants, K/K', need only be greater than 200, in order that the ratio of the concentrations of the complexes in the organic phase, $[MA_N]/[M'A_N]$, can be greater than 100. If the ratio of the extraction constants is large, the metal, M, may be completely separated even when the metal, M', is in excess. Obviously the ideal situation is that in which the complex, MA_N, is much more readily extractable thanthe complexes formed by the acid, HA, with any other metals. Although this is possible in a few cases, often such a system will not be available for a particular metal, but by the use of masking agents and preliminary separations, it has been possible to develope substoichiometric separations for a large number of elements[6,7,9-14,17-20].

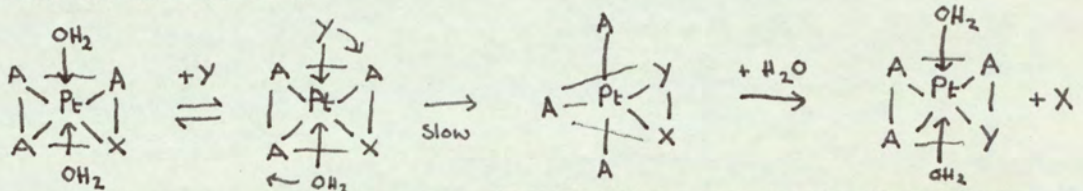
II. The Chemistry and Analysis of Palladium.

Palladium is a second row transition element, having the same outer electronic configuration as nickel and platinum. Like nickel, it is predominantly divalent, but the tetravalent state is quite important and the monovalent and trivalent states are known. A concise account of the chemistry of palladium is given in reference 21. The metal is most easily dissolved by aqua regia, although single mineral acids will attack it slowly in the finely divided form. In the divalent state it forms an oxide, PdO, all four halides, PdX_2, (where X = F, CL, Br or I) a cyanide, $Pd(CN)_2$, and two salts of oxyacids, palladous nitrate, $Pd(NO_3)_2$, and palladous sulphate, $PdSO_4$. All the halides and the cyanide form complex salts with alkali metal halides , of the general formula, M_2PdX_4, (where M = Na or K) and in solutions containing excess of the corresponding halide or cyanide ions, these compounds predominantly exist as the complex tetrahalogenopalladate ion, PdX_4^{2-}, or the tetracyanopalladate ion, $Pd(CN)_4^{2-}$. The palladous ion, Pd^{2+}, is thought to exist[22], but only in small concentrations. In chloride solutions, palladium is known to form six complexes, of the general formula, $PdCl_n^{2-n}$, where n = 1 to 6[23], but the tetrachloro complex, $PdCl_4^{2-}$, is the most important.

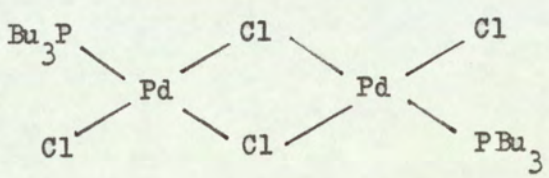
In the tetravalent state, palladium forms an ill-defined oxide, PdO_2, which is only known in the hydrated form and the two halides are only known as their complex salts, of which the anions are the hexachloropalladic ion, $PdCl_6^{2-}$, and the hexabromopalladic ion, $PdBr_6^{2-}$. The tetravalent compounds slowly revert to the divalent state on standing. The main monovalent compound is the oxide, Pd_2O, and the main trivalent compound is the trifluoride, PdF_3, although other compounds are known[24].

Palladium-II complexes are predominantly square planar. Like nickel complexes, they have a low spin d^8 configuration, as shown by

magnetic susceptibility measurements[24]. Palladium tends to form very strong complexes, although not so strong as platinum[21]. All the metals in the group; nickel, palladium, platinum, show a tendency to be slow in their reactions, i.e., to kinetic "inertness", and this tendency increases down the periodic table. For an analagous reaction, e.g., the replacement of chlorine by pyridine in the complex, trans[$M(PEt_3)_2$ - (o-tolyl)Cl] (where M = Ni, Pd or Pt and PEt_3 represents triethylphosphine) the rates of the reactions involving nickel, palladium and platinum respectively are in the approximate ratio $10^6:10^5:1$ [25]. Most work has been done on platinum complexes as the reaction rates involved are easier to measure than the rates of the faster reactions of palladium and nickel, but in general, displacement reactions of square planar complexes are thought to go via five-coordinated intermediates of trigonal bipyramid structure and usually involve solvent participation. The mechanism suggested by Benson[26] for the replacement of a ligand, X, by a ligand, Y, in a square planar platinum complex, PtA_3X, in aqueous solution is as follows:



The difference in reaction rates of the three metals is therefore thought to be due to the increasing difficulty of expansion to a higher coordination number going down the series, nickel, palladium, platinum. This is borne out by work with sterically hindered ligands[26]. Palladium commonly forms mixed complexes, especially with chloride ions, and it also has a tendency to form polynuclear bridged complexes, where the bridging atoms can be halogens, mercaptide anions or thiocyanate ions[22,27]. For example, palladium dichlorotributylphosphate has been shown to have the structure:



These complexes however, usually only exist in solid form or strong solutions. In dilute solutions, they revert to mononuclear states[28].

Analysis

Many accounts are available for general analytical methods for the determination of palladium[21,29,30]. Probably the most widely used reaction for the separation and determination of palladium is the precipitation of the dimethylglyoximate from acid solution. However palladium forms a large number of complexes suitable for analysis purposes, many of which are described in a number of reviews[31-39]. The methods of determination are mainly colourimetric and titrimetric, in fact there are so many colourimetric methods that choice is rendered difficult. The sensitivities of such methods varies but the highest values reported are of the order of parts per million (p.p.m.)[31-34].

Other methods of trace analysis include atomic absorption spectroscopy, spectrochemical methods, X-ray fluorescence and flame spectrometry. These have been reviewed by Beamish et. al.[40] and the most sensitive methods appear to spectrochemical, which is claimed to determine amounts of palladium down to 0.01p.p.m.,[41,42] and fire assay combined with emission spectrography, for which a sensitivity of 0.01ppm. to 0.004ppm. has been claimed[43,44].

Neutron activation methods have also been reviewed by Beamish et. al.[45]. Sensitivities were not quoted in most cases, as these will depend more on irradiation conditions than on the chemical separation. However Vincent and Smales quoted a sensitivity of 0.01 ppm.[46].

Although there are so many complexing agents for palladium, very little data is available on most of them. It should not be difficult to find a reagent suitable for a substoichiometric separation, but many of the complexes would not be completely formed under substoichiometric conditions, where the concentration of the reagent as well as that of the metal is low, because either the reaction does not go to completion unless a large excess of the reagent is present, or because the reaction is kinetically too slow. If palladium is

present in chloride solution, the complex formed must be at least strong enough to compete with the chloro complexes. There are two chelating agents, which are known not only to form complexes with palladium which are more readily extractable than those formed with most other metals, but about which enough is known to indicate that the extraction constants of these complexes are extremely high. These are dithizone, which has been suggested for the substoichiometric separation of palladium by Ruzicka and Stary[3], and diethyldithiocarbamic acid. Both these reagents have been used in a number of substoichiometric separations for other metals[7,9-11]

Dithizone forms extractable complexes into chloroform or carbon tetrachloride with only a few metals, but palladium is reported to form the most readily extractable complex[47]. The highest known extraction constant is that of mercury-II which is 6×10^{26} into carbon tetrachloride[48]. Therefore the extraction constant of palladium dithizonate must be higher than this. However under conditions where palladium is in excess of dithizone, a secondary dithizonate is formed which is reported by Iwantscheff to be very insoluble[49], although Beardsley et. al. [50] have found otherwise. This feature may make dithizone unsuitable for substoichiometry.

The second reagent, diethyldithiocarbamic acid is known to form complexes with a large number of metals[51]. The order of extractability varies with different authors, but it seems possible that mercury-II and gold-III may form more readily extractable complexes than palladium. However, palladium replaces copper-II from its diethyldithiocarbamate, for which a stability constant of $10^{28.8}$ has been determined[52]. Also, attempts to measure the stability constant of palladium diethyldithiocarbamate by competition with palladium dithizonate[53] indicated that the diethyldithiocarbamate was the stronger complex. In fact, the work reported in this thesis shows that palladium diethyldithiocarbamate is more readily extractable than mercury-II under the conditions used

(Ch.4.II.1c), and the reports of the reverse are probably due to a kinetic effect (Ch.2.I)

Palladium dithizonate is discussed more fully in Chapter 6 and palladium diethyldithiocarbamate in Chapter 2.

III The Nuclear Characteristics of Palladium.

1. General Considerations.

Palladium has six stable isotopes and twelve radioactive isotopes (not including metastable states). The properties of these are listed in Table 1.1, together with the products of the stable isotopes on thermal neutron irradiation, that is of (n,γ) reactions. The data in Table 1.1 are taken from reference 54.

It can be seen that the most important product of thermal neutron irradiation, for the purpose of neutron activation analysis is palladium-109. The principal gamma ray energy is 88 keV,[54] and the silver X-radiation, 22 keV.[55] The maximum β^- energy is 1.03 Mev.[54] The γ-ray spectrum of palladium-109 is shown in Figure 1.1. The activities of palladium-103, palladium-107 and palladium-111 will be insignificant compared to that of palladium-109, for periods of a few hours to a few days after irradiation, because of the lower cross-sections and different half-lives. However, after the decay of palladium-109, palladium-103 becomes the most important activity. The formation of palladium-111 and palladium-111m is also important because these decay to silver-111, a radioactive isotope of silver with a half-life of 7.5 days[54]. The specific activity with respect to palladium of this silver-111 is comparable to that of palladium-103, and this will therefore interfere with the use of palladium-103 for tracer work. It is necessary therefore, to separate the silver isotope

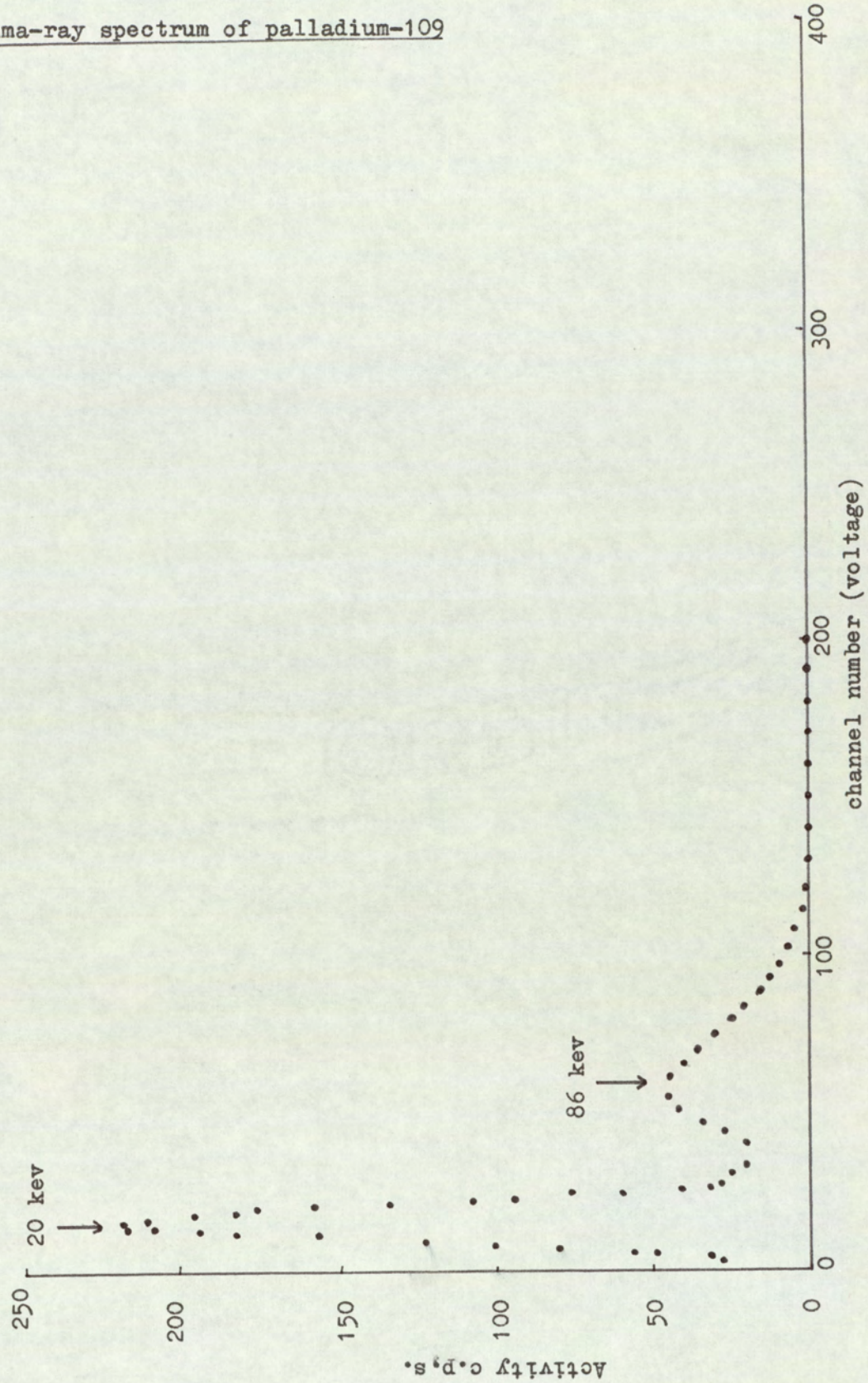
Table 1.1

Stable Isotope Of Palladium	Half-Life	Type of Decay	Isotopic Abundance %	Thermal neutron cross-section (barns)	Product of (n, γ) reaction	Product of radioactive decay
98	17.5m	E.C., γ	-	-	-	-
99	22m	β^+, γ	-	-	-	-
100	4.1d	E.C., γ	-	-	-	-
101	8.5h	E.C., β^+, γ	-	-	-	-
102	stable	-	0.96	4.8	103	^{103}Rh
103	17.0d	E.C., γ	-	-	-	-
104	stable	-	10.97	-	-	-
105	stable	-	22.2	-	-	-
106	stable	-	27.3	0.29	107	^{107}Ag
107m	21.3s	I.T.	-	-	-	-
107	7×10^6 y	β^-, no γ	-	-	-	-
108	stable	-	26.7	12 + 0.2	109+109m	^{109}Ag
109m	4.75m	I.T.	-	-	-	-
109	13.5h	β^-, γ	-	-	-	-
110	stable	-	11.81	0.2+0.04	111+111m	^{111}Ag*
111m	5.5h	I.T., β^-, γ	-	-	-	-
111	22m	β^-, γ	-	-	-	-
112	21h	β^-, γ	-	-	-	-
113	1.4m	β^-, no γ	-	-	-	-
114	2.4m	β^-, no γ	-	-	-	-
115	45s	β^-	-	-	-	-

* radioactive decay product

FIGURE 1.1

Gamma-ray spectrum of palladium-109



after the decay of the 5.5hour palladium-111m. This can be done quite simply by adding inactive silver nitrate solution as carrier to a solution of irradiated palladium and precipitating as silver chloride (Ch.3.II.1). Figure 1.2 shows the mixed γ-ray spectra of palladium-103 and silver-111 before separation and Figures 1.3 and 1.4 show the spectra of the separated isotopes. The principal radiation of palladium-103 is the 20 keV. rhodium X-ray[55], while silver-111 has γ-ray energies of 342 and 247 keV,[54] as well as the 23 keV. cadmium X-ray[55]. Decay curves of the various isotopes were measured by counting samples after different periods of time and the results are given in Table 1.2 and Figure 1.5

Table 1.2

Time(hrs)	Untreated palladium (c.p.s.)	Separated ^{103}Pd (c.p.s.)	Separated ^{111}Ag (c.p.s.)
0	701	250	382
5	598	246	374
20	290	241	348
38	136	234	319
65	65.0	226	293
89	46.3	214	260
112	39.1	208	237
184	30.0	185	202
207	27.9	179	172
232	26.2	169	149
259	24.2	161	137
334	20.2	143	103
399	17.3	128	79.2
519	13.2	102	49.5
691	8.9	77.5	25.5

FIGURE 1.2

Gamma-ray spectrum of natural mixture of palladium-109 and silver-111.

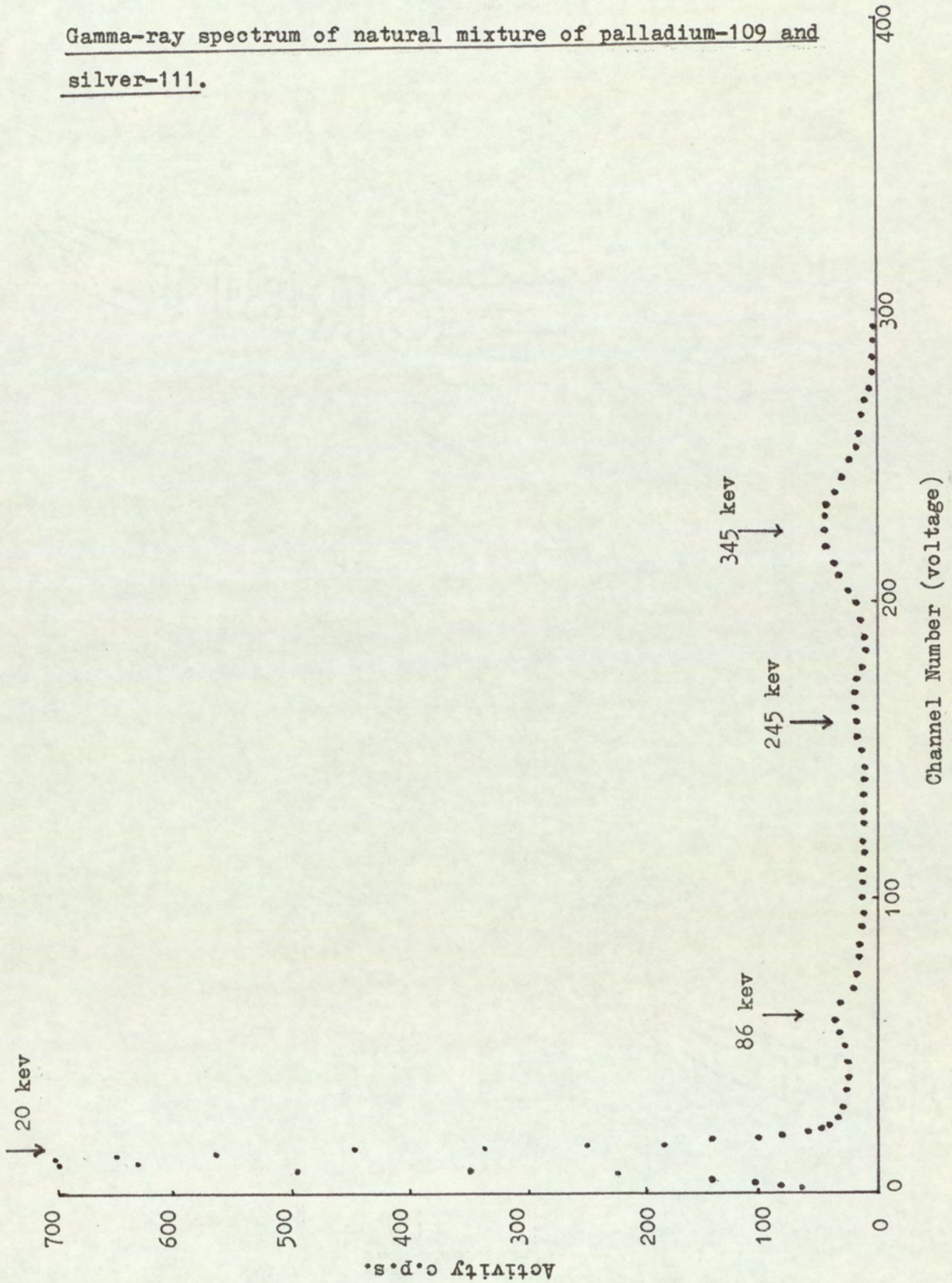
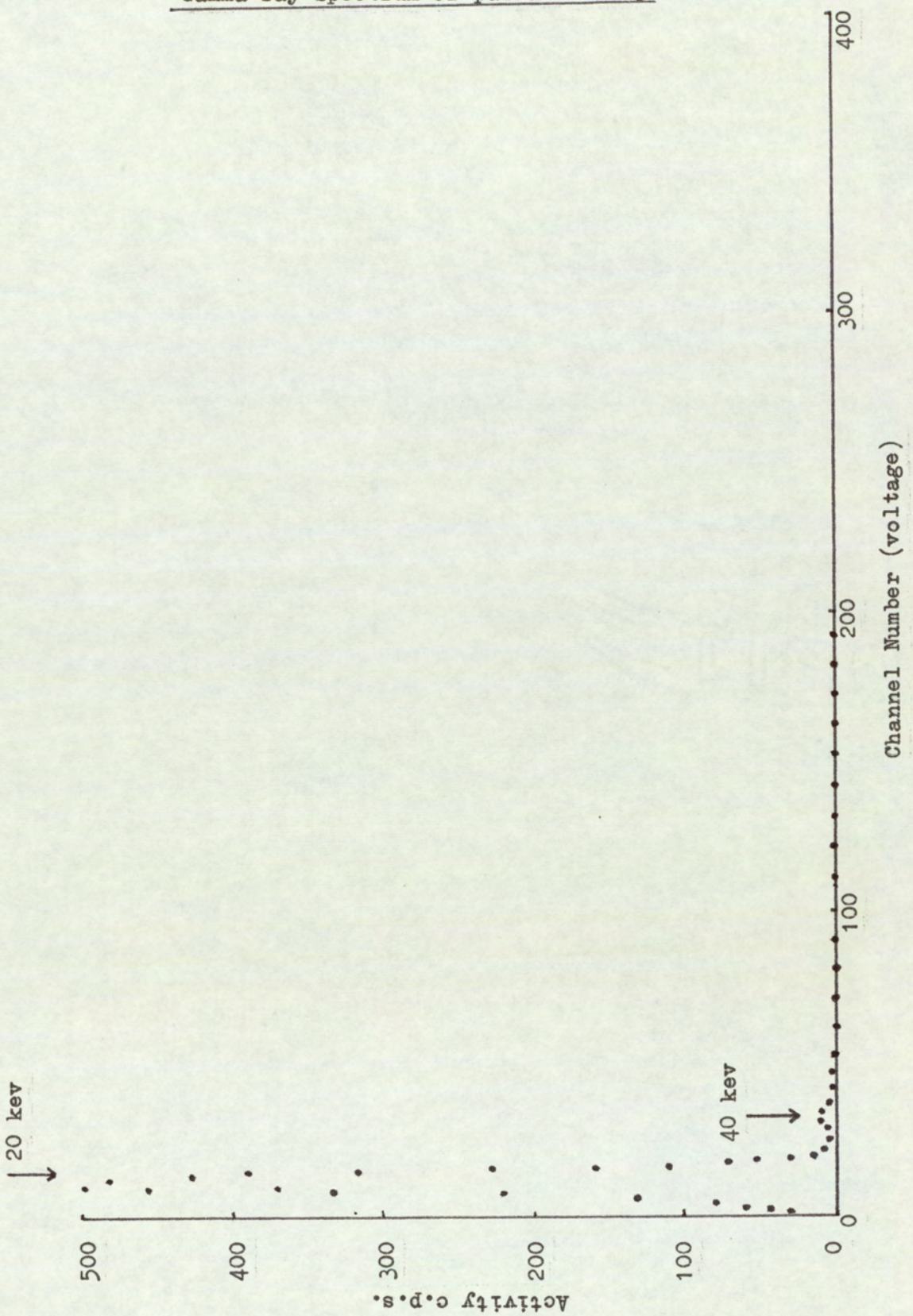


FIGURE 1.3

Gamma-ray spectrum of palladium-103



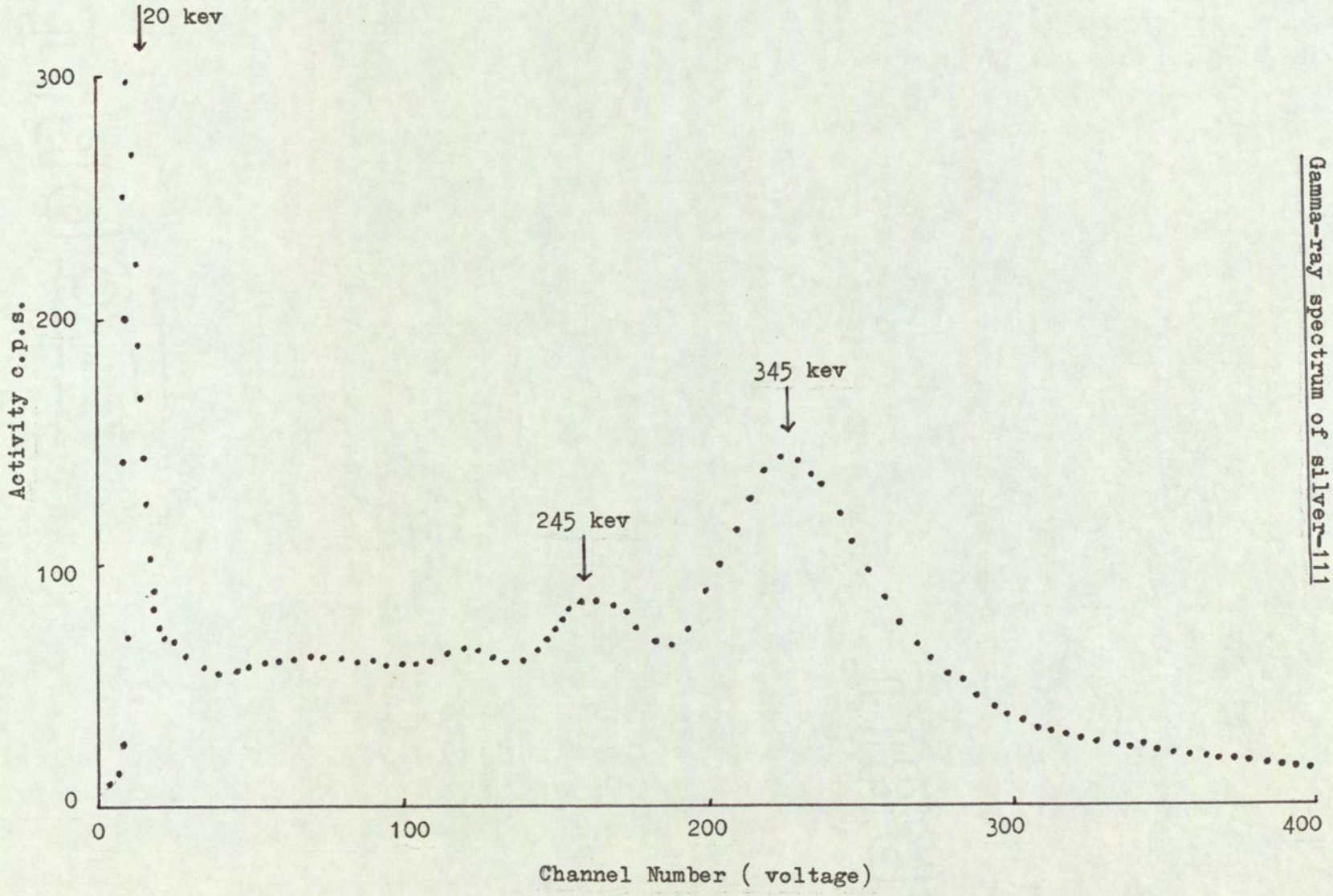


FIGURE 1.4

Gamma-ray spectrum of silver-111

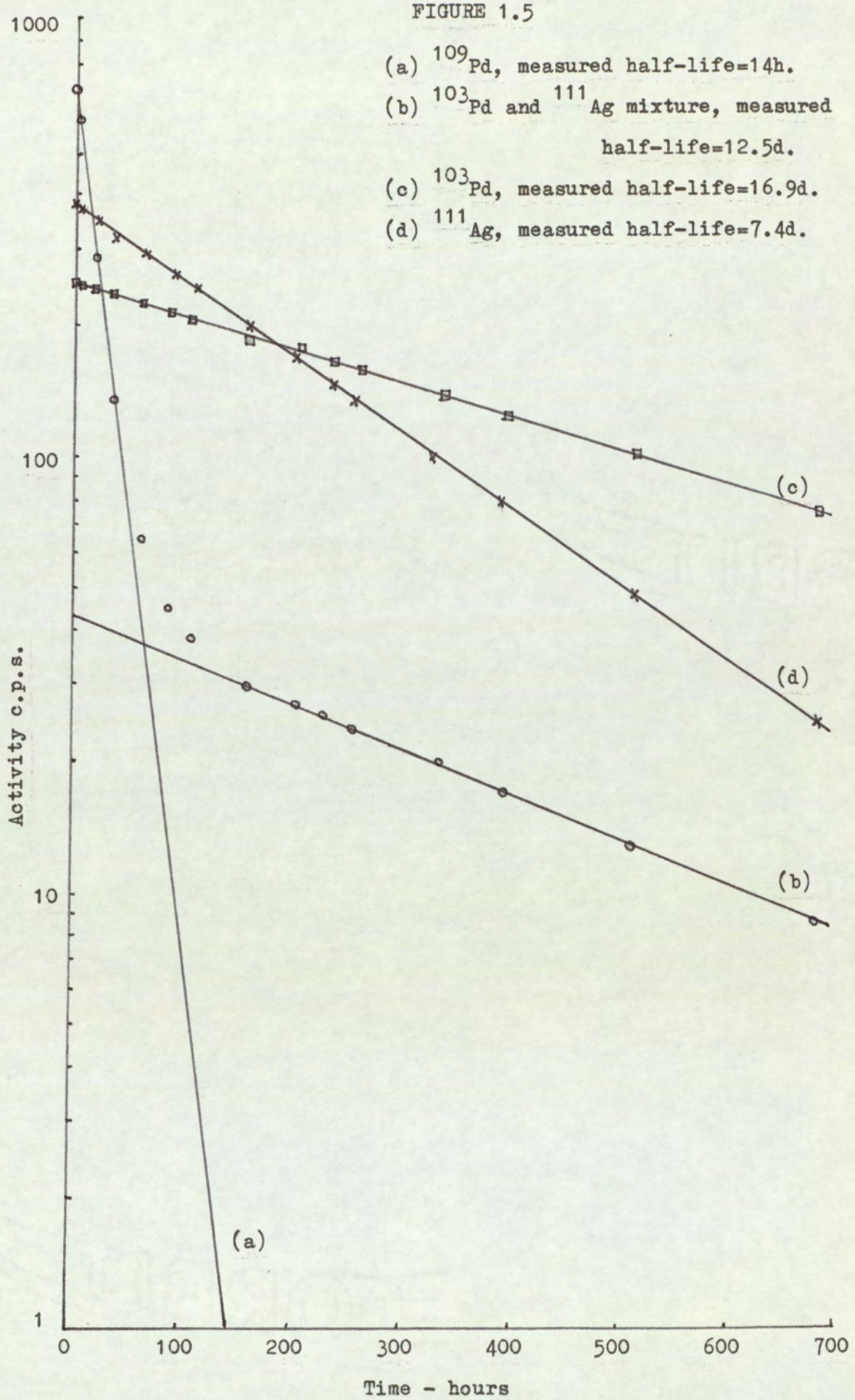
FIGURE 1.5

(a) ^{109}Pd, measured half-life=14h.

(b) ^{103}Pd and ^{111}Ag mixture, measured half-life=12.5d.

(c) ^{103}Pd, measured half-life=16.9d.

(d) ^{111}Ag, measured half-life=7.4d.



2. Detection.

(a) Gamma-ray emitting nuclides.

Palladium isotopes were detected using a well-type, 50x50 mm sodium iodide crystal (activated with thallium), associated with a single channel gamma-ray spectrometer, supplied by Nuclear Enterprises Limited. Both liquid and evaporated samples were counted in 20 mm diameter phials, volume 15 ml.

For palladium-109, a discriminator setting corresponding to 40 keV was used, in order to count the 88 keV peak only, and so eliminate absorption effects (see below) and the need for evaporation of organic solutions. This setting resulted in a background of about 10 c.p.s. However, in the activation analysis of test samples in Chapter 4, the activity of the samples was so low that maximum counting efficiency was necessary, and to achieve this, solutions of both standard and samples were evaporated and counted using a discriminator setting corresponding to 10 - 30 keV. This resulted in a very low background of about 2 c.p.s.. To count both the 22 keV and the 88 keV radiation, a wider channel would have been needed and this would have resulted in a higher background count and hence a lower accuracy [see section (c)].

For palladium-103, a setting corresponding to 10 - 50 keV was used in order to count both the 20 keV and the 40 keV radiation. This resulted in a background of 2 - 3 c.p.s. For the other radioactive nuclides, used for direct interference studies in Chapter 4.II.1d, a setting corresponding to about 20 keV was used.

To count palladium-103 and silver-111 simultaneously (Ch.VII.4a) two channels were used; a 10 - 30 keV channel (A) to count most of the palladium-103 radiation, and a channel of 30 keV upwards (B) to count most of the silver-111 radiation. The activities, x and y, of palladium-103 and silver-111 respectively, could be calculated by counting samples of the individual isotopes under the same conditions.

Suppose: a = activity of palladium-103 in lower channel,

b = activity of palladium-103 in higher channel,

c = activity of silver-111 in lower channel,

d = activity of silver-111 in higher channel,

A = measured activity in lower channel,

B = measured activity in higher channel,

then

$$\frac{a}{a+b}\cdot x + \frac{c}{c+d}\cdot y = A \qquad (1.14)$$

and

$$\frac{b}{a+b}\cdot x + \frac{d}{c+d}\cdot y = B, \qquad (1.15)$$

from which the following expressions can be obtained (see Ch.2.II.3):

$$x = \begin{vmatrix} \frac{c}{c+d} & -A \\ \frac{d}{c+d} & -B \end{vmatrix} \div D \qquad (1.16)$$

and

$$y = \begin{vmatrix} -A & \frac{a}{a+b} \\ -B & \frac{b}{a+b} \end{vmatrix} \div D \qquad (1.17)$$

where

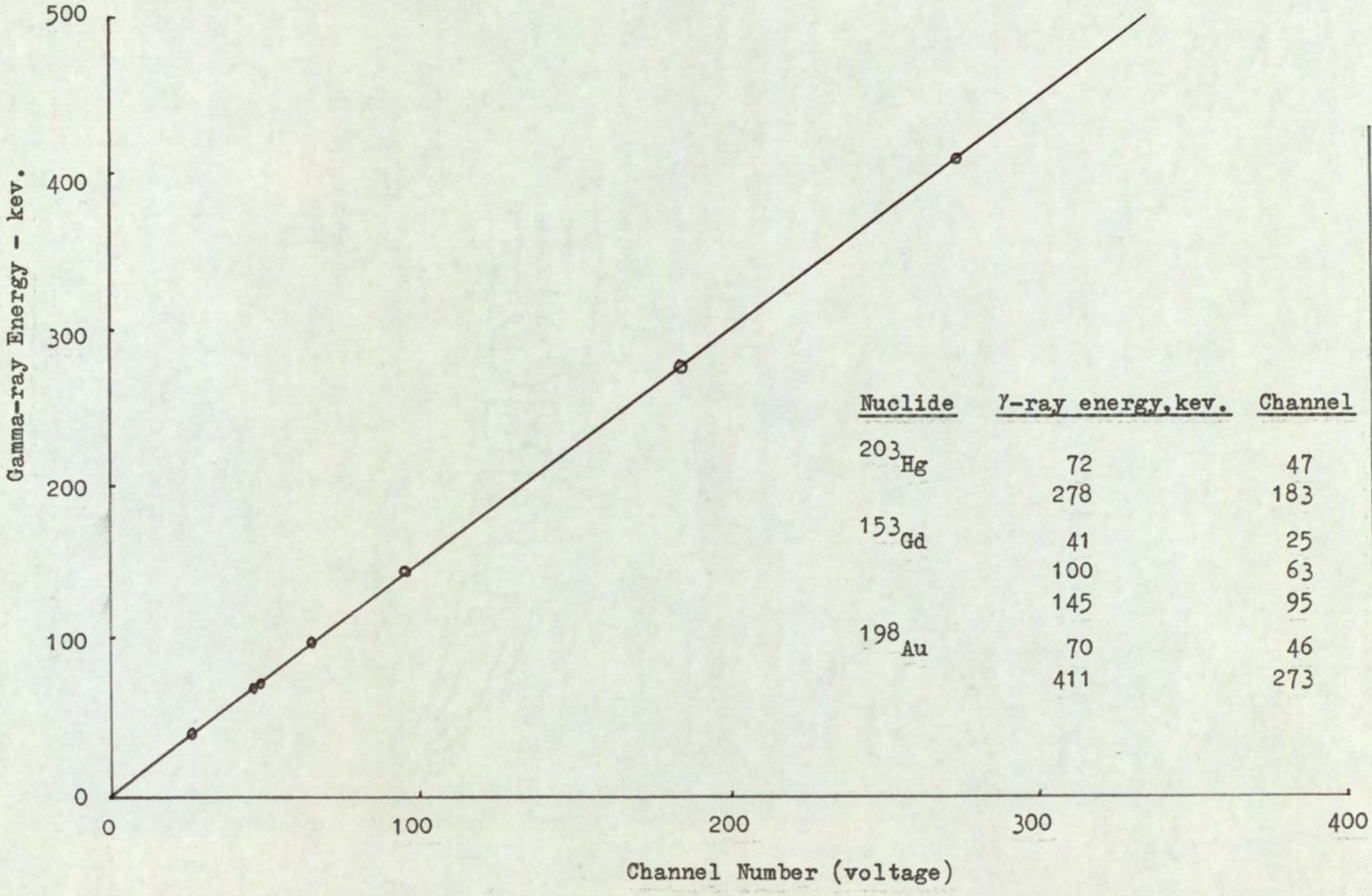
$$D = \begin{vmatrix} \frac{a}{a+b} & \frac{c}{c+d} \\ \frac{b}{a+b} & \frac{d}{c+d} \end{vmatrix} .$$

For the measurement of gamma-ray spectra, a Laben Spectroscope, Model 400, was used. This was connected to the amplifier output of the

single channel gamma-ray spectrometer. The spectra were recorded by printing out on to a typewriter after counting for a set period of time. The Laben Spectroscope was calibrated by the use of nuclides having known gamma-ray energies. The gamma-ray energy was plotted against the number of the channel on the spectroscope at which the corresponding peak appeared, that is against voltage, in Figure 1.6, and by counting the palladium isotopes on the same amplifier setting, it was possible to determine the energies to which the peaks in Figures 1.1 to 1.4 corresponded from the channel number and reference to Figure 1.6. The spectroscope was also used to calibrate the single channel gamma-ray spectrometer, in order to determine the voltage settings suitable for counting particular energies (above).

(b) Chlorine-36.

Chlorine-36 has a half-life of 3×10^5 years and is detected by its β^- emission, which has a maximum energy of 0.714 MeV.[54] This was counted on a liquid scintillation spectroscope, supplied by Nuclear Enterprises Limited, using a suitable discriminator setting for this isotope. The chlorine-36 was initially in the form of a labelled sodium chloride solution and the samples to be counted were in solutions of chloroform. In order to count the samples, 1.0ml of the chloroform solution was mixed with 0.1ml of inactive sodium chloride solution and 10ml of liquid scintillator. For the standards, 0.1ml of the labelled sodium chloride solution was mixed with 1.0ml of chloroform and 10ml of liquid scintillator. The composition of samples and standards was made as similar as possible, as the low energy radiation is subject to absorption, and the volume of chloroform was kept to a minimum as chlorine atoms have a quenching effect. If the organic solution was coloured, as in the case of the dithizonate complexes (Ch.7.I.1), 1.0ml of an inactive solution of the complex was used for the standard instead of chloroform, as coloured substances also tend to have a quenching effect. The scintillator used was NE 220, supplied



Nuclide	γ-ray energy, kev.	Channel
^{203}Hg	72	47
	278	183
^{153}Gd	41	25
	100	63
	145	95
^{198}Au	70	46
	411	273

FIGURE 1.6

Calibration curve for Laben Spectroscope.

by Nuclear Enterprises Limited, which is suitable for internal counting of aqueous solutions.

(c) Statistics of Counting.

Radioactive disintegration is a random process and as such will be subject to fluctuation. Measurements of this process will not give the true disintegration rate, but will vary about a mean rate according to a Poisson distribution[56]. The greater the number of events observed in any measurement, the nearer the observed rate will be to the true or mean rate, as for a Poisson distribution, the standard deviation, s, is given by the expression

$$s = \sqrt{N} \qquad (1.18)$$

where N is the number of events observed. An estimate of the probable error can be obtained from the ratio of the standard deviation to the number of events, s/N. If the number of events, N, is 10,000, from equation 1.18 it can be seen that the standard deviation, s, will be equal to 100, that is, 1% of N. As theory shows that 95% of the observed results will lie within two standard deviations, and 68% will lie within one standard deviation[57], it can be seen that the maximum probable deviation will be less than 2% of the mean. An error of this magnitude is usually permissible, as in experiments of the type carried out in this work, other errors are usually of the same order or higher than this. Hence, as far as possible, a minimum of 10,000 counts was obtained in all experiments. Detection equipment always has a certain background counting rate, which is subject to the same type of statistical variation, as well as variation due to changes in its environment. This will obviously introduce further errors into the observed counting rate and to minimise these it is desirable to have the sample counting rate much higher than the background. As scintillation counting equipment has a fairly high background, if the sample activity is low it is necessary to minimise this background by counting in a narrow voltage channel only, as is described in section (a) for the neutron activation analysis test samples.

3. Absorption of Palladium-103 Radiation.

Attempts to count palladium-103 in chloroform or carbon tetrachloride solution met with little success due to strong absorption of the low energy X-radiation in the solvent. As it was reasonable to assume that other media would also absorb the radiation to a certain extent, an investigation of the effect of a large number of liquids was carried out. To do this a cell was constructed, consisting of a small test tube, diameter 10mm, containing about 0.25ml of an aqueous solution of palladium-103, inserted in a counting phial, diameter 20mm, so that the bottom of the test tube was 5mm from the bottom of the phial. The test tube was fixed in position by attachment to the lid of the phial, and the phial was filled in turn, to a constant level, with the liquids under investigation. In this way it was possible to measure the absorption of the palladium-103 radiation by an effective path length of 5mm in the various liquids by counting in a well type crystal. The results of this experiment are given in Table 1.4

Absorption of γ- or X-radiation in matter follows an exponential law which can be represented by the equation[58]

$$B = B_o e^{-\mu x} \qquad (1.19)$$

for any particular energy of radiation, where

B = intensity of the beam,

B_o = initial intensity of the beam,

x = thickness in atoms.cm^{-2},

μ = absorption coefficient in cm^2.atoms^{-1}.

For a pure liquid, the thickness, x, due to any one type of atom is given by

$$x = n.A.\rho.l/m \qquad (1.20)$$

where n = number of atoms in the molecule,

A = the Avogadro number,

ρ = density,

l = path length,

m = molecular weight.

For a solution, the thickness due to any atom in the solute is given by

$$x = n.M.A.l/10^3 \qquad (1.21)$$

where M = the molarity of the solution.

Hence, if μ is known, the percentage transmission, $B/B_o \times 100$, can be calculated for the cell used above. Siegbahn[58] has listed the values of the absorption coefficient, μ, for some elements, and the values for 20keV. radiation have been given in Table 1.3 and plotted against atomic number in Figure 1.7. From Figure 1.7 it is possible to interpolate values of the absorption coefficient for the other elements and these are also given in Table 1.3. Using the values of the absorption coefficient from Table 1.3 and values of the thickness, x, calculated for a path length of 5mm from equations 1.20 and 1.21, the expected value of the transmission, B/B_o, was calculated. Where more than one atom plays an important part in the absorption, the total transmission is the product of the individual calculated transmissions. The results of these calculations, given in Table 1.4, are in good agreement with the observed transmissions. In practice, however, it is not possible to calculate the transmission when the isotope is dissolved in the liquid rather than surrounded by it, but this experiment enables prediction of the degree of absorption which will occur in various media. In most of this work, it was necessary to compare the activity of chloroform or carbon tetrachloride solutions of palladium-103 with aqueous solutions of this isotope containing hydrochloric acid. In order to count organic solutions at all, the solvent had to be removed by evaporation. This could be done quickly and reproducibly by evaporation on a water bath at 60 - 80°C (see precision experiments, Ch.4.II.1b and Ch.5.II.2c). Evaporation of aqueous solutions was much slower and did not appear to give the same results, so to compare the activities of organic and aqueous phases, residues from evaporated organic phases were dissolved in 1N hydrochloric acid and recounted. The difference in the activity

FIGURE 1.7

Variation of absorption coefficient with atomic number (from Table 1.3)

measured in the two media indicated that only 82% of the activity was measured in 1N hydrochloric acid, compared to that measured after evaporation of an organic solvent. Hence, in all subsequent experiments the measured activity of the aqueous phase was corrected by multiplication by 100/82. No effects were observed due to varying thicknesses of counting phials.

Table 1.3

Absorption coefficients for 20 keV. Radiation

Calculated values[58]			Interpolated values		
Element	Atomic Number (Z)	Absorption Coefficient, μ (10^{-24} cm.^{2} atoms^{-1})	Element	Atomic Number (Z)	Absorption Coefficient, μ (10^{-24} cm.^{2} atoms^{-1})
H	1	0.62	S	16	360
Be	4	3.25	Cl	17	450
C	6	8.24	K	19	680
N	7	13.3	Ni	28	3,060
O	8	21.1	Pd	46	2,350
Na	11	73.8	Ag	47	2,570
Al	13	146	Ce	58	6.800
Si	14	198			
A	18	555			
Ca	20	844			
Fe	26	2,340			
Cu	29	3,530			
Mo	42	1,670			
Sn	50	3,460			
I	53	4,440			
W	74	16,600			
Pt	78	20,400			
Pb	82	24,700			
U	92	30,300			

Table 1.4

Absorbing Medium	Transmitted Activity (c.p.s)	Measured Transmittance, %	Density (at 20–25°C)	x, atoms.cm^{-2} (heaviest atoms)	B/B_o x 100	Total* Transmission (%)
air	100.9	100	-	-	-	-
water	72.5	72.0	-	1.67×10^{22}(O)	70.5(O)	70.5
1N HCl	64.3	63.8	-	3.10×10^{20}(Cl)	87.0(Cl)	61.0
5N HCl	36.6	36.2	-	15.5×10^{20}(Cl)	50.0(Cl)	35.3
1N H_2SO_4	70.2	69.5	-	3.10×10^{20}(S)	89.6(S)	63.1
5N H_2SO_4	51.0	50.4	-	15.5×10^{20}(S)	57.7(S)	40.7
1N HNO_3	72.9	72.4	-	9.30×10^{20}(O)	98.0(O)	
				3.10×10^{20}(N)	100(N)	69.1
5N HNO_3	66.7	66.0	-	46.5×10^{20}(O)	90.5(O)	
				15.5×10^{20}(N)	98.0(N)	62.4
1N KOH	60.3	59.8	-	3.10×10^{20}(K)	83.5(K)	59.0
6N NaOH	69.4	68.8	-	18.6×10^{20}(Na)	86.9(Na)	61.3
1M $Ni(NO_3)_2$	30.3	30.0	-	3.10×10^{20}(Ni)	38.7(Ni)	27.3
1M $Ca(NO_3)_2$	57.5	57.0	-	3.10×10^{20}(Ca)	77.1(Ca)	54.0
1M $AgNO_3$	35.7	35.4	-	3.10×10^{20}(Ag)	44.9(Ag)	31.7
1N $HClO_4$	67.8	67.2	-	3.10×10^{20}(Cl)	87.0(Cl)	61.0
0.7M KI	22.9	22.7	-	2.2×10^{20}(K)	83.5(K)	
				2.2×10^{20}(I)	37.5(I)	22.1
1M $Ce(NO_3)_3$	11.7	11.6	-	3.10×10^{20}(Ce)	13.5(Ce)	9.5
1M $UO_2(NO_3)_2^+$	2.3	2.3	-	3.10×10^{20}(U)	0(U)	0
C_2H_5OH	79.5	79.0	0.789	1.03×10^{22}(C)	92.3(C)	
				0.52×10^{22}(O)	88.7(O)	81.6
CH_3OH	82.9	82.3	0.796	0.75×10^{22}(C)	94.2(C)	
				0.75×10^{22}(O)	85.2(O)	80.2
C_6H_6	88.9	88.0	0.879	2.03×10^{22}(C)	85.2(C)	85.2
$(CH_3)_2CO$	86.3	85.7	0.792	1.2×10^{22}(C)	90.5(C)	
				0.4×10^{22}(O)	91.4(O)	83.0
$(C_2H_5)_2O$	89.1	88.5	0.714	1.2×10^{22}(C)	90.5(C)	
				0.3×10^{22}(O)	94.2(O)	85.4

Table 1.4(continued)

Absorbing Medium	Transmitted Activity (c.p.s.)	Measured Transmittance,%	Density (at 20-25°C)	x, atoms.cm^{-2} (heaviest atoms)	B/B_o x 100	Total* Transmission (%)
$CHCl_3$	1.0	1.0	1.498	1.1×10^{22}(Cl)	0.67(Cl)	0.67
CCl_4	1.0	1.0	1.595	1.25×10^{22}(Cl)	0.37(Cl)	0.37
CS_2	4.3	4.3	1.263	1.0×10^{22}(S)	2.7(S)	2.7
$CH_2Cl.CH_2Cl$	3.8	3.8	1.257	0.77×10^{22}(Cl)	3.3(Cl)	3.3
C_6H_5Cl	24.7	24.5	1.107	1.8×10^{22}(C)	86.1(C)	
				0.3×10^{22}(Cl)	25.9(Cl)	22.3
C_3H_7Br	0	0	1.353	0.3×10^{22}(Br)	0(Br)	0

* absorption of aqueous solutions includes absorption of water

\+ natural uranium activity subtracted.

CHAPTER 2

Palladium Diethyldithiocarbamate Complexes: Theory and Discussion.

I. Formation of palladium diethyldithiocarbamate complexes.

In order to develope a neutron activation method for the determination of traces of palladium, it was necessary to find a chemical separation suitable for separating milligram quantities under conditions which are practicable for the treatment of real samples. As mentioned in Chapter 1, section II, there are two reagents which might be suitable for a substoichiometric separation of palladium, namely dithizone and diethyldithiocarbamic acid. However dithizone is known to form two complexes when palladium is in excess of the reagent, and this might be expected to lead to complications, and so it was decided to investigate the second reagent, diethyldithiocarbamic acid. As both diethyldithiocarbamic acid and its alkali metal salts are known to be unstable, especially in acid solutions[51], heavy metal complexes of the acid, such as cupric diethyldithiocarbamate, in organic solvents, were chosen for this investigation, as similar systems have been used with success in other substoichiometric determinations[10,17,18].

The preliminary experiments, carried out in Chapter 3, sections V and VI, showed that there were three complexes formed by palladium with cupric diethyldithiocarbamate in chloroform. The composition of these complexes were found to correspond to the formulae, $Pd(DDC)_2$, Pd.Cl(DDC) and Pd(DDC) where DDC represents the diethyldithiocarbamate anion. As a substoichiometric separation requires that only one complex is formed under the conditions of the experiment, the formation of these complexes was further investigated by the kinetic study in Chapter 3, section VII. The 1:1 complex, Pd(DDC) had only formed under alkaline conditions (Ch.3.VI) and so this complex was not studied further. As the two complexes, palladium diethyldithiocarbamate,

$Pd(DDC)_2$, and palladium chloride diethyldithiocarbamate, Pd.Cl(DDC), were found to be formed by extraction from media of hydrochloric acid and sulphuric acid respectively,(Ch.3.V),it was obvious that chloride ion concentration and possibly hydrogen ion concentration played an important part in the formation of the two complexes and therefore the effect of these two species on the rate of extraction of palladium into chloroform was studied in some detail in Chapter 3, section VII-1.

The rate curves obtained showed clearly that initially the 1:2 complex, palladium diethyldithiocarbamate was formed, corresponding to the first plateau on the curve (Figures 3.4 to 3.7) and then after varying intervals of time, the 1:1 complex, palladium chloride diethyldithiocarbamate, was formed. The effect of increasing the chloride ion concentration and keeping the hydrogen ion concentration constant was to slow both these reactions down(Figures3.4 to 3.6). This effect, however, was much greater on the second reaction than on the first, so that at high chloride ion concentrations,that is about 5N, palladium chloride diethyldithiocarbamate did not appear to form at all during the time of the experiment. The effect of increasing the hydrogen ion concentration was an increase in the rate of both reactions (Figure 3.7). Hence by choice of conditions it was possible to obtain complete formation of either complex: high hydrogen ion concentration and low chloride ion concentration gave rapid formation of palladium chloride diethyldithiocarbamate, while high hydrogen ion concentration and high chloride ion concentration gave rapid formation of palladium diethyldithiocarbamate which was not followed by any formation of the chloro complex.

The effect of chloride ionson the rate of extraction can be explained by considering the reactions by which the complexes are formed. These can be written

$$Pd^{2+}_{aq} + Cu(DDC)_{2org} \rightleftharpoons Pd(DDC)_{2org} + Cu^{2+}_{aq} \qquad (2.1)$$

and $$Pd^{2+}_{aq} + 2Cl^{-}_{aq} + Pd(DDC)_{2org} \rightleftharpoons 2Pd.Cl(DDC)_{org}. \qquad (2.2)$$

From these reactions it is not obvious why chloride ions should inhibit the extraction, until the reaction between palladium and chloride ions is considered. In Chapter 1, sectionII, it was mentioned that palladium forms six chloro complexes, the main one being the tetrachloro anion, $PdCl_4^{2-}$, and that in chloride solutions the concentration of free palladium-II ions, Pd^{2+}, is very small as chloride ions favour reactions of the type;

$$Pd^{2+} + 4Cl^{-} \rightleftharpoons PdCl_4^{2-}. \qquad (2.3)$$

Therefore, the higher the chloride ion concentration, the lower the concentration of free palladium-II ions and hence high chloride ion concentrations will inhibit both reactions 2.1 and 2.2. It is possible, however, that the formation of the diethyldithiocarbamate complexes does not involve free palladium-II ions, but one or more of the chloro complexes. The reactions might then be written

$$PdCl_{n\,aq}^{(n-2)-} + Cu(DDC)_{2org} \rightleftharpoons Pd(DDC)_{2org} + Cu^{2+}_{aq} + nCl^{-}_{aq} \qquad (2.4)$$

and $$PdCl_{n\,aq}^{(n-2)-} + Pd(DDC)_{2org} \rightleftharpoons 2Pd.Cl(DDC)_{Org} + n\text{-}2Cl^{-}_{aq}. \qquad (2.5)$$

If reaction 2.4 is considered, as the chloro complexes of copper are weaker than those of palladium[59], reaction of any palladium chloro complex will result in chloride ions being produced on the right hand side, and hence,once again, chloride ions will inhibit the reaction. In the case of reaction 2.5, this argument will only apply if n is greater than 2. However, if n is less than 2 or equal to 2, the concentration of the reacting species will be reduced by increasing the chloride ion concentration, for the same reason as the concentration of palladium-II ions will be reduced. This can be seen by considering reactions of the type;

$$PdCl_2 + 2Cl^- \rightleftharpoons PdCl_4^{2-} \qquad (2.6)$$

In reaction 2.5, unlike reaction 2.4, no cupric ions are produced which might consume some of the chloride ions by complexation. Hence it is not surprising that the effect of chloride ions is greater on the rate of formation of palladium chloride diethyldithiocarbamate than on the rate of formation of palladium diethyldithiocarbamate.

In the above discussion, it has been assumed that the observed effects are purely kinetic. However equilibrium effects may well be involved in the case where no palladium chloride diethyldithiocarbamate is formed. The constant, K, for reaction 2.5 can be expressed:

$$K = \frac{[Pd.Cl(DDC)]^2_{org}.[Cl^-]^{n-2}_{aq}}{[PdCl_n^{(n-2)-}]_{aq}.[Pd(DDC)]_{org}} \qquad (2.7)$$

and hence if the chloride ion concentration is sufficiently high, the equilibrium conditions may be such that palladium chloride diethyldithiocarbamate cannot be formed.

If palladium is extracted from a solution containing no chloride ions (Figure 3.5) it can be seen that the rate of extraction is extremely slow. Although nitrate ions do complex palladium[23], it is unlikely that the complexes are comparable with the chloro complexes in strength and therefore it might be expected that the concentration of palladium-II ions would be higher in the absence of chloride ions. As this condition does not appear to favour the formation of either of the diethyldithiocarbamate complexes it seems reasonable to assume that palladium-II ions are not the predominant reacting species and that reactions 2.4 and 2.5 are the most important.

The above investigation was carried out at concentrations suitable for use in an activation analysis method, that is, so that milligram quantities of palladium were extracted, but a separation suitable for an isotope dilution method was also required, involving

much smaller quantities of palladium. To investigate the possibility of using cupric diethyldithiocarbamate for such a separation, a study of the effect of concentration on the rates of formation of both complexes was carried out in Chapter 3, section VII-2. As one would expect, lowering the concentration of the reagent lowered the rate of extraction (Figures 3.8 and 3.9) but it also appeared to lower the percentage of palladium extracted. This was assumed to be due to decomposition of the cupric diethyldithiocarbamate by the strong acids, as the rate of consumption of the reagent was decreased. The effect was noticed at higher concentration when extracting from hydrochloric acid than when extracting from sulphuric acid and it has been shown that cupric diethyldithiocarbamate is less stable to hydrochloric acid than to sulphuric acid (Ch.3.IV.1). This decomposition is probably due to protonation of the small concentration of free diethyldithiocarbamate ions produced by the reaction:

$$Cu(DDC)_2 \rightleftharpoons Cu^{2+} + 2DDC^{-}. \qquad (2.8)$$

The diethyldithiocarbamic acid so formed is readily decomposed in acid solution by the reaction[51]:

$$(C_2H_5)_2NCSS^{-} + H^{+} \rightleftharpoons (C_2H_5)_2NCSSH \longrightarrow (C_2H_5)_2NH + CS_2. \qquad (2.9)$$

(The full formula of diethyldithiocarbamic acid is $(C_2H_5)_2NCSSH$, which has abbreviated to HDDC throughout most of this work.) Hydrochloric acid is more effective in this decomposition than sulphuric acid as the chloride ions complex the cupric ions produced in reaction 2.8, so moving the equilibrium to the right. This decomposition of the reagent at low concentrations indicates that this system is not suitable for separation of amounts of palladium below 10^{-4} to 10^{-5}g.

Chloroform was originally chosen as solvent as it was known

to be the best solvent for heavy metal diethyldithiocarbamate complexes[51], but as the rate of extraction is rather slow for palladium, a solvent in which cupric diethyldithiocarbamate is rather less soluble might be an advantage, as, for a given concentration of reagent in the organic phase, the concentration in the aqueous phase would be higher, and this may speed up the reaction. For this reason, the effect of using cupric diethyldithiocarbamate in carbon tetrachloride and in benzene as extractant was investigated in Chapter 3, sections VII-2 and VII-3. The rate curve of the extraction into benzene was a different shape from that into chloroform (Figure 3.13), but the overall reaction was not significantly faster, and as this solvent is slightly more difficult to separate from the aqueous phase than chloroform, it was not investigated further. Using cupric diethyldithiocarbamate in carbon tetrachloride the rate of extraction was initially slightly faster than in chloroform (Figure 3.12), but upon visible formation of the chloro complex, the palladium appeared to be back extracted into the aqueous phase giving a very low final level of extraction. Similar behaviour was observed at various concentrations (Figures 3.10 and 3.11) as well as the fact that palladium chloride diethyldithiocarbamate appeared to be formed by extraction from 5N hydrochloric acid. It was explained later(Ch.3.IX) by the value of the partition coefficient of this complex between carbon tetrachloride and water. Hence as chloroform appeared to be the most suitable solvent it was used in all further experiments.

Another possibility for accelerating the extraction of palladium was the use of metal complexes of diethyldithiocarbamic acid other than the cupric complex, and this was investigated in Chapter 3, section VII-4. Three complexes were tried; those of zinc, silver and nickel, and as can be seen from Figure 3.18, solutions of silver diethyldithiocarbamate, Ag(DDC), and nickel diethyldithiocarbamate, $Ni(DDC)_2$, in chloroform result in a very much slower

extraction than cupric diethyldithiocarbamate in chloroform. Figure 3.14 shows that zinc diethyldithiocarbamate, $Zn(DDC)_2$, gives a similar overall rate of extraction to the cupric complex although the shape of the rate curve is different. An interesting effect was discovered accidentally by the use of labelled palladium solutions to which silver had been added to remove the silver-111(see Ch.1.III.1) and this was the catalysis of the formation of both palladium complexes (Figures 3.15 and 3.16) by the addition of silver nitrate solution. By the use of two tracers, palladium-103 and silver-111, simultaneously (Figure 3.17) it appeared that the silver was extracted into the organic phase almost instantaneously and was then slowly replaced by palladium. This would indicate that the catalysis is due to palladium reacting more readily with silver diethyldithiocarbamate than with the zinc complex, supposing that the two reactions:

$$2Ag^{+} + Zn(DDC)_2 \rightleftharpoons 2Ag(DDC) + Zn^{2+} \qquad (2.10)$$

and

$$Pd^{2+} + 2Ag(DDC) \rightleftharpoons Pd(DDC)_2 + 2Ag^{+} \qquad (2.11)$$

(the first of which would probably be much faster than any reaction involving palladium) are faster than the reaction:

$$Pd^{2+} + Zn(DDC)_2 \rightleftharpoons Pd(DDC)_2 + Zn^{2+}. \qquad (2.12)$$

However, reaction 2.11 has been shown to be very slow. In low chloride ion concentrations, this catalysis might simply be due to the removal of free chloride ions by complexation with silver to form species of the type, $AgCl_2^{-}$, which is borne out by the fact that when the silver nitrate concentration was very high (Figure 3.15), the reaction was slowed down again and the rate was similar to that previously observed from chloride free solution. However in 5N hydrochloric acid, (Figure 3.16) the lowering of the chloride ion concentration by the silver ions would be insignificant and therefore some other explanation is necessary.

The results obtained using these different diethyldithiocarbamate

complexes indicate that palladium does not react with either free diethyldithiocarbamate ions or with the acid. If this were so, it would be expected that the fastest reaction would be obtained with the weakest complex. The extraction constant of any divalent metal diethyldithiocarbamate complex, $K_{M(DDC)_2}$, is given by

$$K_{M(DDC)_2} = \frac{[M(DDC)_2]_{org}}{[M^{2+}]_{aq}.[DDC^-]^2_{org}} \quad (2.13)$$

Hence, for a given concentration of the complex, $[M(DDC)_2]$, the lower the value of the extraction constant, $K_{M(DDC)_2}$, the greater the concentration of diethyldithiocarbamate ions, $[DDC^-]$, However, the order of decreasing value of the extraction constants is:

silver > copper-II > nickel > zinc,[51]

and so if palladium reacted directly with diethyldithiocarbamate ions, the reaction rates would decrease in the same order. As this is certainly not so, it can be assumed that the reaction is less simple than this.

The behaviour of silver ions when present in palladium solutions has some practical use, as it has enabled easy separation of silver-111 from solutions containing no chloride ions. Shaking such a solution with zinc diethyldithiocarbamate in chloroform results in most of the silver and very little palladium being removed from the aqueous phase, as long as the shaking time is kept short. This method has been utilised in Chapter 3, section II-4 for the preparation of 'chloride free' palladium-103 solutions, where precipitation of silver chloride would have been impossible.

In all these kinetic experiments it was noticed that the "double" shape of the rate curve obtained when extracting palladium with cupric diethyldithiocarbamate in chloroform was characteristic of the system. The only reasonable explanation for such a curve, was that

the second reaction, the formation of palladium chloride diethyldithiocarbamate, was autocatalytic in nature. This was shown to be so,(Ch.3.V) and (Figure 3.19), by addition of previously prepared palladium chloride diethyldithiocarbamate in chloroform to the reaction mixture, which treatment markedly increased the reaction rate.

From the above kinetic studies, it can be seen that cupric diethyldithiocarbamate in chloroform is the best extractant for the palladium diethyldithiocarbamate complexes, and although two complexes are formed, suitable choice of conditions will result in complete formation of either complex. The extraction is reasonably rapid at concentrations suitable for an activation analysis procedure but shows little promise for isotope dilution. However, it would be useful to know whether some of the effects observed are kinetic or thermodynamic in nature, as this may affect the choice of conditions for analysis procedures and will enable prediction of possible interferences and other problems which may occur. For this reason the extraction constants and partition coefficients were measured in Chapter 3, sections VIII and IX and this is discussed in the following section.

II. Equilibria and the Determination of Constants.

1. Introduction.

The extraction constants, K_A and K_B, of the two palladium diethyldithiocarbamate complexes are given by the equations:

$$K_A = \frac{[Pd(DDC)_2]_{org}}{[Pd^{2+}].[DDC^-]^2} \qquad (2.14)$$

and

$$K_B = \frac{[Pd.Cl(DDC)]_{org}}{[Pd^{2+}].[DDC^-].[Cl^-]} \qquad (2.15)$$

where the subscript "aq" has been omitted for simplicity. By combining these equations, the constant for reaction 2.2 and the exchange constant, K_E, for the two complexes is obtained:

$$K_E = \frac{[Pd.Cl(DDC)]^2_{org}}{[Pd(DDC)_2]_{org}.[Pd^{2+}].[Cl^-]^2} = \frac{K_B^2}{K_A}. \qquad (2.16)$$

As mentioned above, the concentration of palladium-II ions will be very low in chloride solutions due to complexation by chloride ions. The most convenient way to handle this in calculations is to use the α coefficient as proposed by Schwarzenbach[60]. This is defined by

$$\alpha_{Pd} = \frac{[Pd']}{[Pd^{2+}]} \qquad (2.17)$$

where $[Pd'] = [Pd^{2+}] + [PdCl^+] + [PdCl_2] +]PdCl_3^-] + [PdCl_4^{2-}] + [PdCl_5^{3-}] + [PdCl_6^{4-}]$.

The stability constants for these chloro complexes have been determined by a number of authors[59] and the agreement is satisfactory. They are as follows:-

$\log K_1 = 6.0$ $\log K_4 = 2.6$

$\log K_2 = 4.5$ $\log K_5 = -2.1$

$\log K_3 = 2.4$ $\log K_6 = -2.1$

where $K_n = \dfrac{[PdCl_n]}{[PdCl_{n-1}].[Cl]}$, omitting charges for simplicity.

The cumulative stability constants, β_n, are given by:

$$\beta_n = \frac{[PdCl_n]}{[Pd].[Cl]^n} = K_1 \times K_2 \times \ldots\ldots K_n. \qquad (2.18)$$

Hence, it is possible to calculate:

$\log \beta_1 = 6.0$ $\log \beta_4 = 15.5$

$\log \beta_2 = 10.5$ $\log \beta_5 = 13.4$

$\log \beta_3 = 12.9$ $\log \beta_6 = 11.3.$

By rearranging equation 2.18,

$$\frac{[PdCl_n]}{[Pd]} = \beta_n.[Cl]^n \qquad (2.19)$$

and hence by substitution into equation 2.17:

$$\alpha_{Pd} = \frac{[Pd']}{[Pd]} = 1 + \frac{[PdCl]}{[Pd]} + \frac{[PdCl_2]}{[Pd]} \text{ etc.}$$

$$= 1 + \sum_{n=1}^{6} \beta_n.[Cl]^n$$

and so,

$$\alpha_{Pd} = 1+10^{6}[Cl] + 10^{10.5}[Cl]^{2}+10^{12.9}[Cl]^{3}+10^{15.5}[Cl]^{4}+10^{13.4}[Cl]^{5} + 10^{11.3}[Cl]^{6}. \quad (2.20)$$

Using equation 2.20 it was possible to calculate the value of the α coefficient, α_{Pd}, for various chloride ion concentrations and the results are given in Table 2.1.

Table 2.1

Chloride ion concentration, [Cl].	α coefficient, α_{Pd}.	log α_{Pd}.
10	3.44×10^{19}	19.54
1	3.20×10^{15}	15.51
10^{-1}	3.26×10^{11}	11.51
10^{-2}	4.29×10^{7}	7.63
10^{-3}	4.40×10^{4}	4.64
10^{-4}	4.26×10^{2}	2.63
10^{-5}	14.2	1.15

From Table 2.1 it was possible to plot log α_{Pd} against chloride ion concentration as in Figure 2.1, from which the value of α_{Pd} at any chloride ion concentration could be interpolated.

By substituting for the concentration of palladium-II ions, $[Pd^{2+}]$, from equation 2.17 into equation 2.16 the following expression is obtained:

$$K_E = \frac{[Pd.Cl(DDC)]^{2}_{org}.\alpha_{Pd}}{[Pd(DDC)_2]_{org}.[Pd'].[Cl^-]}. \quad (2.21)$$

FIGURE 2.1

Variation of log α_{Pd}.

(from Table 2.1)

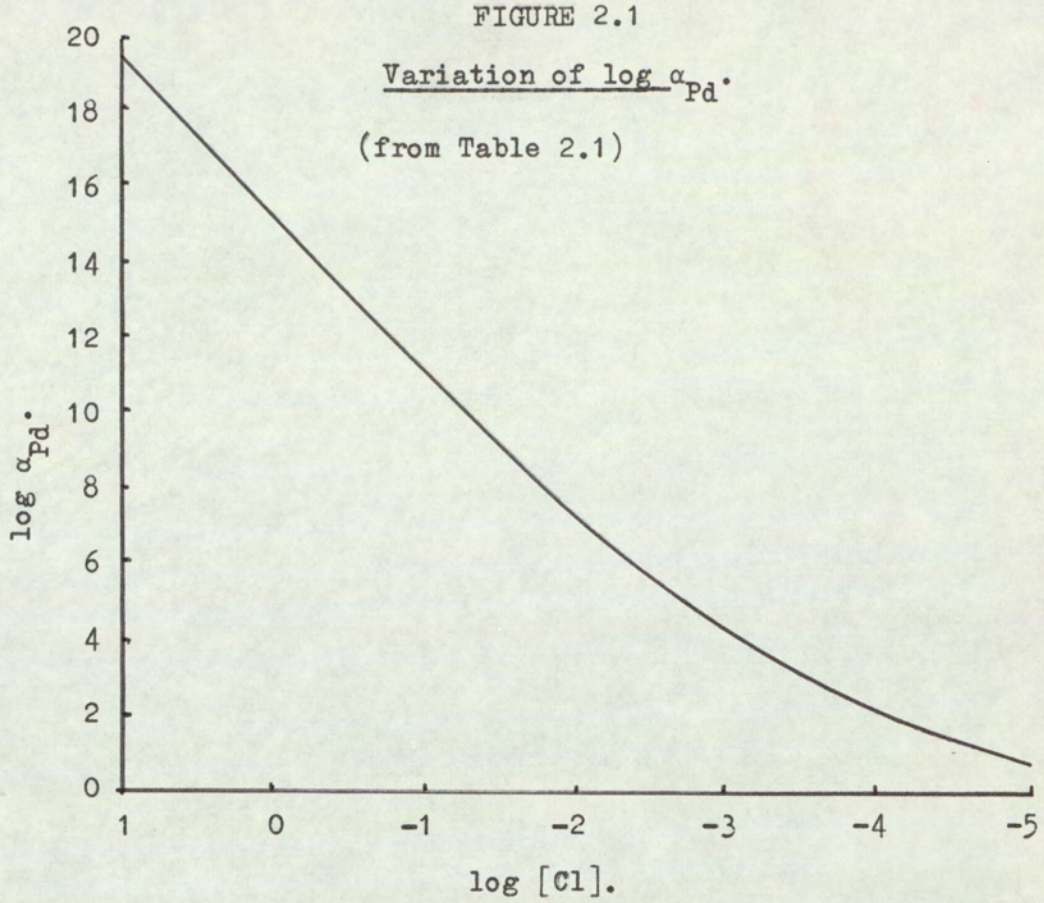
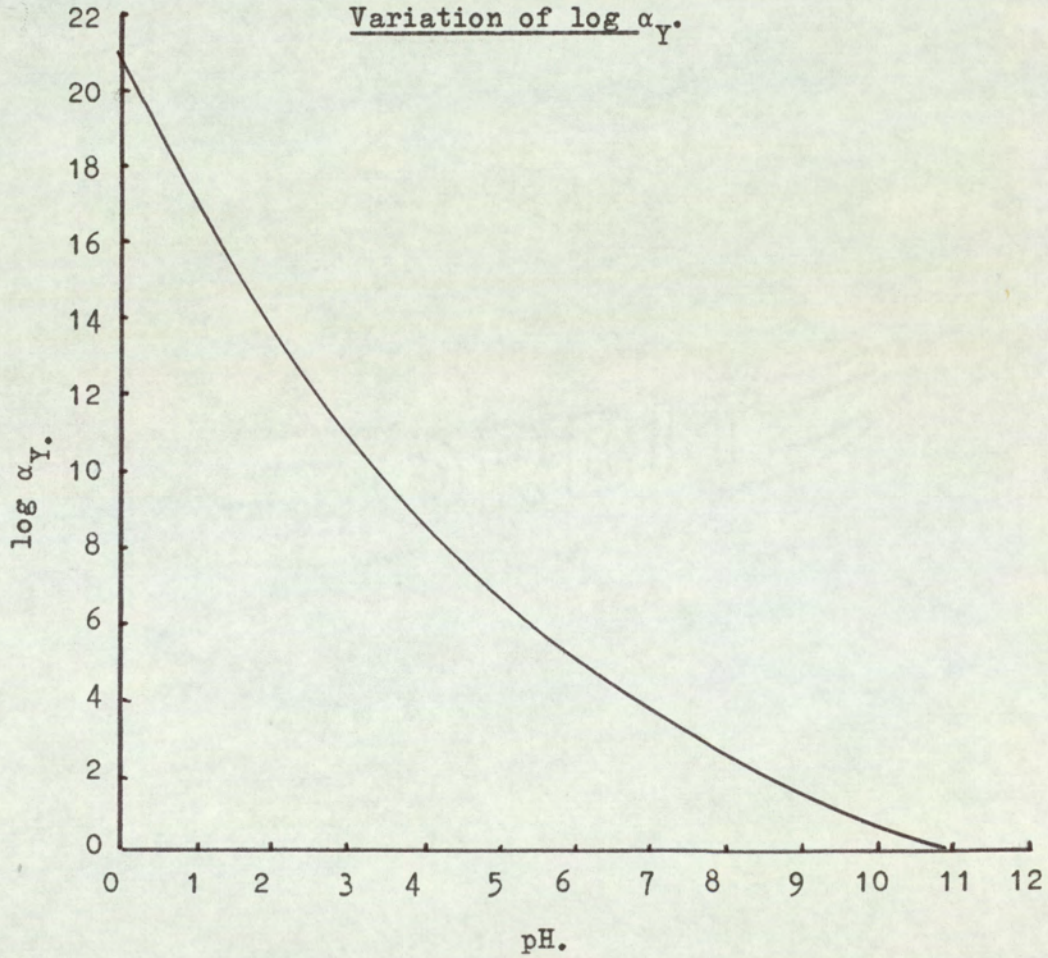


FIGURE 2.2

Variation of log α_{Y}.



2. Determination of K_1.

In order to determine the exchange constant, K_E, a complexing agent is needed for palladium which will compete with the formation of palladium chloride diethyldithiocarbamate and at low pH values, ethylenediaminetetraacetic acid (EDTA) was found to be suitable. At low pH values, the following reaction was assumed between palladium chloride diethyldithiocarbamate and EDTA to give the protonated complex quoted by MacNevin and Kriege[63]:

$$2Pd.Cl(DDC)_{org} + 2H^+ + Y^{4-} \rightleftharpoons H_2PdY + Pd(DDC)_{2org} + 2Cl^- \quad (2.22)$$

where H_4Y represents EDTA. The constant, K_1, for this reaction is given by the equation:

$$K_1 = \frac{[Pd(DDC)_2]_{org}.[H_2PdY].[Cl^-]^2}{[H^+]^2.[Pd.Cl(DDC)]^2_{org}.[Y^{4-}]} = \frac{K_2}{K_E} \quad (2.23)$$

where K_2 is the stability constant for the species H_2PdY and is given by the equation:

$$K_2 = \frac{[H_2PdY]}{[H^+]^2.[Pd^{2+}].[Y^{4-}].} \quad (2.24)$$

The concentration of EDTA ions, $[Y^{4-}]$, can be calculated using the α coefficient again and this has been done by Ringbom[61] using the dissociation constants of the various species. For EDTA the α coefficient is defined as

$$\alpha_Y = \frac{[Y']}{[Y^{4-}]} \quad (2.25)$$

where $[Y'] = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^-] + [H_4Y]$.

The resulting values of log α_Y have been plotted against pH in Figure 2.2.

In order to calculate the concentration of the EDTA complex,

H_2PdY, it is necessary to take into account the complexing power of the chloride ions. Rearranging equation 2.24 and substituting for the EDTA ion concentration, $[Y^{4-}]$, from equation 2.25 the following expression is obtained:

$$[Pd^{2+}] = \frac{[H_2PdY].\alpha_Y}{[H^+]^2.[Y'].K_2}, \qquad (2.26)$$

and by combination with equation 2.17 a further expression is obtained:

$$\frac{[Pd']}{\alpha_{Pd}} = \frac{[H_2PdY].\alpha_Y}{[H^+]^2.[Y'].K_2}. \qquad (2.27)$$

If the concentration of all the palladium species in the aqueous phase is denoted by $[Pd_{aq}]$, then

$$[Pd_{aq}] = [H_2PdY] + [Pd'], \qquad (2.28)$$

and substituting for the expression, $[Pd']$, from equation 2.27 gives

$$[Pd_{aq}] = [H_2PdY] + \frac{[H_2PdY].\alpha_Y.\alpha_{Pd}}{[H^+]^2.[Y'].K_2}. \qquad (2.29)$$

Rearranging equation 2.29 gives

$$[H_2PdY] = \frac{[Pd_{aq}]}{\left\{1 + \frac{\alpha_Y.\alpha_{Pd}}{[H^+]^2.[Y'].K_2}\right\}}, \qquad (2.30)$$

and by substituting from equations 2.25 and 2.30 into equation 2.23:

$$K_1 = \frac{[Pd(DDC)_2]_{org}.[Pd_{aq}].[Cl^-]^2.\alpha_Y}{[H^+]^2[Pd.Cl(DDC)]^2_{org}.[Y']\left\{1 + \frac{\alpha_Y.\alpha_{Pd}}{[H^+]^2.[Y'].K_2}\right\}}. \qquad (2.31)$$

However if the stability constant of the EDTA complex, K_2, is very large in comparison to the α coefficients, α_Y and α_{Pd}, the expression in parentheses approaches unity and equation 2.31 simplifies to

$$K_1 = \frac{[Pd(DDC)_2]_{org}.[Pd_{aq}].[Cl^-]^2.\alpha_Y}{[H^+]^2.[Pd.Cl(DDC)]^2.[Y']} \quad . \qquad (2.32)$$

In practice, equation 2.32 was assumed to be valid under the conditions used and was verified by independent variation of the hydrogen ion, chloride ion and EDTA concentrations. Solutions of palladium chloride diethyldithiocarbamate in chloroform were shaken with aqueous EDTA solutions and the final concentrations of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate were calculated from the activity of the organic phase(Ch.3.VIII.1). If the initial activity in the organic phase, corresponding to 10^{-3}M palladium chloride diethyldithiocarbamate, is A_s and the final activity is A, then the concentration of palladium diethyldithiocarbamate, x, can be calculated as follows:-

$$[Pd.Cl(DDC)] = 10^{-3} - 2x \qquad (2.33)$$

and

$$\frac{[Pd_{org}]}{10^{-3}} = \frac{A}{A_s} = \frac{[Pd(DDC)_2] + [Pd.Cl(DDC)]}{10^{-3}} \qquad (2.34)$$

where $[Pd_{org}]$ represents the total concentration of palladium in the organic phase. Therefore, by rearranging and substituting for the expressions $[Pd(DDC)_2]$ and $[Pd.Cl(DDC)]$ in terms of x:

$$\frac{A}{A_s} \times 10^{-3} = x + (10^{-3} - 2x). \qquad (2.35)$$

Rearranging:

$$x = (1 - A/A_s) \times 10^{-3} = [Pd(DDC)_2]. \qquad (2.36)$$

By substitution from equation 2.36 into equation 2.33:

$$[Pd.Cl(DDC)] = 10^{-3} - 2(1 - A/A_s) \times 10^{-3}$$

$$= A/A_s \times 10^{-3} - (1 - A/A_s) \times 10^{-3}$$

Therefore: $$[Pd.Cl(DDC)] = A/A_s \times 10^{-3} - [Pd(DDC)_2]. \quad (2.37)$$

Taking logarithms, equation 2.32 becomes

$$\log K_1 = 2pH + 2pPd.Cl(DDC) + pY' + \log \alpha_Y - [pPd(DDC)_2 + pPd_{aq} + 2pCl] \quad (2.38)$$

where $pX = -\log[X^{Z+}]$.

Under the experimental conditions used in Chapter 3, section VIII-1, where the volume of the aqueous phase was twice that of the organic phase, it can be seen that

$$[Pd_{aq}] = [Pd(DDC)_2]/2,$$

and, if no extra chloride ions are added

$$[Cl^-] = [Pd(DDC)_2].$$

Hence, by substitution of these expressions into equation 2.38:

$$\log K_1 = 4\log[Pd(DDC)_2] - \log 2 + \log \alpha_Y - 2\log[H^+] - 2\log[Pd.Cl(DDC)] - \log[Y'] \quad (2.39)$$

and by rearranging:

$$2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)] = \tfrac{1}{2}\log[Y'] + \tfrac{1}{2}\log(2.K_1.[H^+]^2/\alpha_Y) \quad (2.40)$$

Hence, a plot of the left hand side versus $\log[Y']$ should give a straight line having a slope of 0.5 and an intercept of $\frac{1}{2}\log(2.K_1.[H^+]^2/\alpha_Y)$. Experimentally a slope of 0.52 was obtained (Figure 3.20, Ch.3.VIII.1e).

Further rearrangement of equation 2.39 gives:

$$4\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log \alpha_Y = 2\log[H^+] + \log(2.K_1.[Y']). \quad (2.41)$$

Hence, a plot of the left hand side versus $\log[H^+]$ should give a straight line having a slope of 2 and an intercept of $\log(2K_1[Y'])$. Experimentally a slope of 1.94 was obtained (Figure 3.21, Ch.3.VIII.1e).

When extra chloride ions were added (Ch.3.VIII.1c), equation 2.39 was no longer valid, and so by substitution for $[Pd_{aq}]$ only, and rearrangement of equation 2.38:

$$2\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log \alpha_Y - 2\log[H^+] = -2\log[Cl^-] + \log 2K_1.[Y']. \quad (2.42)$$

Hence, a plot of the left hand side versus $\log[Cl^-]$ should give a straight line having a slope of -2 and an intercept of $\log(2K_1[Y'])$. Experimentally a slope of -2.12 was obtained (Figure 3.22, Ch.3.VIII.1e).

3. Determination of K_2.

In chloride solution equation 2.24 becomes:

$$K_2 = \frac{[H_2PdY].\alpha_Y.\alpha_{Pd}}{[H^+]^2.[Pd'].[Y']} \quad . \quad (2.43)$$

Hence, the stability constant of the EDTA complex, K_2, can be found by varying the hydrogen ion or the EDTA concentration and determining the ratio of the EDTA complex concentration to the chloro complex concentration, $[H_2PdY]:[Pd']$. The concentrations of these two species were found by absorbance measurements. The chloride ion concentration was 1N and under these conditions palladium will be almost completely present as the tetrachloro anion, $PdCl_4^{2-}$. This was found to have a maximum absorbance at 470nm, which agrees with previous findings[64]. The spectrum of the EDTA complex varied slightly with pH (Figure 3.26), the maximum absorbance occuring at 390 or 400 nm, but this also agreed

with the findings of other authors[63]. By measuring the absorbance of the test solutions at these two wavelengths and comparing with solutions of the pure species, the concentrations of the two species, H_2PdY and $PdCl_4^{2-}$, could be calculated as follows:-

Suppose: a = absorbance of a $2x10^{-3}$M $PdCl_4^{2-}$ solution at 470nm

b = absorbance of a $2x10^{-3}$M $PdCl_4^{2-}$ solution at 390nm

c = absorbance of a $2x10^{-3}$M H_2PdY solution at 470nm

d = absorbance of a $2x10^{-3}$M H_2PdY solution at 390nm

A = measured absorbance at 470 nm

B = measured absorbance at 390 nm

x = molarity of $PdCl_4^{2-}$

y = molarity of H_2PdY,

then

$$\frac{a}{2x10^{-3}}.x + \frac{c}{2x10^{-3}}.y = A \qquad (2.44)$$

and

$$\frac{b}{2x10^{-3}}.x + \frac{d}{2x10^{-3}}.y = B. \qquad (2.45)$$

Using the determinant method, for a pair of simultaneous equations,

$$a_1x + b_1y + c_1 = 0$$

$$a_2x + b_2y + c_2 = 0$$

the unknowns, x and y, are given by the expressions:

$$x = \begin{vmatrix} b_1 & c_1 \\ b_2 & c_2 \end{vmatrix} \div \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix} \quad \text{and} \quad y = \begin{vmatrix} c_1 & a_1 \\ c_2 & a_2 \end{vmatrix} \div \begin{vmatrix} a_1 & b_1 \\ a_2 & b_2 \end{vmatrix}$$

where $\begin{vmatrix} a & b \\ c & d \end{vmatrix} = (ad - bc)$.

Therefore the solutions of equations 2.44 and 2.45 are

$$x = \begin{vmatrix} \frac{c}{2x10^{-3}} & -A \\ \frac{d}{2x10^{-3}} & -B \end{vmatrix} \div D \qquad (2.46)$$

and

$$y = \begin{vmatrix} -A & \frac{a}{2x10^{-3}} \\ -B & \frac{b}{2x10^{-3}} \end{vmatrix} \div D \qquad (2.47)$$

where $D = \begin{vmatrix} a & c \\ b & d \end{vmatrix} \div 4x10^{-6}$.

Taking logarithms, equation 2.43 becomes

$$\log K_2 = 2pH + pPd' + pY' + \log \alpha_Y + \log \alpha_{Pd} - pH_2PdY. \qquad (2.48)$$

Rearranging: $\log[H_2PdY] - \log[Pd'] = \log[Y'] + \log(K_2[H^+]^2/\alpha_Y.\alpha_{Pd})$. (2.49)

Hence, a plot of the left hand side versus log[Y'] should give a straight line having a slope of 1 and an intercept of $\log(K_2[H^+]^2/\alpha_Y.\alpha_{Pd})$. Experimentally a slope of 1.00 was obtained (Figure 3.28, Ch.3.VIII.2).

4. Determination of K_3.

The extraction constant, K_A, of palladium diethyldithiocarbamate was found by back extraction of palladium with potassium cyanide according to the reaction:

$$Pd(DDC)_{2org} + 4(CN)^- \rightleftharpoons Pd(CN)_4^{2-} + 2DDC- \qquad (2.50)$$

where the constant, K_3, of the reaction is given by

$$K_3 = \frac{[Pd(CN)_4^{2-}].[DDC^-]^2}{[Pd(DDC)_2]_{org}.[(CN)^-]^4} = \frac{K_5}{K_A,} \qquad (2.51)$$

where K_5 is the cumulative stability constant (β_4) of the cyanide complex and is given by

$$K_5 = \frac{[Pd(CN)_4^{2-}]}{[Pd^{2+}].[(CN)^-]^4}. \qquad (2.52)$$

Taking logarithms, equation 2.51 becomes

$$\log K_3 = pPd(DDC)_2 + 4pCN - pPd(CN)_4 - 2pDDC \qquad (2.53)$$

Under the conditions used in Chapter 3, section VIII-3, where the volume of the aqueous phase was twice that of the organic phase it can be seen that $[DDC^-] = 2[Pd(CN)_4^{2-}]$.

Therefore substituting for the expression, $[DDC^-]$, and rearranging equation 2.53:

$$3\log[Pd(CN)_4^{2-}] - \log[Pd(DDC)_2] = 4\log[(CN)^-] + \log(K_3/4). \qquad (2.54)$$

Hence, a plot of the left hand side versus $\log[(CN)^-]$ should give a straight line having a slope of 4 and an intercept of $\log(K_3/4)$. Experimentally a slope of 3.9 was obtained (Figure 3.29, Ch.3.VIII.3).

5. Determination of K_6.

To determine the stability constant, K_5, of the palladium cyanide complex, potassium cyanide at low pH values was used to reverse reaction 2.2, giving the overall reaction:

$$2Pd.Cl(DDC)_{org} + 4(CN)^- \rightleftharpoons Pd(DDC)_{2org} + Pd(CN)_4^{2-} + 2Cl^- \quad (2.55)$$

where the constant for the reaction, K_6, is given by

$$K_6 = \frac{[Pd(DDC)_2]_{org}.[Pd(CN)_4^{2-}].[Cl^-]^2}{[Pd.Cl(DDC)]^2_{org}.[(CN)^-]^4} = \frac{K_5}{K_E}. \quad (2.56)$$

The stabilty constant for hydrocyanic acid, K_{HCN}, is given by the expression:[59]

$$K_{HCN} = \frac{[HCN]}{[H^+].[(CN)^-]} = 10^{9.2} \quad (2.57)$$

Therefore, if the pH is less than 10, equation 2.56 becomes

$$K_6 = \frac{[Pd(DDC)_2]_{org}.[Pd(CN)_4^{2-}].[Cl^-]^2.K_{HCN}.[H^+]^4}{[Pd.Cl(DDC)]^2_{org}.[HCN]^4}. \quad (2.58)$$

Taking logarithms, equation 2.58 becomes:

$$\log K_6 = 2pPd.Cl(DDC) + 4pHCN + 4\log K_{HCN} - 4pH - 2pCl - pPd(DDC)_2 - pPd(CN)_4^{2-} \quad (2.59)$$

Under the conditions used in Chapter 3, section VIII-4, where the volume of the aqueous phase was twice that of the organic phase, it can be seen that

$$[Pd(CN)_4^{2-}] = \tfrac{1}{2}[Pd(DDC)_2]$$

and $$[Cl^-] = [Pd(DDC)_2].$$

Therefore by substituting for the expressions $[Pd(CN)_4^{2-}]$ and $[Cl^-]$ and rearranging equation 2.59:

$$2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)] = -2\log[H^+] + \tfrac{1}{2}\log(2K_6[HCN]^4/K_{HCN}^4) \quad (2.60)$$

Hence, a plot of the left hand side versus $\log[H^+]$ should give a

straight line having a slope of -2 and an intercept of $\frac{1}{2}\log(2K_6[HCN]^4/K^4_{HCN})$ if the concentration of hydrocyanic acid is constant. Experimentally a slope of -2.02 was obtained (Figure 3.30, Ch.3.VIII.4).

6. Calculation of Constants.

(a) Errors.

The precision of the determined values of the various constants is quite high, as shown by the standard deviations, although not so high as to justify quoting the second decimal place (Ch.3.VIII). However, it is likely that various errors will have occurred, due to either experimental methods or to incomplete equations having been assumed. Other species may well have been present in significant concentrations which have not been included in the equilibrium equations.

In the determination of K_1, other palladium EDTA complexes may have been present as well as the complex, H_2PdY. This complex is known to predominate at pH 2[63], but by pH 3.8, the complex, $HPdY^-$, may be of importance. However, variation of the hydrogen ion concentration resulted in a fairly good straight line graph (Figure 3.21), so it is reasonable to assume that the other palladium EDTA complexes are not present in significant concentrations.

In the determination of K_2, the most obvious source of error would be the formation of mixed palladium chloro EDTA complexes, such as the complex H_4PdYCl_2, as the concentrations of both EDTA and chloride ions were very high (Ch.3.VIII.2). This particular complex has been isolated[65]. However the concentrations of the EDTA complex, H_2PdY, and the chloro complex, $PdCl_4^{2-}$, were calculated independently and in all cases they added up to give a value which was fairly close to the total palladium concentration. Therefore the concentration of any palladium chloro EDTA complexes could not have been significant,

unless, which would have been an unlikely coincidence, one of these complexes had the same extinction coefficient at 470 or 390 nm as those of the EDTA complex, H_2PdY, or the chloro complex, $PdCl_4^{2-}$.

The determination of K_3 was fairly straightforward. The pH was well above 10 and the concentration of potassium cyanide was high, therefore, although other palladium cyanide complexes undoubtedly do exist, it seems reasonable to assume that the tetracyano complex, $Pd(CN)_4^{2-}$, will predominate under these conditions, as the tetrachloride complex would under analagous conditions. Figure 3.29 confirms this. Some error may have been introduced due to decomposition of the rather unstable diethyldithiocarbamate ions. Although such decomposition is slow in alkaline media, the reaction time involved was very long. However, an apparent equilibrium was reached in the kinetic experiments, and if the diethyldithiocarbamate decomposition was comparable to the rate of reaction, any cyanide concentration would have resulted in complete breakdown of the palladium diethyldithiocarbamate.

In the determination of K_6 there are two important sources of possible error. Firstly, although it is likely that the tetracyano complex, $Pd(CN)_4^{2-}$, is the predominant complex in the determination of K_3, at the low pH values, and hence low cyanide ion concentrations employed in this determination, it is likely that other palladium cyanide complexes may have been present. The only evidence that this is not so is Figure 3.30, which indicates that the pH, and hence the cyanide dependence, is clearly raised to the fourth power. Secondly, it is possible that significant losses of the volatile hydrocyanic acid occured during the experiment. Attempts were made to minimise this by adjusting the pH immediately before shaking the flasks, which were closed and of the smallest volume practicable. Even so, a loss of 10% of the hydrocyanic acid would only alter the value of log K_6 by 0.18.

All the constants determined are apparent rather than thermodynamic constants, due to the fact that, except in the case of hydrogen ions, concentrations rather than activities were measured. Determination at constant ionic strength was impractical; for example, attempts to determine K_1 in 0.1M sodium perchlorate resulted in precipitation which completely upset the reaction. The concentrations used in the various experiments were up to 1M, and therefore corrections were necessary before comparing the individual results. The Davies equation[66] was used for this purpose, i.e.,

$$-\log f \doteq Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - CI] \qquad (2.61)$$

where f = activity coefficient,

I = ionic strength = $\frac{1}{2} \sum c_i z_i^2$,

z = charge on ion,

$A = 0.509$,

$C = 0.2$.

This equation is only claimed to hold up to an ionic strength of 0.1, but it has been shown that between 0.1 and 0.5, log f changes much less than below 0.1[62], and therefore it should give corrections of the right order. Table 2.2 was drawn up by calculating the values of log f at various ionic strengths for mono- and divalent ions.

Table 2.2

Ionic strength, I	-log f	
	z = 1	z = 2
1	0.153	0.610
0.1	0.112	0.451
0.01	0.046	0.185
0.001	0.015	0.062

For K_1, the correction can be calculated by considering equation 2.32. The numerator has only one charged species, viz chloride ions. Hydrogen ion concentration was measured potentiometrically therfore the only species to be considered on the denominator is EDTA. At the pH values used, i.e. 0.3 to 3.8, a mixture of ions would be present but the protonated ions would be most important, and hence it seems reasonable to assume a mean charge of 1. Taking the appropriate values from Table 2.2 for a concentration, and hence an ionic strength, of 0.01, the following equation is obtained:

$$\log K_{1(\text{corrected})} = \log K_{1(\text{observed})} - 2\text{x}0.046 + 0.046. \quad (2.62)$$

As this was the maximum ionic strength used, the maximum correction is 0.046, and as this is barely significant, ionic strength effects were ignored for K_1.

For K_2, considering equation 2.43, at ionic strength 1, the following equation is obtained:

$$\log K_{2(\text{corrected})} = \log K_{2(\text{observed})} + 0.61 + 0.153. \quad (2.63)$$

As K_2 was measured at a constant ionic strength of 1, this gave a correction of +0.743.

The constant, K_3, was determined over a range of ionic strengths from 0.1 to 1. At ionic strength 1, by considering equation 2.51, the following equation is obtained:

$$\begin{aligned} \log K_{3(\text{corrected})} &= \log K_{3(\text{observed})} - 0.610 - 2\text{x}0.153 + 4\text{x}0.153 \\ &= \log K_{3(\text{observed})} - 0.3. \end{aligned} \quad (2.64)$$

At ionic strength 0.1,

$$\log K_{3(\text{corrected})} = \log K_{3(\text{observed})} - 0.23. \quad (2.65)$$

Hence the mean correction is-0.26.

The constant, K_6, was also determined over a range of ionic

strengths from 0.1 to 1. By considering equation 2.58, at ionic strength 1,

$$\log K_{6(\text{corrected})} = \log K_{6(\text{observed})} - 0.610 - 2\text{x}0.153$$

$$= \log K_{6(\text{observed})} - 0.916. \qquad (2.66)$$

At ionic strength 0.1,

$$\log K_{6(\text{corrected})} = \log K_{6(\text{observed})} - 0.675. \qquad (2.67)$$

Hence the mean correction is -0.80. Table 2.3 summarises the determined and corrected constants.

Table 2.3

constant	observed value	corrected value
$\log K_1$	14.46	14.46
$\log K_2$	38.10	38.84
$\log K_3$	-7.21	-7.47
$\log K_6$	37.65	36.85

(b) Calculation.

Using the results in Table 2.3, it is possible to calculate the exchange constant, K_E, as from equation 2.23,

$$\log K_E = \log K_2 - \log K_1$$

and so: $\log K_E = 24.38.$

The extraction constants for the two palladium diethyldithiocarbamate complexes are calculated as follows:

from equation 2.56,

$$\log K_5 = \log K_6 + \log K_E$$

and so $\log K_5 = 61.23.$

Also, from equation 2.51,

$$\log K_A = \log K_5 - \log K_3$$

and so: $\log K_A = 68.70.$

From equation 2.16,

$$2\log K_B = \log K_E + \log K_A$$

and so: $2\log K_B = 93.08,$

and hence: $\log K_B = 46.54.$

The stability constant for palladium diethyldithiocarbamate, $K_{Pd(DDC)_2}$, is given by the equation:

$$K_{Pd(DDC)_2} = \frac{[Pd(DDC)_2]}{[Pd^{2+}].[DDC^-]^2} \qquad (2.68)$$

corresponding to the reaction:

$$Pd^{2+} + 2DDC^- \rightleftharpoons Pd(DDC)_2 \qquad (2.69)$$

taking place in the aqueous phase. The stability constant can be calculated from the extraction constant, K_A, into chloroform, and the partition constant, $P_{Pd(DDC)_2}$, between water and chloroform, as:

$$[Pd(DDC)_2]_{aq} = \frac{[Pd(DDC)_2]_{org}}{P_{Pd(DDC)_2}} . \qquad (2.70)$$

Hence:

$$K_{Pd(DDC)_2} = \frac{K_A}{P_{Pd(DDC)_2}}, \qquad (2.71)$$

and similarly:

$$K_{Pd.Cl(DDC)} = \frac{K_B}{P_{Pd.Cl(DDC)}}, \qquad (2.72)$$

where $K_{Pd.Cl(DDC)}$ is the stability constant of palladium chloride diethyldithiocarbamate and is given by the equation:

$$K_{Pd.Cl(DDC)} = \frac{[Pd.Cl(DDC)]}{[Pd^{2+}].[Cl^-].[DDC^-],} \qquad (2.73)$$

and $P_{Pd.Cl(DDC)}$ is the partition coefficient of palladium chloride diethyldithiocarbamate between water and chloroform.

In Chapter 3, section IX, the partition coefficients of the palladium diethyldithiocarbamate complexes were determined between water and chloroform and between water and carbon tetrachloride. The method used involved measuring the concentrations of two successive equal organic extracts. The partition coefficient, P, of a substance between two immiscible solvents is given by the equation:

$$P = \frac{C_{org}}{C_{aq}} \qquad (2.74)$$

where C_{aq} and C_{org} are the concentrations of the substance in the aqueous and organic phases respectively. As C = w/v, where w = weight and v= volume, equation 2.74 can be written:

$$P = \frac{w/v_{org}}{w/v_{aq}}. \qquad (2.75)$$

Rearranging:

$$\frac{v_{org}}{v_{aq}}.P = \frac{w_{org}}{w_{aq}}. \qquad (2.76)$$

For two successive extractions, where the relative volumes of the two phases are kept constant:

$$\frac{v_{org}}{v_{aq}}.P = \frac{w_{1org}}{w_{1aq}} = \frac{w_{2org}}{w_{2aq}}. \qquad (2.77)$$

As it can be seen that $w_{1aq} = w_{2aq} + w_{2org}$, and $w_{2aq} = \frac{w_{2org}}{(v_{org}/v_{aq}).P}$,

by substituting for w_{1aq} in equation 2.77 the following expression is obtained:

$$\frac{v_{org}}{v_{aq}} \cdot P = \frac{w_{1org}}{w_{2org} + \frac{w_{2org}}{(v_{org}/v_{aq}).P}} . \qquad (2.78)$$

Rearranging:

$$\frac{v_{org}}{v_{aq}} \cdot P. w_{2org} + w_{2org} = w_{1org} \qquad (2.79)$$

and hence:

$$P = \left[\frac{w_{1org} - w_{2org}}{w_{2org}}\right] \frac{v_{aq}}{v_{org}} \qquad (2.80)$$

and therefore:

$$P = \frac{v_{aq}}{v_{org}} \left[\frac{w_{1org}}{w_{2org}} - 1\right]. \qquad (2.81)$$

But as $v_{1org} = v_{2org}$,

$$\frac{w_{1org}}{w_{2org}} = \frac{c_{1org}}{c_{2org}}. \qquad (2.82)$$

Therfore, by substituting from equation 2.82 into equation 2.81:

$$P = \frac{v_{aq}}{v_{org}} \left[\frac{c_{1org}}{c_{2org}} - 1\right]. \qquad (2.83)$$

Using the above equation, from Chapter 3, section IX, the values of the partition coefficients between water and chloroform were found to be as follows:

$$\log P_{Pd(DDC)_2} = 4.84,$$

and $$\log P_{Pd.Cl(DDC)} = 2.55,$$

and hence from equation 2.71, $\log K_{Pd(DDC)_2} = 63.86$,

and from equation 2.72, $\log K_{Pd.Cl(DDC)} = 43.99$.

However, as mentioned in section III, the determined value of the partition coefficient of palladium diethyldithiocarbamate is probably lower than the true value, which would mean that the stability constant of this complex is less than 10^{64}.

(c) Summary.

The constants that have been determined are summarised below:

Palladium Diethyldithiocarbamate.

Extraction constant into chloroform, $\log K_A$, = 68.7.

Partition coefficient between water and chloroform,

$$\log P^{CHCl_3}_{Pd(DDC)_2} = 4.84.$$

Partition coefficient between water and carbon tetrachloride,

$$\log P^{CCl_4}_{Pd.(DDC)_2} = 4.21.$$

Stability constant, $\log K_{Pd(DDC)_2} = 63.9$.

Extinction coefficient in chloroform = 72,000 at λ_{max} = 295 nm.

Palladium Chloride Diethyldithiocarbamate.

Extraction constant into chloroform, $\log K_B$, = 46.5.

Partition coefficient between water and chloroform,

$$\log P^{CHCl_3}_{Pd.Cl(DDC)'} = 2.55.$$

Partition coefficient between water and carbon tetrachloride,

$$\log P^{CCl_4}_{Pd.Cl(DDC)'} = -0.41.$$

Stability constant, $\log K_{Pd.Cl(DDC)'} = 44.0$.

Extinction coefficient in chloroform = 60,000 at λ_{max} = 270 nm.

Palladium Hydroxide Diethyldithiocarbamate.

Extinction coefficient in chloroform = 21,000 at λ_{max} = 300 nm.

Palladium tetracyano complex, $Pd(CN)_4^{2-}$.

Cumulative stability constant, log K_5, = 61.2.

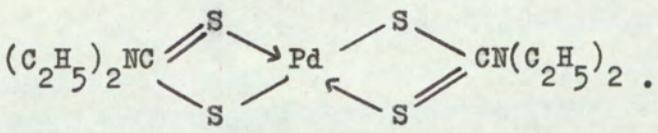
Palladium EDTA complex, H_2PdY.

Stability constant, log K_2, = 38.8.

The extinction coefficient of palladium diethyldithiocarbamate agrees with the value determined by Bode[67]. The stability constant of this complex is very large, but this is not surprising in view of some of the stability constant found for other metal diethyldithiocarbamates, for example, for mercury-II diethyldithiocarbamate, $Hg(DDC)_2$, the logarithm of the stability constant is 38.1[51].

III. Structure and Composition of the Palladium Diethyldithiocarbamate Complexes.

The reaction of palladium-II with excess diethyldithiocarbamic acid to form the yellow palladium diethyldithiocarbamate, $Pd(DDC)_2$, is well known and has been put to various analytical uses[68-75]. This complex has been assigned the structure[70]



No experimental investigation of the structure has been carried out, but an X-ray analysis of the analagous nickel complex, $Ni(DDC)_2$,[76] has shown that it has a square planar arrangement of sulphur atoms round the nickel atom. Magnetic susceptibility measurements have shown that the palladium complex is diamagnetic and hence low spin[77] and so the above structure is very probably correct. This complex corresponds to the complex formed in Chapter 3, section V-1, by the reaction:

$$Pd^{2+} + Cu(DDC)_{2org} \rightleftharpoons Pd(DDC)_{2org} + Cu^{2+}. \qquad (2.84)$$

However, when the metal rather than the reagent is in excess, a further reaction takes place to give the orange palladium chloride diethyldithiocarbamate, Pd.Cl(DDC), (Ch.3.V.2);

$$Pd(DDC)_{2org} + Pd^{2+} + 2Cl^{-} \rightleftharpoons 2Pd.Cl(DDC)_{org}. \qquad (2.85)$$

This complex has a palladium to diethyldithiocarbamate ion ratio of 1:1 and a palladium to chloride ion ratio of 1:1 as shown by tracer studies (Ch.3.V.2).

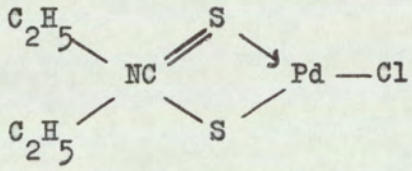
Under alkaline conditions or in the absence of chloride ions, a third complex is formed (Ch.3.V.3), which also has a palladium to diethyldithiocarbamate ion ratio of 1:1 but which contains no chlorine. As diethyldithiocarbamic cannot be dibasic (to form a neutral compound) and palladium does not readily form monovalent compounds, the second valency must be satisfied by a third constituent and the most likely

one seems to be the hydroxide ion, to give another ternary complex, brown palladium hydroxide diethyldithiocarbamate, Pd.OH(DDC), formed by the reaction:

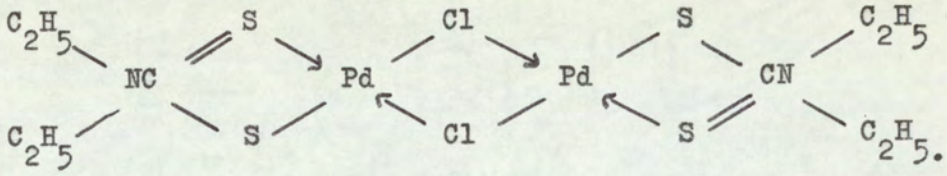
$$Pd(DDC)_{2org} + Pd^{2+} + 2OH^{-} \rightleftharpoons 2Pd.OH(DDC) \qquad (2.86)$$

or: $$Pd.Cl(DDC)_{org} + OH^{-} \rightleftharpoons Pd.OH(DDC) + Cl^{-} \qquad (2.87)$$

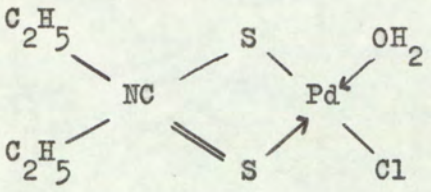
The results of the elemental analyses, (Ch.3.XII) indicate that the assigned formulae are correct, but are not sufficiently accurate to determine whether the complexes contain any coordinated water molecules, although they certainly do not rule out this possibility. The reason for suspecting that the complexes may contain water is due to the difficulty of assigning structures to the two ternary complexes. The structure:



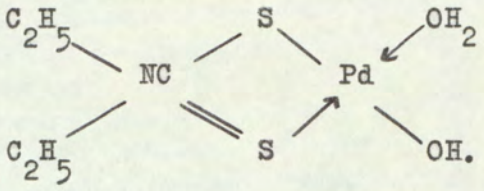
indicates an unusual coordination number for palladium and stereochemical considerations make it seem unlikely that the nitrogen could take part in the bonding without displacing one of the sulphur atoms. Bridged chlorine atom structures have been proposed for palladium complexes[27] and this type of structure might result in a binuclear complex such as:



However an hydroxide ion bridged structure is unusual for palladium and although a binuclear structure may be possible in the solid form, such structures do not usually exist in dilute solutions[28]. Therefore the most likely structures are those in which the fourth coordination point is filled by a water molecule, giving the structures:

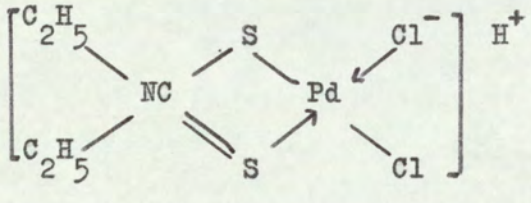


and

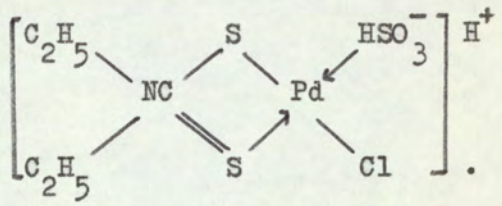


Solubility and partition coefficient data (Ch.3.IX and X) give some indication that these structures are correct. Palladium diethyldithiocarbamate has a very much higher solubility in organic solvents than in water, but for palladium chloride diethyldithiocarbamate the difference in solubility between organic solvents and water is much less. This is as would be expected as it can be said that half the molecule is organic and half inorganic. The order of solubilities is unusual for the chloro complex; it is more soluble in chloroform than in water but more soluble in water than in carbon tetrachloride. If the partition coefficient between chloroform and an acid solution was measured, no difference was observed from that between chloroform and water, but the solubility of palladium chloride diethyldithiocarbamate was greatly increased by an acidic medium when in contact with carbon tetrachloride. If the complex contains a coordinated water molecule, this may well lower its solubility in carbon tetrachloride more than its solubility in chloroform, with which water is much more miscible. (Solubility of water in carbon tetrachloride = 0.008% at 20°C, solubility of water in chloroform = 0.07% at 20°C [78].)

The increased solubility in acid media could be due to the formation of charged species in the aqueous phase, such as



or



Palladium hydroxide diethyldithiocarbamate was also observed to have a very low solubility in carbon tetrachloride, although no quantitative measurements were made.

The calculated solubilities of palladium chloride diethyldithiocarbamate are in good agreement with general observations, however, for palladium diethyldithiocarbamate, the calculated solubility in chloroform is lower than observed. The most likely source of error is the partition coefficient measurement. The partition coefficient of this complex between water and chloroform was the highest of any measured in this work. It may be that what was measured was in fact the limit of the experimental method, i.e., the limit of separation of the phases, rather than the true partition coefficient, which may well be much higher.

CHAPTER 3

Palladium Diethyldithiocarbamate Complexes: Experimental and Results.

I. Apparatus.

For detection of radioactivity see Chapter 1, section III-2.

Spectrometers.

Absorbance measurements were made on a Unicam SP600 visible spectrometer. Ultra-violet spectra were hand plotted from a Uvispek H700 spectrometer.

pH Meter. E.I.L. model 23A.

Filter Papers.

Unless otherwise stated a dry Whatman No.41 filter paper was used in all experiments.

II. Preparation of Solutions.

All reagents used were analytical grade unless otherwise stated.

1. Metal Diethyldithiocarbamate Solutions.

As sodium diethyldithiocarbamate tends to decompose even in the solid form, this reagent was first purified by dissolving in a minimum quantity of acetone and then adding a large excess of ether. The resulting precipitate was filtered off and dried in a vacuum dessicator.

To about 0.45g of this purified sodium diethyldithiocarbamate dissolved in water, 5 ml of a 0.5M cupric sulphate solution was added, and the resulting precipitate was extracted into the appropriate organic solvent. The organic layer was separated, filtered and diluted to 100 ml. In this way the following solutions were prepared:

10^{-2}M Cupric diethyldithiocarbamate in chloroform,

2×10^{-3}M (saturated) Cupric diethyldithiocarbamate in carbon tetrachloride,

10^{-2}M cupric diethyldithiocarbamate in benzene.

Other metal diethyldithiocarbamates were prepared by replacing the

cupric sulphate solution used above with a similar aqueous solution of the metal required. In this way the following solutions were prepared:

10^{-2}M zinc diethyldithiocarbamate in chloroform,

10^{-2}M nickel diethyldithiocarbamate in chloroform,

saturated silver diethyldithiocarbamate in chloroform.

When more dilute solutions were required the above stock solutions were diluted immediately before use.

2. Inactive Palladium Solutions.

Palladium chloride solutions were prepared by dissolving about 0.25g spectrographically standardised palladium sponge (supplied by Johnson Matthey and Company, Ltd.) in a small volume of aqua regia. The solution was evaporated to dryness several times with concentrated hydrochloric acid to remove oxides of nitrogen, the residue dissolved in hydrochloric acid and the solution diluted to 250 ml to give an approximately 10^{-2}M solution of palladium chloride in 1N hydrochloric acid.

Palladium nitrate solutions were prepared by dissolving the above palladium sponge in concentrated nitric acid, containing a small amount of concentrated sulphuric acid. The solution was evaporated to dryness several times, adding a small quantity of distilled water between evaporations, and then diluted to 250 ml to give an approximately 10^{-2}M solution of palladium nitrate.

3. Palladium-109 Solutions.

These were prepared as above using thermal neutron irradiated palladium sponge, specific activity 100 mCi/g as supplied by the Radiochemical Centre, Amersham.

4. Low Specific Activity Palladium-103 Solutions.

About 0.25 g thermal neutron irradiated palladium sponge, specific activity of palladium-103, 1 mCi/g, (after the palladium-109 had decayed) was dissolved in a small quantity of aqua regia. The solution

was diluted to about 100 ml, a few millilitres of 1M silver nitrate solution added, and the precipitate centrifuged off. This treatment was repeated once, to ensure complete removal of the silver-111 (Ch.1.III.1). The solution was then evaporated to dryness several times with concentrated hydrochloric acid and diluted to 250 ml to give an approximately 10^{-2}M solution of palladium chloride in 1N hydrochloric acid.

Palladium nitrate solutions were prepared as in section 2, but only diluted to about 100 ml. This solution was shaken for 1 to 2 minutes with 50 ml of 10^{-3}M zinc diethyldithiocarbamate solution in chloroform before final dilution to 250 ml. This treatment was found to remove most of the silver-111 (see section VII-4a).

5. Carrier Free Palladium-103 Solutions.

Carrier free palladium-103, prepared by cyclotron irradiation of rhodium, was supplied by the Radiochemical Centre, Amersham, as palladium chloride in 1N hydrochloric acid. However, attempts to mix this solution directly with inactive palladium chloride solutions resulted in inconsistent experimental data being obtained and further investigation showed that this carrier free palladium-103 was soluble in chloroform, and therefore it was obviously not in the chemical form stated. The carrier free palladium-103 solution was diluted to 100 ml with water and one drop of the resulting solution mixed with (a) 10 ml distilled water and (b) 10 ml 5N hydrochloric acid. These aqueous solutions were each shaken for about 2 minutes with 5 ml of chloroform and the activity of the aqueous and organic layers measured:-

	activity of aqueous layer, c.p.s.
(a)	109
(b)	198
	activity of organic layer, c.p.s.
(a)	288
(b)	211

As this indicates the presence of an organic complex of palladium attempts were made to destroy this by the following treatment:

A. The carrier free palladium-103 solution was evaporated to dryness, the residue dissolved in aqua regia and evaporated to dryness several times with hydrochloric acid before dissolving in further hydrochloric acid, and the resulting solution diluted so that it was 1N with respect to hydrochloric acid.

The palladium-103 was no longer soluble in chloroform after this treatment, but still isotopic equilibrium did not appear to be reached when the solution was mixed with inactive palladium chloride solution, and so further treatment was carried out:

B. The palladium-103 solution from A was diluted to about 200 ml, 5 ml of an approximately 0.1M sodium diethyldithiocarbamate solution in water added, and the resulting precipitate extracted into chloroform. The chloroform layer was separated, filtered and evaporated to dryness and then treatment A was repeated.

The above treatment must result in palladium being present as the chloride, and it was found to mix isotopically with inactive palladium chloride solutions, as shown by the following experiment:

Carrier free palladium-103 solution in 1N hydrochloric acid was used to label a 10^{-2}M solution of palladium in 1N hydrochloric acid, both after treatment A only, and after treatments A and B. The labelled solution was diluted to 10^{-3}M in 10 ml portions of 5N hydrochloric acid and shaken for 5 minutes with 5 ml 5×10^{-4}M cupric diethyldithiocarbamate in chloroform. The results in Table 3.1 were obtained on counting 3.0 ml aliquots of the separated organic layers.

Subsequently, treatments A and B were carried out on all carrier free palladium-103 solutions and this eliminated the inconsistent behaviour.

Table 3.1

Sample	After treatment A only Activity of organic phase, c.p.s.	After treatments A and B. Activity of organic phase, c.p.s.
1	48	31.8
2	140	33.0
3	17	32.2
4	18	32.4
5	16	33.1
6	367	32.0

6. Chlorine-36 Solutions.

Chlorine-36 was supplied by the Radiochemical Centre, Amersham, as a solution of sodium chloride in water, specific activity 13.5 mCi/g. This solution was used to directly label inactive sodium chloride solutions of known concentration.

III. Standardisation of Solutions.

1. Metal diethyldithiocarbamate Solutions.

Cupric diethyldithiocarbamate in carbon tetrachloride was standardised by measuring the absorbance at 436 nm[79]. The extinction coefficient at this wavelength is 13,000.

Cupric diethyldithiocarbamate in chloroform was standardised in the same way. The extinction coefficient was shown to be the same in chloroform as in carbon tetrachloride as follows:

About 5 ml of an approximately 1M solution of sodium diethyldithiocarbamate was added to two 10.0 ml aliquots of an approximately 10^{-4}M solution of cupric sulphate. One of the resulting precipitates was extracted into 5.0 ml of chloroform and the other into 5.0 ml of carbon tetrachloride and the absorbancies of the two organic solutions were measured at 436 nm in 1 mm cells against the constituent solvent of each. The chloroform solution had an absorbance of 0.213 and the carbon tetrachloride solution had an absorbance of 0.212.

Zinc diethyldithiocarbamate in chloroform was standardised by shaking with an excess of aqueous cupric sulphate and measuring the absorbance of the organic layer at 436 nm.

2. Palladium Solutions.

Palladium solutions are usually standardised gravimetrically, the most popular method being that involving precipitation of the dimethylglyoximate. However such methods are both time consuming and require the use of large amounts of palladium to give accurate results and these factors are serious disadvantages when dealing with radioactive solutions. Therefore the possibility of using the back titration method with EDTA developed by MacNevin and Kriege[80] was investigated. This method was claimed to be usable over the range 0.1M to 0.001M with respect to the EDTA concentration. However it was found

that, using 0.01M solutions, the end-point was masked by the colour of the palladium EDTA complex, while using 0.001M solutions resulted in the end-point being too indefinite to give reproducible results. Therefore, use of an intermediate concentration, $3x10^{-3}$M was found to give optimum results, the end-point being definite and clearly visible.

EDTA solution.

EDTA (disodium salt) was weighed (0.558g), dissolved in distilled water and diluted to 500 ml. This solution was standardised against metallic zinc by dissolving about 0.006g in a few drops of concentrated hydrochloric acid and diluting to 20 ml. About 5ml of an ammonium chloride/ammonium hydroxide buffer solution (pH 10) was added and the zinc solution titrated with the EDTA solution using Eriochrome Black T indicator.

Zinc nitrate solution.

Zinc nitrate (0.42g $Zn(NO_3)_2.6H_2O$) was dissolved in distilled water and diluted to 500 ml. This solution was standardised against the EDTA solution using Eriochrome Black T at pH 10.

Indicator solution.

About 0.1g Eriochrome Black T was dissolved in 50 ml distilled water which had been made slightly alkaline with 3 drops 1N potassium hydroxide solution.

Procedure.

To 5.0 ml of an approximately 10^{-2}M palladium chloride solution, 25.0 ml of standard $3x10^{-3}$M EDTA solution was added. The pH was adjusted to $10^{\pm}$ 1 using 1N potassium hydroxide solution (buffer materials complex with palladium). A few drops of indicator solution were added and the solution titrated with standard $3x10^{-3}$M zinc nitrate solution until the colour changed from green to pink.

In order to compare this method with the gravimetric method, palladium solutions were standardised by both methods and the results compared in Table 3.2.

Gravimetric Procedure.

A 20.0 ml aliquot of an approximately 10^{-2}M palladium chloride solution was diluted to 150 ml with distilled water and heated to about 70°C. About 20 ml of a 1% solution of dimethylglyoxime in ethanol was added dropwise with stirring and the precipitate digested at about 60°C for 1½ hours, cooled to room temperature and allowed to stand for 1 hour. The precipitate was filtered on to a number 4, sintered glass crucible, previously washed, dried at 110°C and weighed to constant weight. The precipitate was washed, dried at 110°C, cooled in a dessicator and weighed to constant weight.

Table 3.2

Palladium solution	Concentration by dimethylglyoxime method, M.	Concentration by EDTA titration method, M.
1	0.983×10^{-2}	0.985×10^{-2}
	0.998×10^{-2}	0.983×10^{-2}
2	0.896×10^{-2}	0.896×10^{-2}

Each result quoted is a mean of two determinations.

The error in the dimethylglyoxime method is about 1 mg, which gives an error of 1.5% using the above quantities, while the error in the titration method, 0.1 ml, only gives an error of 0.6%. Therefore the titration method is more precise and as the results in Table 3.2 show good agreement, it can be no less accurate than the gravimetric method. Hence the EDTA titration method was used throughout this work.

3. Chlorine-36 Solutions.

A 1.0 ml aliquot of the active sodium chloride solution was evaporated in a previously dried and weighed silica crucible at 50°C and weighed as sodium chloride.

IV. Use and Stability of Solutions.

1. Metal Diethyldithiocarbamate Solutions.

Solutions of cupric diethyldithiocarbamate in chloroform and carbon tetrachloride of concentrations of 10^{-3}M or above could be kept without noticeable change for several months when stored in glass in a dark cupboard. Zinc diethyldithiocarbamate was less stable and a 10^{-2}M solution in chloroform showed significant change in concentration after 1 - 2 weeks. The stability of cupric and zinc diethyldithiocarbamates in chloroform towards acids was investigated under the conditions used in palladium extractions:

A 5 ml portion of a 5×10^{-4}M solution of the metal diethyldithiocarbamate in chloroform was shaken for various lengths of time with 5 ml of hydrochloric or sulphuric acid. After shaking, the absorbance of the organic phase was measured in a 1 mm cell at 436 nm for cupric diethyldithiocarbamate, while the zinc diethyldithiocarbamate was shaken with a few millilitres of a 0.1M cupric sulphate solution before measuring the absorbance as above. The results of this experiment are given in Table 3.3. It can be seen that cupric diethyldithiocarbamate is stable to 2N hydrochloric acid or 5N sulphuric acid but would only be

Table 3.3

	Time(minutes)	Absorbance at 436 nm.			
		2N HCl	5N HCl	2N H_2SO_4	5N H_2SO_4
$Cu(DDC)_2$	5	0.607	0.612	-	0.612
	10	0.612	0.587	-	0.602
	20	0.605	0.563	-	0.616
	40	0.602	0.495	-	0.602
$Zn(DDC)_2$	5	0.550	0.175	0.562	0.572
	10	0.527	0.076	0.565	0.522
	20	0.531	0.032	0.558	0.442
	40	0.478	0.014	0.559	0.432

suitable for use with 5N hydrochloric acid if the reaction was fairly fast. Zinc diethyldithiocarbamate is not suitable for use with strong acids, being only stable towards 2N sulphuric acid.

2. Palladium Solutions.

Using the method of standardisation described in section III-2, no change in concentration was observed in any palladium solutions as long as the acid concentration was 0.1N or above. More dilute solutions, down to 10^{-6}M, also did not appear to deteriorate.

The choice of active solution was governed by the purpose of the experiment. Because of the absorption of palladium-103 radiation (Ch.1.III.3), direct comparison of specific activities between aqueous and organic phases was difficult, therefore when accurate comparison was neccessary, as in the determination of the composition of the complexes in section V, palladium-109 solutions were used. The specific activity of palladium-109 was such that solutions down to 10^{-5}M could be used for the first few half-lives.

Low specific activity palladium-103 solutions, because of the long half-life and ready availability of this isotope, were most convenient for most of the work, but could only be used at concentrations of 10^{-4}M or above. Hence, for lower concentrations, use of carrier free palladium-103 solutions was necessary.

V. Formation and Composition of the Palladium Diethyldithiocarbamate Complexes.

1. Formation of Palladium Diethyldithiocarbamate.

An aliquot of 1.0 ml of a 0.980×10^{-3}M palladium chloride solution (^{109}Pd) in 0.1N hydrochloric acid was diluted to 10 ml in 5N hydrochloric acid and shaken for various lengths of time with 5 ml of a 5.50×10^{-5}M solution of cupric diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.4 and figure 3.1. From the concentrations of the solutions used, a 1:2 complex corresponds to 28.0% extraction of palladium.

Table 3.4

Shaking Time(minutes)	Activity of Organic Phase, c.p.s.	% Extraction
½	15.8	13.1
1	23.0	19.1
2	30.3	25.3
5	33.3	27.7
10	32.0	26.7
20	33.0	27.5
30	31.3	26.1
60	33.6	28.0

initial activity of aqueous phase = 120c.p.s.

2. Formation of palladium chloride diethyldithiocarbamate.

Experiment 1 was repeated using 5N sulphuric acid instead of 5N hydrochloric acid and a 5.93×10^{-5}M solution of cupric diethyldithiocarbamate. The results are given in Table 3.5 and Figure 3.2. From the concentrations of the solutions used, a 1:2 complex corresponds to 30.3% extraction of palladium, while a 1:1 complex corresponds to 60.6% extraction.

Table 3.5

Shaking Time(minutes)	Activity of Organic Phase, c.p.s.	% Extraction
½	471.7	31.6
1	483.9	32.6
2	494.6	33.2
4	583.6	39.2
8	825.0	55.5
12	895.8	60.2
20	887.3	59.8
30	890.0	60.0

initial activity of aqueous phase = 1486 c.p.s.

The above experiment was repeated using an inactive 10^{-3}M palladium chloride solution labelled with 1 ml of a 0.1M sodium chloride solution (^{36}Cl), such that the final chloride ion concentration was the same as before i.e. 10^{-2}M. Aliquots of 1.0 ml of the organic phase were counted and the results are given in Table 3.6 and Figure 3.3. It can be seen that the final activity of the organic phase corresponds to 0.1 ml of the active sodium chloride solution, i.e. the organic phase was 10^{-4}M with respect to chlorine. This corresponds to a palladium:chlorine ratio of 1:1.

Table 3.6

Shaking Time(minutes)	Activity of Organic Phase, c.p.s.
1	1.3
1½	1.3
3	4.7
5	7.9
7	8.4

activity of 0.1 ml 10^{-3}M sodium chloride solution = 8.2 c.p.s.

FIGURE 3.1

Formation of Palladium Diethyldithiocarbamate.

(labelled palladium - from Table 3.4)

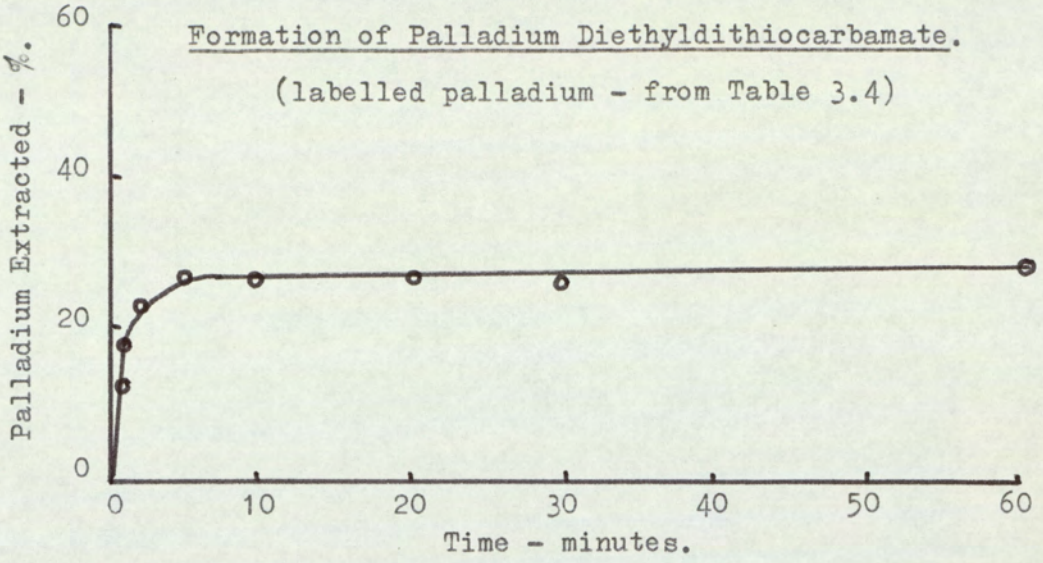


FIGURE 3.2

Formation of Palladium Chloride Diethyldithiocarbamate.

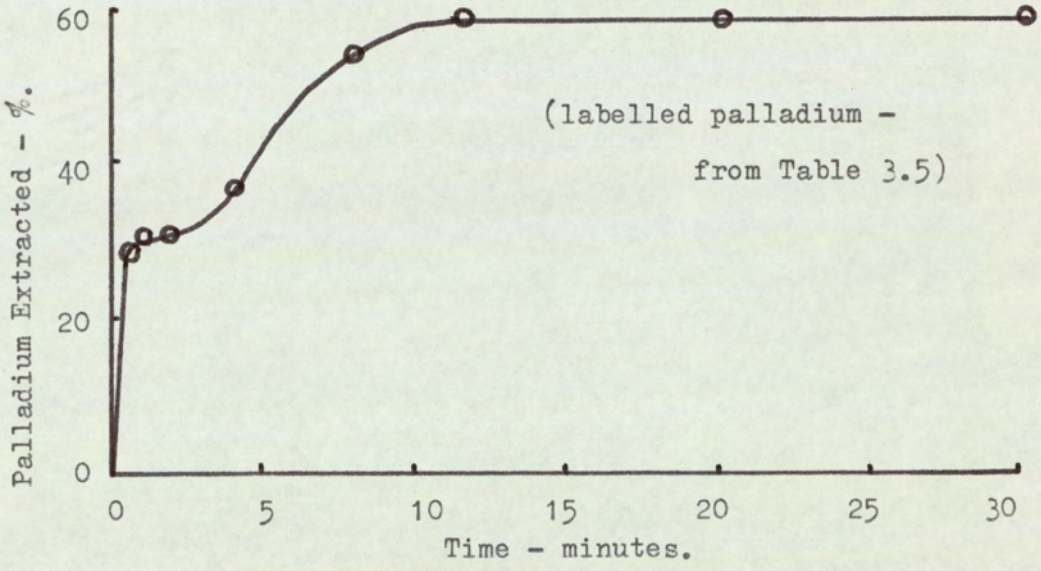
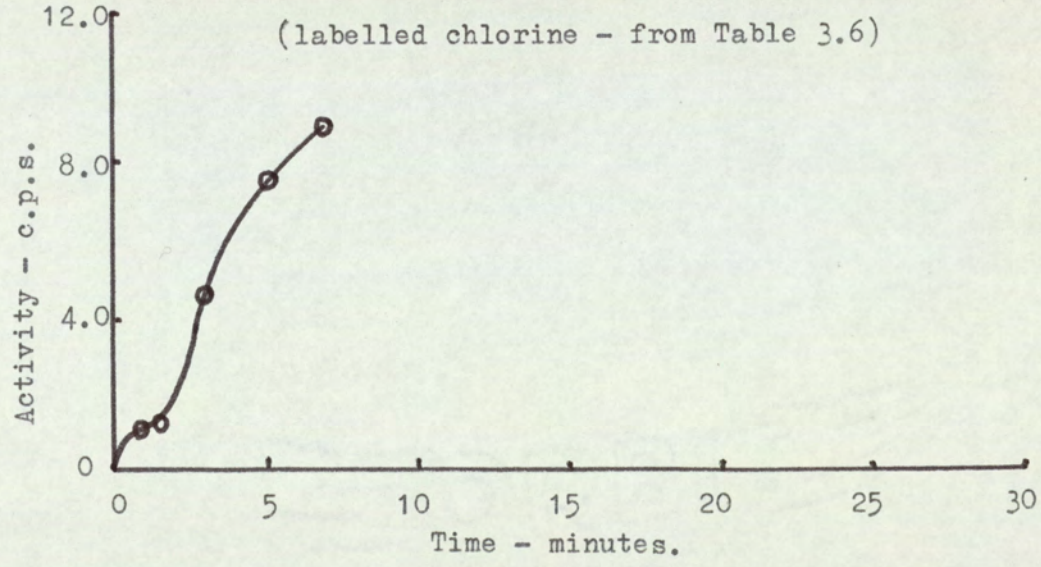


FIGURE 3.3

Formation of Palladium Chloride Diethyldithiocarbamate.

(labelled chlorine - from Table 3.6)



3. Formation of Palladium Hydroxide Diethyldithiocarbamate.

From chloride free palladium solutions, extraction with cupric diethyldithiocarbamate in chloroform did not result in formation of palladium chloride diethyldithiocarbamate, and the formation of palladium diethyldithiocarbamate was very slow (see section VII-1), however on prolonged shaking a brown solution was formed in the organic phase, and the activity of the organic phase tended towards that which would correspond to a 1:1 complex. A similar solution was formed, but much more readily, by shaking a solution of palladium chloride diethyldithiocarbamate in chloroform with aqueous sodium hydroxide, the activity of the organic phase being unchanged. A solution of palladium chloride diethyldithiocarbamate, labelled with chlorine-36 instead of palladium-109, was produced as in experiment 2 and after removing 1.0 ml for counting, was shaken for about 2 minutes with sodium hydroxide solution. A 1.0 ml aliquot was counted, giving the following results:

Activity of 1.0 ml organic phase before shaking with sodium hydroxide = 187.2 c.p.s.

Activity of 1.0 ml organic phase after shaking with sodium hydroxide = 1.3 c.p.s.

Activity of 0.1 ml of sodium chloride solution = 185.3 c.p.s.

Hence this complex contains no chlorine.

VI. The Reactions of the Palladium Diethyldithiocarbamate Complexes.

1. Palladium Diethyldithiocarbamate.

This complex was found to be very stable. The activity of a 5×10^{-4}M solution of palladium diethyldithiocarbamate in chloroform was unaffected by shaking for 1 hour with 5N hydrochloric acid, 5N sulphuric acid or 6N sodium hydroxide solution. It was also unaffected by EDTA, potassium iodide, sodium sulphite and dithizone (Ch.4.II.1c) and the only substance tried which decomposed it was potassium cyanide. Some of the above substances appeared to stop the formation of palladium diethyldithiocarbamate when attempts were made to prepare it in their presence, but this was almost certainly a kinetic effect. Solutions of palladium diethyldithiocarbamate in chloroform, carbon tetrachloride or benzene were yellow in colour, and on evaporation produced yellow needle shaped crystals which were readily redissolved.

2. Palladium Chloride Diethyldithiocarbamate.

The activity of a 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform was also unaffected by shaking for 1 hour with 5N hydrochloric acid or 5N sulphuric acid, but on shaking with even dilute sodium hydroxide a colour change occurred . As the brown solution formed was shown (above) to contain no chlorine, the chlorine must go into the aqueous phase, and this was confirmed by acidifying the aqueous layer with nitric acid and adding a few drops of silver nitrate solution. The turbidity produced was similar to that produced by a 10^{-3}M solution of sodium chloride under the same conditions. Solutions of palladium chloride diethyldithiocarbamate in chloroform or carbon tetrachloride were orange in colour and on evaporation gave red rosettes of small needle shaped crystals, which redissolved slowly.

3. Palladium Hydroxide Diethyldithiocarbamate.

Solutions of palladium hydroxide diethyldithiocarbamate in chloroform were not reconverted to palladium chloride diethyldithiocarbamate on shaking for 1 hour with hydrochloric acid. These solutions were brown in colour and on evaporation gave black mica-like plates.

VII. A Kinetic Study of the Formation of the Palladium Diethyldithiocarbamate Complexes.

1. The Effect of Hydrogen and Chloride Ion Concentrations.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 0.1N hydrochloric acid was diluted to 10 ml, and the hydrogen ion and chloride ion concentrations adjusted with hydrochloric acid, sodium chloride and sulphuric acid. This solution was shaken for various lengths of time with 5 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Tables 3.7 to 3.9 and Figures 3.4 to 3.7. (A 10^{-2}M palladium nitrate solution was used for the 'chloride free' experiment.)

Table 3.7

Effect of chloride ion concentration on rate of extraction from 0.1N acid.

Shaking Time,	0.1N chloride		1N chloride		4N chloride	
minutes.	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
½	31.4	32.2	-	-	-	-
1	34.4	35.3	11.0	11.3	7.2	7.4
2	31.6	32.4	18.3	18.8	12.1	12.4
4	-	-	-	-	19.5	20.0
5	43.6	44.7	25.2	25.9	-	-
8	-	-	-	-	26.3	26.0
10	64.1	65.8	23.8	24.4	-	-
20	66.2	67.9	-	-	-	-
25	-	-	-	-	27.3	28.0
30	-	-	24.9	25.5	-	-
60	-	-	31.1	31.9	27.5	28.2
85	-	-	45.0	46.2	-	-
100	-	-	-	-	26.3	26.0

initial activity of aqueous phase = 97.5 c.p.s.

Effect of chloride ion concentration on rate of extraction of palladium from 0.1N acid.

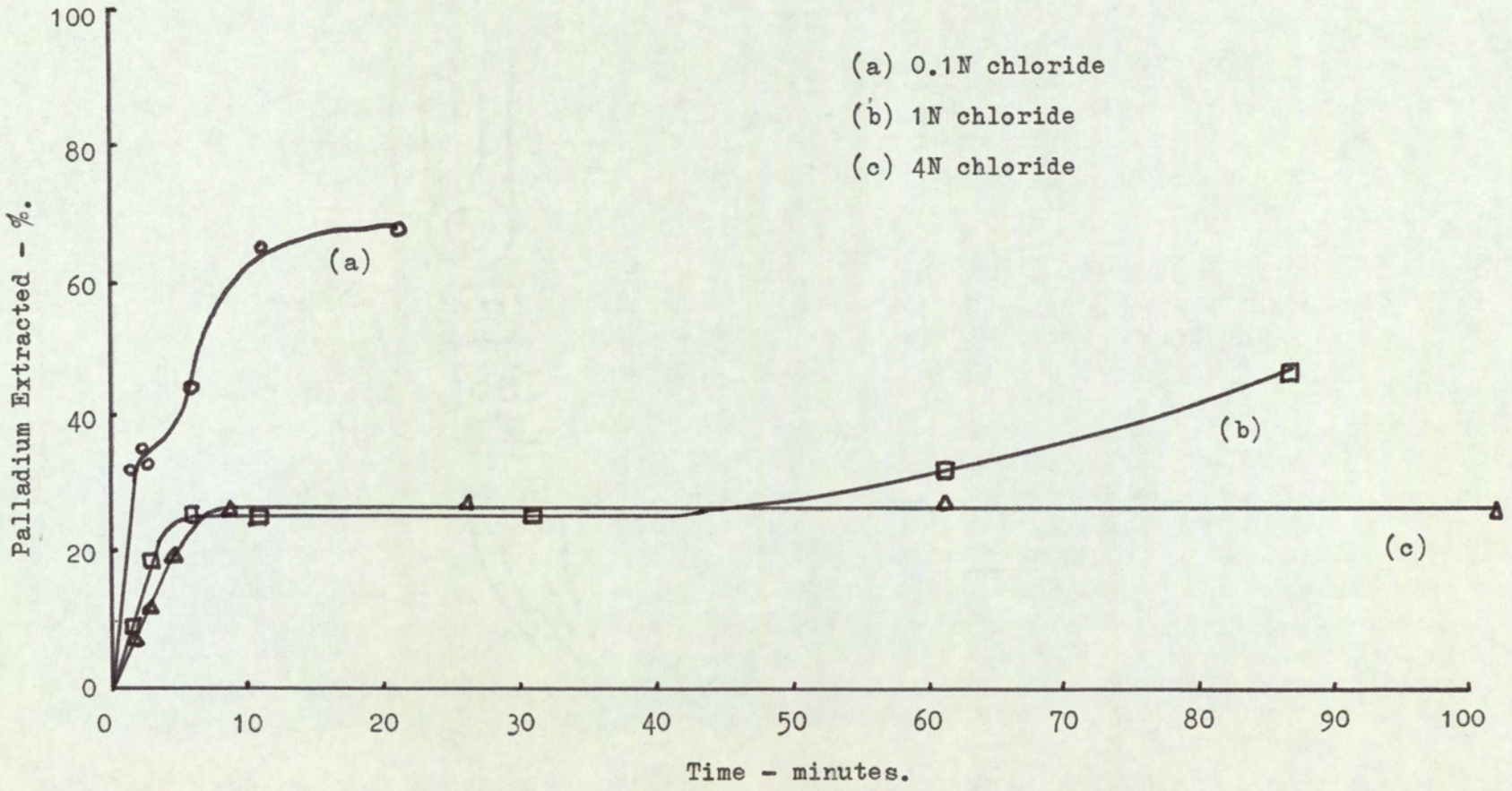


FIGURE 3.4
(from Table 3.7)

Table 3.8

Effect of chloride ion concentration on rate of extraction from 1N acid.

Shaking Time, minutes.	no chloride		0.1N chloride		1N chloride		5N chloride	
	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
½	1.3	1.5	23.6	28.1	-	-	6.1	7.3
1	1.8	2.1	24.0	28.5	21.2	25.1	-	-
1½	-	-	-	-	-	-	18.0	21.4
2	1.8	2.1	25.1	29.8	-	-	-	-
3	-	-	-	-	22.6	26.8	-	-
4	-	-	-	-	-	-	22.7	27.0
5	3.0	3.6	26.9	32.0	22.4	26.6	-	-
7	-	-	43.4	51.7	-	-	-	-
10	4.2	5.0	45.8	54.5	22.1	26.3	-	-
12	-	-	-	-	-	-	21.3	25.3
15	5.9	7.0	43.0	51.0	-	-	-	-
20	8.0	9.5	-	-	22.0	26.2	-	-
30	10.8	12.8	-	-	23.0	27.3	22.8	27.1
40	-	-	-	-	25.6	30.4	-	-
60	-	-	-	-	38.0	45.2	23.6	28.1
110	-	-	-	-	-	-	25.1	29.8

initial activity of aqueous phase = 84.2 c.p.s.

Effect of chloride ion concentration on rate of extraction of palladium from 1N acid.

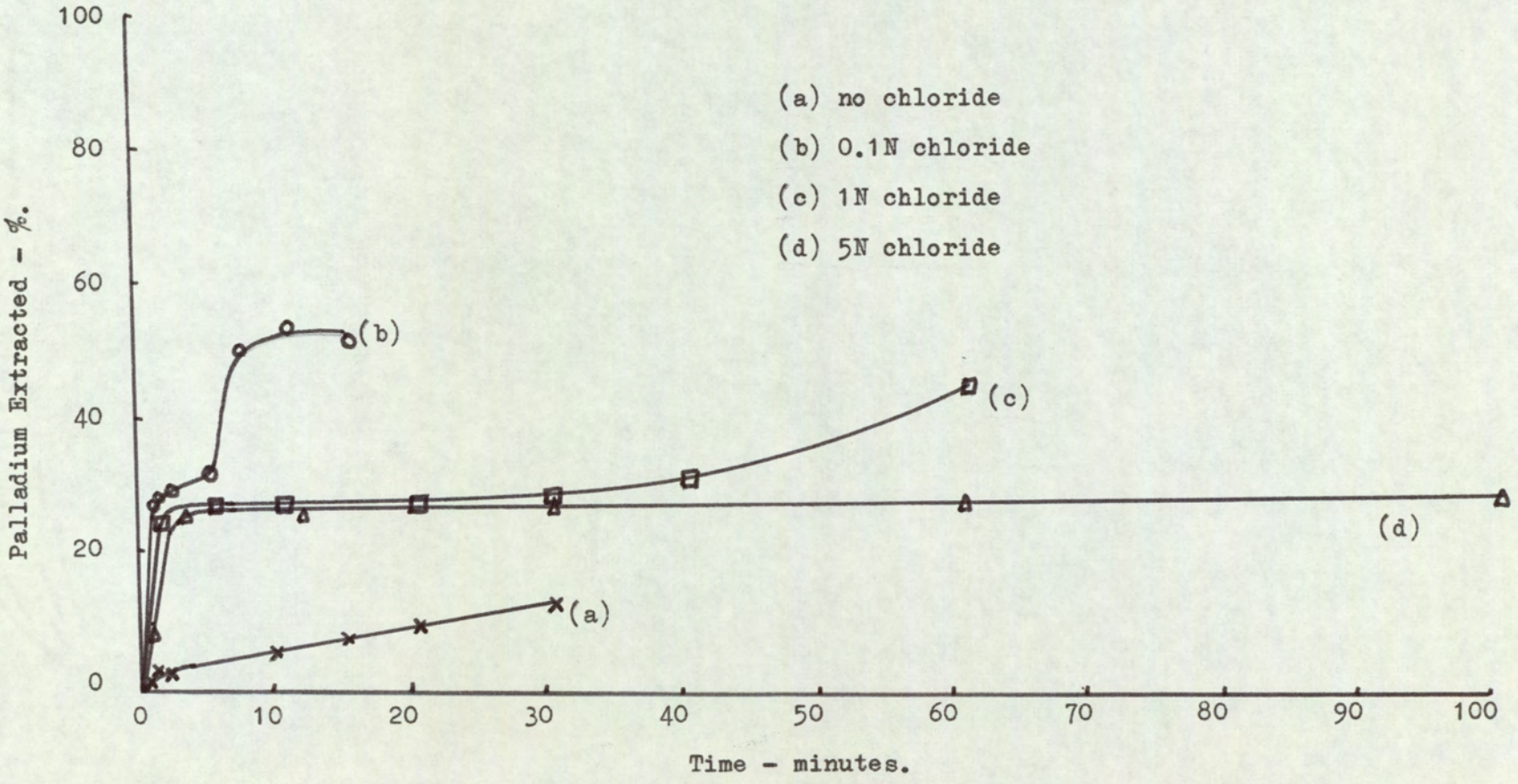


FIGURE 3.5
(from Table 3.8)

Table 3.9

Effect of chloride ion concentration on rate of extraction from 5N acid.

Shaking Time, minutes	0.1N chloride		1N chloride		5N chloride	
	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
½	25.0	29.7	22.9	27.2	-	-
1	24.8	29.5	21.6	25.7	21.6	25.6
2	24.8	29.5	23.4	27.8	-	-
3	26.8	31.9	-	-	20.7	24.7
4	32.3	38.4	-	-	-	-
5	-	-	23.0	27.3	21.6	25.6
6	44.0	52.2	-	-	-	-
10	44.8	53.3	22.2	26.4	21.6	25.6
20	-	-	28.3	33.6	23.0	27.4
30	-	-	34.1	40.5	22.8	27.1
40	-	-	-	-	22.8	27.1
60	-	-	-	-	22.8	27.1
85	-	-	-	-	22.9	27.2
90	-	-	-	-	21.9	26.0
105	-	-	-	-	23.2	27.6
120	-	-	-	-	23.1	27.5

initial activity of aqueous phase = 84.2 c.p.s.

Effect of chloride ion concentration on rate of extraction of palladium from 5N acid.

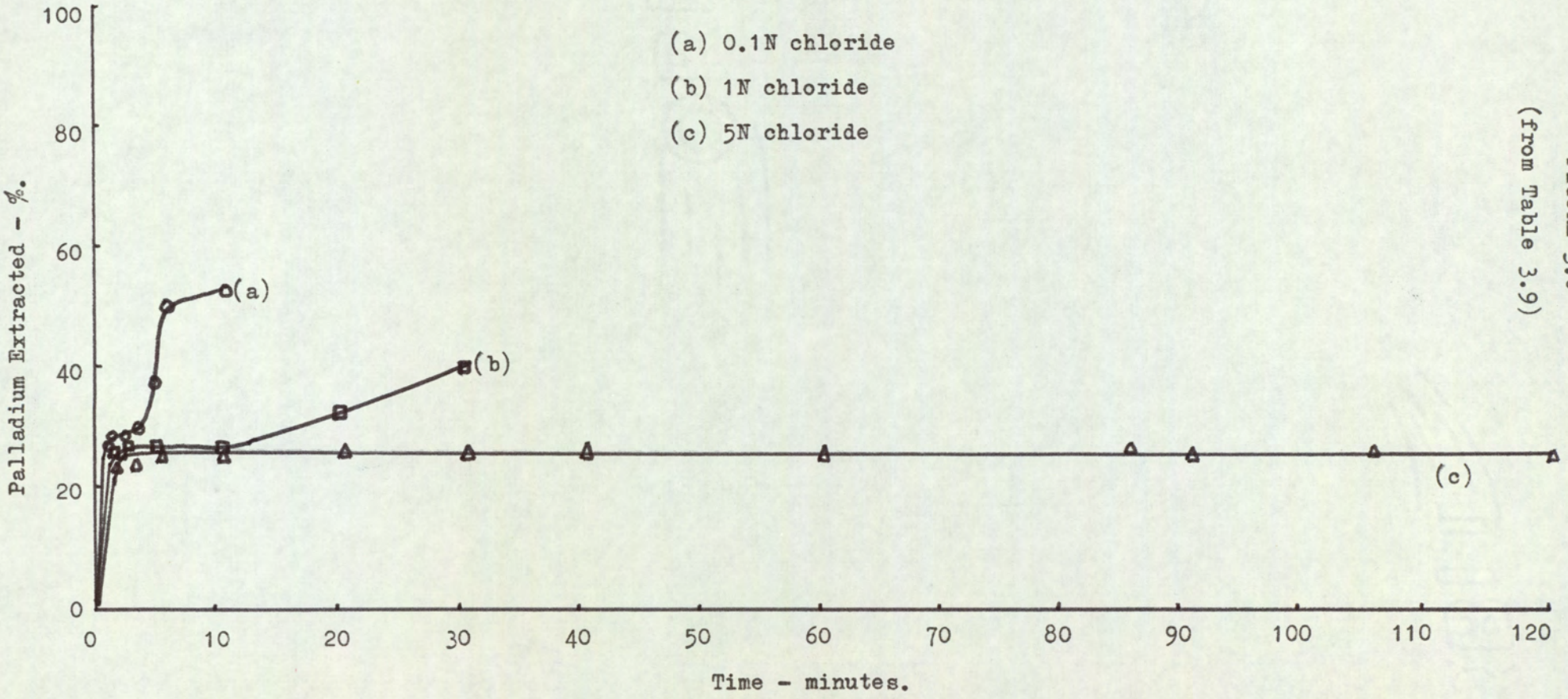


FIGURE 3.6
(from Table 3.9)

Effect of hydrogen ion concentration on rate of extraction of palladium from 1N chloride.

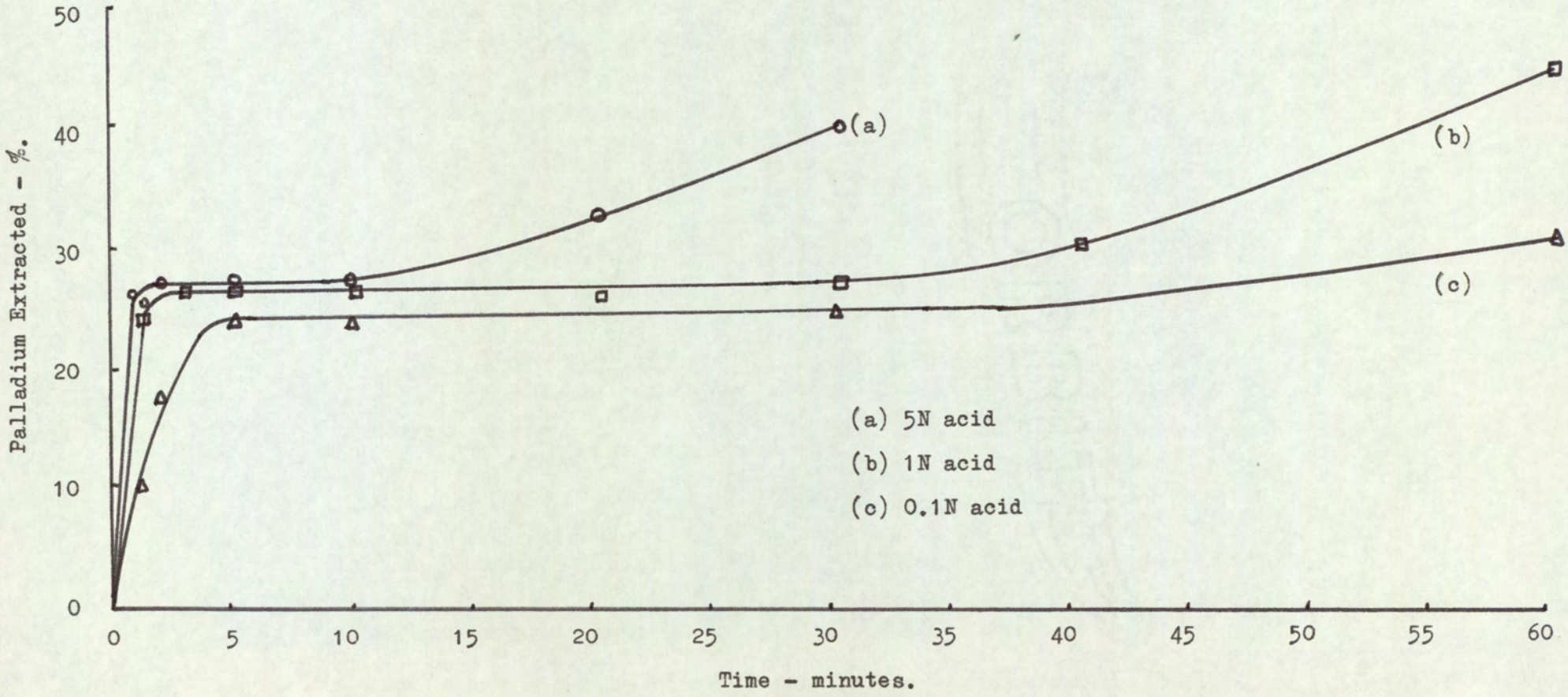


FIGURE 3.7 (from Tables 3.7, 3.8, 3.9)

2. The Effect of Reagent Concentration.

(a) Extraction of Palladium from 5N Hydrochloric acid into Chloroform.

An aliquot of 1.0 ml of a palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml in 5N hydrochloric acid and shaken for various lengths of time with 5 ml of a solution of cupric diethyldithiocarbamate in chloroform. The concentrations of the solutions were chosen such that the molar concentration of the cupric diethyldithiocarbamate in the organic phase was half that of the palladium chloride in the aqueous phase. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.10 and Figure 3.8.

Table 3.10

Shaking Time,	$5x10^{-5}$M $Cu(DDC)_2$		$5x10^{-6}$M $Cu(DDC)_2$	
minutes	c.p.s.	% ext.	c.p.s.	% ext.
½	15.8	13.2	-	-
1	23.0	19.2	6.0	5.0
2	30.3	25.2	10.3	8.6
4	-	-	13.7	11.4
5	33.3	27.8	-	-
6	-	-	14.5	12.1
10	32.5	27.1	22.3	18.5
20	33.0	27.4	24.0	20.0
30	31.3	26.1	23.6	19.7
60	33.6	27.9	-	-

initial activity of aqueous phase = 120 c.p.s.

Effect of Concentration on Extraction of Palladium Diethyldithiocarbamate into Chloroform

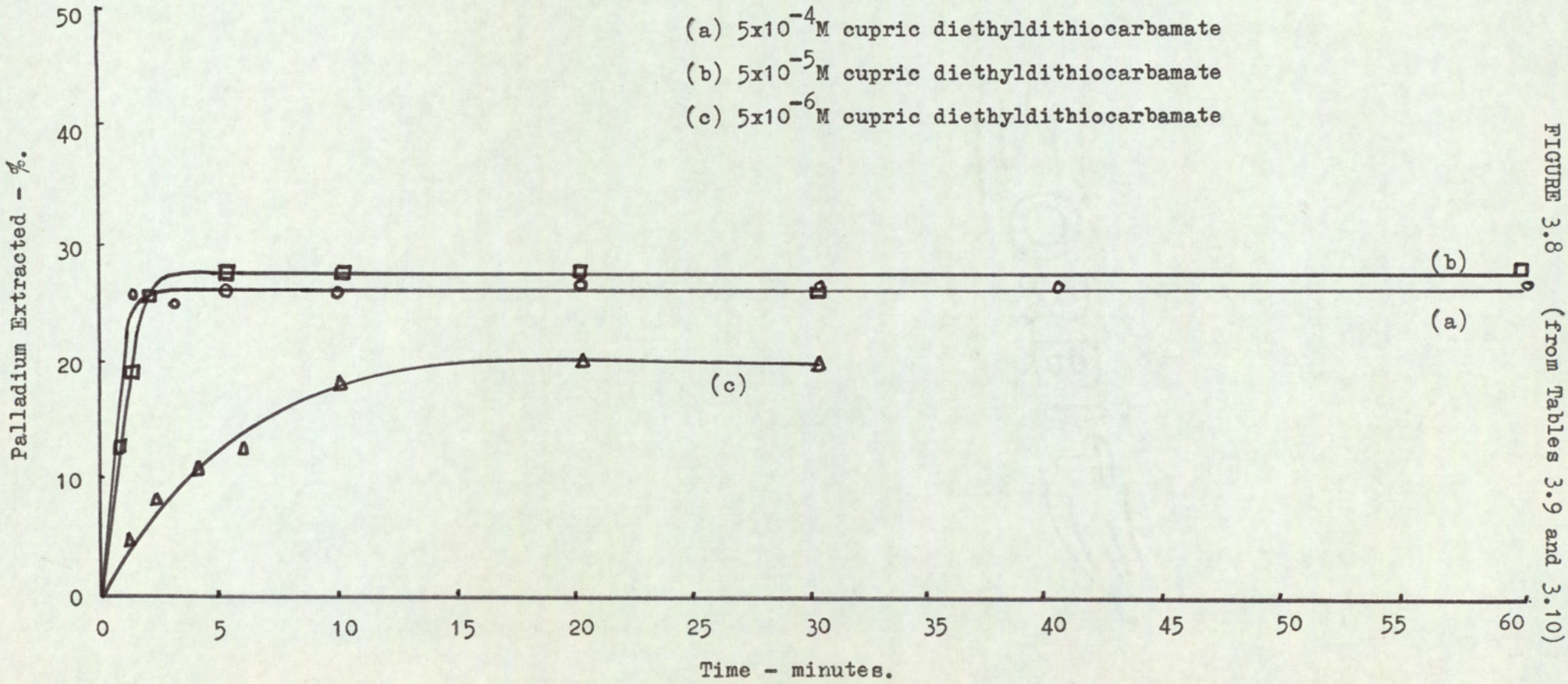


FIGURE 3.8 (from Tables 3.9 and 3.10)

(b) Extraction of palladium from 5N sulphuric acid into chloroform.

The experiment was carried out as in (a), replacing the 5N hydrochloric acid by 5N sulphuric acid. The results are given in Table 3.11 and Figures 3.9 and 3.12.

Table 3.11

Shaking Time, minutes.	$5x10^{-5}$M $Cu(DDC)_2$		$5x10^{-6}$M $Cu(DDC)_2$		$5x10^{-7}$M $Cu(DDC)_2$		$5x10^{-8}$M $Cu(DDC)_2$	
	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
½	152.0	31.7	-	-	-	-	-	-
1	155.9	32.5	27.2	5.7	-	-	-	-
2	159.2	33.2	-	-	24.0	5.0	-	-
3	-	-	44.1	9.2	-	-	-	-
4	186.8	38.9	-	-	60.6	12.6	-	-
5	-	-	-	-	-	-	42.8	8.9
6	-	-	-	-	87.1	18.1	-	-
7	-	-	56.5	11.8	105.0	21.9	-	-
8	265.5	55.2	-	-	-	-	-	-
9	-	-	-	-	111.4	23.2	-	-
10	-	-	-	-	-	-	44.7	9.3
12	288.4	60.1	116.1	24.2	126.8	26.4	-	-
15	-	-	-	-	137.3	28.6	51.5	10.7
20	286.2	59.7	150.9	31.4	142.0	29.6	60.1	12.5
25	-	-	-	-	137.3	28.6	68.7	14.3
30	286.8	59.9	166.2	34.6	137.3	28.6	68.7	14.3
40	-	-	-	-	142.0	29.6	-	-
45	-	-	154.8	32.3	-	-	80.0	16.7
60	-	-	212.8	44.3	-	-	108.7	22.6

initial activity of aqueous phase = 480 c.p.s.

Effect of concentration on extraction of palladium chloride diethyldithiocarbamate into chloroform.

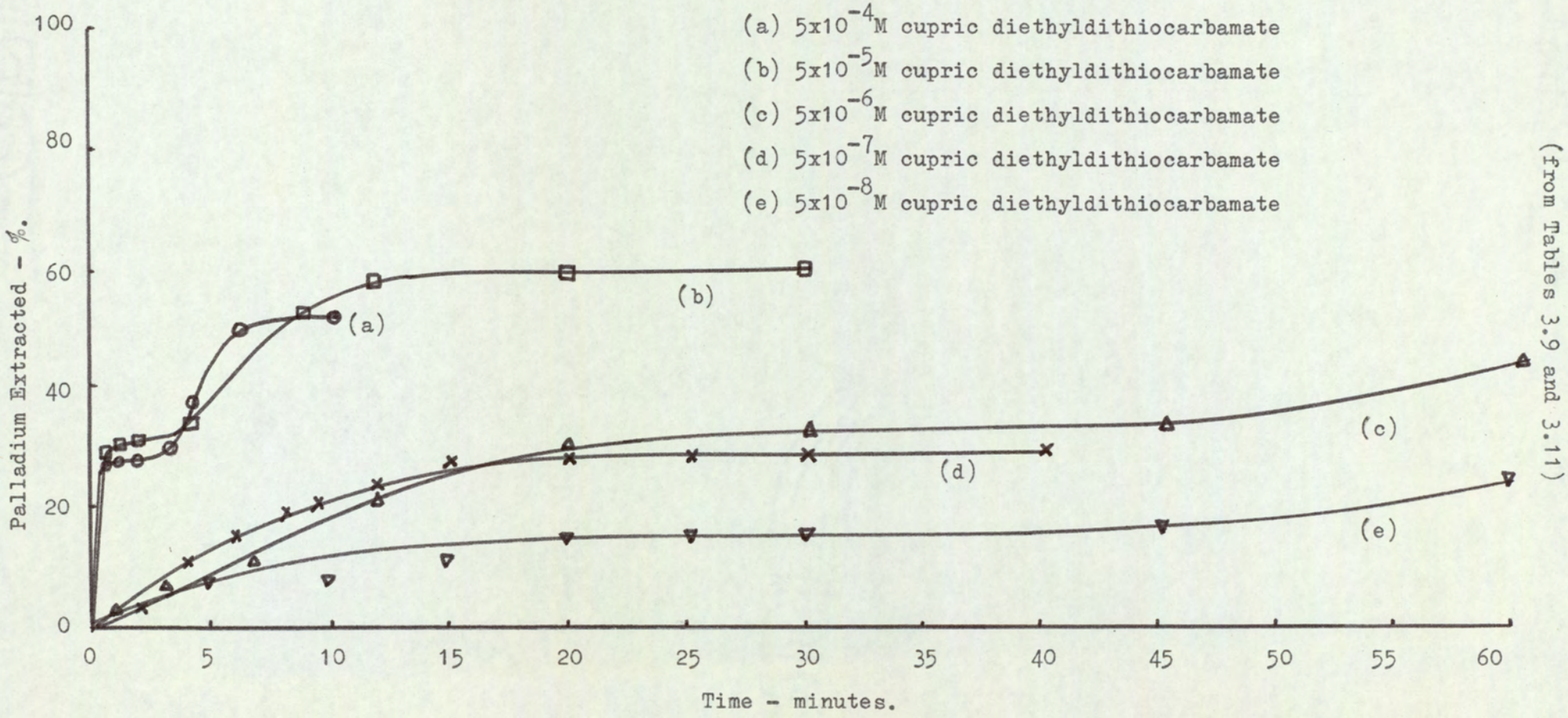


FIGURE 3.9
(from Tables 3.9 and 3.11)

(c) Extraction of palladium from 5N hydrochloric acid into carbon tetrachloride.

The experiment was carried out as in (a), replacing the cupric diethyldithiocarbamate in chloroform by cupric diethyldithiocarbamate in carbon tetrachloride. The results are given in Table 3.12 and Figure 3.10.

Table 3.12

Shaking Time, minutes	5×10^{-5} M $Cu(DDC)_2$		5×10^{-6} M $Cu(DDC)_2$	
	c.p.s.	% ext.	c.p.s.	% ext.
½	71.3	15.8	-	-
1	72.5	16.1	42.3	9.4
2	73.1	16.2	51.2	11.4
5	62.6	13.9	77.9	17.3
10	64.1	14.2	61.4	13.7
15	-	-	54.9	12.2
20	50.2	11.2	45.7	10.1
30	20.3	4.5	31.6	7.0
45	-	-	27.5	6.1
60	3.4	0.8	-	-

initial activity of aqueous phase = 450 c.p.s.

(d) Extraction of palladium from 5N sulphuric acid into carbon tetrachloride.

The experiment was carried out as in (b), replacing cupric diethyldithiocarbamate in chloroform by cupric diethyldithiocarbamate in carbon tetrachloride. The results are given in Table 3.13 and Figures 3.11 and 3.12.

Effect of concentration on rate of extraction of palladium from 5N hydrochloric acid into carbon tetrachloride.

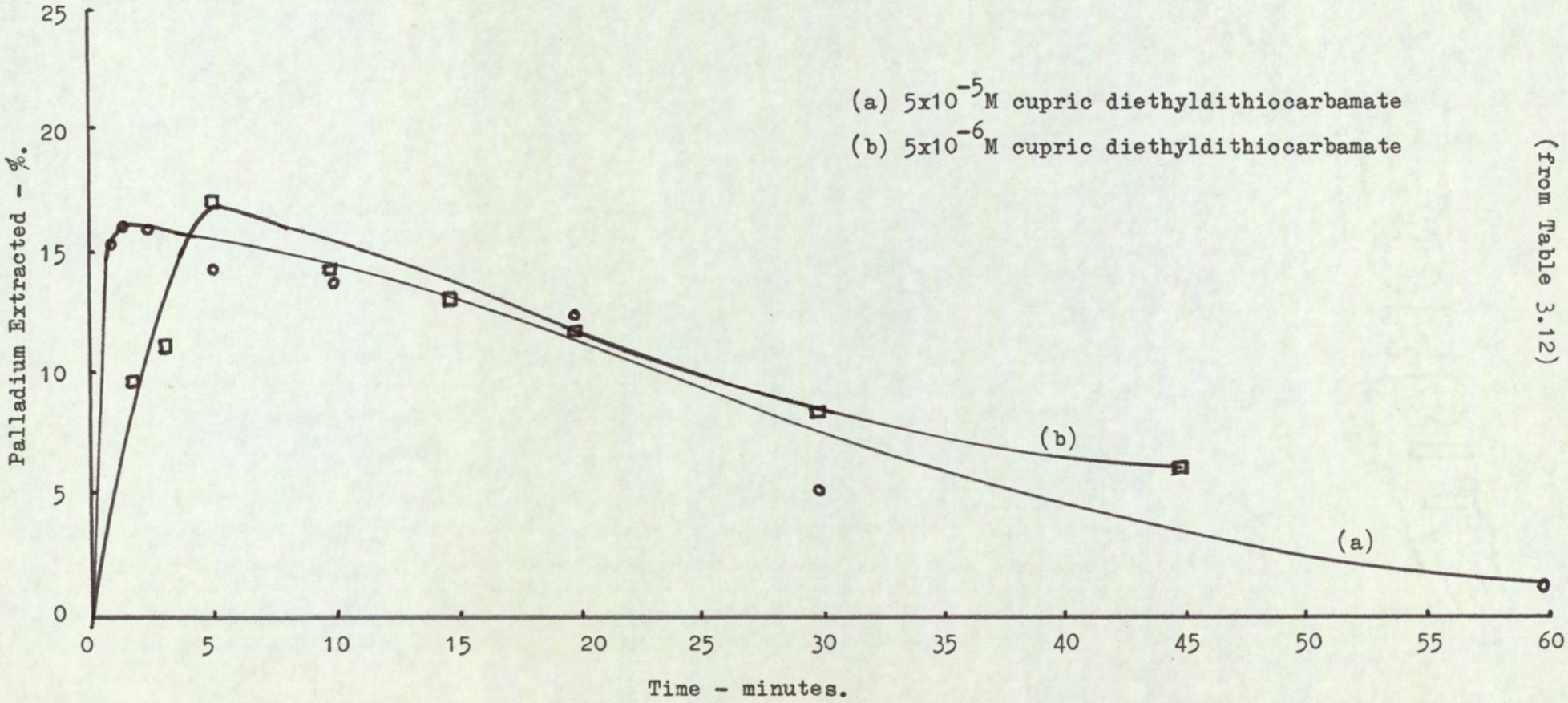


FIGURE 3.10
(from Table 3.12)

Effect of concentration on rate of extraction of palladium from 5N sulphuric acid into carbon tetrachloride.

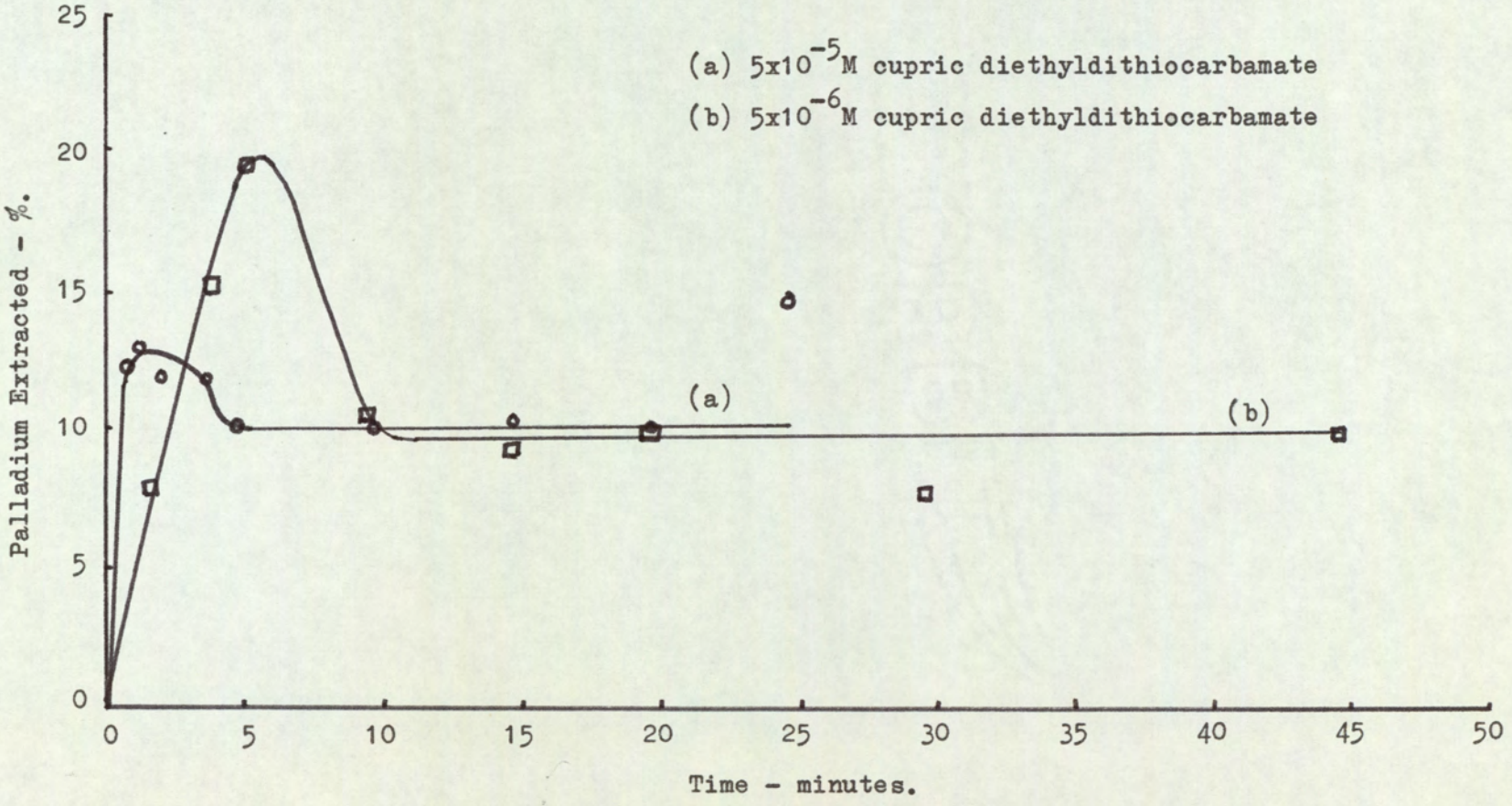


FIGURE 3.11
(from Table 3.13)

FIGURE 3.12

Comparison of chloroform and carbon tetrachloride.

(from Tables 3.11 and 3.13)

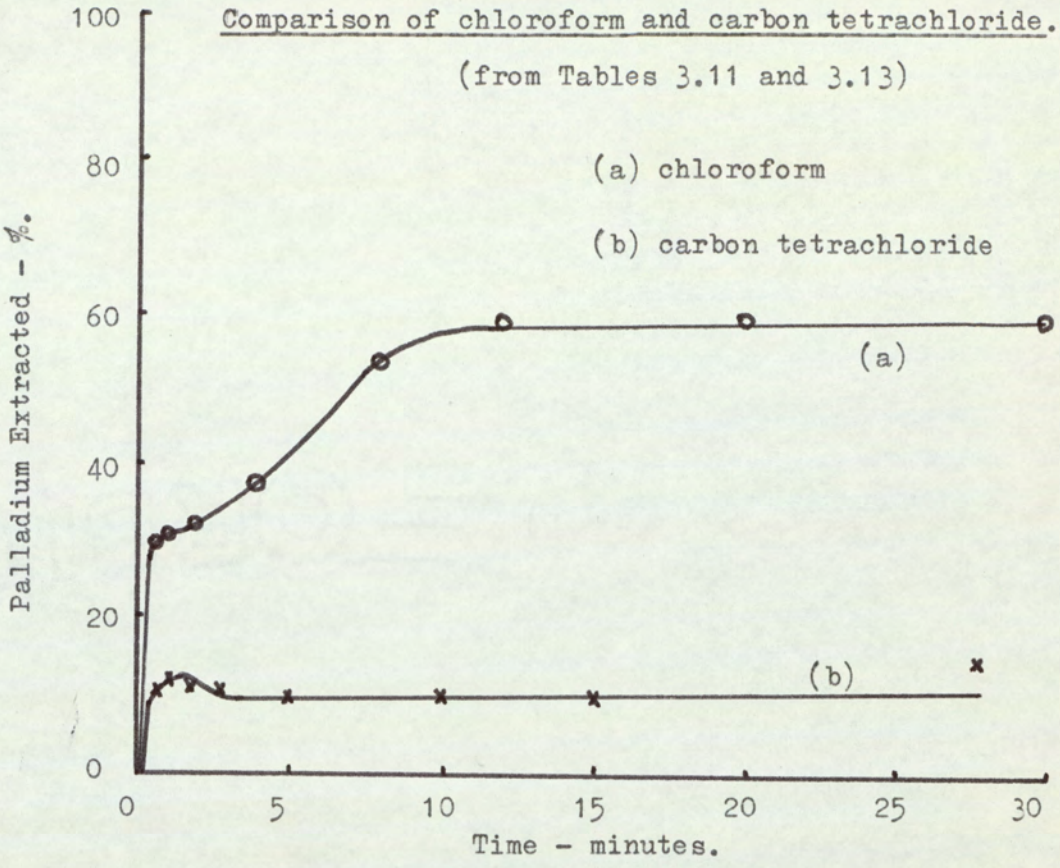


FIGURE 3.13

Comparison of chloroform and benzene.

(from Tables 3.8 and 3.14)

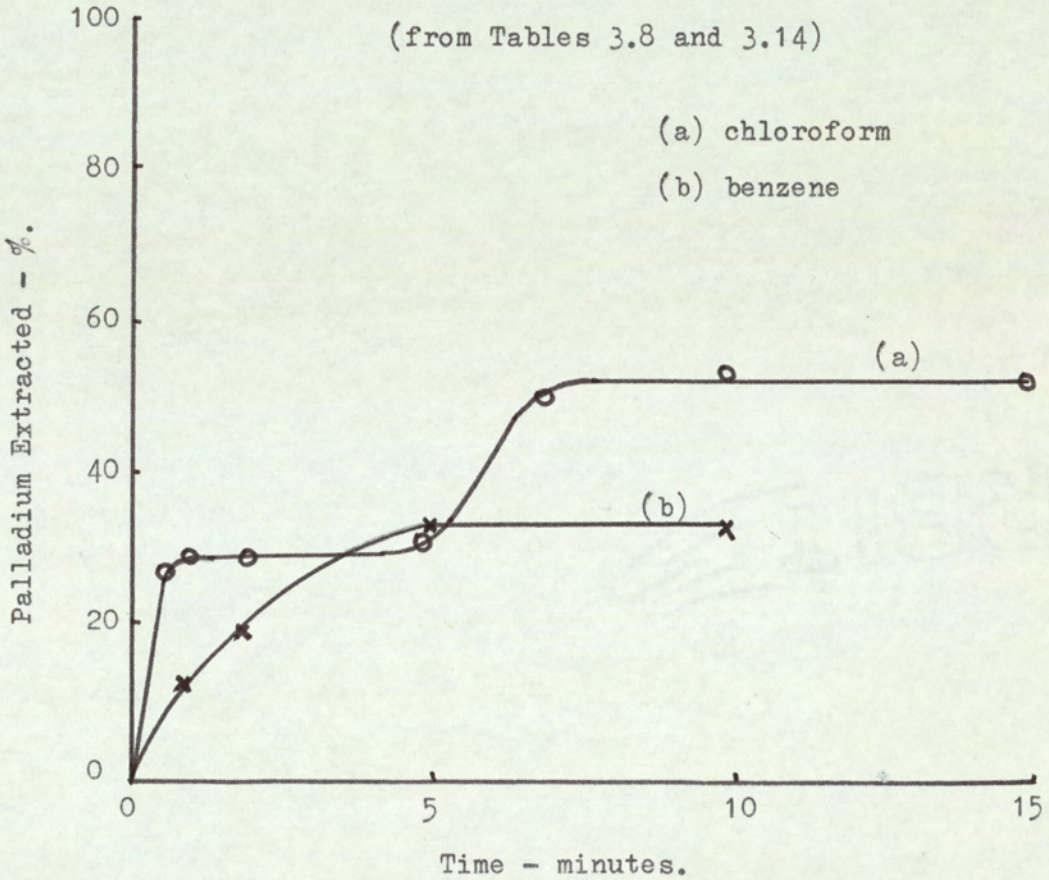


Table 3.13

Shaking Time, minutes	$5x10^{-5}$M $Cu(DDC)_2$		$5x10^{-6}$M $Cu(DDC)_2$	
	c.p.s.	% ext.	c.p.s.	% ext.
½	59.2	12.4	-	-
1	60.7	12.9	38.7	8.6
2	55.4	11.6	-	-
3	55.5	11.8	74.5	15.8
5	45.5	9.7	94.8	20.2
10	47.6	10.1	49.5	10.5
15	48.5	10.8	40.3	8.6
20	-	-	48.9	10.4
25	66.6	14.8	-	-
30	-	-	31.6	6.7
45	-	-	52.9	11.2

initial activity of aqueous phase = 470 c.p.s.

3. The Effect of Different Organic Solvents.

Chloroform and carbon tetrachloride have already been compared in section 2, Figure 3.12.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml in 1N sulphuric acid and shaken for various lengths of time with 5 ml of a $5x10^{-4}$M solution of cupric diethyldithiocarbamate in benzene. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.14 and Figure 3.13.

Table 3.14

Shaking Time, minutes	Activity, c.p.s.	% extraction
1	26.1	12.4
2	39.7	18.4
5	65.7	31.3
10	65.0	30.9

initial activity of organic phase = 210 c.p.s.

4. The Effect of Different Metal Diethyldithiocarbamates.

(a) Zinc diethyldithiocarbamate.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml in 1N sulphuric acid and shaken for various lengths of time with 5 ml of a $5x10^{-4}$M solution of zinc diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.15 and Figure 3.14.

Table 3.15

Shaking Time, minutes	Activity, c.p.s.	% Extraction
1	34.2	10.1
2	67.7	19.9
3	91.5	26.9
5	197.5	58.1
7	195.9	57.6
10	187.3	55.0
15	197.3	58.0
20	194.6	57.2

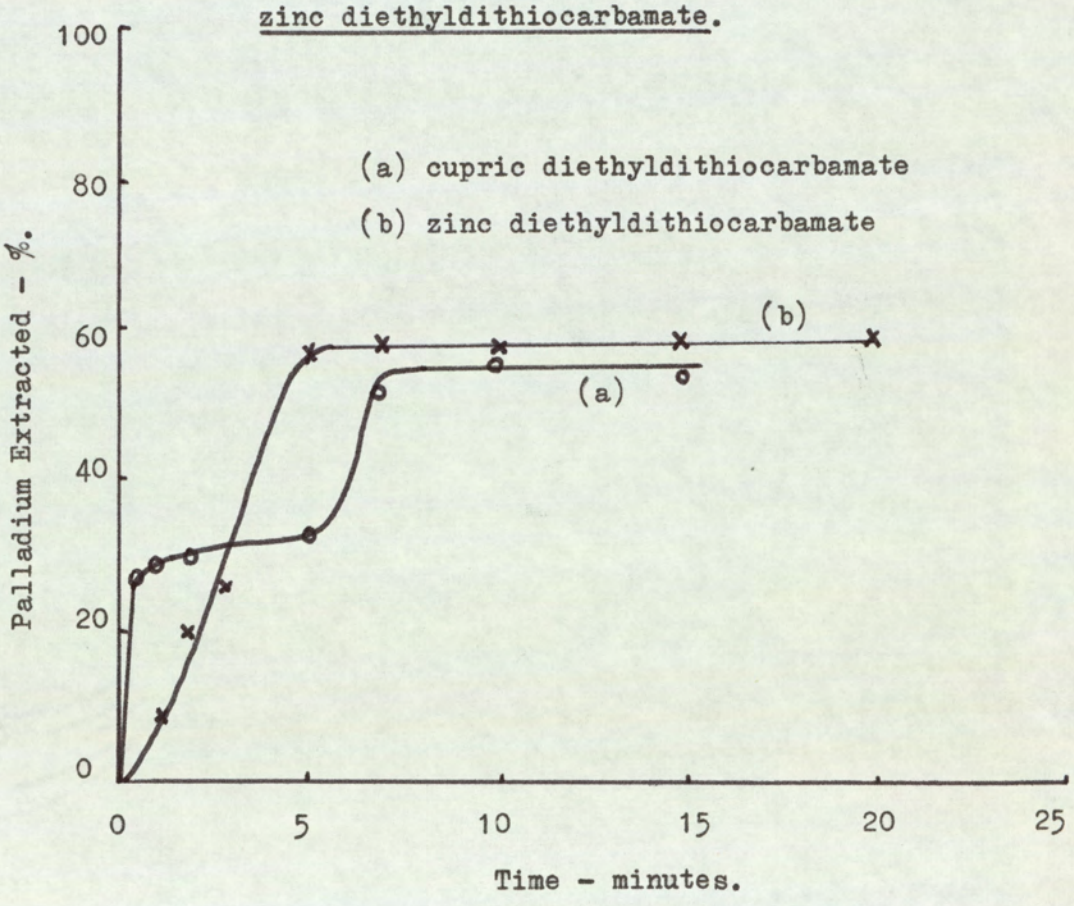
initial activity of aqueous phase = 340 c.p.s.

The above experiment was repeated, adding various amounts of silver nitrate solution to the aqueous phase. The results are given in Table 3.16 and Figure 3.15.

FIGURE 3.14

(from Tables 3.8 and 3.15)

Comparison of cupric diethyldithiocarbamate and zinc diethyldithiocarbamate.



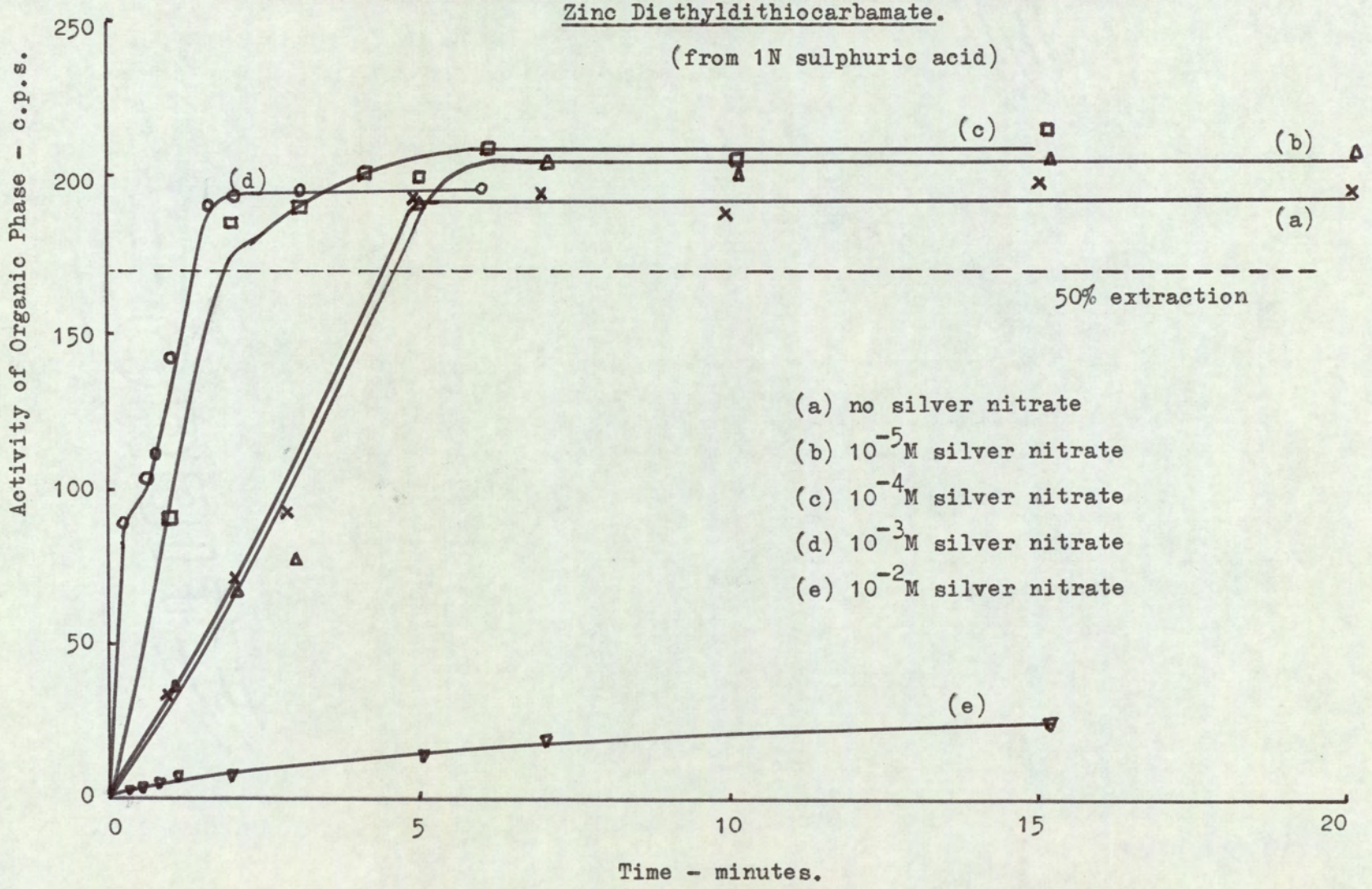


FIGURE 3.15
(from Tables 3.15 and 3.16)

Table 3.16

Shaking Time, minutes.	10^{-5}M $AgNO_3$ Activity, c.p.s	10^{-4}M $AgNO_3$ c.p.s.	10^{-3}M $AgNO_3$ * c.p.s.	10^{-2}M $AgNO_3$ + c.p.s.
1/4	-	-	90.9	3.5
1/2	-	-	104.2	5.4
3/4	-	-	111.9	5.0
1	36.2	92.2	142.4	7.4
1½	-	-	193.2	-
2	65.0	188.2	195.8	7.4
3	77.4	190.7	196.4	-
4	-	201.7	-	-
5	194.9	199.1	-	12.3
6	-	211.0	199.5	-
7	205.0	-	-	17.0
10	201.3	206.0	-	-
15	209.2	216.0	-	23.9
20	212.7	-	-	-

initial activity of aqueous phase = 340 c.p.s.

* slight precipitate of silver chloride occurred.

+ heavy precipitate of silver chloride occurred.

The above experiment was repeated, replacing the 1N sulphuric acid by 1N hydrochloric acid. The results are given in Table 3.17 and Figure 3.16.

Effect of silver nitrate concentration on extraction of palladium with zinc diethyldithiocarbamate.

(from 1N hydrochloric acid)

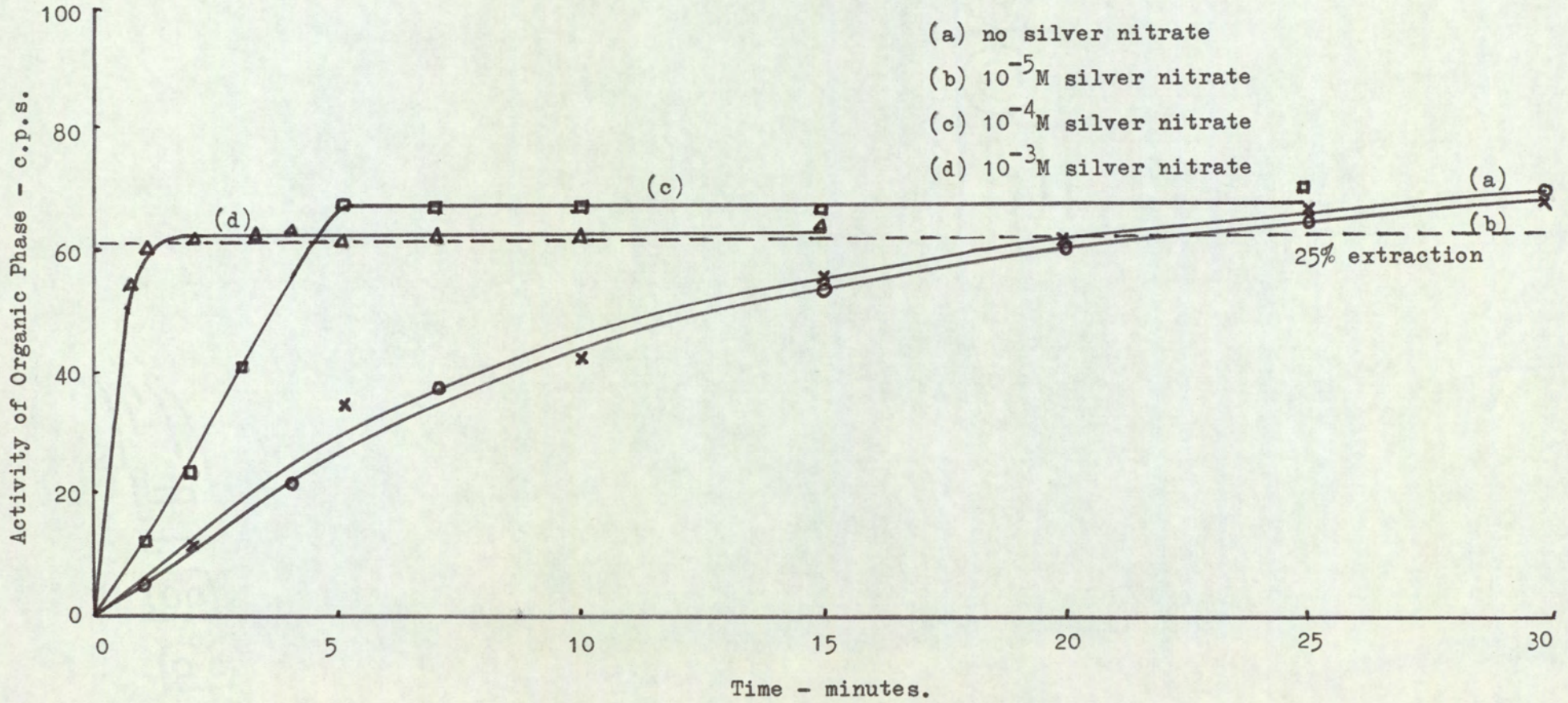


FIGURE 3.16 (from Table 3.17)

Table 3.17

Shaking Time, minutes.	No $AgNO_3$ c.p.s.	10^{-5}M $AgNO_3$ c.p.s.	10^{-4}M $AgNO_3$ c.p.s.	10^{-3}M $AgNO_3$ c.p.s.
1	5.6	-	12.4	61.2
2	10.6	10.8	24.4	62.7
3	-	-	41.1	64.1
4	21.6	-	-	63.2
5	-	34.4	68.7	61.7
7	38.0	-	65.0	62.5
10	-	42.0	65.2	63.0
15	54.5	57.1	64.7	65.7
20	62.8	63.6	-	-
25	68.1	69.8	70.2	-
30	70.1	68.3	-	-

initial activity of aqueous phase = 254 c.p.s.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd), in 1N hydrochloric acid, from which the silver-111 had not been separated, was diluted to 10 ml in 1N sulphuric acid and shaken for various lengths of time with 5 ml of a $5x10^{-4}$M solution of zinc diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The palladium-103 and the silver-111 were counted simultaneously and the true activities calculated using equations 1.16 and 1.17 (Ch.1.III.2a). The results are given in Table 3.18 and Figure 3.17.

FIGURE 3.17

(from Table 3.18)

Simultaneous following of extraction with zinc diethyl-dithiocarbamate with palladium-103 and silver-111.

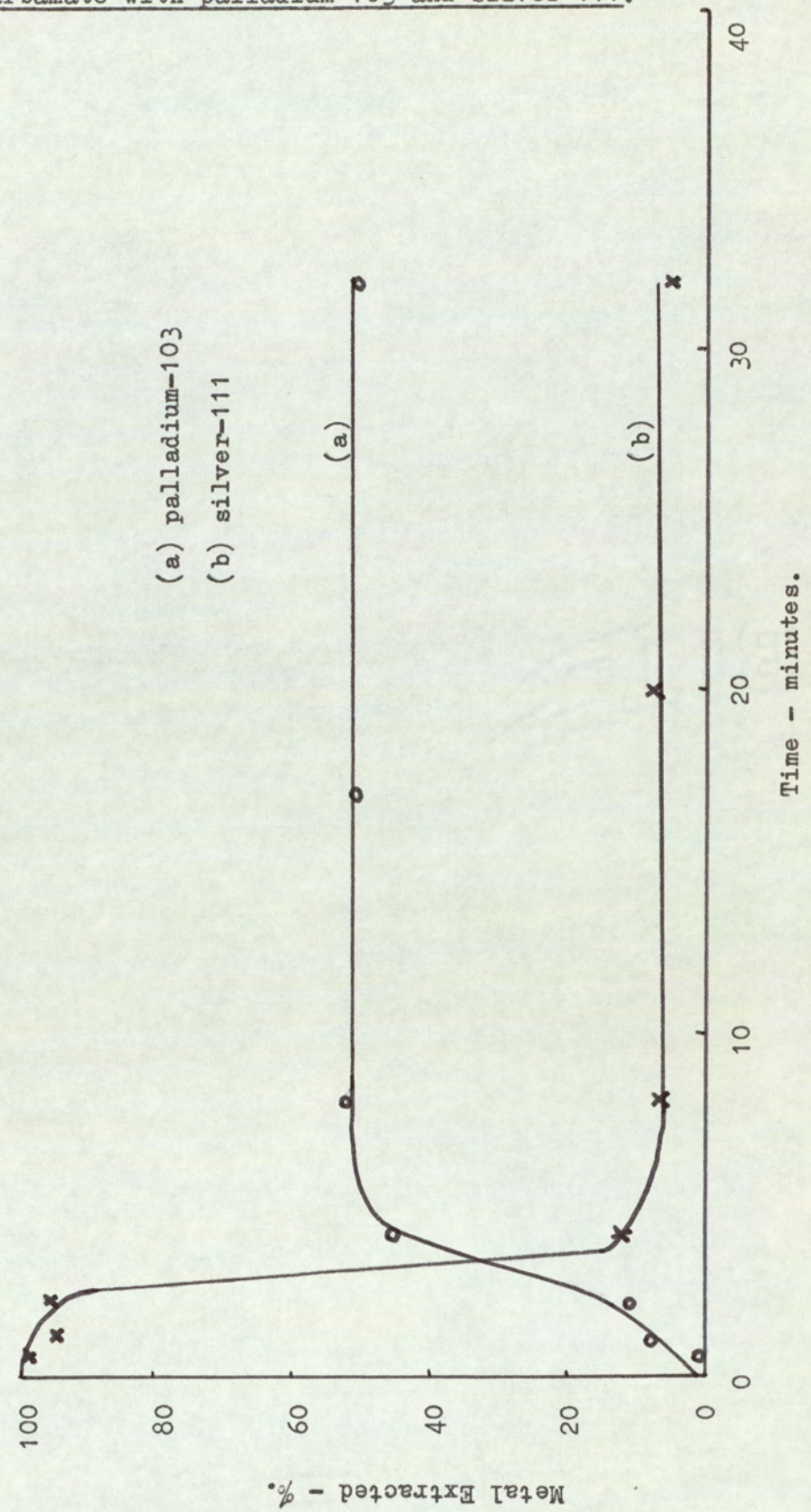


Table 3.18

Shaking Time, minutes.	Palladium-103 activity c.p.s	% ext.	Silver-111 activity c.p.s.	% ext.
½	0	0	238	100
1	22	7.8	225	95.0
2	29	10.3	230	97.0
4	132	46.4	28	11.8
8	150	53.1	18	7.6
17	144	51.1	20	8.4
32	143	50.8	11	4.7

initial palladium-103 activity of aqueous phase = 292 c.p.s.

initial silver-111 activity of aqueous phase = 237 c.p.s.

(b) Nickel diethyldithiocarbamate.

An aliquot of 1.0 ml of a 10^{-3}M palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml in (i) 5N hydrochloric acid and (ii) 5N sulphuric acid, and shaken for various lengths of time with 5 ml of a $5x10^{-5}$M solution of nickel diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.19 and Figure 3.18.

Table 3.19

Shaking Time, minutes.	Extraction from 5N HCl c.p.s.	% ext.	Extraction from 5N H_2SO_4 c.p.s.	% ext.
½	0	0	1.8	0.83
1	0.3	0.14	4.0	1.84
2	0.5	0.23	6.5	3.20
5	1.5	0.69	14.8	6.82

initial activity of aqueous phase = 217 c.p.s.

Comparison of cupric, nickel and silver diethyldithiocarbamates.

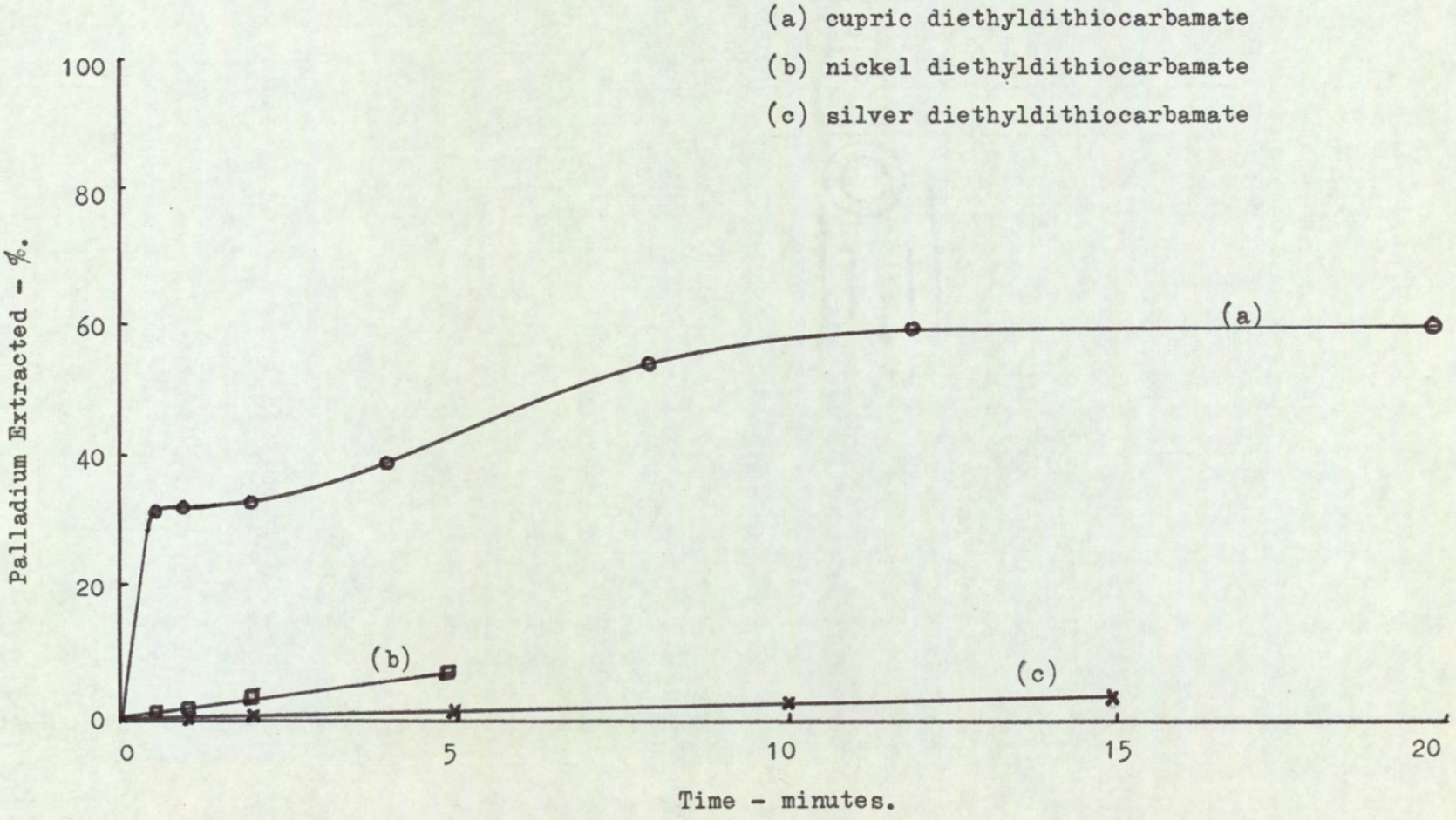


FIGURE 3.18
(from Tables 3.11, 3.19 and 3.20)

(c) Silver diethyldithiocarbamate.

The experiment was carried out as in (b) using 5N sulphuric acid and replacing the $5x10^{-5}$M nickel diethyldithiocarbamate by 10^{-4}M silver diethyldithiocarbamate in chloroform. The results are given in Table 3.20 and Figure 3.18.

Table 3.20

Shaking Time, minutes.	Activity, c.p.s.	% Extraction
1	0.4	0.2
2	0.5	0.3
5	0.8	0.4
10	2.5	1.4
15	4.8	2.8

initial activity of aqueous phase = 174 c.p.s.

5. The Effect of the Addition of Previously Prepared Palladium Chloride Diethyldithiocarbamate.

An aliquot of 2.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml with distilled water and shaken for various lengths of time with 5 ml of a $5x10^{-4}$M solution of cupric diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. This experiment was then repeated, adding (i) 1 ml and (ii) 2 ml of a previously prepared 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform, to the organic phase after 5 minutes shaking. The results are given in Table 3.21 and Figure 3.19.

Table 3.21

Shaking Time, minutes.	Volume of Pd.Cl(DDC) solution added. none	1 ml	2 ml
	Activity, c.p.s.	Activity, c.p.s.	Activity, c.p.s.
2	4.7	-	-
4	4.9	-	-
5	5.2	-	-
6	4.9	-	6.1
7	-	5.9	-
9	4.9	6.9	-
10	5.2	-	8.8
12	5.1	7.9	8.9
14	5.1	-	9.1
15	5.6	9.0	-
16	5.7	-	8.9
18	7.5	-	8.8
20	8.0	-	9.2
30	8.7	-	9.3

initial activity of aqueous phase = 20.1 c.p.s.

Effect of the addition of previously prepared palladium chloride diethyldithiocarbamate in chloroform on rate of extraction.

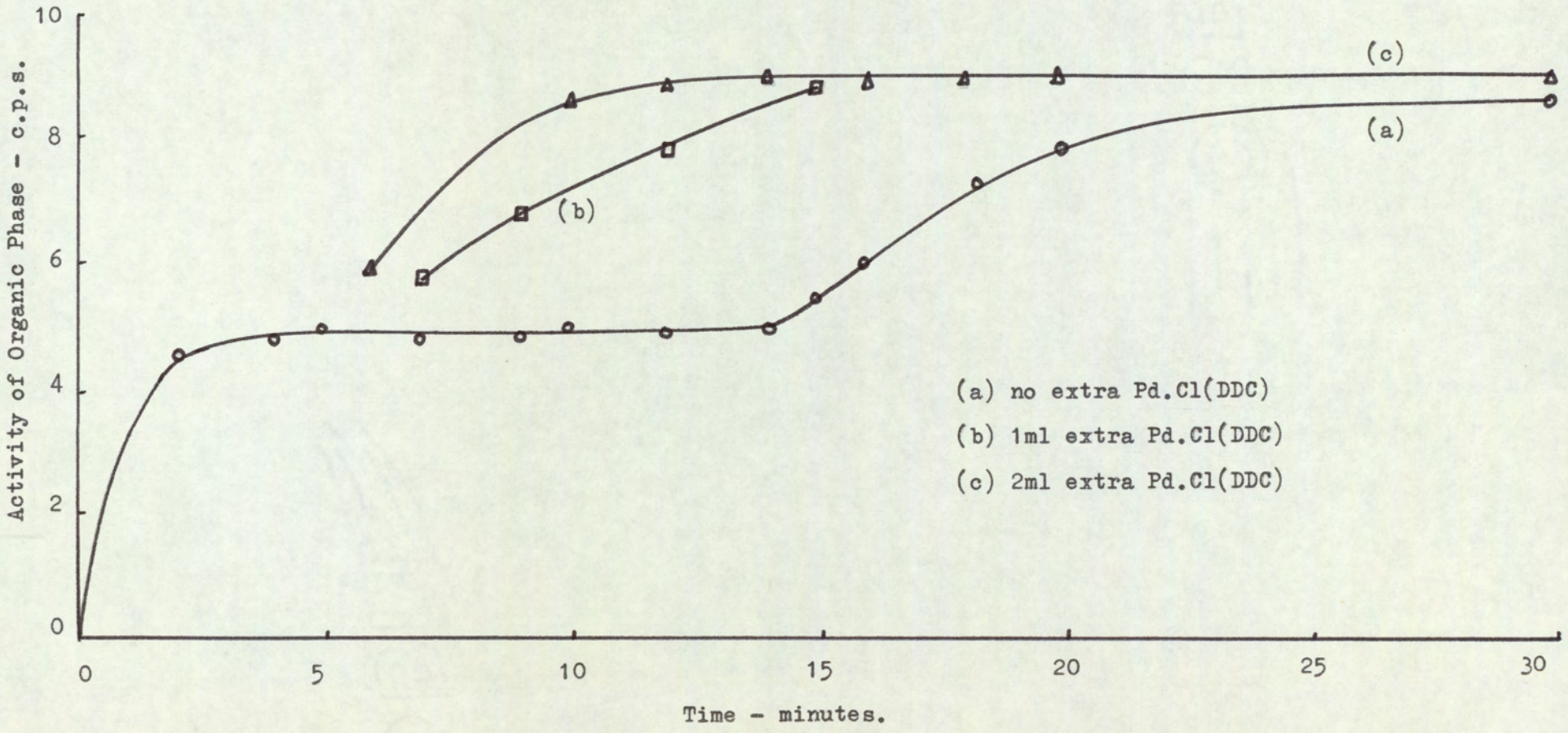


FIGURE 3.19 (from Table 3.21)

VIII. Determination of Extraction and Stability Constants.

1. Determination of K_1.

(a) Variation of EDTA concentration.

A 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform was prepared by shaking 100 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes with an excess (20 ml) of a 10^{-2}M palladium chloride solution (^{103}Pd) diluted to 100 ml in 5N sulphuric acid.

In order to determine the time required to reach equilibrium, 5 ml of the above solution was shaken for various lengths of time with 10 ml portions of aqueous EDTA (disodium salt) of different concentrations. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.22.

Table 3.22

Shaking Time, minutes.	10^{-4}M EDTA c.p.s.	3×10^{-4}M EDTA c.p.s.	5×10^{-4}M EDTA c.p.s.	10^{-3}M EDTA c.p.s.
2	98.4	-	-	-
5	100.7	83.8	69.4	62.5
10	94.0	77.5	65.2	61.8
15	93.1	77.1	65.0	60.5
20	91.7	77.8	65.3	61.8
25	91.0	-	-	-
30	92.2	-	-	-
35	90.9	-	-	-

initial activity of organic phase = 110 c.p.s.

A series of aqueous solutions, volume 10 ml, were prepared containing EDTA over the concentration range 10^{-3} to 10^{-4}M. These solutions were shaken for 30 minutes with 5 ml of a 10^{-3}M solution

of palladium chloride diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered and the pH measured. The final concentrations of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate were calculated from the activity of the organic phase using equations 2.36 and 2.37 (Ch.2.II.2). The results are given in Table 3.23.

Table 3.23

Initial EDTA concentration, M	Activity of organic phase, c.p.s.	pH	[Pd.Cl(DDC)] x 10^{-4}	[$Pd(DDC)_2$] x 10^{-4}
2.0×10^{-4}	67.9	3.60	3.00	3.50
2.5×10^{-4}	62.1	3.60	1.90	4.06
3.25×10^{-4}	59.9	3.60	1.48	4.26
4.2×10^{-4}	58.6	3.60	1.24	4.38
5.0×10^{-4}	57.6	3.60	1.10	4.46
5.2×10^{-4}	57.5	3.60	1.00	4.50
7.0×10^{-4}	57.0	3.70	0.92	4.54
8.0×10^{-4}	56.4	3.80	0.80	4.60
1.1×10^{-3}	54.9	3.85	0.50	4.75

initial activity of organic phase = 104.3 c.p.s.

(b) Variation of hydrogen ion concentration.

A series of 10 ml portions of a 10^{-3}M aqueous EDTA solution were adjusted to various pH values using sulphuric or perchloric acids. These solutions were shaken for 30 minutes with 5 ml of a 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered and the final pH measured. The concentrations of the two complexes were calculated as in (a) and the results are given in Table 3.24.

Table 3.24

pH	Activity of organic phase, c.p.s.	[Pd.Cl(DDC)] $\times 10^{-4}$	[$Pd(DDC)_2$] $\times 10^{-4}$
3.60	49.8	0.50	4.75
2.20	55.0	1.63	4.19
1.50	64.0	3.52	3.23
1.35	64.6	3.64	3.18
0.80	74.9	5.82	2.09
0.35	80.6	7.05	1.48

initial activity of organic phase = 94.7 c.p.s.

(c) Variation of chloride ion concentration.

A series of 10 ml portions of a 10^{-3}M aqueous EDTA solution were adjusted to various chloride ion concentrations using hydrochloric acid. These solutions were shaken for 30 minutes with 5 ml of a 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered and the pH measured. The concentrations of the two complexes were calculated as in (a) and the results are given in Table 3.25.

Table 3.25

Initial HCl concentration, M	Activity of organic phase c.p.s.	pH	$[Pd.Cl(DDC)]$ $\times 10^{-4}$	$[Pd(DDC)_2]$ $\times 10^{-4}$
-	22.8	3.65	4.53	0.94
1.0×10^{-3}	22.9	3.50	4.50	1.00
2.0×10^{-3}	24.1	3.44	4.24	1.54
3.0×10^{-3}	26.3	3.36	3.69	2.62
4.0×10^{-3}	26.9	3.22	3.55	2.90
5.0×10^{-3}	29.1	3.10	3.03	3.96
6.0×10^{-3}	31.1	2.96	2.54	4.92
8.0×10^{-3}	31.8	2.88	2.37	5.26
1.0×10^{-2}	38.6	2.22	0.74	8.51

initial activity of organic phase = 41.7 c.p.s.

(d) Calculation of results.

From the results in Tables 3.23 to 3.25, the following quantities were calculated using the equations:

$$[Pd_{aq}] = [Pd(DDC)_2]/2$$

$$[Cl^-] = [Pd(DDC)_2] + \text{initial}[Cl^-]$$

$$[Y'] = \text{initial } [EDTA] - [Pd_{aq}].$$

Values for log α_Y were obtained from Figure 2.2, and taking logarithmic values for the concentrations of the various species, Table 3.26 was compiled. The values of log K_1 were calculated using equation 2.38 (Ch.2.II.2).

Table 3.26

$pPd(DDC)_2$	$pPd.Cl(DDC)$	pPd_{aq}	pCl^-	pH	pY'	$\log \alpha_Y$	$\log K_1$
Variation of $[Y']$							
3.456	3.523	3.757	3.456	3.60	4.602	9.4	14.12
3.392	3.721	3.693	3.392	3.60	4.328	9.4	14.50
3.371	3.830	3.672	3.371	3.60	3.947	9.4	14.42
3.358	3.907	3.660	3.358	3.60	3.701	9.4	14.38
3.351	3.958	3.658	3.351	3.60	3.553	9.4	14.36
3.347	4.000	3.648	3.347	3.60	3.536	9.4	14.45
3.343	4.036	3.644	3.343	3.70	3.321	9.2	14.32
3.337	4.097	3.638	3.337	3.80	3.249	9.0	14.39
3.323	4.301	3.623	3.323	3.85	3.060	8.9	14.67
Variation of $[H^+]$							
3.323	4.301	3.623	3.323	3.60	3.118	9.4	14.73
3.378	3.790	3.678	3.378	2.20	3.050	13.0	14.23
3.490	3.454	3.790	3.490	1.50	3.102	15.3	14.02
3.498	3.439	3.798	3.498	1.35	3.048	16.0	14.33
3.680	3.235	3.980	3.680	0.80	3.047	18.0	14.10
3.830	3.152	4.131	3.830	0.35	3.033	19.9	14.32
Variation of $[Cl^-]$							
3.344	4.027	3.644	3.344	3.65	3.112	9.3	14.09
3.347	4.000	3.648	2.839	3.50	3.111	9.6	15.04
3.372	3.812	3.674	2.616	3.44	3.103	9.7	15.02
3.433	3.582	3.733	2.472	3.36	3.089	9.9	14.76
3.450	3.538	3.750	2.360	3.22	3.085	10.2	14.88
3.520	3.402	3.821	2.276	3.10	3.071	10.6	14.78
3.595	3.308	3.896	2.205	2.96	3.059	10.9	14.59
3.625	3.279	3.926	2.084	2.88	3.054	11.0	14.65
4.131	3.070	4.432	1.971	2.22	3.017	12.9	13.99

From Table 3.26, the mean value of log K_1 is 14.46 (24 determinations) and the standard deviation, s, calculated by the equation:

$$s^2 = \frac{\sum \Delta^2}{n - 1}$$

where Δ = the deviation from the mean,

and n = the number of determinations,

was found to be 0.33.

(e) Verification of Equation 2.38.

Variation of EDTA concentration.

Values of the expression, $2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)]$, were calculated from Table 3.26 and are given in Table 3.27. These were plotted against the expression, log[Y'] in Figure 3.20.

Table 3.27

$2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)]$	log[Y']
-3.389	-4.602
-3.063	-4.328
-2.912	-3.947
-2.809	-3.701
-2.744	-3.553
-2.694	-3.536
-2.677	-3.249
-2.650	-3.321
-2.345	-3.060

From Figure 3.20, the slope of the line = 0.522 and the intercept of the line = -0.83. Hence,

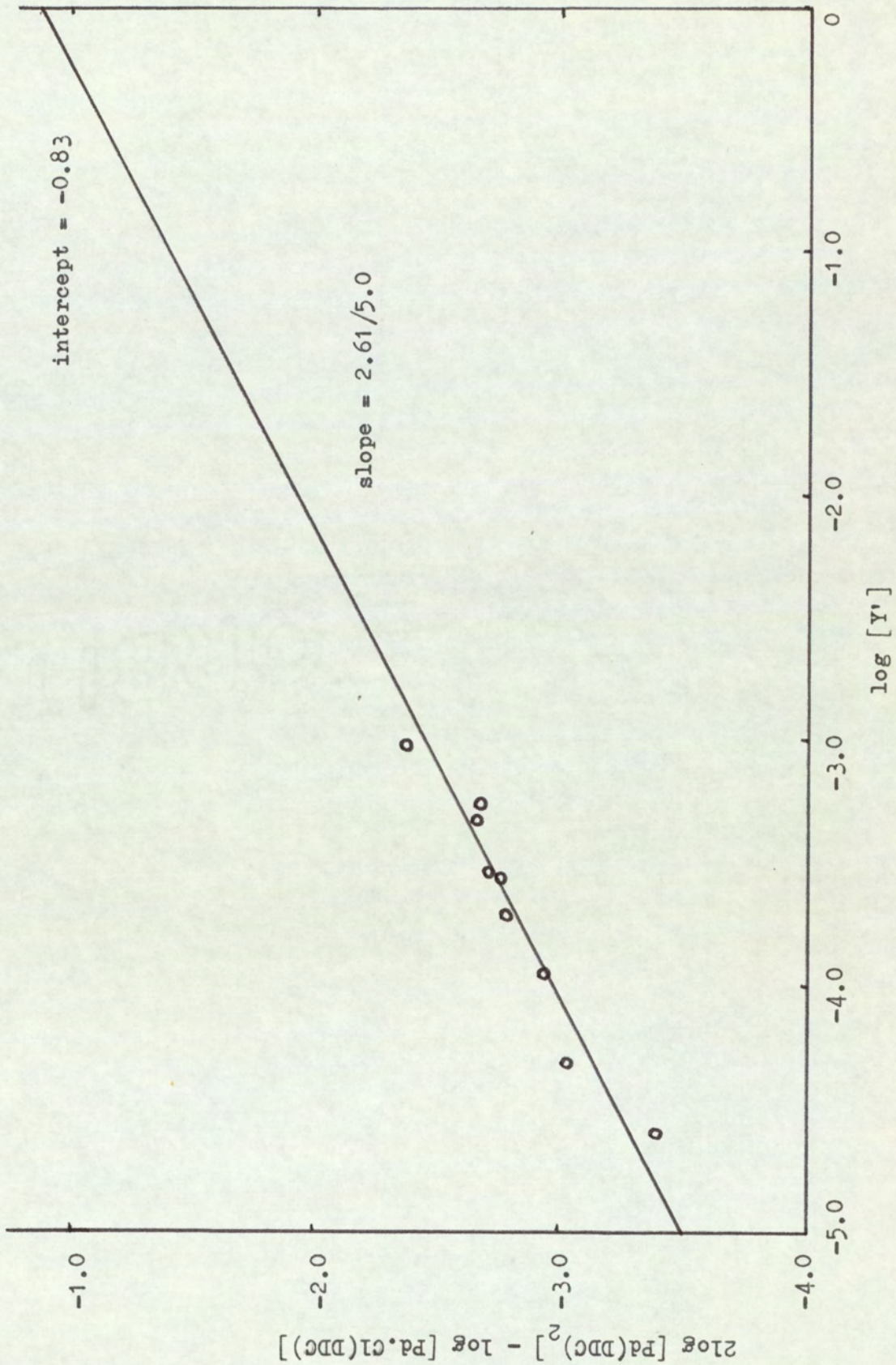
$$\tfrac{1}{2}\log(2K_1[H^+]^2/\alpha_Y) = -0.83$$

and therefore log K_1 = 14.6

FIGURE 3.20

Variation of EDTA concentration.

(from Table 3.27)



Variation of Hydrogen ion concentration.

Values of the expression, $4\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log\alpha_Y$, were calculated from Table 3.26 and are given in Table 3.28. These were plotted against the expression, $\log[H^+]$, in Figure 3.21.

Table 3.28

$4\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log\alpha_Y$	$\log[H^+]$
4.710	-3.60
7.068	-2.20
8.248	-1.50
8.886	-1.35
9.750	-0.80
10.864	-0.35

From Figure 3.21, the slope of the line = 1.94 and the intercept of the line = 11.4. Hence,

$$\log(2K_1[Y']) = 11.4$$

and therefore $\log K_1 = 14.7$.

Variation of chloride ion concentration.

Values of the expression,

$$2\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log\alpha_Y - 2\log[H^+],$$

were calculated from Table 3.26 and are given in Table 3.29. These were plotted against the expression, $\log[Cl^-]$, in Figure 3.22.

From Figure 3.22, the slope of the line = -2.12 and the intercept of the line = 11.6. Hence,

$$\log(2K_1[Y']) = 11.6$$

and therefore, $\log K_1 = 14.9$.

FIGURE 3.21

Variation of hydrogen ion concentration.

(from Table 3.28)

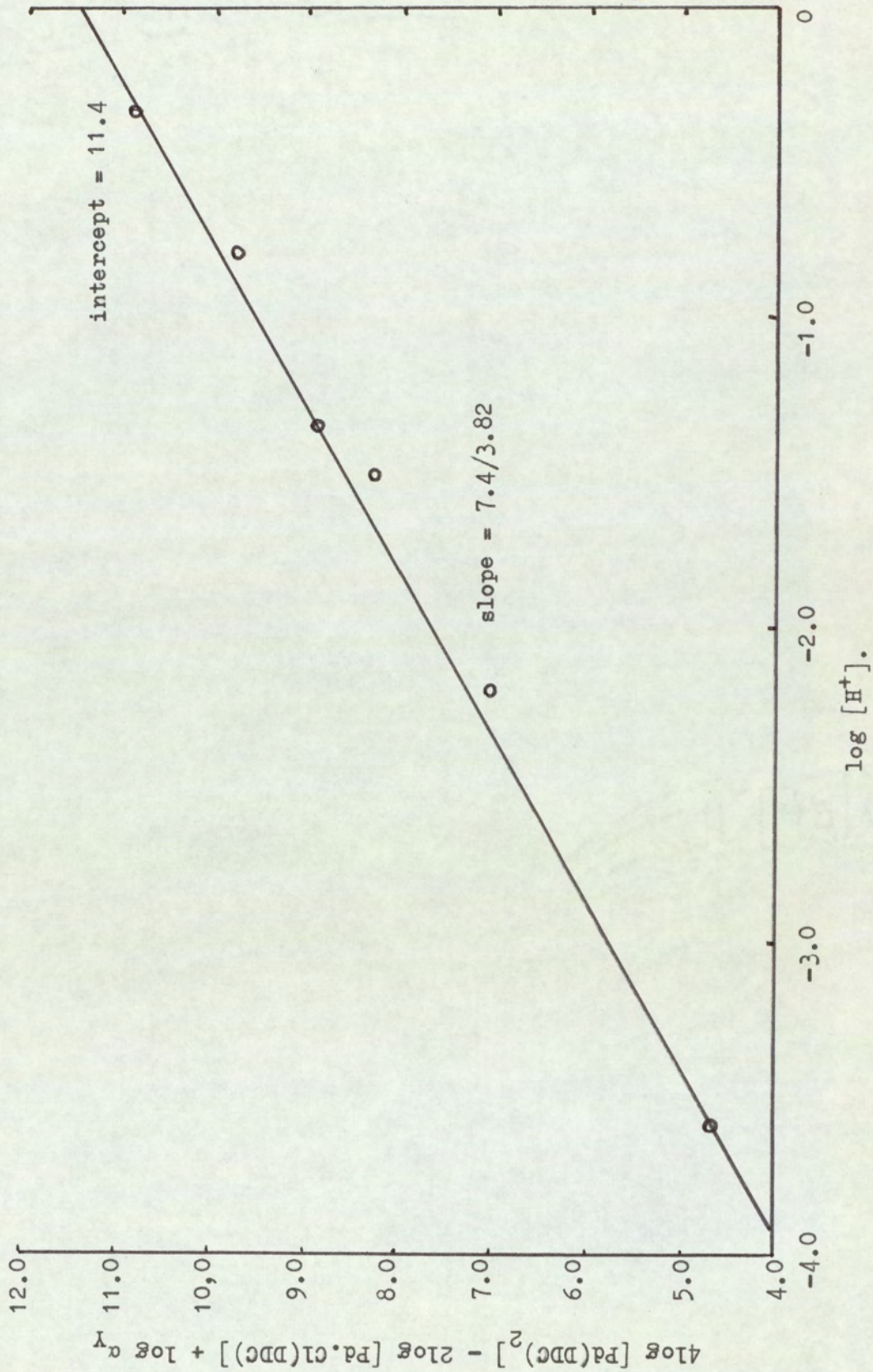


FIGURE 3.22

Variation of chloride ion concentration.

(from Table 3.29)

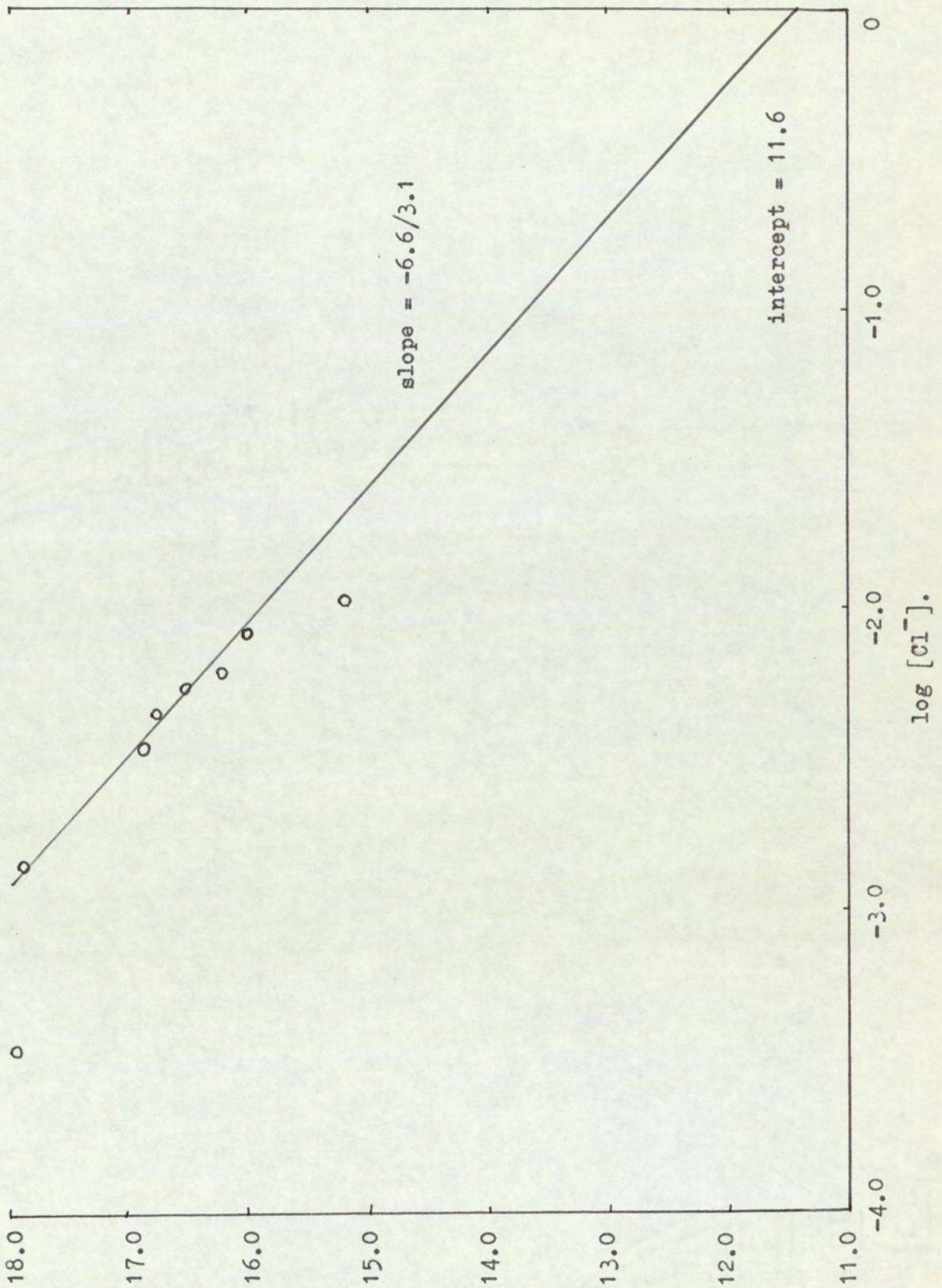


Table 3.29

$2\log[Pd(DDC)_2] - 2\log[Pd.Cl(DDC)] + \log \alpha_Y - 2\log[H^+]$.	$\log[Cl^-]$
17.966	-3.440
17.906	-2.839
17.456	-2.616
16.918	-2.472
16.816	-2.360
16.564	-2.276
16.246	-2.205
16.068	-2.084
15.218	-1.971

2. Determination of K_2.

The visible spectrum of the ion, $PdCl_4^{2-}$, was investigated by measuring the spectra of solutions containing palladium over a range of hydrogen and chloride ion concentrations. The results of this experiment are given in Figures 3.23 and 3.24, and it can be seen that the absorbance peak at 470 nm is unchanged over the pH range 0 to 3, and the chloride ion concentration range 0.5N to 2N. Various volumes of an inactive, 10^{-2}M palladium chloride solution were diluted to 10 ml in 1N hydrochloric acid and the absorbance of the resulting solutions was measured at 470 nm against distilled water in a 10 mm cell. The results are given in Table 3.30 and Figure 3.25. It can be seen that Beer's Law is obeyed over the palladium concentration range 5×10^{-4}M to 8×10^{-3}M.

The spectrum of the palladium EDTA complex, H_2PdY, was investigated by measuring the spectra of solutions containing palladium in 0.1M EDTA over a range of hydrogen ion concentrations. The results of this experiment are given in Figure 3.26, and it can be seen that

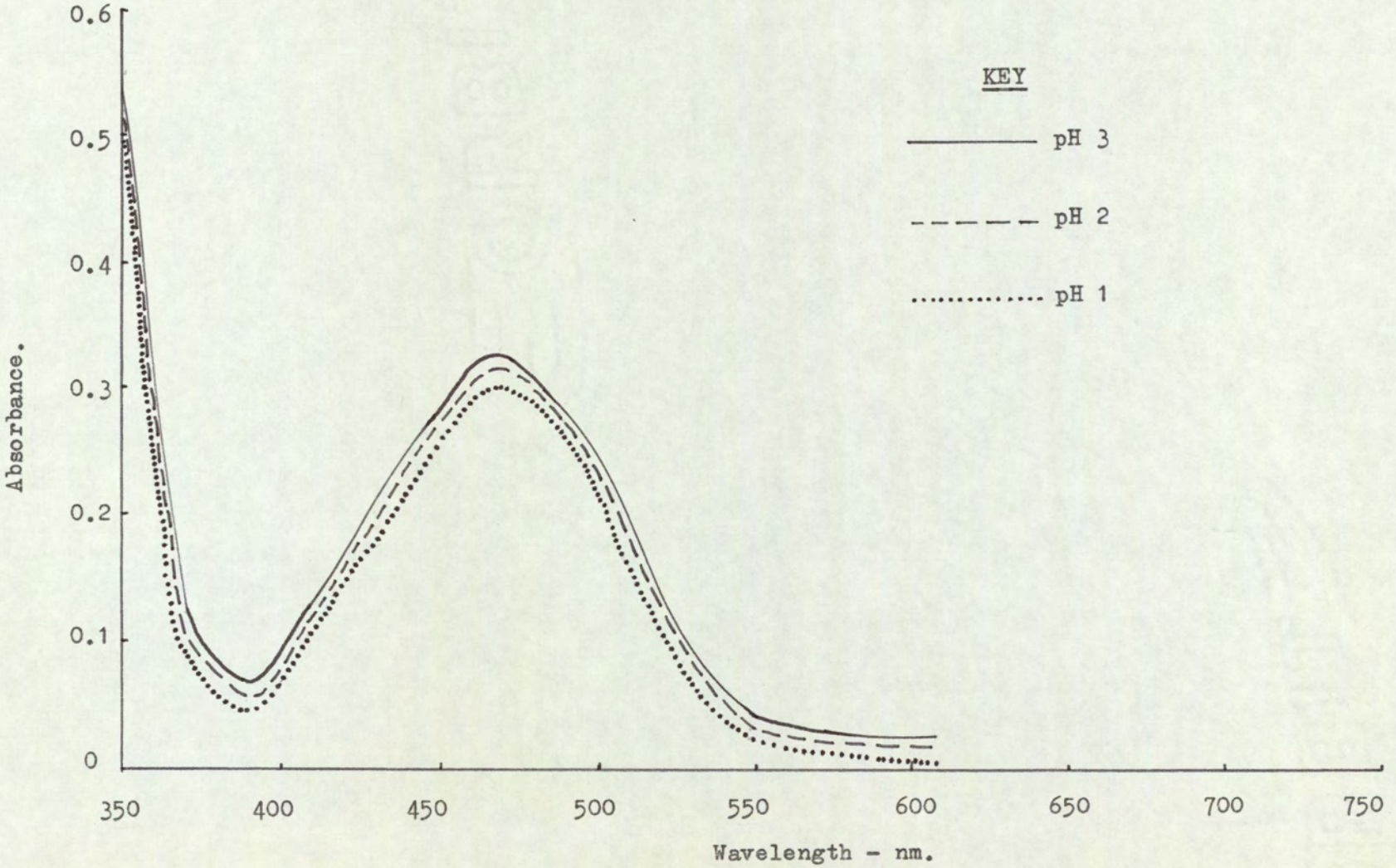


FIGURE 3.23

Effect of pH on the spectrum of the anion, $PdCl_4^{2-}$.

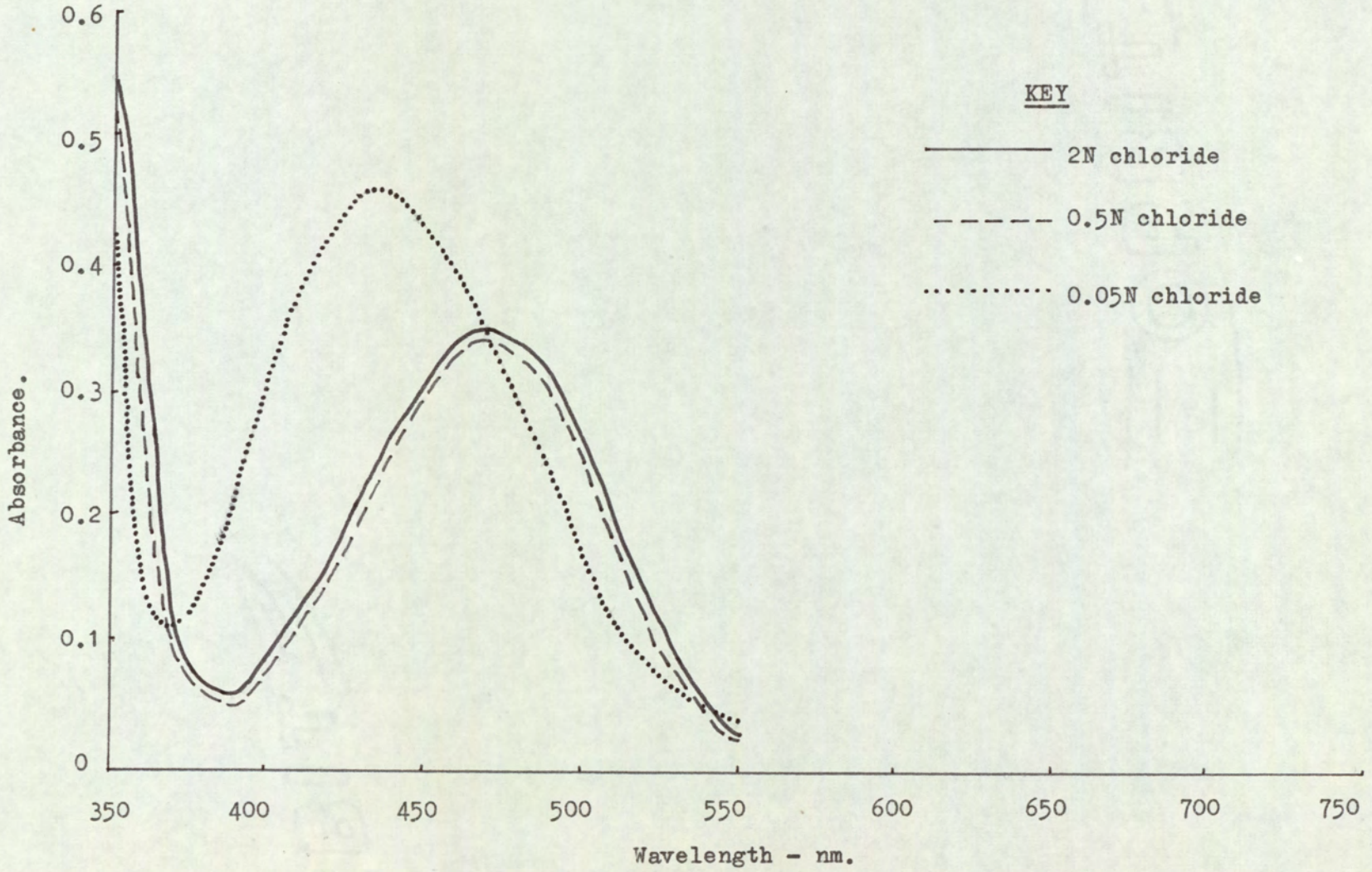


FIGURE 3.24

Effect of chloride ion concentration on the spectrum of the anion, $PdCl_4^{2-}$.

FIGURE 3.25

Calibration curve for the anion, $PdCl_4^{2-}$, at 470nm.

(from Table 3.30)

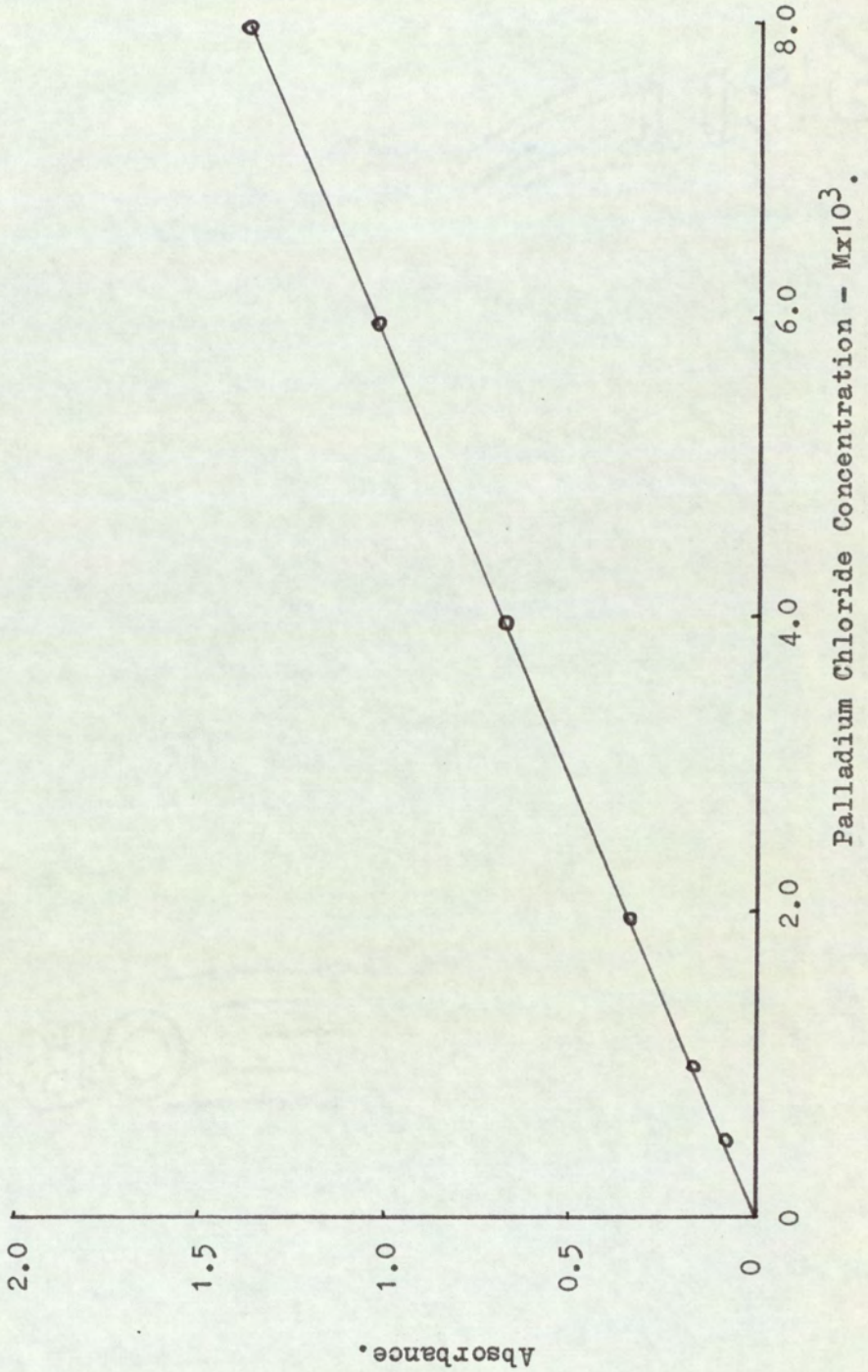


Table 3.30

Concentration of $PdCl_2$ M x 10^{-3}	Absorbance at 470 nm.
0.5	0.085
1.0	0.172
2.0	0.340
4.0	0.690
6.0	1.040
8.0	1.400

the absorbance peak at 390 mn which occurs at pH 1 to 2, moves to 400 nm at lower pH values. Various volumes of an inactive, 10^{-2}M palladium chloride solution were diluted to 10 ml in 0.1M EDTA and the pH adjusted with hydrochloric acid. The absorbance of the resulting solutions was measured at 390 or 400 nm against distilled water in a 10 mm cell. The results are given in Table 3.31 and Figure 3.27. It can be seen that Beer's Law is only approximately obeyed.

Table 3.31

Concentration of $PdCl_2$ M x 10^{-3}	Absorbance at 400 nm. (pH=0.5)	Absorbance at 390 nm. (pH=2)
0.5	0.201	0.262
1.0	0.390	0.450
2.0	0.740	0.910
4.0	1.210	1.740

A series of solutions were prepared by diluting 2.0 ml of an inactive palladium chloride solution to 10.0 ml in EDTA over the concentration range 10^{-4} to 10^{-2}M. The pH was adjusted with hydrochloric acid over the range 0 to 2 and the chloride ion concentration

FIGURE 3.26

Effect of pH on the spectrum of the complex, H_2PdY.

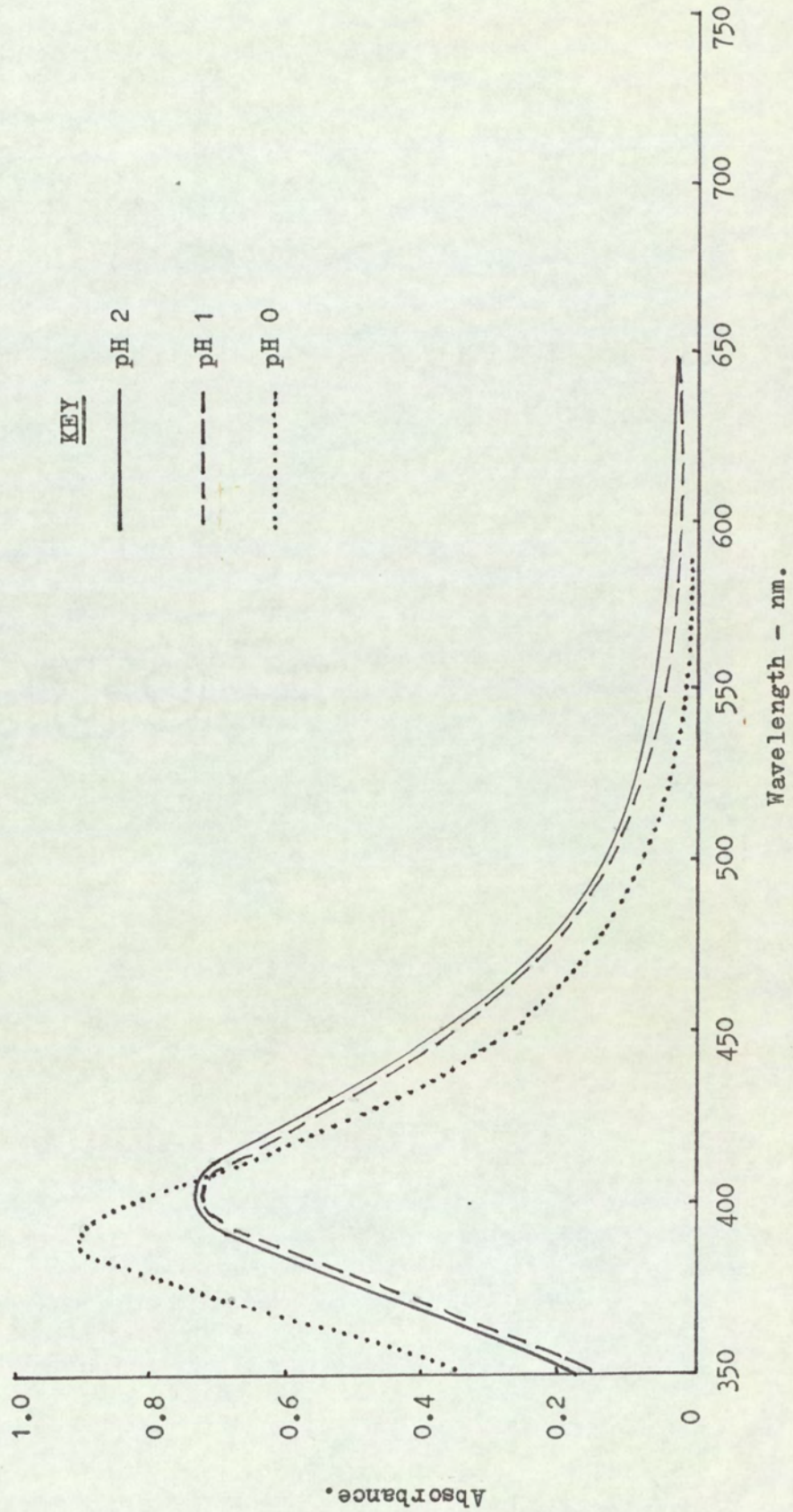
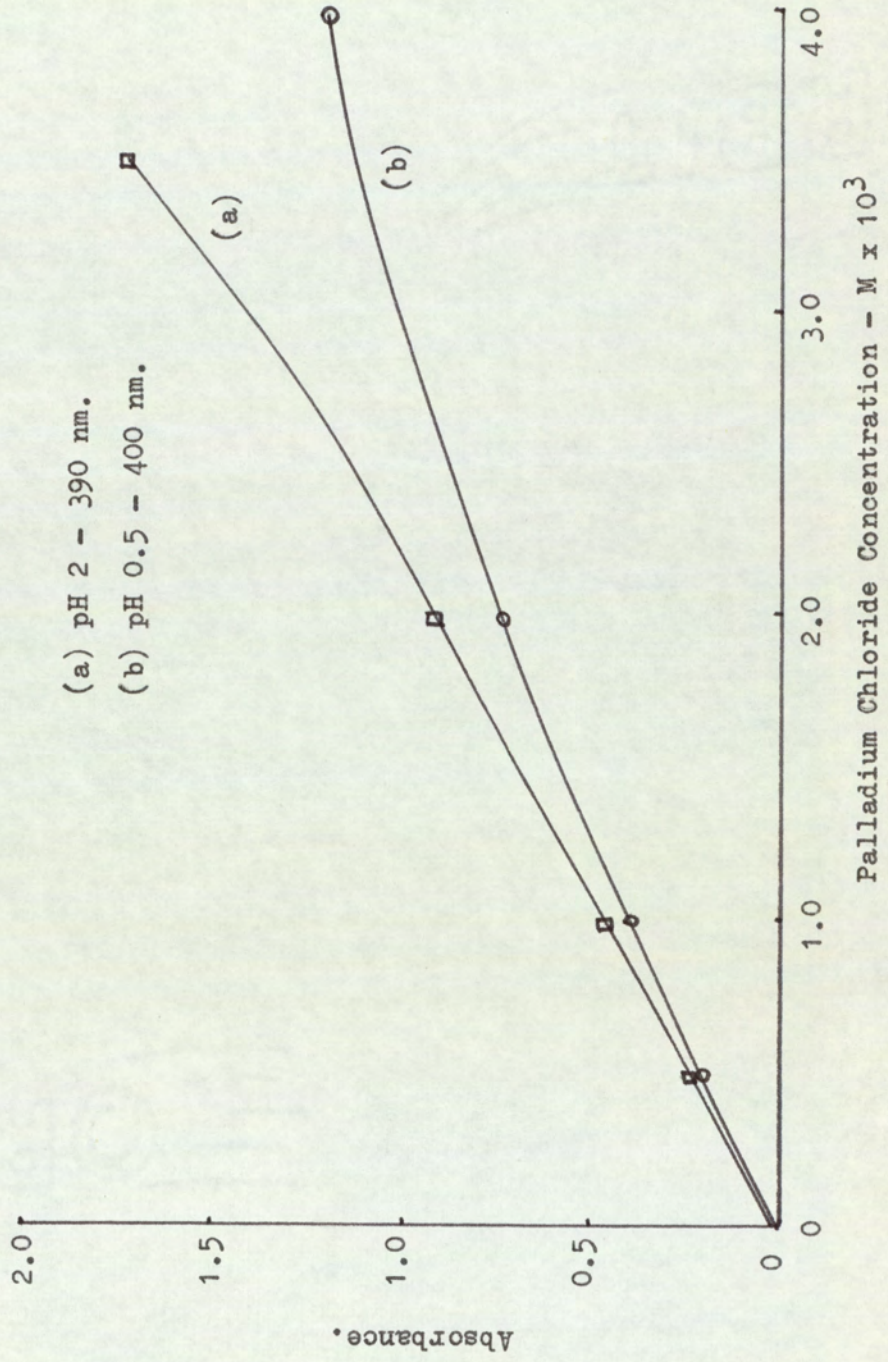


FIGURE 3.27

Calibration Curve for the Complex, H_2PdY, at 390 and 400 nm.

(from Table 3.31)



made 1N with sodium chloride. These solutions were allowed to stand for at least 1 hour to reach equilibrium (no colour change was observed after the first 5 to 10 minutes), and then the pH was measured and the absorbance at 470 nm and 390 or 400 nm measured against distilled water in a 10 mm cell. The concentrations of the two species, $PdCl_4^{2-}$ and H_2PdY, were calculated from the absorbance measurements using equations 2.46 and 2.47 (Ch.2II.3) which become:

$$[PdCl_4^{2-}] = (293A - 72.5B)/4.9\times10^4,$$

and $$[H_2PdY] = (188B - 77A)/4.9\times10^4 \quad \text{at pH 0.5,}$$

or at pH 1 - 2:

$$[PdCl_4^{2-}] = (419A - 67B)/8.15\times10^4$$

and $$[H_2PdY] = (180B - 46A)/8.15\times10^4.$$

The results are given in Table 3.32 and Table 3.33.

Table 3.32

Initial EDTA concentration, M	pH	Absorbance at 470 nm	Absorbance at 400 nm	$[PdCl_4^{2-}]$ $\times10^{-3}$	$[H_2PdY]$ $\times10^{-3}$
5×10^{-4}	0.50	0.346	0.210	1.74	0.26
1×10^{-3}	0.50	0.342	0.214	1.71	0.28
2×10^{-3}	0.50	0.310	0.257	1.43	0.57
4×10^{-3}	0.50	0.263	0.365	1.02	0.98
5×10^{-3}	0.50	0.260	0.378	0.98	1.03
7×10^{-3}	0.50	0.243	0.416	0.83	1.20
1×10^{-2}	0.50	0.212	0.486	0.55	1.51
2×10^{-2}	0.50	0.182	0.518	0.32	1.68
-	-	0.376	0.153	2.00	-
10^{-1}	-	0.145	0.586	-	2.00

Table 3.33

Initial EDTA concentration, M	pH	Absorbance at 470 nm	Absorbance at 390 nm	$[PdCl_4^{2-}]$ $\times 10^{-3}$	$[H_2PdY]$ $\times 10^{-3}$
2×10^{-4}	1.30	0.337	0.159	1.81	0.18
5×10^{-4}	1.33	0.308	0.254	1.50	0.46
1×10^{-3}	1.40	0.264	0.369	1.15	0.85
2×10^{-3}	1.41	0.173	0.691	0.36	1.61
3×10^{-3}	1.43	0.152	0.789	0.15	1.87
4×10^{-3}	1.50	0.141	0.806	0.06	1.92
5×10^{-3}	1.55	0.139	0.814	0.05	1.94
-	-	0.359	0.091	2.00	-
10^{-1}	-	0.134	0.838	-	2.00

From the results in Tables 3.32 and 3.33, the following quantities were calculated using the equations:

$$[Pd'] = [PdCl_4^{2-}]$$

$$[Y'] = \text{initial } [EDTA] - [H_2PdY].$$

Values of $\log \alpha_{Pd}$ and $\log \alpha_Y$ were obtained from Figures 2.1 and 2.2, and taking logarithmic values for the concentrations of the various species, Table 3.34 was compiled. The values of $\log K_2$ were calculated using equation 2.48 (Ch.2.II.3)

From Table 3.34, the mean value of $\log K_2$ is 38.10 (15 determinations) and the standard deviation was found to be 0.16.

Table 3.34

pPd'	pH_2PdY	pH	log α_Y	log α_{Pd}	pY'	log K_2
2.759	3.585	0.50	19.2	15.5	3.620	38.49
2.767	3.553	0.50	19.2	15.5	3.143	38.06
2.845	3.244	0.50	19.2	15.5	2.845	38.15
2.991	3.009	0.50	19.2	15.5	2.520	38.20
3.009	2.987	0.50	19.2	15.5	2.401	38.12
3.180	2.921	0.50	19.2	15.5	2.237	38.10
3.260	2.821	0.50	19.2	15.5	2.071	38.21
3.495	2.775	0.50	19.2	15.5	1.737	38.20
2.742	3.745	1.30	16.1	15.5	4.699	37.90
2.824	3.337	1.33	16.0	15.5	4.398	38.05
2.939	3.071	1.40	15.8	15.5	3.824	37.79
3.444	2.793	1.41	15.8	15.5	3.409	38.18
3.824	2.728	1.43	15.7	15.5	2.947	38.10
4.222	2.717	1.50	15.4	15.5	2.682	38.09
4.301	2.712	1.55	15.2	15.5	2.514	37.90

Verification of Equation 2.48 by Variation of EDTA concentration.

Values of the expression, $\log[H_2PdY] - \log[Pd']$, were calculated from Table 3.34 and are given in Table 3.35. These were plotted against the expression, $\log[Y']$, in Figure 3.28.

From Figure 3.28, the slope of the line = 1.00 and the intercept of the line = 2.46. Hence,

$$\log(K_2[H^+]/\alpha_Y.\alpha_{Pd}) = 2.46$$

and therefore $\log K_2 = 38.16$.

FIGURE 3.28

Variation of EDTA concentration.

(from Table 3.35)

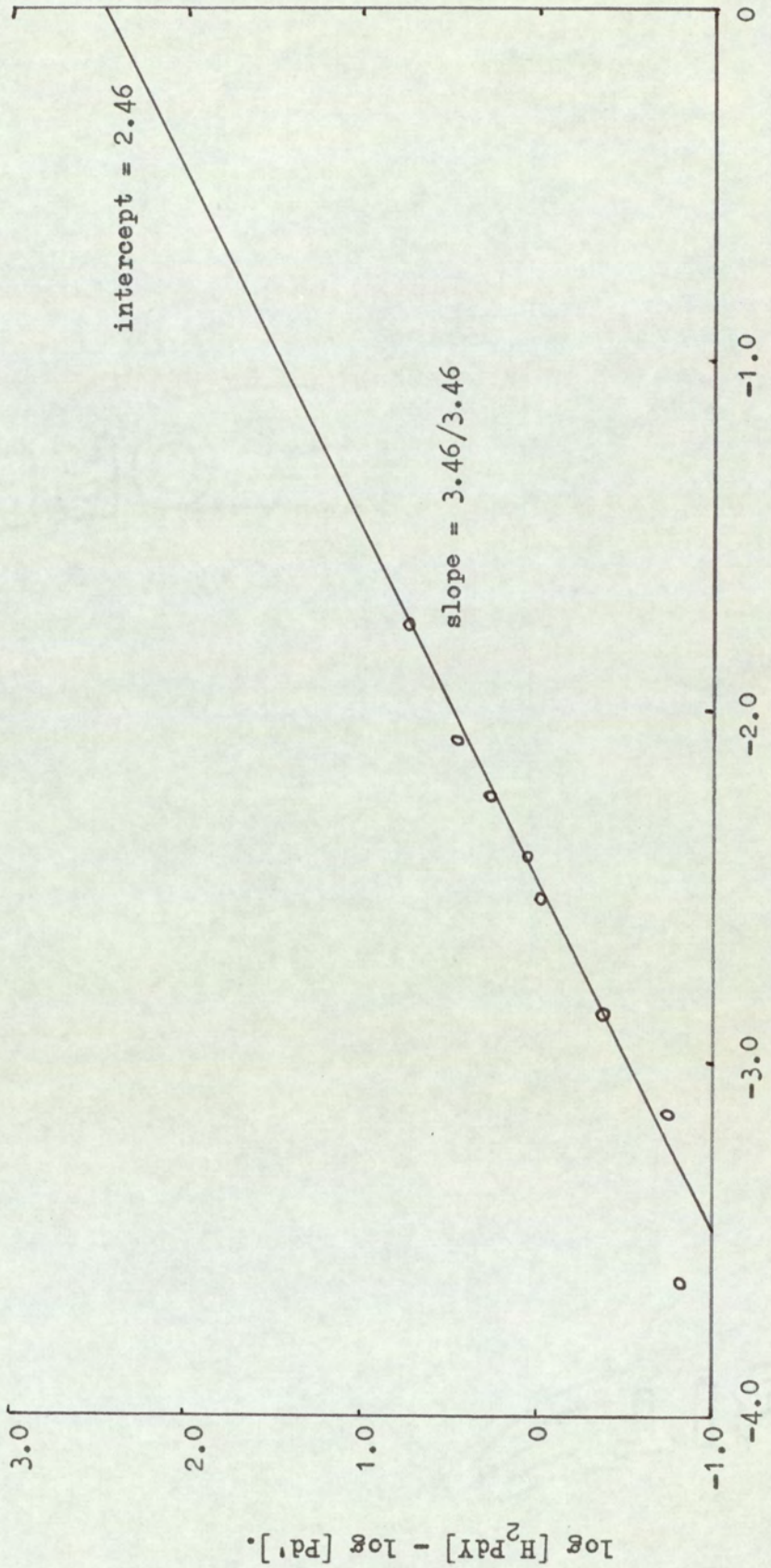


Table 3.35

$\log [H_2PdY] - \log[Pd']$	$\log[Y']$
-0.826	-3.620
-0.786	-3.143
-0.399	-2.845
-0.018	-2.520
0.022	-2.401
0.259	-2.237
0.439	-2.071
0.720	-1.737

3. Determination of K_3.

A 5×10^{-4}M solution of palladium diethyldithiocarbamate in chloroform was prepared by shaking 100 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes with an excess (20 ml) of a 10^{-2}M palladium chloride solution (^{103}Pd) diluted to 100 ml in 5N hydrochloric acid.

In order to determine the time required to reach equilibrium, 5 ml of the above solution was shaken for various lengths of time with 10 ml portions of potassium cyanide solution of different concentrations. The organic layer was separated, filtered and the absorbance at 350 nm measured in a 1mm cell against chloroform. The results are given in Table 3.36. It can be seen that equilibrium is reached in about 3 hours.

Table 3.36

Shaking Time,	Absorbance at 350 nm.		
hours.	0.1M KCN	0.5M KCN	1.0M KCN
1/6	0.365	0.362	0.349
1/2	0.340	0.343	0.325
1	0.341	0.326	0.276
2	0.340	0.284	0.176
3	0.344	0.253	0.130
4	0.346	0.251	0.120
5	0.345	0.254	0.129

A series of aqueous solutions, volume 10 ml, were prepared containing potassium cyanide over the concentration range 0.1 to 1.0M. These solutions were shaken for 4 hours with 5 ml of a 5×10^{-4}M solution of palladium diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 3.37.

Table 3.37

Initial KCN concentration, M	Activity of organic phase, c.p.s.	$[Pd(DDC)_2]\times10^{-4}$M
0.1	24.5	4.80
0.2	23.3	4.57
0.2	23.0	4.50
0.3	21.6	4.23
0.5	18.0	3.53
0.5	18.7	3.60
1.0	10.7	2.10
1.0	11.1	2.18
1.0	10.0	1.96

initial activity of organic phase = 25.5 c.p.s.

From Table 3.37, the following quantities were calculated using the equations:

$$\tfrac{1}{2}[DDC^-] = [Pd(CN)_4^{2-}] = \tfrac{1}{2}(5\times10^{-4} - [Pd(DDC)_2])$$

$$[(CN)^-] = \text{initial } [KCN]$$

Taking logarithmic values for the concentrations of the various species Table 3.38 was compiled. The values of log K_3 were calculated using equation 2.53 (Ch.2.II.4).

Table 3.38

pCN	$pPd(CN)_4$	$pPd(DDC)_2$	pDDC	log K_3
1.000	5.000	3.319	4.699	-7.08
0.699	4.668	3.340	4.367	-7.36
0.699	4.603	3.347	4.302	-7.16
0.523	4.414	3.374	4.103	-7.18
0.301	4.134	3.452	3.833	-7.15
0.301	4.155	3.444	3.854	-7.22
0	3.839	3.678	3.538	-7.24
0	3.851	3.661	3.550	-7.34
0	3.818	3.708	3.517	-7.15

From Table 3.38 the mean value of K_3 is -7.21 (9 determinations) and the standard deviation was found to be 0.08.

Verification of equation 2.53 by variation of potassium cyanide concentration.

Values of the expression, $3\log[Pd(CN)_4^{2-}] - \log[Pd(DDC)_2]$, were calculated from Table 3.38 and are given in Table 3.39. These were plotted against the expression, $\log[(CN)^-]$ in Figure 3.29.

From Figure 3.29, the slope of the line = 3.9 and the intercept of the line = -7.84. Hence,

$$\log(K_3/4) = -7.84$$

and therefore $\log K_3 = -7.24$.

FIGURE 3.29

Variation of cyanide ion concentration.

(from Table 3.39)

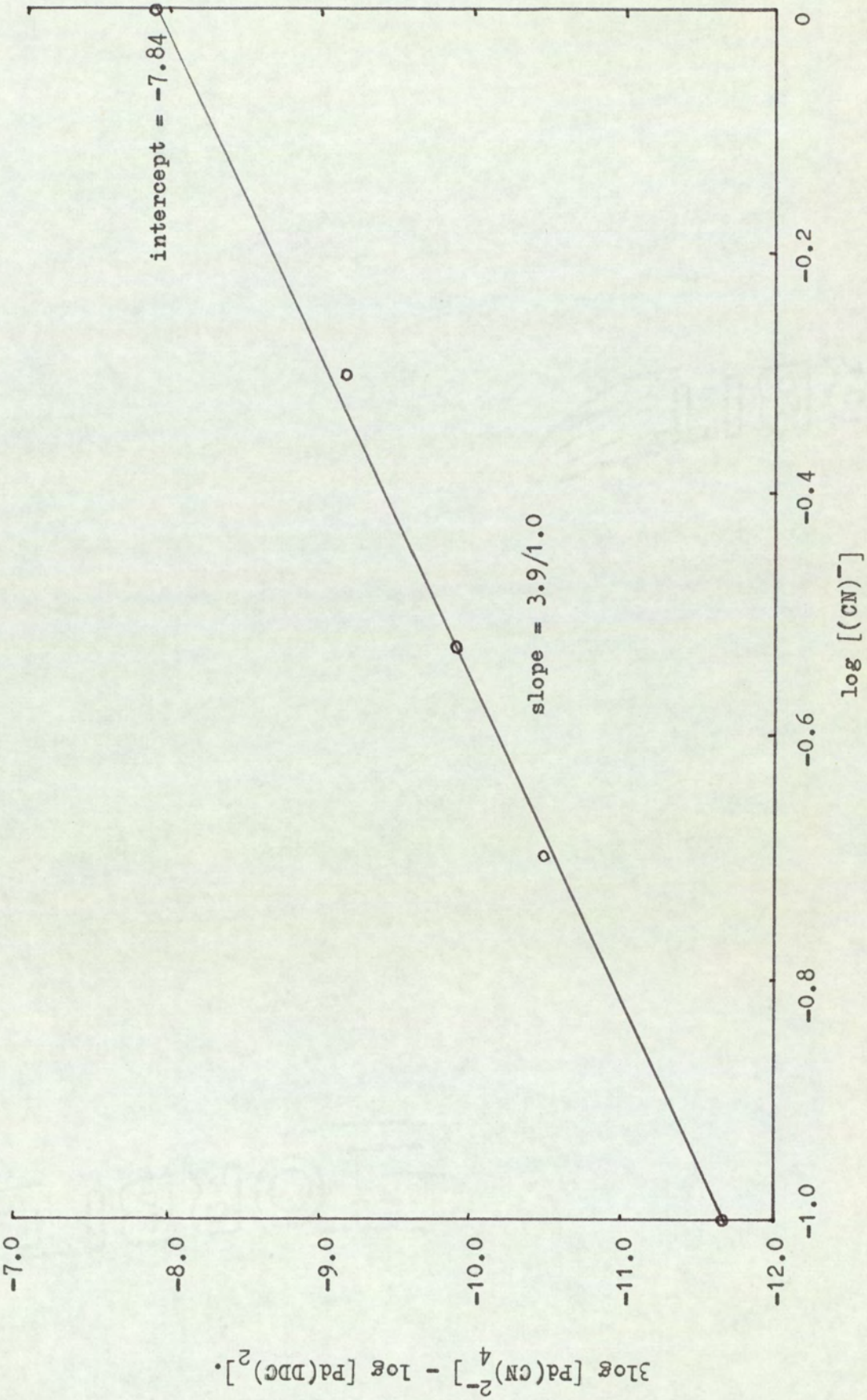


Table 3.39

$3\log[Pd(CN)_4^{2-}] - \log[Pd(DDC)_2]$		$\log[(CN)^-]$
-11.681		-1.000
-10.644		
-10.462	mean = -10.553	-0.699
-9.868		-0.523
-8.950		
-9.021	mean = -8.968	-0.301
-7.839		
-7.939	mean = -7.841	0
-7.746		

4. Determination of K_6.

A 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform was prepared as in section 1a. In order to determine the time required to reach equilibrium, 5 ml of this solution was shaken for various lengths of time with 10 ml portions of potassium cyanide solution, concentration 10^{-2}M, the pH of which had been adjusted with perchloric acid. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered and the pH measured. The results are given in Table 3.40

Table 3.40

Shaking Time, minutes.	Activity of organic phase, c.p.s.		
	pH=0.7	pH=0	pH=-0.3
5	13.0	16.7	19.0
10	12.9	16.6	18.9
15	13.1	16.5	19.1
20	13.1	16.6	18.9

initial activity of organic phase = 25.3c.p.s.

It can be seen from Table 3.40 that equilibrium is reached in under 5 minutes.

A series of 10 ml portions of a 10^{-2}M aqueous potassium cyanide solution were adjusted to various pH values using perchloric acid. These solutions were shaken for 10 minutes with 5 ml of a 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered and the pH measured. The concentrations of the two complexes were calculated as in section 1a and the results are given in Table 3.41.

Table 3.41

pH	Activity of organic phase, c.p.s.	$[Pd.Cl(DDC)]x10^{-4}$	$[Pd(DDC)_2]$ $x10^{-4}$
0.50	13.9	0.50	4.50
0.20	15.2	2.00	4.00
0	16.6	3.30	3.30
-0.10*	17.7	4.00	3.00
-0.30*	19.0	5.00	2.50

initial activity of organic phase = 25.3 c.p.s.

* calculated pH values.

From Table 3.41 the following quantities were calculated using the equations:

$$[Pd(CN)_4^{2-}] = [Pd(DDC)_2]/2$$

$$[Cl^-] = [Pd(DDC)_2]$$

$$[HCN] = \text{initial}[KCN].$$

Taking logarithmic values for the concentrations of the various species, Table 3.42 was compiled. The values of log K_6 were calculated using equation 2.59 (Ch.2.II.5).

Table 3.42

pPd.Cl(DDC)	$pPd(DDC)_2$	$pPd(CN)_4$	pCl	pHCN	pH	$\log K_6$
4.301	3.347	3.648	3.347	2.0	0.50	37.71
3.699	3.398	3.699	3.398	2.0	0.20	37.51
3.481	3.481	3.782	3.481	2.0	0	37.53
3.398	3.523	3.824	3.523	2.0	-0.10	37.60
3.301	3.602	3.902	3.602	2.0	-0.30	37.89

From Table 3.42, the mean value of $\log K_6$ is 37.65 (5 determinations) and the standard deviation was found to be 0.14.

Verification of equation 2.59 by variation of hydrogen ion concentration.

Values of the expression, $2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)]$, were calculated from Table 3.42 and are given in Table 3.43. These were plotted against the expression, $\log[H^+]$, in Figure 3.30.

Table 3.43

$2\log[Pd(DDC)_2] - \log[Pd.Cl(DDC)]$	$\log[H^+]$
2.393	-0.50
3.097	-0.20
3.481	0
3.648	0.10
3.901	0.30

From Figure 3.30, the slope of the line = -2.02 and the intercept of the line = -3.4. Hence,

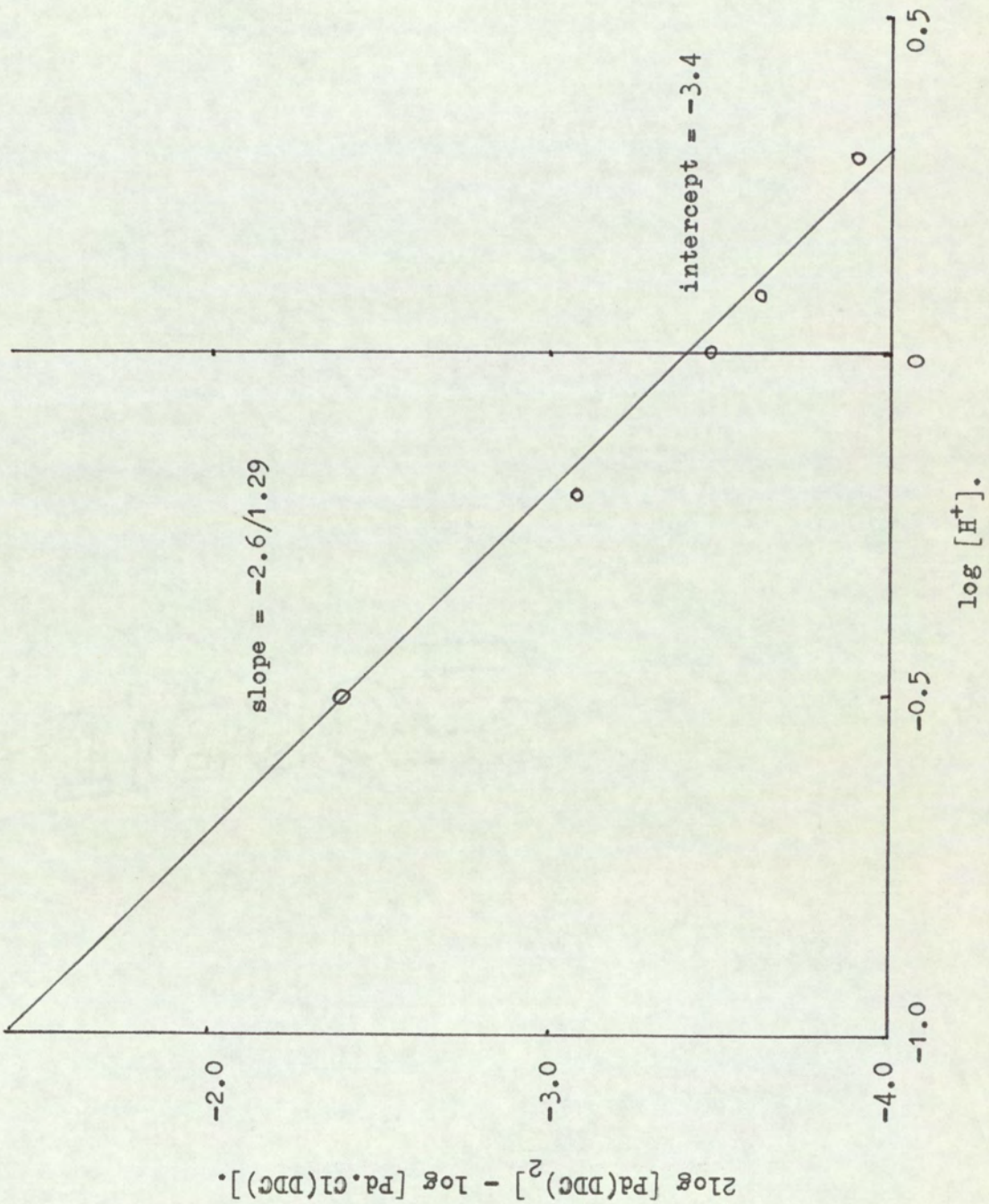
$$\tfrac{1}{2}\log(2K_6[HCN]^4/K_{HCN}^4) = -3.4$$

and therefore $\log K_6 = 37.7$.

FIGURE 3.30

Variation of hydrogen ion concentration.

(from Table 3.43)



IX. Determination of the Partition Coefficients of the Palladium Diethyldithiocarbamate Complexes.

A 10^{-2}M solution of palladium diethyldithiocarbamate in chloroform was prepared by shaking 100 ml of a 10^{-2}M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes with 200 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 5N hydrochloric acid.

A 10^{-3}M solution of palladium diethyldithiocarbamate in carbon tetrachloride was prepared by shaking 100 ml of a 10^{-3}M solution of cupric diethyldithiocarbamate in carbon tetrachloride for 5 minutes with 20 ml of a palladium chloride solution (^{103}Pd), concentration 10^{-2}M, diluted to 100 ml in 5N hydrochloric acid.

A 10^{-3}M solution of palladium chloride diethyldithiocarbamate in chloroform was prepared by shaking 100 ml of a $5x10^{-4}$M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes with 20 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) diluted to 100 ml in 5N sulphuric acid.

A saturated solution of palladium chloride diethyldithiocarbamate in carbon tetrachloride was prepared by shaking 100 ml of a 10^{-3}M solution of cupric diethyldithiocarbamate in carbon tetrachloride for 5 minutes with 40 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) diluted to 100 ml in 5N sulphuric acid.

A 10 ml portion of each of the first three solutions was shaken with 500 ml of distilled water for about 5 minutes. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered through a Whatman No. 42 filter paper and then shaken for a further 5 minutes with 10 ml of the pure solvent. The organic layer was separated and counted as before. Alternatively, the absorbance of the two organic layers was measured at 350 nm against the pure solvent, after dilution where necessary.

The value of the partition coefficient, P, was calculated using

equation 2.83 (Ch.2II.6b) and the results are given in Tables 3.44 to 3.46.

Table 3.44

Palladium Diethyldithiocarbamate in Chloroform.

Absorbance of first organic layer at 350 nm.	Absorbance of second organic layer at 350 nm.	Ratio of concs. of organic layers.	P
160.0	0.015	1,070	53,500
165.0	0.110	1,500	75,000
190.0	0.190	1,000	50,000
168.0	0.129	1,300	65,000
95.0	0.050	1,900	94,000
Activity of first layer, c.p.s.	Activity of second layer, c.p.s.		
1502	1.0	1,500	75,000
		mean P =	68,800

Table 3.45

Palladium Diethyldithiocarbamate in Carbon Tetrachloride.

Activity of first organic layer, c.p.s.	Activity of second organic layer, c.p.s.	Ratio of concs. of organic layers.	P
1895	5.0	379	18,950
1980	7.2	274	13,700
1490	4.3	347	17,350
1435	4.7	305	15,250
		mean P =	16,310

Table 3.46

Palladium Chloride Diethyldithiocarbamate in Chloroform.

Absorbance of first organic layer at 350 nm.	Absorbance of second organic layer at 350 nm.	Ratio of concs. of organic layers	P
2.37	0.289	8.2	360
2.72	0.384	7.1	305
3.85*	0.455	8.45	373
3.12	0.351	8.9	395
2.34+	0.330	7.1	305
Activity of first organic layer, c.p.s.	Activity of second organic layer, c.p.s.		
36.7	4.3	8.5	375
29.8+	3.5	8.5	375

* 500 ml 1N H_2SO_4 as aqueous layer mean P = 355.

\+ 500 ml 0.1N HCl as aqueous layer.

A 10 ml portion of the saturated solution of palladium chloride diethyldithiocarbamate in carbon tetrachloride was shaken for 5 minutes with 10 ml of distilled water. The layers were separated, filtered and the activity of a 3.0 ml aliquot of each determined:

activity of organic phase = 7.0 c.p.s.

activity of aqueous phase = 18.1 c.p.s.

Hence, the partition coefficient, P, = 0.39.

This experiment was repeated, replacing the 10 ml distilled water with 10 ml 5N sulphuric acid:

activity of organic phase = 4.3 c.p.s.

activity of aqueous phase = 380 c.p.s.

Hence, the partition coefficient, P, = 1.16×10^{-2}.

The partition coefficients are summarised in Table 3.47.

Table 3.47

Complex	P in chloroform	P in carbon tetrachloride
$Pd(DDC)_2$	68,800	16,310
Pd.Cl(DDC)	355	0.39

X. The Solubilities of the Palladium Diethyldithiocarbamate Complexes.

1. Palladium Diethyldithiocarbamate in carbon tetrachloride.

A 5 ml portion of a 10^{-2}M palladium chloride solution (^{103}Pd) was added to about 5 ml of a 0.1M solution of sodium diethyldithiocarbamate in water and the resulting precipitate was shaken for about 30 minutes with 5 ml carbon tetrachloride. The organic layer was separated, filtered and 1.0 ml evaporated for counting. The results were as follows:

activity of 1.0 ml of organic phase = 40.77, 34.85 c.p.s.

activity of 1.0 ml 0.88×10^{-2} $PdCl_2$ solution = 401 c.p.s.

Hence, solubility of $Pd(DDC)_2$ = 0.89×10^{-3}M, 0.77×10^{-3}M

mean = 0.83×10^{-3}M.

2. Palladium chloride diethyldithiocarbamate in carbon tetrachloride.

An aliquot of 2.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 1N hydrochloric acid was diluted to 10 ml in 5N sulphuric acid and shaken for 30 minutes with 5 ml of a 10^{-3}M solution of cupric diethyldithiocarbamate in carbon tetrachloride. At this concentration precipitation occurs. The organic layer was separated, filtered and 1.0 ml evaporated for counting. The aqueous layer containing the precipitate was then shaken for a further 30 minutes with 5 ml carbon tetrachloride. The organic layer was separated and counted as before. The results were as follows:

activity of 1.0 ml of first organic phase = 1.1 c.p.s.

activity of 1.0 ml of second organic phase = 1.2 c.p.s.

activity of 1.0 ml 0.88×10^{-2}M $PdCl_2$ solution = 150 c.p.s.

Hence, solubility of Pd.Cl(DDC) = 0.65×10^{-4}M, 0.67×10^{-4}M

mean = 0.66×10^{-4}M.

Knowing the solubilities of the two complexes in carbon tetrachloride and the partition coefficients between this solvent and water, and between chloroform and water, it is possible to calculate the

solubilities in chloroform and water from the equations:

$$S_{H_2O} = \frac{S_{CCl_4}}{P_{CCl_4}},$$

and $$S_{CHCl_3} = S_{H_2O} \times P_{CHCl_3}.$$

The measured and calculated solubilities are summarised in Table 3.48. The solubility of palladium chloride diethyldithiocarbamate in chloroform agreed with previous observations, but that of palladium diethyldithiocarbamate in chloroform is too low as solutions of this complex in chloroform have been prepared up to 10^{-2}M.

Table 3.48

Complex	Solvent		
	Chloroform	Carbon tetrachloride	Water
$Pd(DDC)_2$	3.6×10^{-3}M	8.3×10^{-4}M	5.2×10^{-8}M
Pd.Cl(DDC)	5.3×10^{-2}M	6.7×10^{-5}M	1.8×10^{-4}M

XI. The Ultraviolet and Visible Spectra of the Palladium Diethyldithiocarbamate Complexes.

Solutions of palladium diethyldithiocarbamate and palladium chloride diethyldithiocarbamate in chloroform were prepared as in section IX, using inactive palladium chloride solutions. A solution of palladium hydroxide diethyldithiocarbamate in chloroform was prepared by shaking 20 ml of the 10^{-3}M solution of palladium chloride diethyldithiocarbamate for 1 - 2 minutes with 20 ml of a 1N sodium hydroxide solution.

The spectra of each of the above solutions were measured, after dilution if necessary, in a 10 mm cell against the constituent solvent, chloroform. The results are given in Figure 3.31. The extinction coefficients, ε_{max}, for the complexes are summarised in Table 3.49.

Table 3.49

Complex	ε_{max} in chloroform.
$Pd(DDC)_2$	$\varepsilon_{295} = 7.2 \times 10^4$
Pd.Cl(DDC)	$\varepsilon_{270} = 6.0 \times 10^4$
Pd.OH(DDC)	$\varepsilon_{300} = 2.1 \times 10^4$

Spectra of the palladium diethyldithiocarbamates in chloroform.

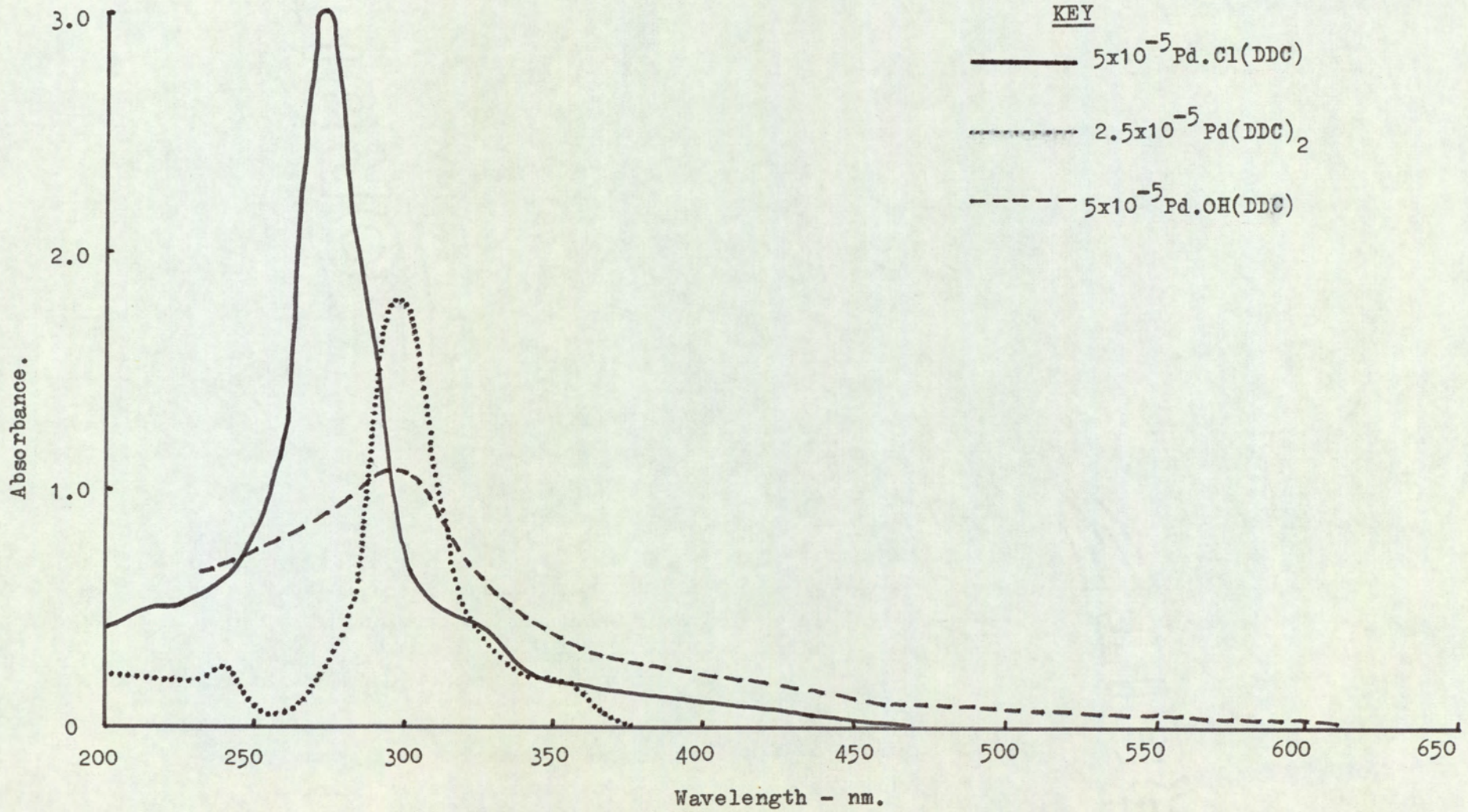


FIGURE 3.31

XII. Analysis of the Palladium Diethyldithiocarbamate Complexes.

Samples of the three complexes in solid form, prepared by evaporation of their chloroform solutions, were submitted to elemental analysis. The samples were analysed for carbon, hydrogen and nitrogen on an F. and M. Scientific 185 Carbon Hydrogen Nitrogen Analyzer. The sulphur and chlorine contents were determined by fusion with sodium peroxide. The results, together with the theoretical compositions, are given in Table 3.50.

Table 3.50

Complex.	C %	H %	N %	S %	Cl %
$Pd(DDC)_2$:					
found:	28.80	5.04	6.75	31.59	0
calculated for $Pd(DDC)_2$:	29.7	5.00	6.95	31.8	0
Pd.Cl(DDC):					
found:	20.13	3.37	4.10	19.51	12.67
calc. for Pd.Cl(DDC):	20.6	3.47	4.83	22.10	12.2
calc. for $Pd.Cl(DDC)H_2O$:	19.5	3.90	4.64	20.80	11.5
Pd.OH(DDC):					
found:	21.25	3.44	4.82	22.03	0
calc. for Pd.OH(DDC):	22.1	4.06	5.18	23.6	0
calc. for $Pd.OH(DDC).H_2O$:	20.7	4.48	4.84	22.1	0

CHAPTER 4

Substoichiometric Determination of Traces of Palladium by Neutron Activation Analysis.

I. Theory and Discussion.

Neutron activation analysis has been used to determine traces of palladium in rocks,[46,81] ores,[82] meteorites[83-85] and various metals.[86-89] Most of the previously reported methods involved precipitation or solvent extraction of palladium dimethylglyoximate and because of the incompleteness of this process, these methods involve many successive separation steps which make the analysis complicated and time consuming. This chemical separation has been greatly simplified by use of the substoichiometric principle.

The products of the thermal neutron irradiation of palladium are given in Table 1.1 (Ch.1.III.1). The irradiation facilities normally available have thermal neutron fluxes from 10^{12} to 6×10^{12} neutrons.cm^{-2}.sec^{-1} and therefore by using equation 1.1 (Ch.1.I.1) it is possible to estimate the sensitivity of a neutron activation method for palladium. The most suitable palladium isotope for use in neutron activation analysis is palladium-109, which can be detected either by the beta radiation or the gamma radiation and silver X-radiation associated with its decay (Ch.1.III.1).

If $F = 10^{12}$ neutrons.cm^{-2}.sec^{-1}, and the sample is irradiated to saturation, then from equation 1.1:

$$A = \frac{6.023\times10^{23}}{106.4} \times 10^{12} \times 12.2\times10^{-24} \times \frac{26.7}{100}$$

Hence, A 2×10^{10} d.p.s., for 1 g of palladium, as for palladium-109, $\sigma = 12.2\times10^{-24}$ cm^2 and $\theta = 26.7\%$ (Table 1.1)

If 50% of the palladium is separated and it is possible to count activities down to 1 d.p.s., then theoretically, amounts of palladium

down to 10^{-10}g could be determined. However, in practice, as the energy of the radiation is low and hence it will be significantly absorbed by the containers etc. (Ch.1.III.3), the efficiency of detection will be low, i.e. probably between 1 and 10%. Therefore it would be expected that amounts of palladium down to about 10^{-8}g could be determined, and this was found to be so.

For a substoichiometric determination it is necessary to have a chelating agent which forms a strong, readily extractable complex. From Chapters 2 and 3 it can be seen that the palladium diethyldithiocarbamate complexes have very high extraction constants and therefore are likely to be suitable for substoichiometry. As palladium diethyldithiocarbamate is known to be more readily extractable than most other metal diethyldithiocarbamates (Ch.1.II) the separation should be very selective. It is possible (Ch.1.I.1) to add milligram quantities of inactive palladium to the sample after irradiation and therefore a separation is required which is usable at concentrations of the order of 10^{-3}M. As shown in Chapter 3, section VII-1, at this concentration, by choosing the right conditions it is possible to get either quick formation of palladium chloride diethyldithiocarbamate from a medium of 5N sulphuric acid by extracting with cupric diethyldithiocarbamate in chloroform, or quick formation of palladium diethyldithiocarbamate and no formation of palladium chloride diethyldithiocarbamate from a medium of 5N hydrochloric acid. It appears that either complex could be used for a substoichiometric separation and this is confirmed by the good substoichiometric reproducibility curves obtained in section II, Figure 4.1. However, the dissolution of the samples in real analyses must be considered and it would almost certainly be more convenient to have high chloride ion concentrations permissible, and so it was decided to use palladium diethyldithiocarbamate in the analysis.

From Chapter 3, section VII-1, it can be seen that, using 25% stoichiometry, extraction of palladium from 5N hydrochloric acid using

5 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform as extractant, reached equilibrium in under one minute and was unaffected by further shaking for up to 2 hours. Hence, these were the conditions used for the separation, with an extraction time of about 5 minutes. Under these conditions good substoichiometric reproducibility (Figure 4.1) and precision (Table 4.2) were obtained.

In order to determine the selectivity of the separation, it was necessary to consider two types of interference; (a) indirect interference, i.e., depression of the extracted palladium activity by the presence of other species in the aqueous phase, and (b) direct interference, i.e., extraction of small amounts of highly radioactive materials present in the irradiated sample. In section II-1c, a large number of foreign species were investigated for interference of type (a). Of the substances which did interfere: antimony-V, cerium-IV, gold-III, iron-III, molybdenum-VI, selenium-IV, selenium-VI, tellurium-VI, uranium-VI, vanadium-V, vanadium-VI, hydrogen peroxide and nitrate ions, many are oxidising agents and hence much of this interference was prevented by the addition of sodium sulphite solution. The only substances which still interfered were gold-III, selenium-IV and selenium-VI. Gold-III appeared to form a more readily extractable complex than palladium, while selenium interfered by being reduced to metallic selenium by the sodium sulphite and then reducing the palladium-II to the metallic state. Sodium sulphite will reduce palladium-II from thermodynamic considerations, but the reduction is normally so slow as to be unimportant.

In section II-1d, a few species were investigated for interference of type (b). All the platinum metals (except rhodium which only produces a very short-lived isotope on thermal neutron irradiation) and the metals known to form strong diethyldithiocarbamate complexes were looked at. The only substances which interfered were gold-III, as expected, and platinum-IV. Platinum also appeared to form a more

readily extractable complex than palladium, but due to its usual "inertness" (Ch.1.II) the extraction is so slow, that even with an excess of platinum not enough platinum is extracted to significantly depress the extracted palladium activity.

As gold becomes highly radioactive on thermal neutron irradiation, it was necessary to separate the gold before determination of the palladium. Separation of platinum was not necessary in the samples which only contained trace quantities of this element, but in the platinum sample, not only did interference occur from the platinum itself, but also from its active decay product, gold-199, which is the daughter of the 30 minute half-lived platinum-199. It was therefore necessary to carry out a preliminary separation with dimethylglyoxime after the addition of gold hold-back carrier. Even after further separation of gold, some gold-199 still appeared in the separated palladium samples, but by counting the 22 kev radiation of palladium-109 only, it was thought that the gold would have little effect on the results.

The samples used for test analyses were two standard rocks, a diabase, W1, and a peridotite, PCC1, a biological material, dried leaves of kale, and a sample of platinum.

The diabase, W1, is known to contain trace amounts of some 40 elements, larger amounts of 6 other elements with the main constituents being silica and aluminium oxide[90]. The peridotite, PCC1, is known to contain trace amounts of 10 elements, larger amounts of 6 other elements, with the main constituents being silica and magnesium oxide[91]. Both these samples were provided by the U.S. Geological Survey, Washington D.C., U.S.A.

The kale is a complicated organic matrix[92] and was provided by H.J.M.Bowen, The University, Reading, England.

The platinum sample contains trace amounts of selenium, tellurium, osmium, iridium, iron, gold, ruthenium, cobalt, arsenic and antimony and is sample Pt 3 of reference 93, provided by D.F.C.Morris, Brunel University, London.

From section III, it can be seen that the reproducibility of the test analyses results is good. Variation of sample size indicates that no self-shielding effects occurred. The radiochemical purity of the palladium extracts was confirmed by decay measurements and gamma-ray spectra (Figures 4.2 and 4.3) except in the case of the platinum samples where some gold-199 is present.

The results obtained are slightly higher than those obtained by other authors in the case of the rocks and slightly lower in the case of the platinum.

These results indicate, as expected, that the substoichiometric separation of palladium by cupric diethyldithiocarbamate in chloroform is very selective. Similar methods have been developed for arsenic[10] and gold[17] using metallic salts of diethyldithiocarbamic acid as extractants. As platinum is probably one of the most difficult matrices to analyse for palladium, it can be assumed that this separation might be applied to almost any type of matrix.

II. Experimental.

For solutions and apparatus see Chapter 3, sections I - IV.

Irradiation.

The test samples were weighed (see Table 4.5), sealed in quartz ampoules and irradiated in a reactor simultaneously with a standard of palladium chloride containing 10.0 μg of palladium. Times of irradiation were 12 hours or 7 days at thermal neutron fluxes of 10^{12} or 6×10^{12} neutrons.cm^{-2}.sec^{-1}. For irradiations the Harwell DIDO and the Universities of Manchester and Liverpool Research Reactors were used.

Radioactive Tracers.

The radioactive tracers used in the direct interference studies were obtained as follows:

Copper-64, gold-198, ruthenium-97, osmium-193, iridium-194 and platinum-197 were obtained by irradiating samples of the metals for 12 hours in the Universities of Manchester and Liverpool Research Reactor.

Mercury-203, cerium-144, cobalt-60, thallium-204 and iodine-131 were obtained from the Radiochemical Centre, Amersham.

Silver-111 was obtained by separation from irradiated palladium (Ch.3.II.4).

1. Development of Method.

(a) Reproducibility.

To ascertain that exactly equal amounts of palladium could be extracted from solutions of varying palladium concentration, a series of solutions of palladium chloride (^{103}Pd) in 5N hydrochloric acid were shaken with 5 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes. The organic layer was separated, filtered and 3.0 ml evaporated for counting.

The above experiment was repeated, replacing the 5N hydrochloric acid by 5N sulphuric acid (keeping the chloride ion concentration at 0.1N). The results are given in Table 4.1 and Figure 4.1.

Table 4.1

Palladium added, mg.	5N hydrochloric acid		5N sulphuric acid	
	Activity c.p.s.	Palladium ext., mg.	Activity c.p.s.	Palladium ext., mg.
0.1	166	0.092	201	0.110
0.2	364	0.202	357	0.198
0.3	459	0.255	550	0.305
0.5	470	0.261	895	0.497
0.75	462	0.257	910	0.504
1.0	469	0.260	912	0.506
2.0	474	0.262	909	0.504
5.0	474	0.262	906	0.503

activity of 0.1 mg of palladium = 180c.p.s.

(b) Precision.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) was diluted to 10 ml in 5N hydrochloric acid and shaken for 5 minutes with 5 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The standard deviation, s, of seven samples was calculated using the expression:

$$s^2 = \frac{\Sigma \Delta^2}{n-1}$$

where Δ = deviation from mean,

and n = number of samples.

The results are given in Table 4.2

Substoichiometric Reproducibility Curve for the Extraction of Palladium.

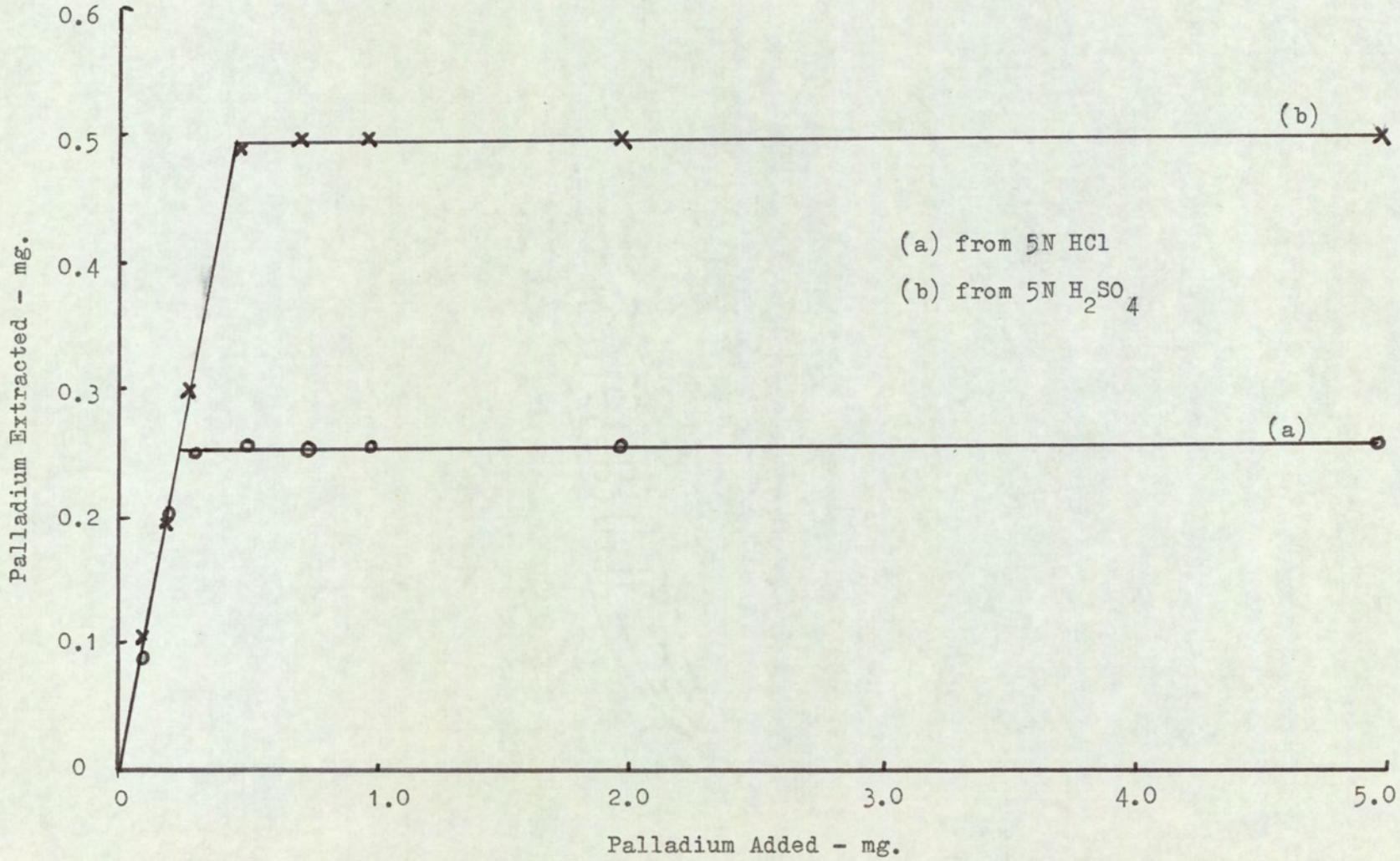


FIGURE 4.1
(from Table 4.1)

Table 4.2

Activity of organic phase, c.p.s.	mean activity, c.p.s.	Standard deviation
267.3		
262.7		
265.4		
270.0	265.4	4.5 (1.7%)
268.3		
257.1		
269.2		

(c) Indirect Interference.

An aliquot of 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) was mixed with a solution of the foreign species under investigation and diluted to 10 - 20 ml in 5N hydrochloric acid. This solution was shaken for 5 minutes with 5 ml of a $5x10^{-4}$M solution of cupric diethyldithiocarbamate in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The activity of this organic phase was compared with that of a standard in which no foreign substance was present. A substance was considered to interfere if the activity of the sample was less than 95% of that of the standard. Where possible, the aqueous phase contained a thousandfold excess of the foreign ion over palladium. However, when the species under investigation was insufficiently soluble, a saturated solution was used. For those substances which were found to interfere, the above experiment was repeated, adding 5 ml of a freshly prepared solution of sodium sulphite (saturated). The results are given in Table 4.3.

Table 4.3

Foreign ion added.	Activity c.p.s.	Activity with Na_2SO_3 c.p.s.	Foreign ion added.	Activity c.p.s.	Activity with Na_2SO_3 c.p.s.
none	175	-	osmium-IV(50mg)	-	166
aluminium	170	-	platinum-IV(10mg)	-	172
antimony-III	171	-	potassium	175	-
antimony-V	2.6	175	rhenium-VII	-	177
arsenic-III	171	-	rhodium-III(40mg)	-	182
arsenic-V	174	-	ruthenium-IV(10mg)	-	172
barium*	173	-	selenium-IV	117	45.4
beryllium	175	-	selenium-IV(1mg)	-	164
bismuth	171	-	selenium-VI	9.8	93.7
boron	172	-	selenium-VI(10mg)	-	167
bromide	174	-	silicon*	166	-
cadmium	171	-	silver-I*	174	-
cerium-III	177	-	sodium	175	-
cerium-IV	0.9	478	strontium	183	-
calcium	178	-	sulphate	178	-
perchlorate	173	-	sulphite	171	-
chromium-III	172	-	tellurium-IV	177	-
cobalt-II	174	-	tellurium-VI	132	180
copper-II	174	-	thallium-I*	177	-
gallium	172	-	thorium-IV	174	-
germanium*	178	-	tin-II	181	-
gold-III(100mg)	1.2	9.8	tin-IV	169	-
indium-III	174	-	titanium-IV	169	-
iodide	177	-	tungsten-VI*	171	-
iridium-IV	-	180	uranium-VI	148	171
iron-II	170	-	vanadium-V	96.2	176
iron-III	44.6	170	vanadium-VI	2.6	174
magnesium	177	-	zinc	182	-
manganese-II	170	-	zirconium-IV	181	-
mercury-I*	181	-	lead-II*	177	-
mercury-II	173	-	phosphate	173	-
molybdenum-VI	117	174	acetate	171	-
niobium-V*	173	-	ammonia	175	-
nickel	173	-	hydrogen peroxide	2.8	173
nitrate	7.0	177			

* saturated solution.

10^{-2} mole of all species present unless otherwise stated.

(d) Direct Interference.

The experiment was carried out as in (c) except that an inactive palladium chloride solution was used with labelled solutions of the species under investigation. The results are given in Table 4.4, and it can be seen that a small amount of activity is always extracted due to incomplete separation of the phases by filtration. This can be eliminated by washing the organic layer.

Table 4.4

Foreign ion added.	Labelling radioisotope	Total activity added, c.p.s.	Activity of organic phase, c.p.s.	Radioactive ion extracted, c.p.s.
mercury-II, 2.0g	^{203}Hg	7,340	1.3	0.02
cerium-IV, 0.14g	^{144}Ce	3,330	0.36	0.01
silver-I, satd.	^{111}Ag	1,050	0.30	0.03
cobalt-II, 0.6g	^{60}Co	13,070	0.38	0.003
thallium-I, satd.	^{204}Tl	10,460	0.003	$3x10^{-5}$
iodide, 1.3g	^{131}I	18,600	10.4	0.05
copper-II, 0.6g	^{64}Cu	29,000	1.0	0.003
gold-III, 0.02g	^{198}Au	23,390	166.3	0.7
ruthenium-IV, 0.01g	^{97}Ru	7,780	1.4	0.02
osmium-IV, 0.05g	^{193}Os	5,233	1.1	0.02
iridium-IV, 0.01g	^{194}Ir	72,777	1.0	0.0014
platinum-IV, 0.1g	^{197}Pt	800,000	1,600	0.2

2. Analysis of Test Samples.

(a) Elimination of Interferences.

Gold, when present in trace quantities was removed by extraction of gold-III chloride from the sample solution in 5N hydrochloric acid with diethyl ether.

When 10 mg of gold (labelled with gold-198) and 1.0 ml of a 10^{-2}M, inactive palladium chloride solution were diluted to 10 ml in 5N hydrochloric acid and extracted with three 50 ml portions of diethyl ether before carrying out a substoichiometric separation of the palladium, a decontamination factor of about 2,000 was obtained. This decreased somewhat on lowering the gold concentration, as for a solution containing only 0.01 mg of gold, the decontamination factor was only 200. In the test analyses, where the gold was only present in trace quantities, however, three ether extractions with no carrier added were found to be quite sufficient. For the platinum sample, where a large activity of carrier free gold-199 is present, the concentration of gold was far too low to give a large enough decontamination factor and so addition of gold carrier was necessary.

In the test analysis of the platinum sample it was found that a preliminary separation of palladium was necessary, which was done by precipitation of the dimethylglyoximate. This reduced the platinum concentration sufficiently to prevent its interference. As selenium does not interfere in quantities of less than 1 mg, no separation was necessary for the samples analysed. For high selenium content samples, a preliminary separation would probably be necessary.

(b) Dissolution of Samples.

The procedures detailed below were tested by adding 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) to the non-irradiated matrix. After dissolution the palladium was extracted with 5 ml of a 5x01^{-4}M solution of cupric diethyldithiocarbamate in chloroform. No significant losses of palladium were observed.

Rocks.

To the irradiated test matrix in a 50 ml teflon beaker, 1.0 ml of a 10^{-2}M inactive palladium chloride solution was added and the matrix dissolved in a mixture of hydrofluoric (10 ml), nitric (10 ml) and hydrochloric (2 ml) acids. After the silicon had been fumed off, four evaporations to dryness were carried out with 5 ml portions of hydrochloric acid, to remove oxides of nitrogen. The final residue was dissolved in 5 ml concentrated hydrochloric acid.

Biological Material (kale).

To the irradiated test matrix in a 150 ml beaker, 1.0 ml of a 10^{-2}M inactive palladium chloride solution was added. After dissolution in 5 ml nitric acid, the solution was evaporated to dryness. This was repeated several times until all the carboniferous material had been oxidised. Four evaporations to dryness were carried out with 5 ml portions of hydrochloric acid, to remove oxides of nitrogen, before dissolving the final residue in 5 ml concentrated hydrochloric acid.

Platinum.

To the irradiated test matrix in a 150 ml beaker, 1.0 ml of a 10^{-2}M inactive palladium chloride solution and 1 ml of gold carrier solution (1 mg/ml) were added. The matrix was dissolved in 10 ml aqua regia and the resulting solution diluted to about 100 ml with distilled water before adding 2 ml of a 1% solution of dimethylglyoxime in ethanol. The solution was warmed and stirred. The palladium dimethylglyoximate formed was filtered off and washed, first with dilute hydrochloric acid and then with distilled water. This precipitate was then dissolved through the paper by the addition of hot, concentrated nitric acid. A further 1 ml of gold carrier solution was added and the resulting solution evaporated to dryness and the residue dissolved in 5 ml hydrochloric acid. Four evaporations to dryness were carried out to remove oxides of nitrogen, and the final residue dissolved in 5 ml concentrated hydrochloric acid.

(c) Extraction Procedures.

The dissolved samples were diluted with 5 ml of distilled water and extracted with three 50 ml portions of diethyl ether for 1 - 2 minutes. The ether layers were discarded and the aqueous phase shaken with 20 ml chloroform for 30 seconds (to remove any chloroform soluble substances). The separated aqueous phase was warmed to remove final traces of the organic solvents. After adding 5 ml freshly prepared, saturated sodium sulphite solution and 5 ml concentrated hydrochloric acid, extraction was carried out by shaking with 5 ml of a 5×10^{-4}M solution of cupric diethyldithiocarbamate in chloroform for 5 minutes. The organic layer was separated, washed with two 10 ml portions of 5N hydrochloric acid (to remove traces of the highly radioactive aqueous phase), filtered and 3.0 ml evaporated for counting. Two extractions were carried out on each sample as a check.

The irradiated palladium standard (x_s) was dissolved in 5 ml concentrated hydrochloric acid after the addition of 1.0 ml of a 10^{-2}M inactive palladium chloride solution. A 5 ml portion of freshly prepared, saturated sodium sulphite solution was added to this solution and extraction with cupric diethyldithiocarbamate carried out as for the test samples, omitting the washing of the organic layer. The activities of the equal, 3.0 ml aliquots of the organic phases from the test (a) and standard (a_s) samples were determined by counting the 22 keV radiation of palladium-109 as in Chapter 1, section III-2a, and the amount of palladium in the sample calculated from equation 1.7:

$$x = x_s . \frac{a}{a_s} .$$

The radiochemical purity of the extracts was checked by counting the samples after various intervals of time and determining the half-lives. Also the gamma-ray spectra were recorded.

III. Results.

The results of the test analyses are given in Table 4.5. Results of other authors have been included for comparison. Decay curves and gamma-ray spectra for one of each type of sample are given in Figures 4.2 and 4.3.

Table 4.5

Sample	Sample weight g.	Pd std. activity c.p.s.	Pd sample activity c.p.s.	Pd found µg.	Pd found p.p.m.	mean value p.p.m.	Results of other authors p.p.m.
W1	1.0059	870	3.4	3.9×10^{-2}	3.9×10^{-2}		
	1.0006	1320	4.8	3.6×10^{-2}	3.6×10^{-2}	3.9×10^{-2}	1.9×10^{-2}*
	0.5404	450	1.0	2.2×10^{-2}	4.1×10^{-2}		1.4×10^{-2}**
	0.6672	1950	5.4	2.8×10^{-2}	4.2×10^{-2}		
PCC1	1.0052	870	2.8	3.2×10^{-2}	3.2×10^{-2}		
	1.0033	1320	3.2	2.4×10^{-2}	2.4×10^{-2}		
	0.5602	1130	1.7	1.5×10^{-2}	2.9×10^{-2}	2.9×10^{-2}	0.7×10^{-2}**
	0.5687	1130	1.9	1.7×10^{-2}	3.0×10^{-2}		
	0.6948	1950	4.0	2.1×10^{-2}	2.9×10^{-2}		
Kale	1.0031	450	1.3	2.8×10^{-2}	2.8×10^{-2}		
	0.4919	1950	2.8	1.4×10^{-2}	2.9×10^{-2}	2.6×10^{-2}	-
	0.4894	1950	2.1	1.1×10^{-2}	2.2×10^{-2}		
	0.4730	1950	2.5	1.3×10^{-2}	2.6×10^{-2}		
Pt	0.2615	240	8.4	0.350	1.34		
	0.2510	240	7.1	0.296	1.18	1.29	2.13+
	0.2541	940	35.0	0.373	1.46		
	0.2514	940	28.2	0.300	1.20		

* reference 94; ** reference 43 ; + reference 86.

All standards were 10.0 µg.

FIGURE 4.2

Decay Curves of Typical Cupric Diethyldithiocarbamate Extracts.

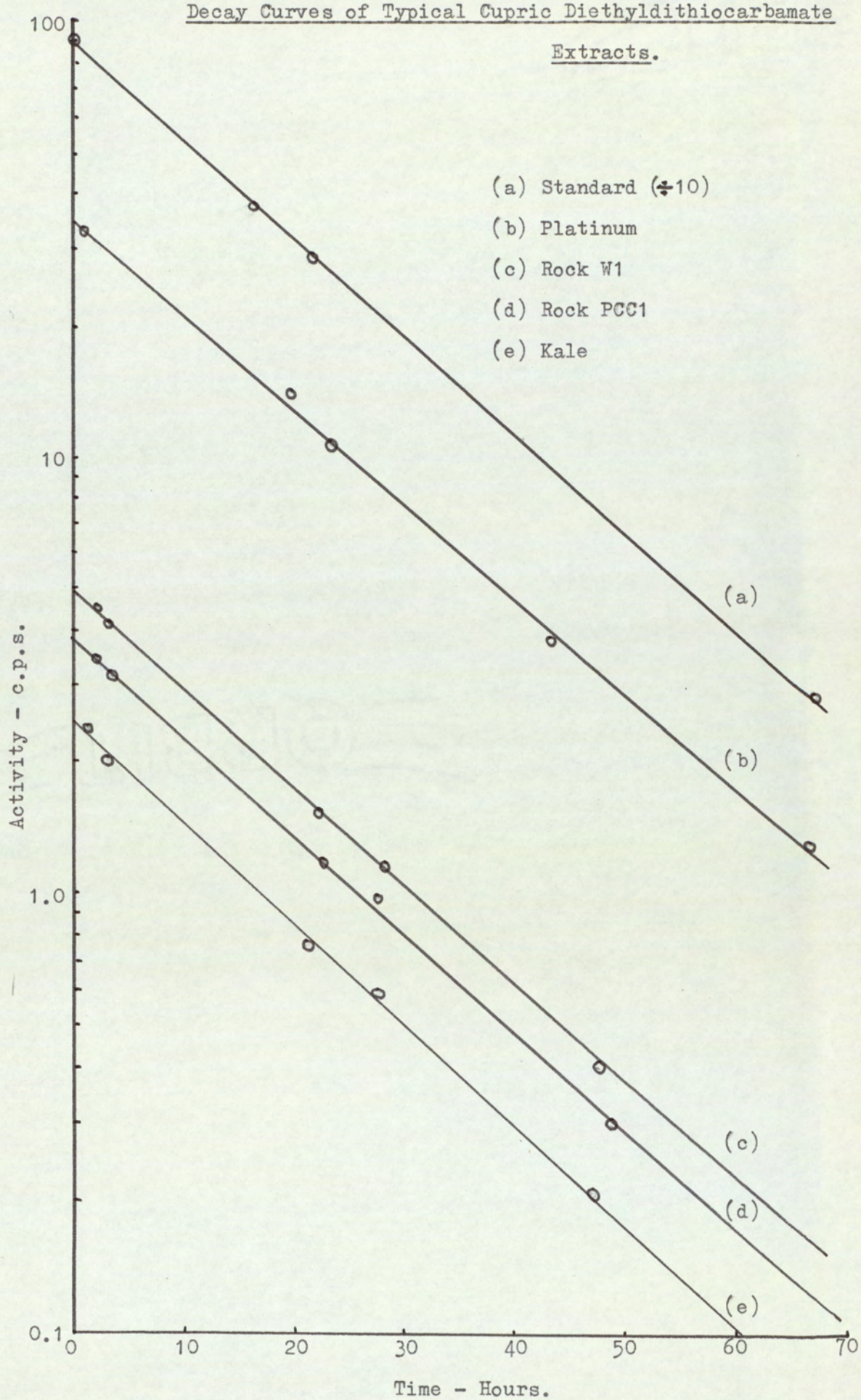
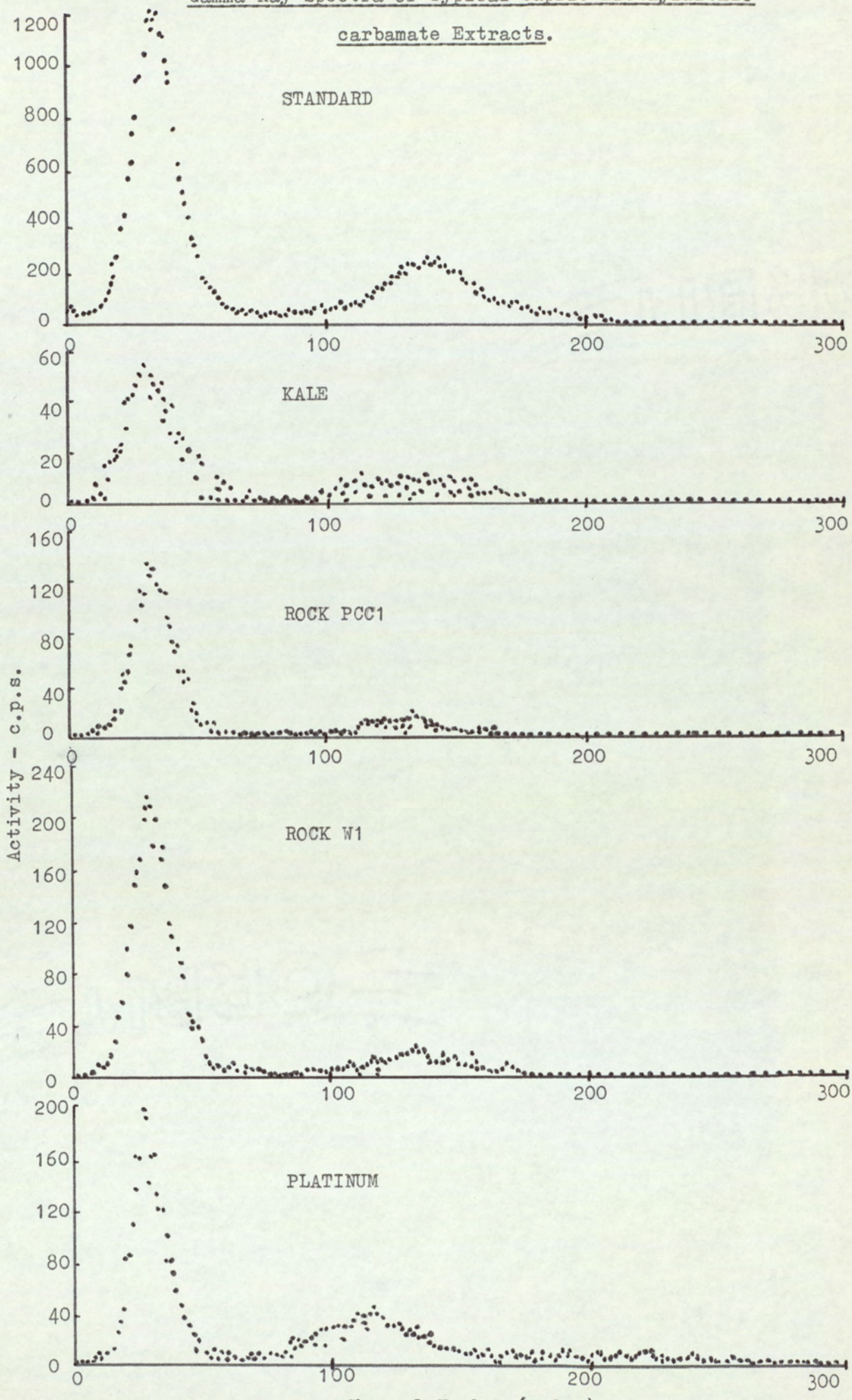


FIGURE 4.3

Gamma-Ray Spectra of Typical Cupric Diethyldithio-carbamate Extracts.



CHAPTER 5

Substoichiometric Determination of Traces of Palladium by Radioactive Isotope Dilution Analysis.

I. Theory and Discussion.

Following the success of the neutron activation method for the determination of traces of palladium, it was thought that a similar separation might be used for isotope dilution analysis. As mentioned in Chapter 1, section I, substoichiometry enables the technique of isotope dilution to be as sensitive or more so than neutron activation analysis, and it eliminates the irradiation step. Where amounts of palladium greater than 10^{-6} g are to be determined, isotope dilution analysis has little to offer over the spectrophotometric and other methods (Ch.1.II), therefore attention has been concentrated on amounts below this level. Conventional isotope dilution analysis has been applied to the determination of a large number of elements[95], but no reference can be found describing its application to the determination of palladium.

In Chapter 3, section VII-2, the effect of concentration on the extraction of the palladium diethyldithiocarbamate complexes indicated that this system was not suitable for use at concentrations lower than 10^{-5}M, even under ideal conditions, therefore the system shows little promise for use in an analytical method. Hence, it was decided to examine the extraction of palladium by dithizone. Palladium dithizonate is known to have a high extraction constant (Ch.1.II) and therefore the extraction would be expected to be selective and to go to completion under substoichiometric conditions. This system was not considered at the milligram level for use in activation analysis because of the formation of an insoluble secondary complex which was known to occur under substoichiometric conditions[49], but it was thought that either this complex would not be formed at very low concentrations, or it might be sufficiently soluble to be used itself

for the separation. Carbon tetrachloride was chosen as the solvent, as, due to the lower solubility of dithizone in this solvent than in chloroform, the extraction might be expected to be faster (Ch.2.I). In order to find the optimum conditions for extraction at low concentrations a kinetic study was carried out in section II-2a. As hydrogen ion and chloride ion concentration were found to be important in the extraction of the palladium diethyldithiocarbamate complexes (Ch.2.I), the effect of these was studied in some detail. As it can be seen in Figure 5.2, the hydrogen ion concentration appeared to have little effect over the range 0.01N to 10N. In Figure 5.3, it can be seen that increasing the chloride ion concentration above 0.01N both slows the reaction down and lowers the final level of extraction. Below 0.01N chloride, extraction equilibrium appears to be reached in about 15 minutes at a reagent concentration of 10^{-7}M.

In the above experiments, it can be seen that the final level of extraction is about 25%, which corresponds to a palladium to dithizone ratio of 1:2, i.e. the primary dithizonate, $Pd(HDz)_2$, where H_2Dz represents dithizone. This condition is known as 25% stoichiometry. Alteration of the stoichiometry, i.e. the initial relative concentrations of palladium and dithizone, might be expected to affect the reaction rate. Although higher stoichiometry is optimum, as it gives better counting accuracy, if the reaction is slowed down significantly this advantage is lost. In section II-2a(ii), Figure 5.4, the effect of altering the stoichiometry to 15% and 50% can be seen. The higher stoichiometry, 50%, results in a much slower reaction than at 25%, while 15% stoichiometry does not increase the rate significantly. Hence , at a reagent concentration of 10^{-7}M, the optimum conditions for extraction were found to be pH 2 to 10N acid, 0.01N or less chloride ion concentration and 25% stoichiometry.

The reagent concentration used in analysis, however, will depend on the amount of palladium in the sample. The most accurate results

will be obtained if the palladium in the sample is approximately equal to the radioactive palladium added. The range over which the separation can be applied therefore determines the range of the analysis method. In order to determine this range, the rate of extraction was examined over a range of reagent concentrations, such that the amount of palladium in the aqueous phase was 10^{-6} to 10^{-9}g. Section II-2a(iii), Figure 5.5, gives the results of this investigation, and it can be seen that both the rate and the level of extraction are not much different over the range 10^{-6} to 10^{-8} g of palladium, i.e. 10^{-6} to 10^{-8}M dithizone, but at 10^{-9}M the level of extraction is low and erratic. This is probably due to decomposition of the reagent. For subsequent experiments a shaking time of 30 minutes was used for reagent concentrations of 10^{-6} and 10^{-7}M, and 45 minutes for lower concentrations.

In order to test further, reproducibility experiments were carried out at a number of concentrations in section II-2b. Figure 5.6 shows that substoichiometric reproducibility is good over the reagent concentration range 10^{-6} to 5×10^{-9}M, except near the equivalence points. This discrepancy is due to the reaction being incomplete in the time under such conditions.

The precision, Table 5.8, is satisfactory down to a reagent concentration of 10^{-8}M.

The selectivity, Table 5.9, was shown to be very high. Of all the species investigated, only mercury-I, mercury-II, gold-III and cerium-IV interfered when present in a thousandfold excess over palladium, and even these did not interfere at a tenfold excess. The mercury and gold may well have competed for the dithizone thermodynamically, or more likely, kinetically and the cerium probably oxidised the reagent. These interferences are not likely to be important as mercury would be lost in the dissolution procedures and gold will only be present in similar quantities to palladium in most samples. The oxidation of the cerium, however, indicates that other oxidising

agents might also interfere.

The test samples analysed were the same samples which had been analysed by neutron activation: standard rocks W1 and PCC1, standard kale and platinum. A number of dissolution methods were tried for the rocks and the kale, but direct separation with dithizone gave erratic results. The platinum posed an obvious problem, as platinum does not readily go into solution except in fairly high chloride ion concentrations. Therefore, it was necessary to carry out a preliminary separation with dimethylglyoxime. As this separation was quick and simple and eliminated some of the care necessary in the dissolution procedure, it was decided to use this separation for all the samples.

The results, section III, Table 5.10, show that the method is extremely sensitive and reproducible. Amounts of palladium down to $3x10^{-9}$ g were determined. In the activation analysis the smallest amount of palladium determined was 10^{-8} g: a limit of the nuclear characteristics of palladium rather than of the separation. This demonstrates very well the high sensitivity which can be achieved by the application of substoichiometry to isotope dilution analysis. The results are in good agreement with those obtained by activation analysis. As stated in Chapter 4, section I, the samples contain a large number of elements and platinum is one of the most difficult matrices to analyses for palladium. Hence, this method is likely to be applicable to almost any type of matrix.

II. Experimental.

1. Preparation, standardisation and stability of solutions.

For palladium solutions and apparatus see Chapter 3, sections I to IV.

Dithizone Solutions.

(a) Preparation and Standardisation.

Dithizone was purified to remove the products of oxidation, by dissolving in chloroform 0.25 g of the solid and shaking the resulting solution with about 200 ml dilute ammonia solution. The dithizone went into the aqueous phase, leaving the impurities in the organic phase. The aqueous layer was washed twice with small volumes of chloroform, acidified with dilute hydrochloric acid, and the resulting precipitate of dithizone was extracted with chloroform or carbon tetrachloride. The organic layer was separated, filtered and diluted to 100 ml. In this way the following solutions were prepared:

10^{-2}M dithizone in chloroform.

2×10^{-3}M dithizone in carbon tetrachloride.

The molarity of the dithizone was checked by measuring the absorbance at 605 nm in chloroform or 620 nm in carbon tetrachloride. The extinction coefficients at these wavelengths are 32,800 and 40,000 in chloroform and carbon tetrachloride respectively[96].

(b) Stability.

Solutions of dithizone in chloroform and carbon tetrachloride do not deteriorate noticeably for 1 - 2 weeks when kept in glass in a dark cupboard at concentrations down to 10^{-3}M. Stabilities of dithizone in these two solvents at concentrations of 50 mg/ml have been reported to be 2 days for carbon tetrachloride and 12 - 17 days for chloroform[97]. However the 2×10^{-3}M solution of dithizone in carbon tetrachloride prepared above appeared to be saturated and this agrees with solubilities reported[49], so the existance of a 50 mg/ml solution seems doubtful.

Solutions of lower concentrations were obviously rather unstable and were therefore prepared by dilution immediately before use. The stability of low concentrations of dithizone in carbon tetrachloride was investigated as follows:

10^{-5}M

A 10^{-5}M solution of dithizone in carbon tetrachloride was stored in glass in a dark cupboard and the absorbance measured at various intervals in a 10 mm cell against carbon tetrachloride at 620 nm.

10^{-6}M

This was treated as the 10^{-5}M solution, except that the absorbance was measured in a 40 mm cell.

10^{-7}M

A 10^{-7}M solution of dithizone in carbon tetrachloride was stored in glass in a dark cupboard. After various intervals of time, 5 ml of this solution were shaken for 30 minutes with 1.0 ml of a 10^{-6}M solution of palladium chloride (^{103}Pd) in 0.1N hydrochloric acid, diluted to 10 ml in 0.1N sulphuric acid. The organic layer was separated, filtered and 3.0 ml evaporated for counting.

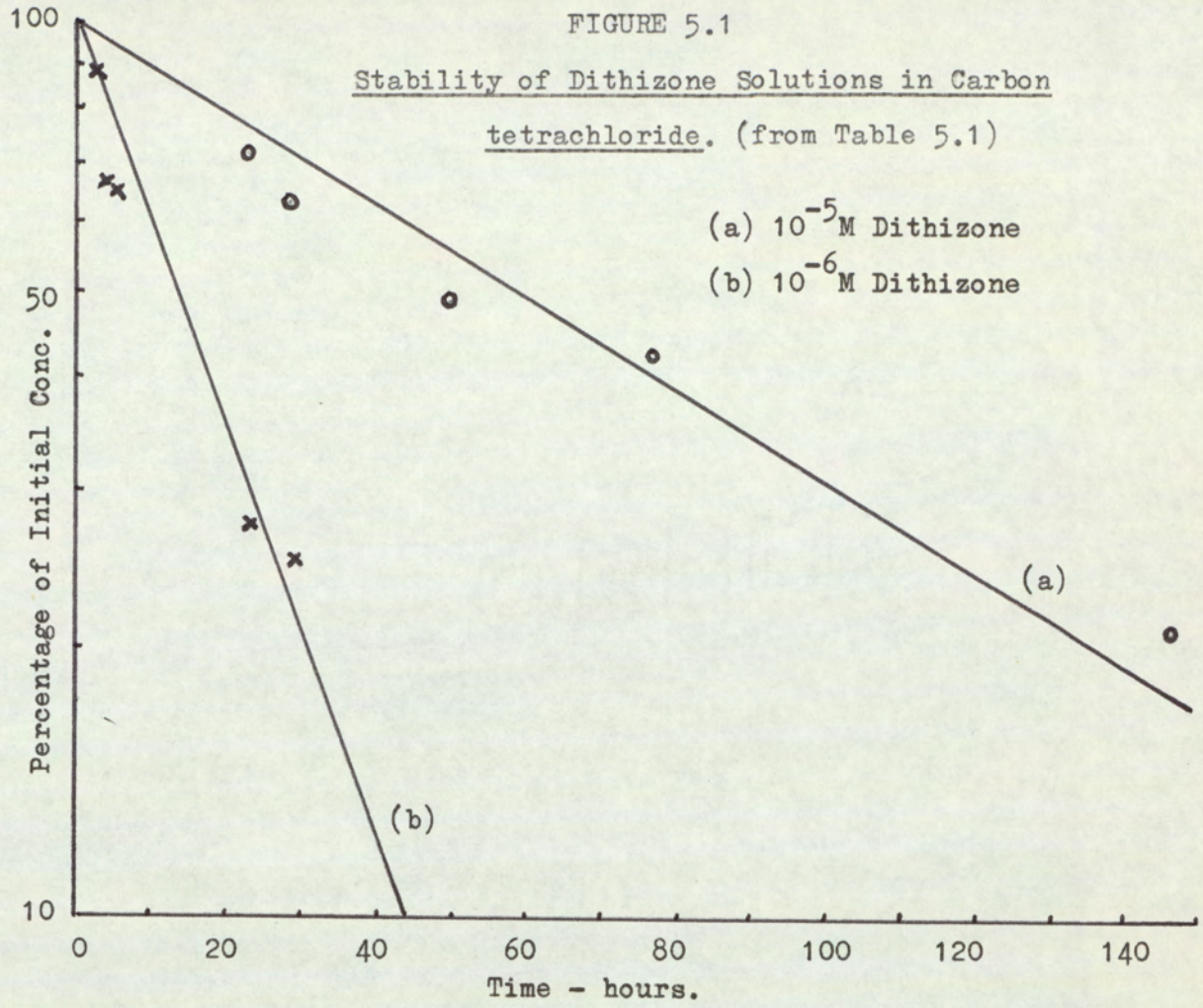
10^{-8}M

This was treated as the 10^{-7}M solution, except that it was shaken for 45 minutes with 1.0 ml of a 10^{-7}M palladium chloride solution.

The results are given in Table 5.1 and Figure 5.1. From Figure 5.1 the approximate half-lives of the solutions can be determined and the time for 10% decomposition. These are given in Table 5.2. It can be seen that at 10^{-8}M, the limit of usage is very near.

FIGURE 5.1

Stability of Dithizone Solutions in Carbon tetrachloride. (from Table 5.1)



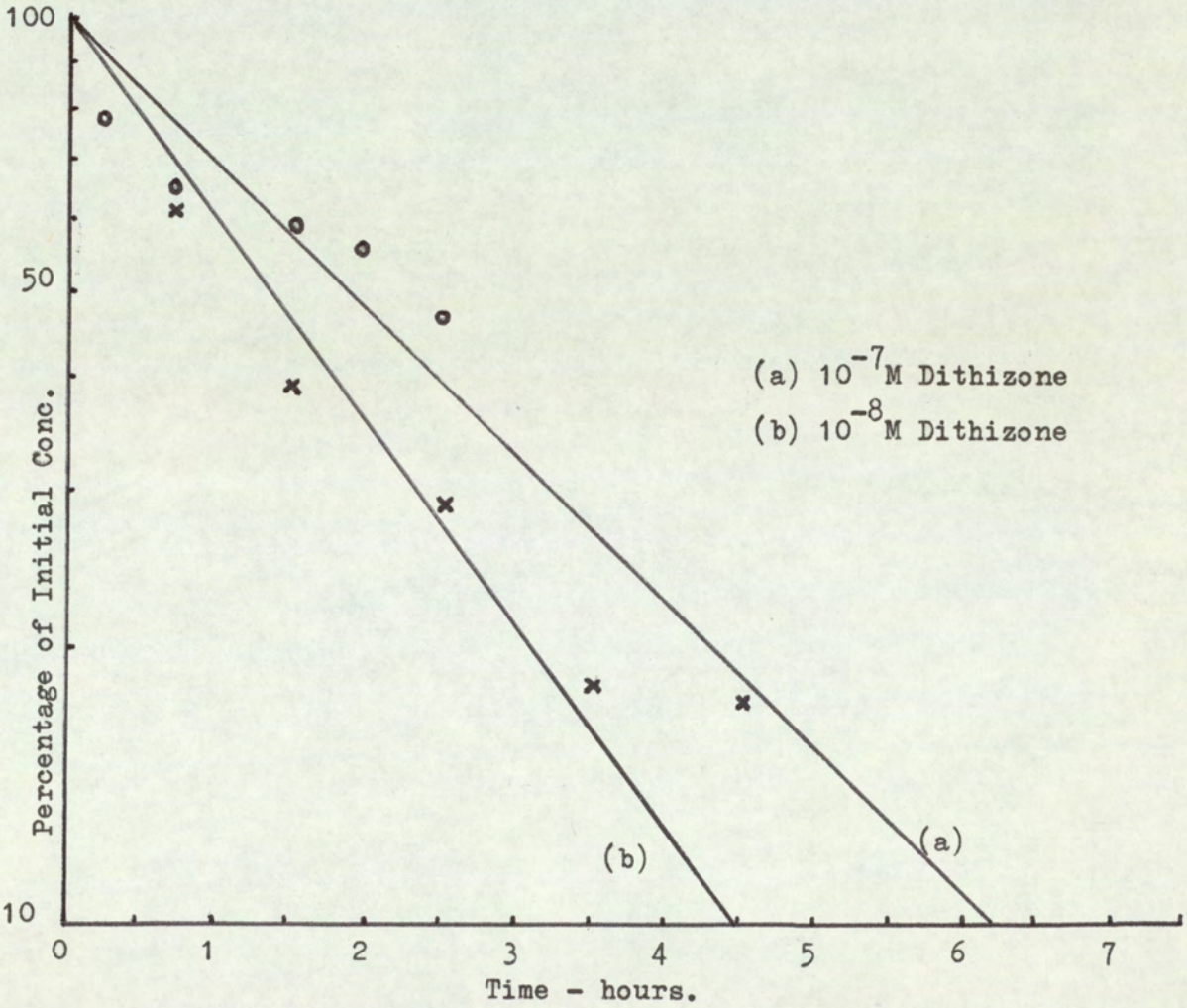


Table 5.1

Time, hours	Absorbance at 620 nm.				Activity of organic phase, c.p.s.			
	10^{-5}M H_2Dz		10^{-6}M H_2Dz		10^{-7}M H_2Dz		10^{-8}M H_2Dz	
		% left		% left		% left		% left
0	0.274	100	0.128	100	12.0	100	12.0	100
1/4	-	-	-	-	9.3	77.4	-	-
1/2	-	-	0.128	100	-	-	-	-
3/4	-	-	-	-	8.0	66.7	7.4	61.7
1½	-	-	-	-	7.1	59.2	4.7	39.2
2	-	-	-	-	6.9	57.5	-	-
2½	-	-	0.112	87.6	5.7	47.5	3.5	29.2
3½	-	-	-	-	-	-	2.2	18.3
4½	-	-	0.085	66.4	-	-	2.1	17.5
6	-	-	0.083	64.8	-	-	-	-
23	0.193	70.5	0.035	27.3	-	-	-	-
29	0.172	62.7	0.032	25.0	-	-	-	-
50	0.134	48.9	0	0	-	-	-	-
77	0.126	46.0	-	-	-	-	-	-
147	0.058	21.2	-	-	-	-	-	-

Table 5.2

$[H_2Dz]$	Half-life, hours.	Time for 10 % decomposition, hours.
10^{-5}	59	8.5
10^{-6}	12.5	1.9
10^{-7}	1.9	0.3
10^{-8}	1.3	0.2

2. Development of Method.

(a) Kinetics.

(i) The Effect of Hydrogen and Chloride ion concentration.

An aliquot of 1.0 ml of a 10^{-6}M palladium chloride solution (^{103}Pd) in 0.05N hydrochloric acid was diluted to 10 ml and the hydrogen ion and chloride ion concentrations adjusted with hydrochloric acid and sulphuric acid. This solution was shaken for various lengths of time with 5 ml of a 10^{-7}M solution of dithizone in carbon tetrachloride. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Tables 5.3 and 5.4 and Figures 5.2 and 5.3.

Table 5.3

The effect of hydrogen ion concentration on extraction from 0.01N chloride.

Shaking Time, minutes.	0.01N acid		0.1N acid		1N acid		5N acid		10N acid	
	c.p.s.	% ext.	c.p.s.	%ext.	c.p.s.	%ext.	c.p.s.	%ext.	c.p.s.	%ext.
2	4.8	8.2	6.0	10.3	5.0	8.6	5.6	9.6	6.2	10.7
5	8.5	14.6	7.6	13.1	5.5	9.4	-	-	10.2	17.6
8	-	-	-	-	-	-	9.3	16.0	-	-
10	11.7	20.1	9.2	15.8	10.9	18.7	10.3	17.7	10.8	18.6
15	12.9	22.1	11.6	20.0	10.4	17.9	13.3	22.9	11.6	19.9
20	13.9	24.0	11.8	20.3	12.2	21.0	14.5	24.9	13.2	22.7
30	15.3	26.3	15.0	25.8	13.3	22.9	15.7	27.0	15.2	26.1
45	-	-	-	-	15.1	26.0	-	-	-	-
60	16.0	27.5	14.0	24.1	15.2	26.2	15.5	26.6	15.0	25.9
90	15.5	26.6	15.2	25.1	-	-	15.8	27.2	18.5	31.8

initial activity of aqueous phase = 58.2 c.p.s.

FIGURE 5.2

(from Table 5.3)

Effect of hydrogen ion concentration on rate of extraction of palladium from 0.01N chloride.

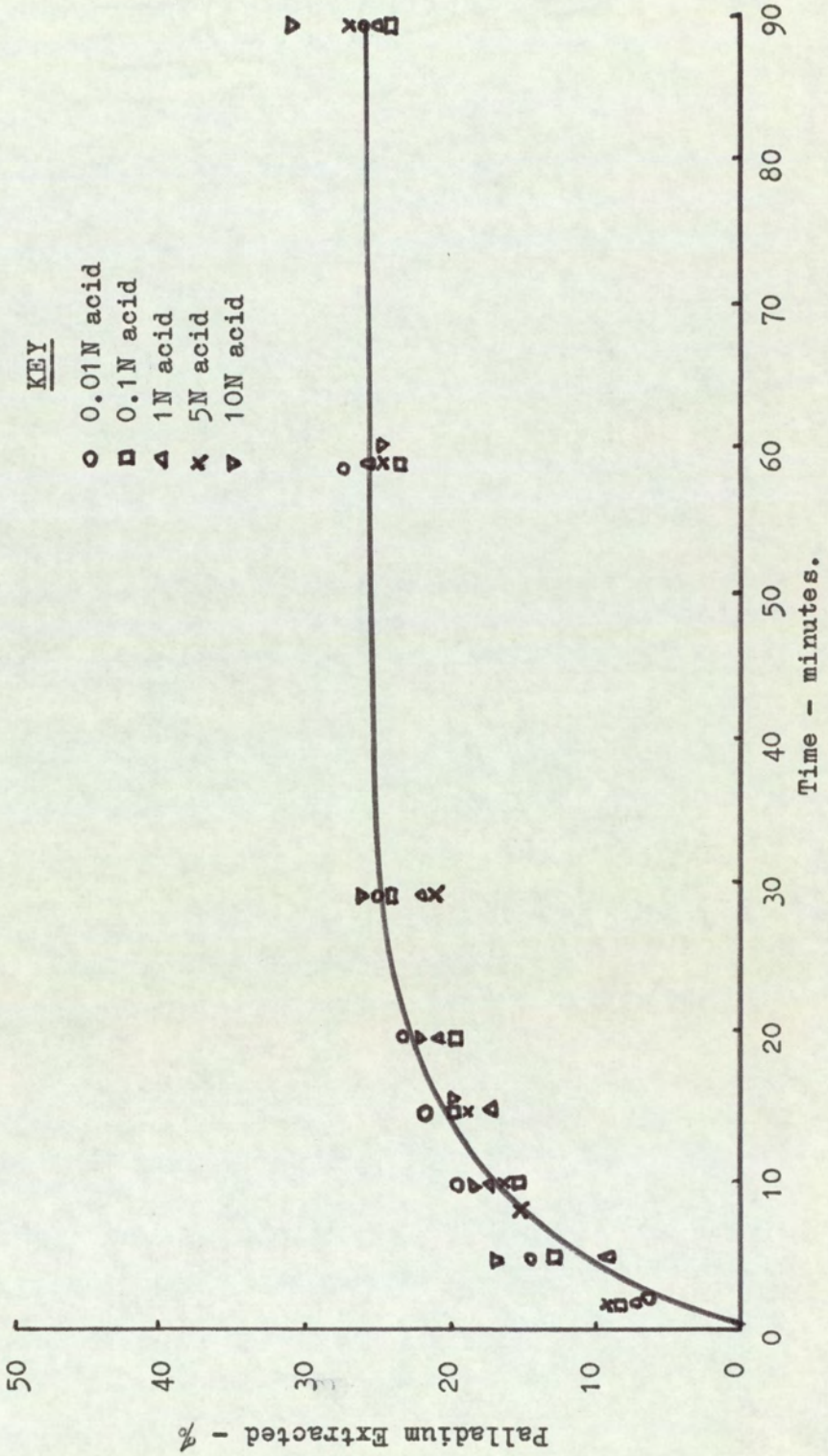


FIGURE 5.3

(from Tables 5.3 and 5.4)

Effect of chloride ion concentration on rate of extraction of palladium from 5N acid.

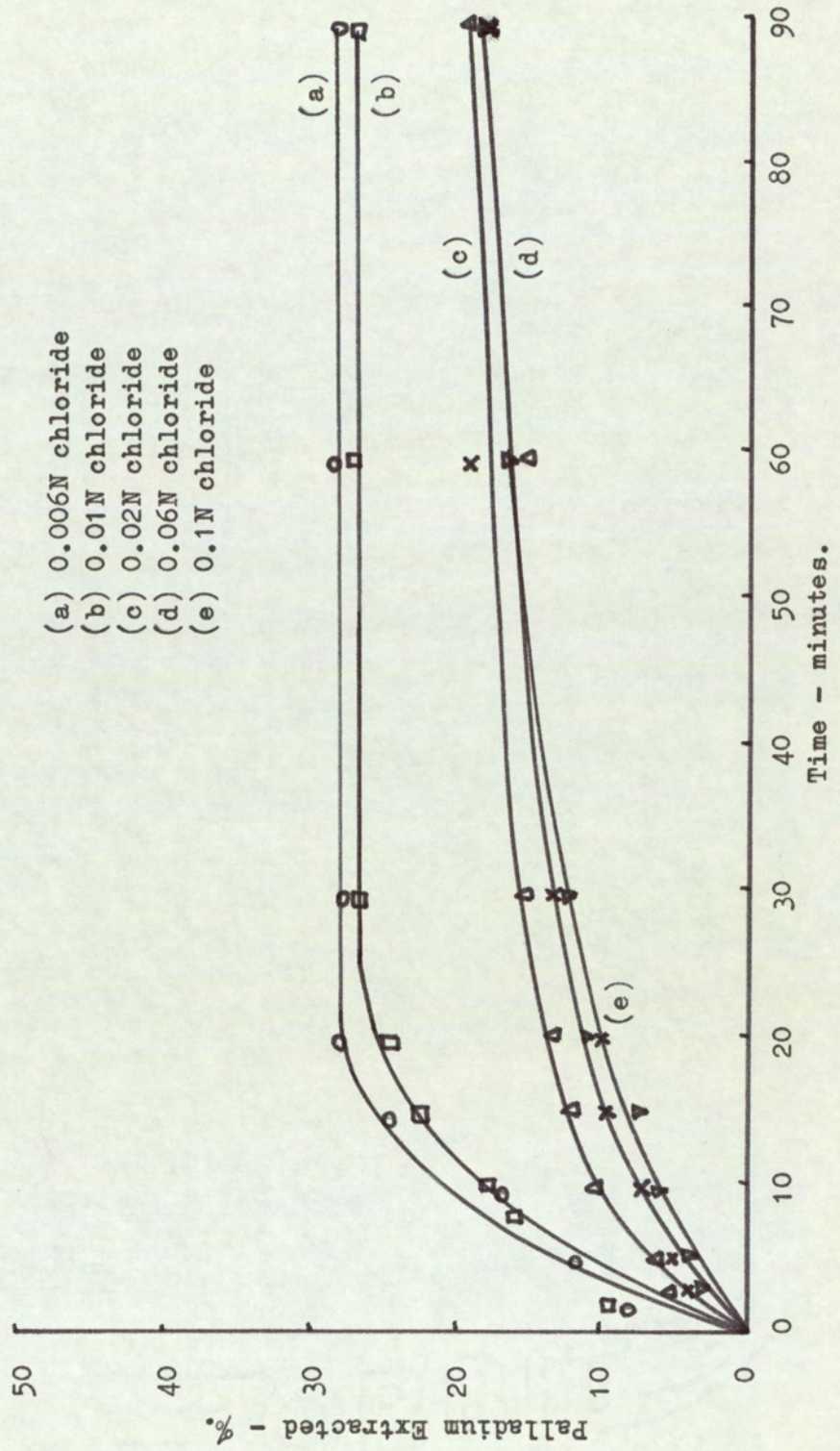


Table 5.4

The effect of chloride ion concentration on extraction from 5N acid.

Shaking Time, minutes.	0.006N chloride		0.02N chloride		0.06N chloride		0.1N chloride	
	c.p.s.	%ext.	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
2	7.2	8.3	5.2	6.0	4.0	4.7	3.4	3.9
5	10.2	11.8	5.4	6.2	4.6	5.3	4.3	5.0
10	14.8	17.1	9.4	10.9	6.2	7.2	5.6	6.5
15	21.4	24.8	10.3	11.9	7.6	8.8	6.1	7.1
20	24.4	28.2	11.4	13.2	10.0	11.6	8.4	9.8
30	24.0	27.8	13.3	15.4	10.2	11.8	10.8	12.4
60	25.0	28.9	13.1	15.2	16.8	19.4	14.4	16.7
90	24.6	28.4	16.8	19.4	16.2	18.7	-	-

initial activity of aqueous phase = 86.5 c.p.s.

(ii) The Effect of Stoichiometry.

An aliquot of 1.0 ml of a 10^{-6} M palladium chloride solution (^{103}Pd) in 0.01N hydrochloric acid was diluted to 10 ml in 0.1N sulphuric acid and shaken with 5 ml of a solution of dithizone in carbon tetrachloride for various lengths of time. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 5.5 and Figure 5.4.

FIGURE 5.4

(from Tables 5.5 and 5.6)

Effect of stoichiometry on rate of extraction of palladium.

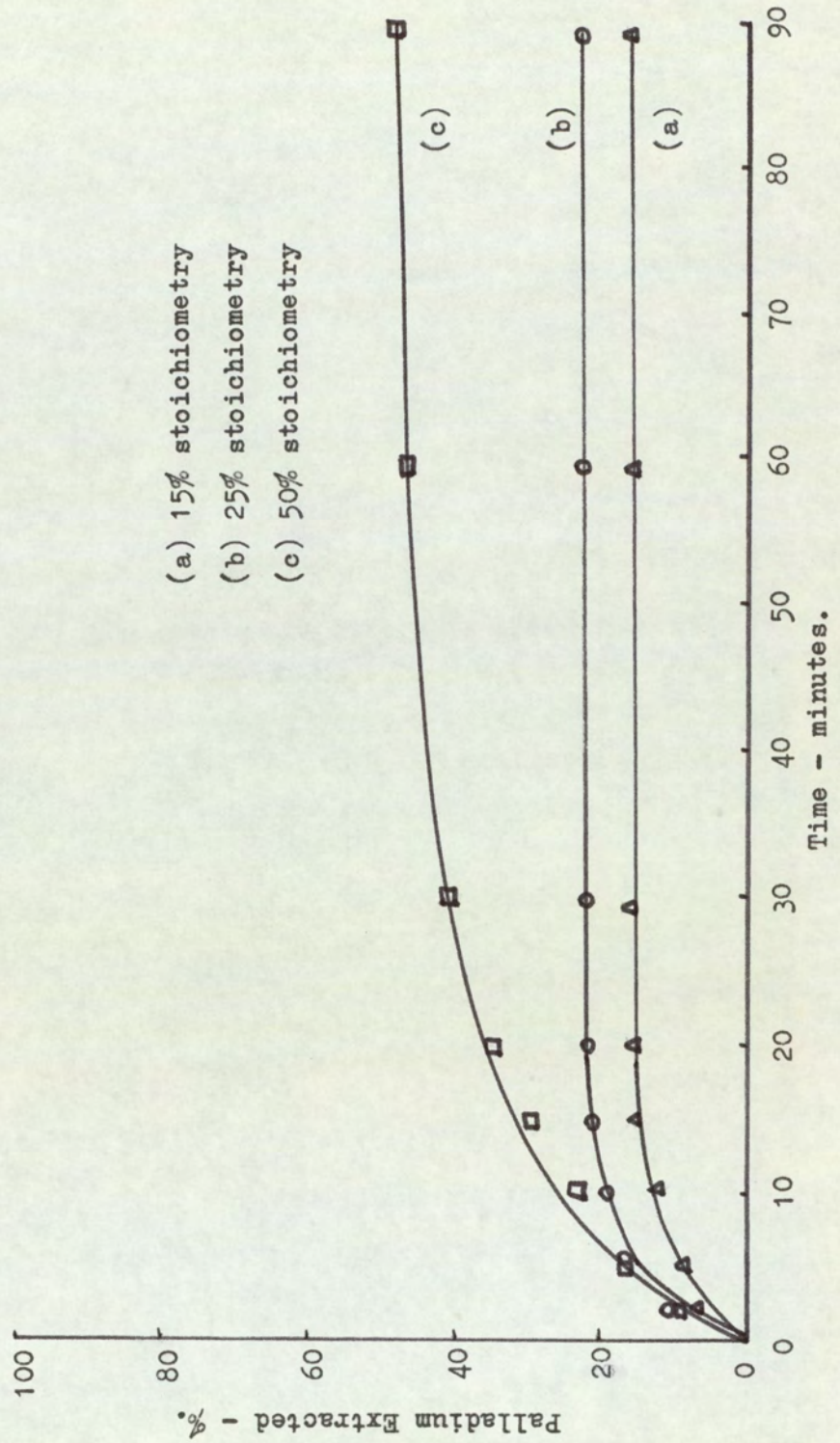


Table 5.5

Shaking Time, minutes	15% stoichiometry (5×10^{-8} M H_2Dz)		50% stoichiometry (2×10^{-7} M H_2Dz)	
	c.p.s.	% extraction	c.p.s.	% extraction
2	4.0	7.8	4.6	9.0
5	4.6	9.0	8.6	16.8
10	5.9	11.5	11.2	21.9
15	8.2	16.0	14.6	28.5
20	8.2	16.0	18.0	35.1
30	8.8	17.2	20.8	40.6
60	8.3	16.2	24.0	46.9
90	8.5	16.6	25.0	48.9

initial activity of aqueous phase = 51.2 c.p.s.

(iii) The Effect of Concentration.

An aliquot of 1.0 ml of a palladium chloride solution (^{103}Pd) in 0.1N hydrochloric acid was diluted to 10 ml in 0.1N sulphuric acid and shaken for various lengths of time with 5 ml of a solution of dithizone in carbon tetrachloride, such that the molar concentration of dithizone in the organic phase was equal to that of the palladium in the aqueous phase. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 5.6 and Figure 5.5.

FIGURE 5.5

(from Table 5.6)

Effect of concentration on rate of extraction of palladium.

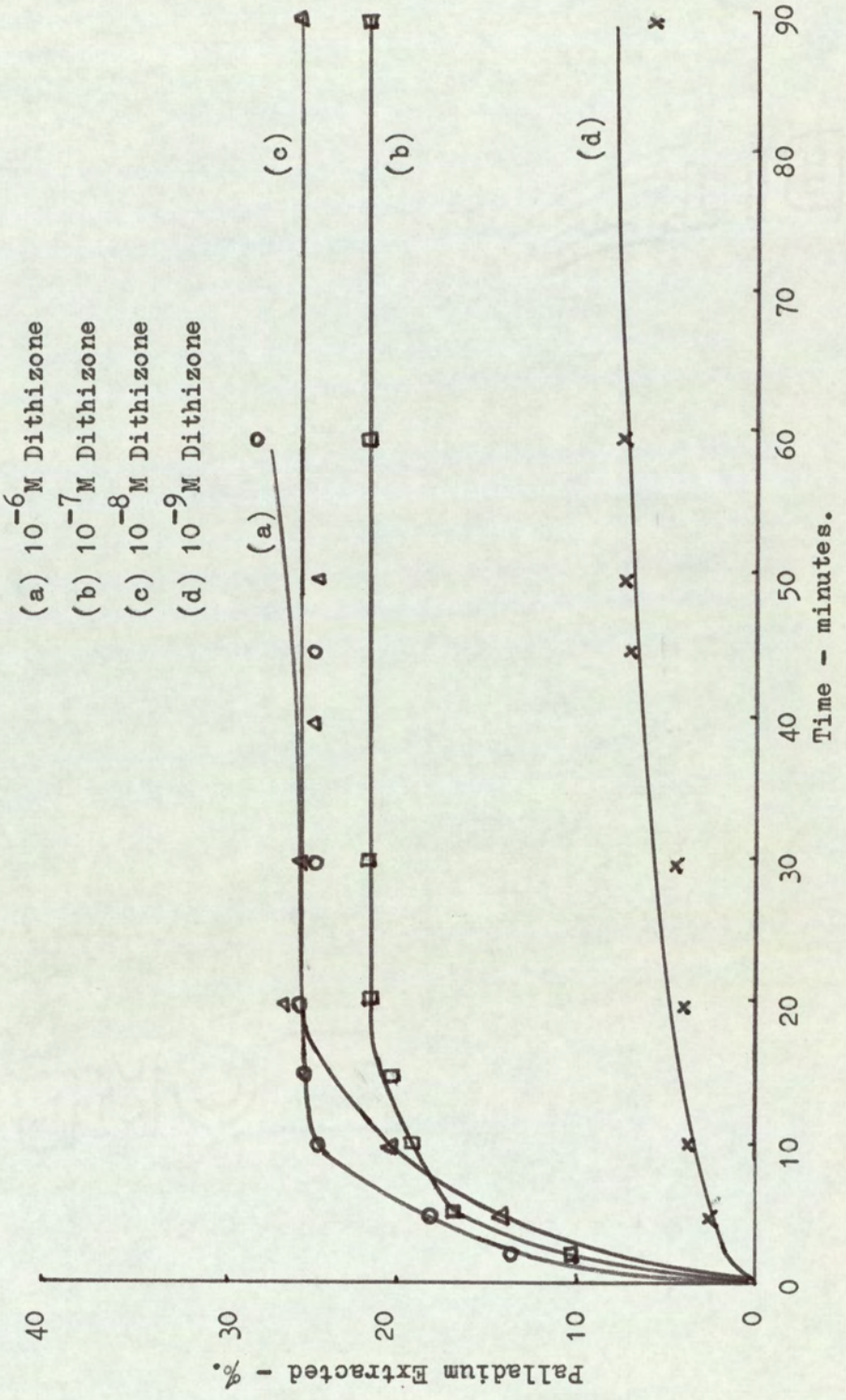


Table 5.6

Shaking Time	10^{-6} M H_2Dz		10^{-7} M H_2Dz		10^{-8} M H_2Dz		10^{-9} M H_2Dz	
minutes.	c.p.s.	% ext.	c.p.s.	%ext.	c.p.s.	% ext.	c.p.s.	% ext.
2	23.8	14.2	18.3	10.9	-	-	-	-
5	30.5	18.3	29.1	17.3	23.8	14.3	4.8	2.8
10	42.7	25.4	33.0	19.6	34.8	20.7	6.7	4.0
15	43.8	26.1	35.0	20.9	-	-	-	-
20	44.9	26.6	37.5	22.4	45.6	27.2	6.7	4.0
30	40.8	24.3	37.5	22.4	43.2	25.8	7.7	4.6
40	-	-	-	-	40.0	23.8	-	-
45	41.2	24.5	-	-	-	-	11.5	6.9
50	-	-	-	-	39.5	23.5	12.5	7.4
60	49.7	29.5	38.0	22.6	-	-	12.5	7.4
90	-	-	38.0	22.6	44.0	26.1	9.6	5.7

initial activity of aqueous phase = 168 c.p.s.

(b) Reproducibility.

In order to test for substoichiometric reproducibility, different volumes of palladium chloride solutions (^{103}Pd) were added to a series of separating funnels, made up 0.01N chloride and 0.1N sulphuric acid, and shaken for a constant time with 5 ml portions of dithizone in carbon tetrachloride. The organic layer was separated, filtered and 3.0 ml evaporated for counting. This experiment was carried out using several different dithizone concentrations and the results are given in Table 5.7 and Figure 5.6. Below a dithizone concentration of 5×10^{-9}M the results were erratic.

$5x10^{-9}$ M H_2Dz			10^{-8} M H_2Dz			10^{-7} M H_2Dz			10^{-6} M H_2Dz		
Pd added µg.	c.p.s.	Pd ext. µg.	Pd added µg.	c.p.s.	Pd ext. µg.	Pd added µg.	c.p.s.	Pd ext. µg.	Pd added µg.	c.p.s.	Pd ext. µg.
0.0005	4.0	0.00043	0.001	12.0	0.00083	0.01	9.0	0.0088	0.1	6.4	0.110
0.0010	6.8	0.00073	0.002	18.1	0.00126	0.02	12.1	0.0119	0.2	10.4	0.180
0.0025	8.3	0.00089	0.005	24.5	0.00170	0.05	20.2	0.0198	0.5	12.8	0.223
0.0050	9.8	0.00105	0.010	28.0	0.00194	0.10	26.0	0.0255	1.0	13.8	0.238
0.0075	10.0	0.00108	0.015	27.9	0.00194	0.15	25.5	0.0250	1.5	13.7	0.237
0.0100	10.0	0.00108	0.020	28.1	0.00195	0.20	25.6	0.0251	2.0	13.5	0.233
0.0125	10.1	0.00109	0.025	28.5	0.00198	0.25	26.0	0.0255	2.5	13.4	0.231
0.0150	10.0	0.00108	0.030	27.9	0.00194	0.30	25.9	0.0254	3.0	14.0	0.241

activity of 0.001µg = 9.3 c.p.s.

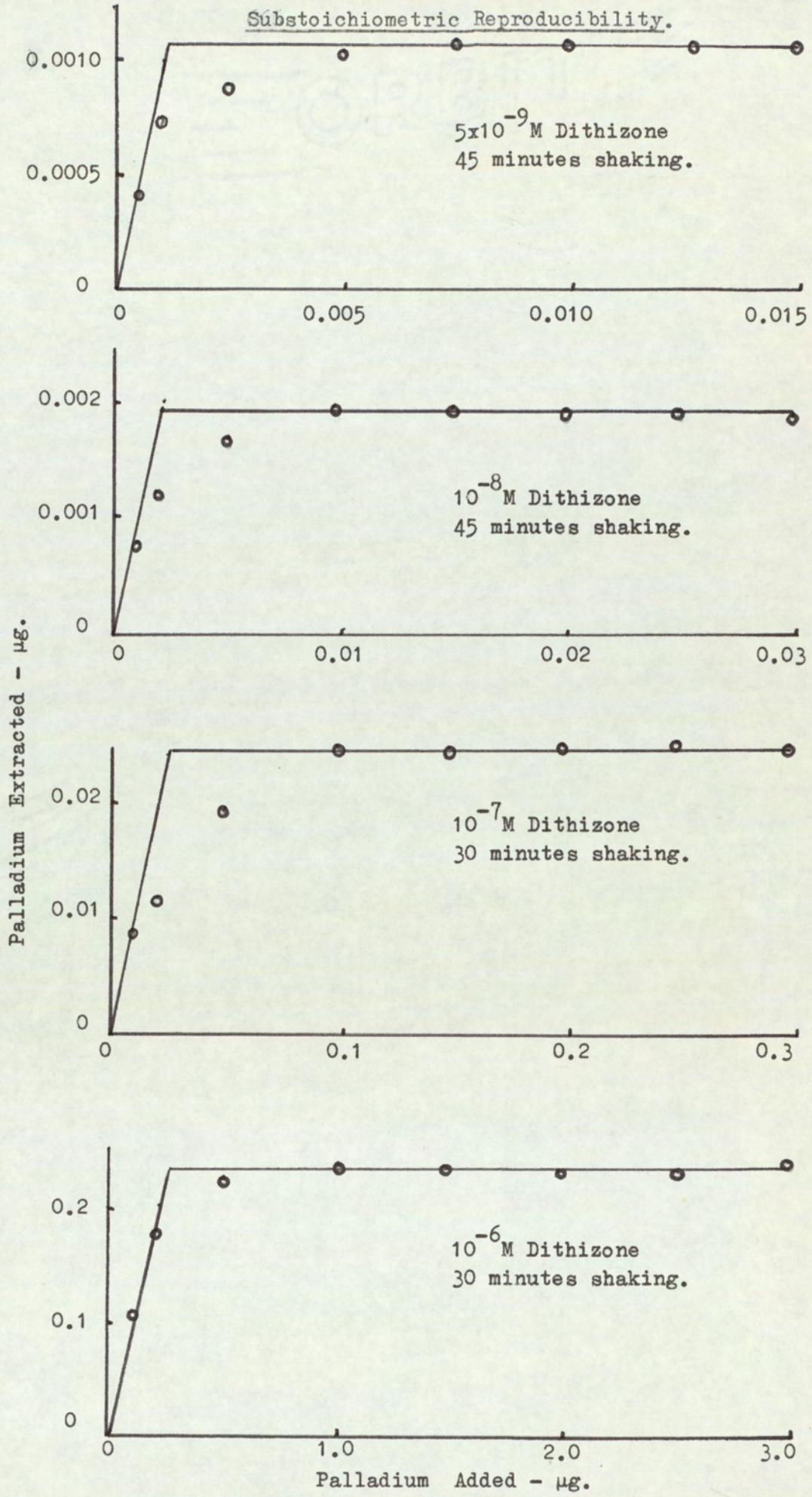
activity of 0.001µg = 14.4 c.p.s.

activity of 0.01µg = 10.2 c.p.s.

activity of 0.1µg = 5.8 c.p.s.

Table 5.7

FIGURE 5.6 (from Table 5.7)



(c) Precision.

To test the precision of the extraction at various concentrations, 1.0 ml aliquots of a palladium chloride solution (^{103}Pd) in 0.1N hydrochloric acid were diluted to 10 ml in 0.1N sulphuric acid and shaken for a constant time with 5 ml of a solution of dithizone in carbon tetrachloride. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The concentrations were such that the molar concentration of dithizone in the organic phase was equal to the concentration of palladium in the aqueous phase, i.e., 25% stoichiometry. The shaking time was 45 minutes for 10^{-8} M dithizone and 30 minutes for the higher concentrations. The standard deviation was calculated as before (Ch.4.II.1b) and the results are given in Table 5.8.

Table 5.8

Weight of Pd added, µg.	H_2Dz conc. M	Activity of organic phase, c.p.s.		mean activity, c.p.s.	Standard deviation
		88.6	87.5		
1.0	10^{-6}	91.4	90.9	90.0	1.22
		89.7	90.2		(1.4%)
		90.5	90.8		
		76.7	78.5		
0.10	10^{-7}	75.5	77.6	77.4	1.08
		79.1	77.2		(1.4%)
		76.0	78.9		
		35.2	37.0		
0.010	10^{-8}	33.9	34.5	34.9	1.23
		33.1	34.8		(3.5%)
		35.6	35.3		

(d) Selectivity.

The selectivity was examined in the presence of a large number of foreign ions that were thought likely to be present in test samples. The effect of high concentrations of substances that might be used in dissolution procedures was also investigated. An aliquot of 1.0 ml (0.1 μg) of a 10^{-6}M palladium chloride solution (^{103}Pd) in 0.1N hydrochloric acid was diluted to 10 ml in 0.1N sulphuric acid and a solution of the ion under investigation. This solution was shaken for 30 minutes with 5 ml of a 10^{-7}M solution of dithizone in carbon tetrachloride. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The amount of the foreign ion present was 1 mg or above, i.e., at least a ten thousandfold excess over palladium, but if interference occurred lower concentrations were tried. The species under investigation was considered to interfere if the activity of the sample was less than 95% of that of a standard in which no foreign ions were present. The results are given in Table 5.9. It can be seen that the only substances which interfere when present in a thousandfold excess over palladium are mercury-I, mercury-II, cerium-IV and gold-III.

Table 5.9

Foreign ion added	Activity, c.p.s.	Foreign ion added	Activity, c.p.s.
none	112.2	mercury-II, 0.01mg	78.5
aluminium, 100mg	111.6	mercury-II, 0.001mg	118.1
antimony-III, 1mg	120.0	molybdenum-VI, 10mg	115.1
antimony-V, 1mg	58.5	nickel, 100mg	118.3
antimony-V, 0.1mg	109.7	niobium-V, 1mg	11.8
arsenic-III, 1mg	119.0	niobium-V, 0.1mg	108.2
arsenic-V, 10mg	119.0	osmium-VI, 1mg	107.0
barium, 100mg	106.5	platinum-IV, 1mg	113.0
beryllium, 100mg	116.8	potassium, 100mg	111.5
bismuth, 1mg	106.0	rhenium-VII, 1mg	84.2
boron, 10mg	112.1	rhenium-VII, 0.1mg	112.2
cadmium, 100mg	117.0	rhodium-IV, 1mg	114.3
calcium, 10mg	115.8	ruthenium-IV, 10mg	119.1
cerium-III, 10mg	106.8	selenium-IV, 10mg	108.4
cerium-IV, 1mg	8.4	selenium-VI, 10mg	112.0
cerium-IV, 0.1mg	39.4	silicon, 10mg	109.5
cerium-IV, 0.01mg	56.2	silver-I, 10mg	107.2
cerium-IV, 0.001mg	112.0	sodium, 100mg	112.2
chromium-III, 10mg	108.3	strontium, 10mg	107.2
cobalt-II, 100mg	108.8	tellurium-IV, 10mg	109.5
copper-II, 1mg	109.6	tellurium-VI, 10mg	107.2
gallium, 1mg	120.1	thallium-I, 10mg	114.8
germanium, 1mg	105.5	thorium-IV, 100mg	109.5
gold-III, 1mg	2.9	tin-II, 1mg	93.8
gold-III, 0.1mg	5.9	tin-II, 0.1mg	114.5
gold-III, 0.01mg	21.5	tin-IV, 1mg	112.0
gold-III, 0.001mg	106.6	titanium-III, 1mg	114.5
indium-III, 10mg	107.5	titanium-IV, 10mg	108.8
iridium-IV, 1mg	28.1	tunsten-VI, 10mg	109.5
iridium-IV, 0.1mg	119.1	uranium-VI, 10mg	106.8
iron-II, 100mg	116.8	vanadium-IV, 10mg	112.2
iron-III, 100mg	106.2	zinc, 10mg	113.5
lead-II, 10mg	110.1	zirconium-IV, 10mg	114.8
magnesium, 100mg	108.8	fluoride, 10mg	115.2
manganese-II, 10mg	106.8	iodide, 10mg	112.5
mercury-I, 1mg	4.8	acetate, 10mg	109.2
mercury-I, 0.1mg	12.2	sulphite, 10mg	111.9
mercury-I, 0.01mg	91.0	EDTA, 1mg	97.0
mercury-I, 0.001mg	106.8	EDTA, 0.1mg	109.2
mercury-II, 1mg	61.5	bromide, 1M	111.8
mercury-II, 0.1mg	68.5	orthophosphate, 1M	110.1
		perchlorate, 1M	108.0
		nitrate, 1M	110.0

3. Analysis of Test Samples.

Four samples were used for test analyses; the standard rocks W1 and PCC1, dried leaves of kale and platinum (Ch.4.I). The following dissolution and separation procedures were used.

(a) Rocks.

To the test sample in a 25 ml Teflon beaker, a weight, x_s g, of palladium labelled with palladium-103 was added (as palladium chloride solution) approximately equal to the expected weight of palladium in the sample. A mixture of 5 ml concentrated nitric acid, 5 ml hydrofluoric acid and 1 ml concentrated hydrochloric acid was added to the sample and the mixture boiled until the volume was reduced to 3 - 4 ml. About 5 ml aqua regia was added and the solution boiled until no more brown fumes were evolved, cooled and diluted to about 500 ml in a separating funnel. About 3 ml of a 1% solution of dimethylglyoxime in ethanol was added to this solution, which was then shaken with 5 ml chloroform for 5 minutes. The organic layer was separated and the aqueous layer washed with a further 5 ml chloroform. The combined organic extracts were filtered and evaporated to dryness. To the residue 5 ml concentrated nitric acid and 2 ml perchloric acid were added and the resulting solution was boiled until white fumes of perchloric acid were evolved and then diluted with about 5 ml distilled water. This was repeated twice and the solution was cooled, transferred to a 50 ml separating funnel and diluted to 10 - 15 ml with distilled water. To this solution, 5 ml dithizone in carbon tetrachloride was added and the mixture shaken for 30 or 45 minutes, according to the dithizone concentration used. The dithizone concentration was such that 25% of x would be consumed. The organic layer was separated, filtered and 3.0 ml evaporated for counting. For the standard, the same weight, x_s g, of labelled palladium was diluted to 10 ml in 0.1N sulphuric and 0.01N hydrochloric acid and extracted with the same dithizone solution as the sample. The activity of 3.0 ml aliquot of the organic phase was determined. The amount of palladium in the sample, x, was calculated

from the separated activities of the sample and standard, a and a_s, using equation 1.10:

$$x = (a_s/a - 1).x_s.$$

(b) Kale

The kale was first dried for 24 hours at 80°C. To the test sample in a 150 ml beaker a weight, x_s g, of labelled palladium was added, followed by 5 ml concentrated nitric acid and 5 ml concentrated sulphuric acid. The mixture was heated until charring occurred and then a further 5 ml concentrated nitric acid and 2 ml perchloric acid were added and the solution boiled to fumes of sulphuric and perchloric acids several times (diluting with distilled water each time), until the solution was colourless; two or three times was usually sufficient. The solution was cooled, transferred to a separating funnel and treated as for the rock samples.

(c) Platinum.

To the test sample in 100 ml beaker a weight, x_s g, of labelled palladium was added followed by 10 ml aqua regia. The mixture was heated gently until all the platinum was dissolved and the resulting solution cooled, transferred to a separating funnel and treated as for the rock samples.

(d) Reagent Blanks.

Known weights of labelled palladium were added to the same quantities of reagents which had been used to dissolved each type of sample. The resulting solutions were treated exactly the same as the samples, and the weigth of palladium in the reagents calculated. In all cases no palladium was found.

III. Results.

A large number of samples were analysed, varying the ratio of the weights, $x:x_s$, to check for errors and taking sample weights so that the lower limit of the determination could be investigated. The results are given in Table 5.10. The standard deviation of the results for each sample have been determined using the expression in Chapter 4, section II-1b, and the activation analysis results from Chapter 4, section III, (Table 4.5) have been included for comparison.

Table 5.10

Sple.	Sple. wt.,g	Pd std. µg.	act. of std c.p.s.	act. of sple. c.p.s.	Pd found p.p.m.	mean p.p.m.	Std. deviation, p.p.m.	Act. anal. results p.p.m.	Results of other authors, p.p.m.
W1	0.2501	0.108	16.8	15.5	0.036				
	0.2497	0.108	26.9	24.6	0.040				
	0.2510	0.108	26.9	24.5	0.042				
	0.4772	0.108	50.1	42.0	0.044				
	0.5086	0.108	50.1	41.6	0.043				
	0.4987	0.054	35.1	25.4	0.041				
	0.4869	0.054	35.1	26.0	0.039	0.041	0.0028	0.039	0.019[94]
	0.7549	0.054	42.0	27.2	0.039		(6.9%)		0.014[43]
	0.7408	0.054	42.0	27.0	0.040				
	0.5125	0.027	19.1	11.0	0.039				
	0.7671	0.027	19.1	9.2	0.038				
	0.1001	0.0054	13.0	7.1	0.045				
	0.0944	0.0054	11.1	6.2	0.045				
PCC1	0.2512	0.108	24.7	23.2	0.028				
	0.2498	0.108	49.3	46.1	0.030				
	0.2495	0.108	49.3	46.5	0.026				
	0.4932	0.108	50.1	44.7	0.026				

Table 5.10 (continued)

Sple.	Sple. wt.,g.	Pd std. µg.	Act. of std. c.p.s.	Act. of sple. c.p.s.	Pd found p.p.m.	Mean p.p.m.	Std. deviation, p.p.m.	Act. anal. p.p.m.	Results of other authors, p.p.m.
PCC1	0.5049	0.108	50.1	45.6	0.021				
(cont)	0.4935	0.054	35.1	28.0	0.028				
	0.5013	0.054	35.1	26.8	0.033	0.028	0.0033	0.029	0.007[43]
	0.7710	0.054	42.0	30.1	0.028		(11.9%)		
	0.7548	0.054	42.0	29.0	0.032				
	0.4917	0.027	19.0	12.1	0.031				
	0.7610	0.027	19.0	10.2	0.031				
	0.0868	0.0054	7.3	5.2	0.025				
	0.1061	0.0054	7.3	4.6	0.030				
Kale	0.2522	0.108	24.7	23.0	0.032				
	0.4792	0.108	50.1	45.0	0.026				
	0.4815	0.108	50.1	44.2	0.030	0.032	0.0036	0.026	-
	0.4821	0.054	35.1	27.1	0.033		(11.2%)		
	0.7499	0.054	42.0	30.1	0.028				
	0.5101	0.027	19.0	11.5	0.034				
	0.7564	0.027	19.0	9.5	0.036				
	0.0895	0.0054	7.3	4.5	0.037				
Pt	0.0396	0.054	45.8	19.8	1.79				
	0.0384	0.054	45.8	22.0	1.52				
	0.0309	0.054	35.8	17.9	1.75				
	0.0135	0.054	35.8	25.1	1.71				
	0.0593	0.054	20.0	7.1	1.65				
	0.0504	0.054	39.0	16.0	1.54	1.65	0.074	1.29	2.13[86]
	0.0499	0.054	25.0	10.1	1.60		(4.5%)		
	0.0588	0.054	25.0	8.9	1.66				

Table 5.10 (continued)

Sple.	Sple. wt.,g.	Pd std. µg.	Act. of std c.p.s.	Act. of sple. c.p.s.	Pd found p.p.m.	Mean p.p.m.	Std. deviation, p.p.m	Act. anal. p.p.m.	Results of other authors, p.p.m.
Pt (cont)	0.0848	0.054	33.0	8.8	1.75				
	0.0685	0.054	33.0	10.8	1.62				
	0.0089	0.0054	7.3	2.0	1.61				

CHAPTER 6

Palladium Dithizonate Complexes: Theory and Discussion.

I. Kinetic Studies.

At low concentrations, dithizone was found to be suitable for a substoichiometric separation of palladium and this has been used for an isotope dilution procedure in Chapter 5. The experiments carried out for the purpose of developing the analytical method indicated the formation of a 1:2 complex which is presumably primary palladium dithizonate, $Pd(HDz)_2$. Kinetic studies in Chapter 5, section II-2a, indicated that the formation of this complex was little affected by hydrogen ion concentration but was slowed down considerably by increasing the chloride ion concentration. As mentioned in Chapter 1, section II, however, palladium is thought to form another complex with dithizone, secondary palladium dithizonate, PdDz. Little evidence was found for this in Chapter 5, except for a slight upward slope in the rate curve using 10^{-6}M dithizone (Figure 5.5), which might indicate some formation of a 1:1 complex. In order to investigate the apparent discrepancy between the results in Chapter 5 and those reported in the literature, the palladium dithizonate system was studied at higher concentrations.

In the preliminary experiments (Ch.7.I and II) it was found that in fact three complexes were formed, primary palladium dithizonate, secondary palladium dithizonate and palladium chloride dithizonate, Pd.Cl(HDz). The secondary complex appeared to be formed only under alkaline conditions and hence it is not surprising that it did not appear in Chapter 5. However the chloro complex, which is formed slowly after initial formation of the primary complex (Figure 7.2) is formed under conditions similar to those used in the separation procedure developed in Chapter 5, except for the concentration of the reagents, and therefore its lack of appearance was probably a kinetic effect. In order to confirm this a kinetic study was carried out at

high reagent concentrations (Ch.7.III) to compare with the kinetic experiments carried out at low concentrations in Chapter 5. As use of dithizone in carbon tetrachloride as extractant resulted in the formation of a precipitate, chloroform was used as solvent.

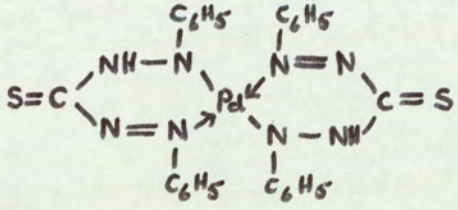
By comparison of Chapter 5, section II-2a and Chapter 7, section III-1, it can be seen that hydrogen ion concentration appeared to have little more effect at high concentrations than at low, on either the fast initial formation of primary palladium dithizonate or the slow formation of palladium chloride dithizonate (Figures 5.2 and 7.3). Similarly, it can be seen that increasing the chloride ion concentration slows down the formation of both complexes (Figures 5.3 and 7.4.). The latter effect can be explained by similar reasoning to that used in Chapter 2, section I, to explain the inhibition of the formation of the palladium diethyldithiocarbamate complexes by chloride ions. However, unlike the diethyldithiocarbamic acid system, chloride free solutions resulted in fast formation of primary palladium dithizonate, which indicates either that free palladium-II ions are the main reacting species, or that the palladium nitrate complexes react as fast or faster than the chloro complexes.

As the basic extraction reaction appears to be similarly affected by hydrogen and chloride ion concentrations at both high and low reagent concentrations, the effect of reagent concentration itself was next examined, both in chloroform and carbon tetrachloride (Ch.7.III.2). At high concentrations, i.e., 10^{-4}M dithizone in carbon tetrachloride and 10^{-3}M dithizone in chloroform, precipitation of the chloro complex occurs, giving the downward sloping curves in Figures 7.5 and 7.6. Figure 7.7 shows that the reaction is slightly faster with carbon tetrachloride than with chloroform as expected. By using the results from both Table 5.6 and Table 7.6 in Figure 7.6, the effect of concentration over the range 10^{-4}M to 10^{-9}M can be seen and this shows that the formation of palladium chloride dithizonate simply becomes slower with decreasing reagent concentration, until

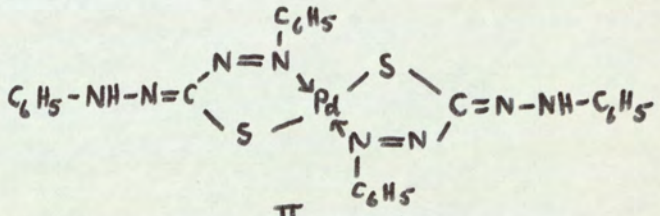
at 10^{-6}M, it is hardly noticeable and at lower concentrations it does not appear at all. Hence the reason why this complex did not interfere in the isotope dilution procedure was a kinetic one . Obviously, however, as predicted in Chapter 1, section II, this system would not have been suitable for a substoichiometric separation at higher concentrations and therefore would have been little use for activation analysis.

II. Formation and Composition.

The reaction of palladium with dithizone has been studied by a number of workers[98-101] and is generally assumed to form two complexes, a primary complex, $Pd(HDz)_2$, and a secondary complex, PdDz. The structure of these complexes has not been studied, but primary dithizonates are assumed to have either structure I, postulated by Fischer[103], or structure II, postulated by Geiger[102].



I.



II.

X-ray studies have confirmed structure II for copper-II[104] and mercury-II[105] dithizonates and so it is reasonable to assume that most primary dithizonates are similar. The 1:2 complex formed in Chapter 7, section I-1, is the primary palladium complex, formed by the reaction:

$$Pd^{2+} + 2H_2Dz \rightleftharpoons Pd(HDz)_2 + 2H^+. \qquad (6.1)$$

It was found to be dark green in colour, the spectrum (Ch.7.VI) agreeing with previous workers[101]. However various authors have reported a variety of colours for this complex: dirty grey with a red precipitate[103], brown-red[98], blue[99], violet or brown[106], dirty brown-green[101] and dark green[107]. Meriwether et al[100] have reported that primary palladium dithizonate has three forms: green, violet and red, the latter being a product of a photochemical reaction. The composition of these forms has been confirmed by elemental analysis in this case, but it seems likely that in some of the above cases, some of the ternary complex, palladium chloride dithizonate was present, as most workers were using excess metal in chloride solution. Under these conditions it was found that the following reaction took place (Ch.7.I.2):

$$Pd(HDz)_2 + Pd^{2+} + 2Cl^- \rightleftharpoons 2Pd.Cl(HDz) \qquad (6.2)$$

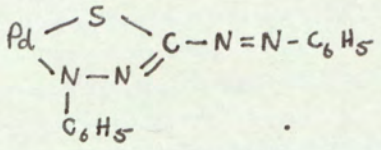
The composition of palladium chloride dithizonate was indicated by tracer studies with palladium-103 and chlorine-36. This complex is clear red in colour, but the sequence of colours observed during its formation can be described as:

green → grey → brown → dull pink → red

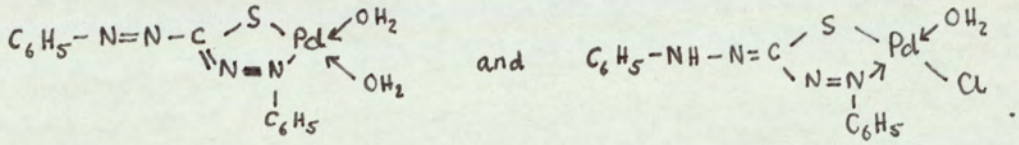
and these colours may well be the cause of some of the above confusion. It also seems likely that this complex has been observed and distinguished from the primary complex but then reported to be the secondary complex. Secondary palladium dithizonate has been reported to be pink[99], brown-violet[101] and violet[50,100]. It is usually considered to be insoluble in most solvents, e.g. the solubility in both chloroform and carbon tetrachloride has been reported to be less than 10^{-6}M[49], but Beardsley et al found it to be moderately soluble[50], which agrees with the results in this work (Ch.7.V), whether they were observing the secondary or the chloro complex. A complex of the formula, $PdDz_3$,[107] has been reported and one of the formula, $PdDz_2$,[99] but little evidence is given to support these structures. In most cases the so-called secondary complex has been formed under the conditions used in Chapter 7, section I-2, to form the chloro complex. Its composition was determined by Meriwether et al[100] using elemental analysis and found to correspond to the formula: $PdDz.2H_2O$, but this formula has almost exactly the same constitution with respect to the elements determined as the formula: Pd.Cl(HDz). Fischer[98], however, has reported a violet secondary complex formed under alkaline conditions, and this may well be the same complex as that formed by the action of an alkaline solution on the chloro complex (Ch.7.I.3) according to the reaction:

$$Pd.Cl(HDz) + OH^- \rightleftharpoons PdDz + Cl^- + H_2O. \qquad (6.3)$$

The secondary complexes of dithizone have been assigned the structure[103]



However, in view of the fact that the elemental analysis results (Ch.7.VII) indicate that the formula of this complex is $PdDz.2H_2O$, and the obvious parallel with the diethyldithiocarbamate complexes in Chapter 2, it seems reasonable to suggest that the two water molecules make up a square planar complex, possibly with partial protonation of the dithizonate part of the molecule, so that the formula might be more correctly written: $Pd.OH(HDz).H_2O$. As the chloro complex also appears to have the formula: $Pd.Cl(HDz).H_2O$, the structures of these two complexes could be:



Primary palladium dithizonate has been put to a number of analytical uses, including qualitative detection[108], separation of palladium fission products[106], emission spectral analysis[109] and chromatographic separations[107,110,111].

The solubility and partition coefficient data (Ch.7.IV and V) shows that palladium chloride dithizonate and secondary palladium dithizonate are very similar in this respect, which tends to confirm the similar structures proposed above. Their solubility in organic solvents is less than that of primary palladium dithizonate, which is to be expected. The value of the solubility of primary palladium dithizonate agrees with that reported by Iwantscheff[49] i.e. 4.5×10^{-4}M, but as mentioned above the secondary (or chloro)complex is much more soluble than reported. This may be due to the fact that, once precipitated, the dithizonates tend to be very slow to redissolve.

The extinction coefficients of primary palladium dithizonate in carbon tetrachloride (Ch.7.VI) are also similar to the following values reported by Iwantscheff[96]:

$$\varepsilon_{280} = 3.8 \times 10^4$$

$$\varepsilon_{450} = 3.4 \times 10^4$$

$$\varepsilon_{640} = 2.8 \times 10^4.$$

CHAPTER 7

Palladium Dithizonate Complexes: Experimental and Results.

For apparatus and palladium solutions see Chapter 3, sections I to IV. For dithizone solutions see Chapter 5, section II-1.

I. Formation and Composition of the Palladium Dithizonate Complexes.

1. Formation of Primary Palladium Dithizonate.

An aliquot of 1.0 ml of a 0.88×10^{-3}M palladium nitrate solution (^{109}Pd) was diluted to 10 ml in 5N sulphuric acid and shaken for various lengths of time with 5 ml of a 0.88×10^{-4}M solution of dithizone in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 7.1 and Figure 7.1. From the concentrations of the solutions used, a 1:2 complex corresponds to 25.0% extraction.

Table 7.1

Shaking Time, minutes	Activity of organic phase, c.p.s.	palladium extracted, %
½	57.8	21.4
1	66.6	24.7
2	69.2	25.6
4	62.0	22.9
8	65.2	24.3
15	68.6	25.5
30	70.0	25.9
60	63.8	24.7

initial activity of aqueous phase = 270 c.p.s.

FIGURE 7.1

Formation of primary palladium dithizonate.

(from Table 7.1)

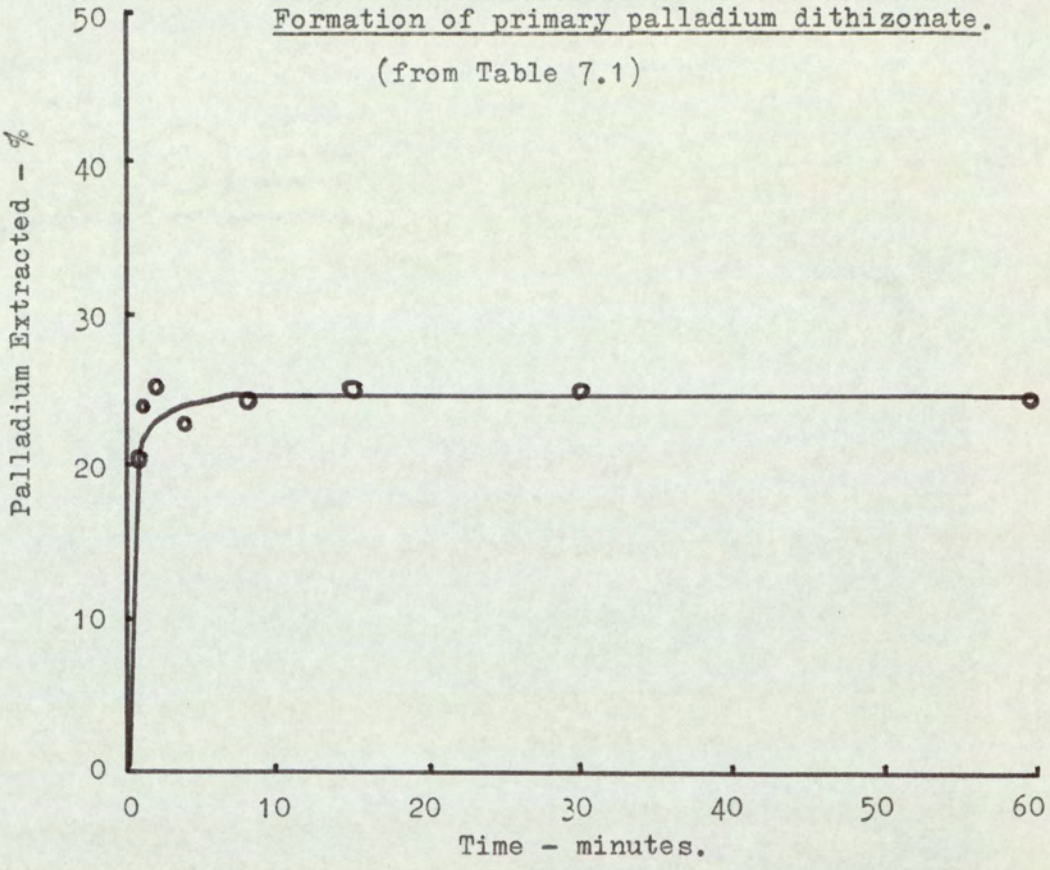
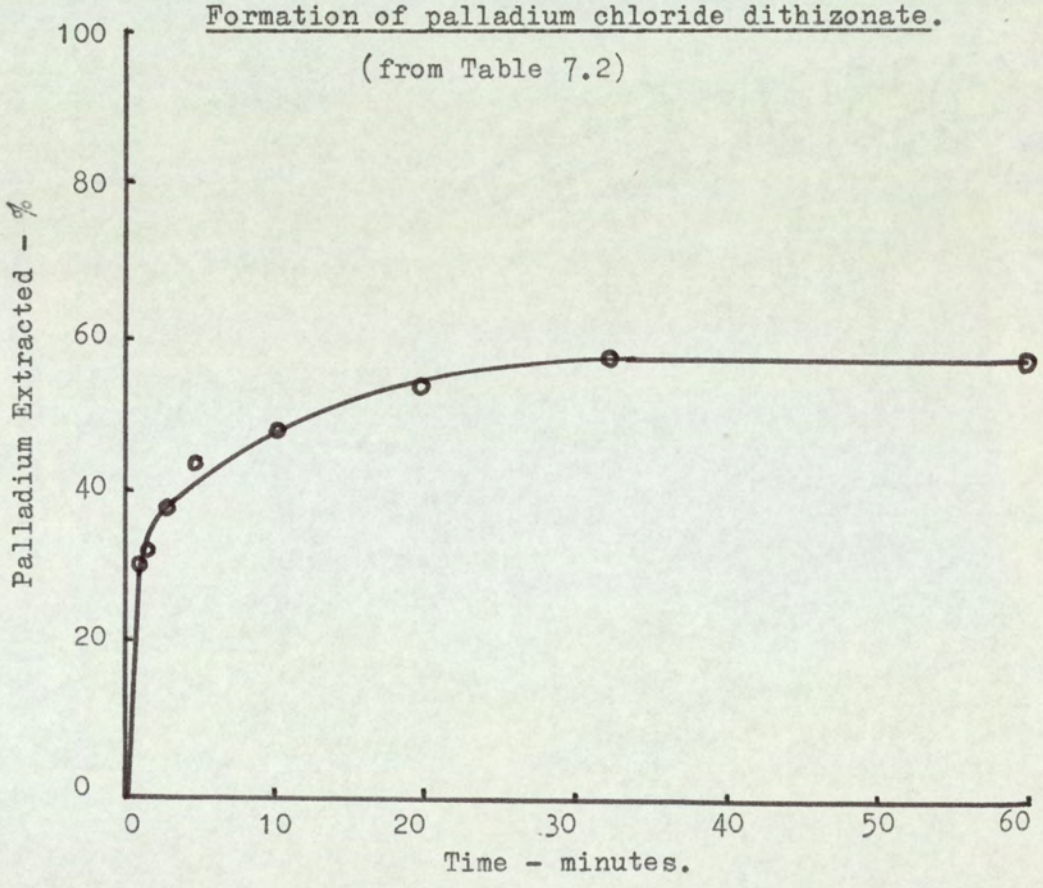


FIGURE 7.2

Formation of palladium chloride dithizonate.

(from Table 7.2)



The above complex was prepared by shaking 1.0 ml of a 10^{-3}M inactive palladium nitrate solution labelled with 1.0 ml of a 10^{-3}M sodium chloride solution (^{36}Cl) in 10 ml 1N sulphuric acid for 5 minutes with 5 ml of a 10^{-4}M solution of dithizone in chloroform. The organic layer was separated, filtered and 1.0 ml counted. The chlorine-36 standard was mixed with 1.0 ml of an inactive primary palladium dithizonate solution in chloroform prepared as above but omitting the sodium chloride solution.

Activity of 1.0 ml of primary palladium dithizonate solution
= 3.3 c.p.s.

Activity of 0.1 ml 10^{-3}M sodium chloride solution (^{36}Cl)
= 145.3 c.p.s.

Hence, this complex contains no chlorine.

2. Formation of palladium chloride dithizonate.

An aliquot of 1.0 ml of a 0.88×10^{-3}M palladium chloride solution (^{109}Pd) was diluted to 10 ml in 5N sulphuric acid and 0.01N chloride and shaken for various lengths of time with 5 ml of a 1.03×10^{-4}M solution of dithizone in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 7.2 and Figure 7.2. From the concentrations of the solutions used, a 1:1 complex corresponds to 58.4% extraction.

The above complex was prepared by shaking 1.0 ml of a 10^{-3}M inactive palladium chloride solution labelled with 1.0 ml of a 0.1M sodium chloride solution (^{36}Cl) in 10 ml 5N sulphuric acid for 30 minutes with 5 ml of a 10^{-4}M solution of dithizone in chloroform. The organic layer was separated, filtered and 1.0 ml counted. The chlorine-36 standard was mixed with 1.0 ml of an inactive palladium chloride dithizonate solution in chloroform prepared as above using inactive sodium chloride solution.

Activity of 1.0 ml palladium chloride dithizonate solution = 155 c.p.s.

Activity of 0.1 ml 10^{-3}M sodium chloride solution (^{36}Cl) = 151 c.p.s.

These results indicate that the organic phase was 10^{-4}N with respect to chloride, which corresponds to a palladium to chlorine ratio of 1:1.

Table 7.2

Shaking time, minutes		Activity of organic phase, c.p.s.	Palladium extracted, %
	3/4	18.4	32.8
	1½	18.7	33.3
	3	21.8	38.8
	5	25.4	45.2
	10	28.0	49.9
	20	30.4	54.2
	32	33.1	58.8
60	60	32.8	58.3

initial activity of aqueous phase = 56.2 c.p.s.

3. Formation of Secondary Palladium Dithizonate.

A 5 ml portion of a 10^{-4}M solution of palladium chloride dithizonate (^{109}Pd) prepared as in 2 was shaken for 2 - 3 minutes with 10 ml 1N sodium hydroxide solution. A colour change occurred and 1.0 ml of the organic layer was separated for counting:

Initial activity of 1.0 ml palladium chloride dithizonate solution = 10.2 c.p.s.

Activity of 1.0 ml of same solution after shaking with sodium hydroxide = 10.3 c.p.s.

The above experiment was repeated using a 10^{-4}M solution of palladium chloride dithizonate (^{36}Cl) prepared as in 2.

Activity of 1.0 ml palladium chloride dithizonate solution = 112.2 c.p.s.

Activity of 1.0 ml of same solution after shaking with sodium hydroxide = 3.6 c.p.s.

Hence, this complex has a palladium to dithizone ratio of 1:1 and contains no chlorine.

II. Reactions of the Palladium Dithizonate Complexes.

1. Primary Palladium Dithizonate.

The activity of a solution of primary palladium dithizonate in chloroform was unchanged by shaking for several hours with 5N sulphuric acid or 6N sodium hydroxide solution. However, shaking with hydrochloric acid resulted in slow conversion to the chloro complex. Solutions of palladium dithizonate in chloroform or carbon tetrachloride were dark green in colour and on evaporation gave small black crystals.

2. Palladium Chloride Dithizonate.

A solution of palladium chloride dithizonate in chloroform or carbon tetrachloride was unaffected by shaking with 5N sulphuric or 5N hydrochloric acids, but on shaking with even dilute sodium hydroxide solution was rapidly converted to secondary palladium dithizonate. The palladium concentration of the organic solution was unchanged (section I-3) and no free dithizone was observed in either phase, but if the aqueous phase, after shaking with an equal volume of 10^{-4}M palladium chloride dithizonate in chloroform, was acidified with nitric acid and treated with a few drops of 1M silver nitrate solution, the turbidity produced was similar to that produced by a 10^{-4}M sodium chloride solution under the same conditions. Solutions of palladium chloride dithizonate were red in colour and on evaporation gave small dark red crystals.

3. Secondary Palladium Dithizonate.

Solutions of secondary palladium dithizonate in chloroform were slowly reconverted to the chloro complex on shaking with dilute hydrochloric acid, with no change in the specific activity of the solution. Solutions of secondary palladium dithizonate were violet in colour and on evaporation gave small black crystals.

III. A kinetic study of the formation of the palladium dithizonate complexes.

1. The effect of hydrogen ion and chloride ion concentrations.

An aliquot of 1.0 ml of a 10^{-3}M solution of palladium chloride (^{103}Pd) in 0.1N hydrochloric acid was diluted to 10 ml and the hydrogen ion and chloride ion concentrations adjusted with hydrochloric and sulphuric acids. This solution was shaken for various lengths of time with 5 ml of a 10^{-4}M solution of dithizone in chloroform. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Tables 7.3 and 7.4 and Figures 7.3 and 7.4.

Table 7.3

Effect of hydrogen ion concentration on extraction from 0.01N chloride.

Shaking time,	0.01N acid		0.1N acid		1N acid		5N acid	
minutes	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
3/4	17.6	31.3	14.5	25.8	14.9	26.5	18.4	32.8
1½	19.2	34.2	17.5	31.2	17.6	31.4	18.7	33.2
3	22.2	39.6	17.8	31.7	18.3	32.6	21.8	38.8
5	23.1	41.1	19.6	34.9	19.6	34.9	25.4	45.2
10	23.4	41.6	19.4	34.5	21.6	38.4	28.0	49.7
20	22.0	39.2	21.6	38.5	24.0	42.7	30.4	54.2
35	27.5	49.0	23.8	42.5	25.8	46.0	33.1	59.0
60	28.0	49.8	24.2	43.0	27.1	48.2	32.8	58.4

initial activity of aqueous phase = 56.2 c.p.s.

FIGURE 7.3

Effect of hydrogen ion concentration on rate of extraction of palladium from 0.01N chloride.

(from Table 7.3)

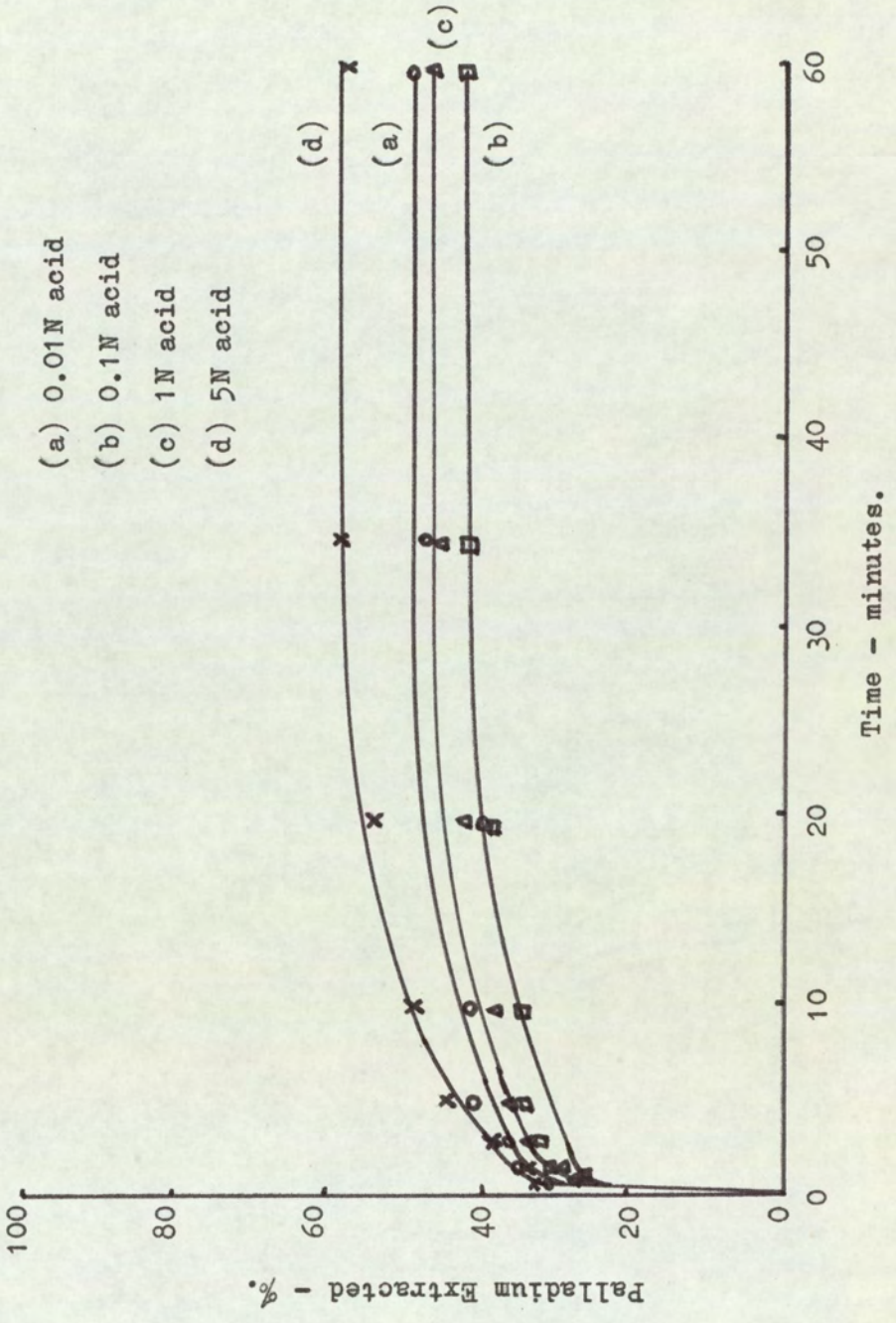


FIGURE 7.4

Effect of chloride ion concentration on extraction of palladium from 5N acid.

(from Tables 7.3 and 7.4)

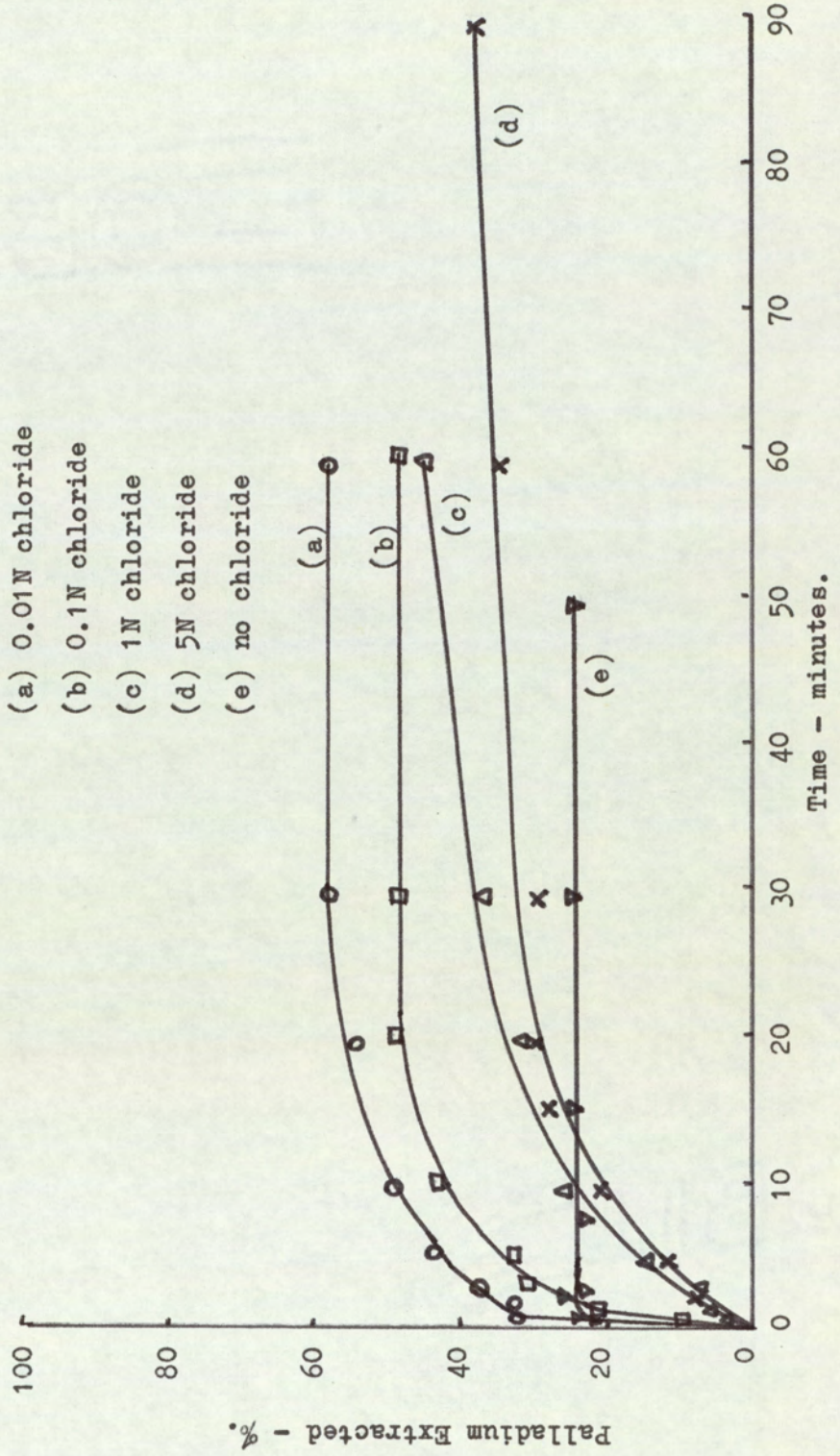


Table 7.4

Effect of chloride ion concentration on extraction from 5N acid.

Shaking time,	0.1N chloride		1N chloride		5N chloride	
minutes	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
3/4	5.1	9.5	1.8	3.4	-	-
1½	11.4	21.3	2.8	5.2	-	-
2	-	-	-	-	3.6	6.7
3	16.8	31.4	3.1	5.8	-	-
5	17.4	32.4	7.3	13.6	5.4	10.1
10	23.8	44.4	13.5	25.2	10.7	20.0
15	-	-	-	-	15.5	28.9
20	26.9	50.1	16.8	31.4	16.5	30.8
30	26.3	49.1	19.6	36.6	15.5	28.9
60	26.2	49.0	24.6	46.0	18.1	33.7
90	-	-	-	-	21.0	39.2

initial activity of aqueous phase = 53.6 c.p.s.

2. The Effect of Reagent Concentration.

(a) The extraction of palladium with dithizone in chloroform.

An aliquot of 1.0 ml of a palladium chloride solution (^{103}Pd) in 0.1N hydrochloric acid was diluted to 10 ml in 0.1N sulphuric acid and shaken for various lengths of time with 5 ml of a solution of dithizone in chloroform. The molar concentration of dithizone in the organic phase was equal to that of the palladium in the aqueous phase. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The results are given in Table 7.5 and Figures 7.5 and 7.7. (Visible precipitation occured in the experiment with 10^{-3}M dithizone.)

Table 7.5

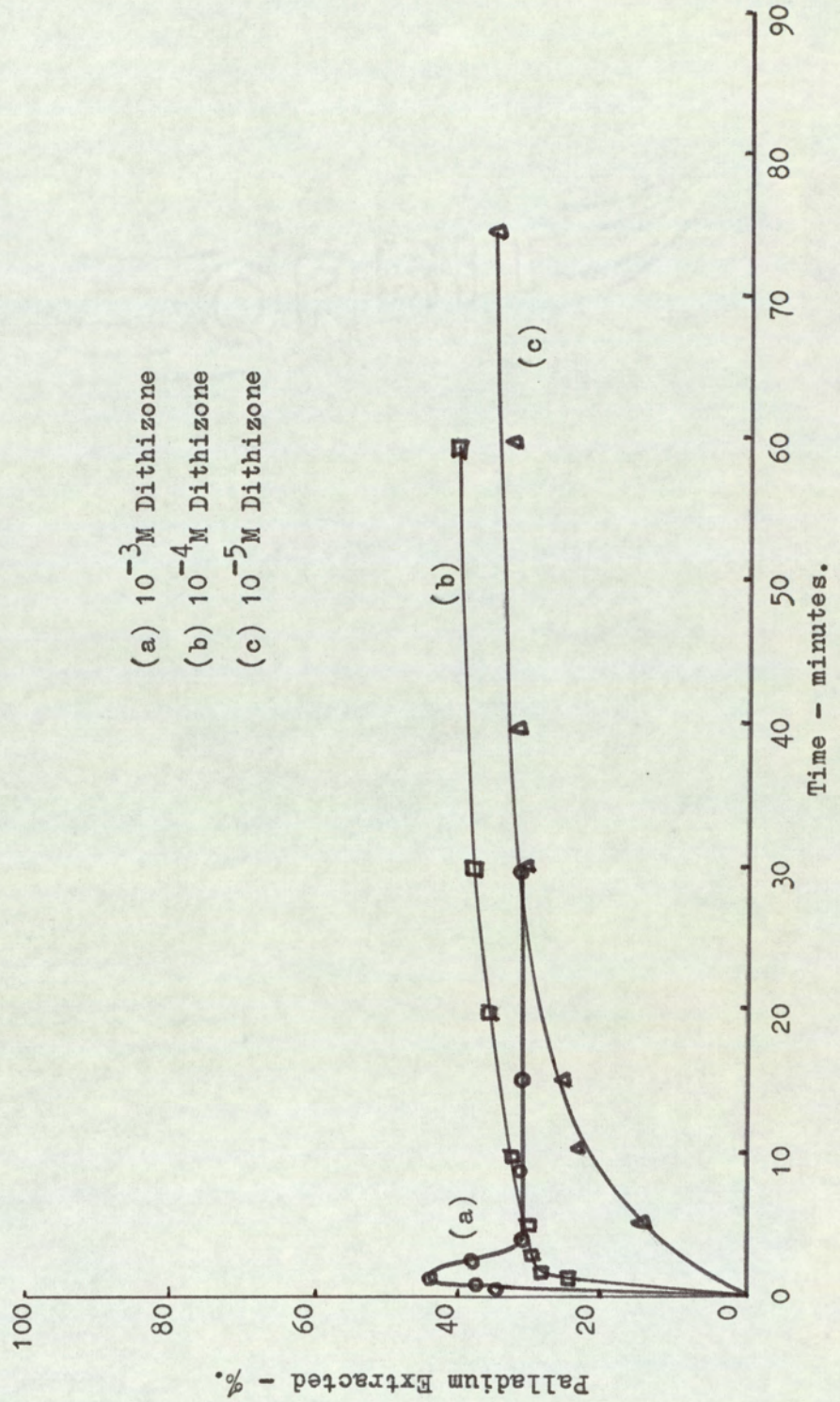
Shaking time,	10^{-3}M H_2Dz		10^{-4}M H_2Dz		10^{-5}M H_2Dz	
minutes	c.p.s.	% ext.	c.p.s.	% ext.	c.p.s.	% ext.
1/4	187.3	35.9	-	-	-	-
1/2	203.0	39.0	-	-	-	-
3/4	-	-	136.0	26.2	-	-
1	235.5	45.2	-	-	-	-
1½	-	-	153.6	29.5	-	-
2	203.6	39.0	-	-	-	-
3	-	-	159.2	30.6	-	-
4	163.0	31.4	-	-	-	-
5	-	-	164.2	31.5	81.6	15.7
8	170.0	32.7	-	-	-	-
10	-	-	174.1	33.4	124.6	24.0
15	165.8	32.1	-	-	131.1	25.2
20	-	-	189.7	36.4	-	-
30	168.0	32.3	200.0	38.4	166.2	31.9
40	-	-	-	-	168.4	32.3
60	-	-	213.9	41.2	173.6	33.3
75	-	-	-	-	188.0	36.1
90	-	-	-	-	203.1	39.0

initial activity of aqueous phase = 520 c.p.s.

FIGURE 7.5

Effect of concentration on extraction of palladium with dithizone in chloroform.

(from Table 7.5)



(b) The extraction of palladium with dithizone in carbon tetrachloride.

The experiment was carried out as in (a) replacing dithizone in chloroform by dithizone in carbon tetrachloride. The results are given in Table 7.6 and Figures 7.6 and 7.7, along with the results from Table 5.6 (Ch.5.II.2a). (Visible precipitation occurred in the experiment with 10^{-4}M dithizone.)

Table 7.6

Shaking time, minutes	10^{-4}M H_2Dz		10^{-5}M H_2Dz	
	c.p.s.	% extraction	c.p.s.	% extraction
½	42.5	25.2	-	-
1	45.3	27.0	21.1	12.6
2	55.6	33.1	32.3	19.2
3	66.7	39.6	-	-
4	-	-	40.9	24.3
5	62.1	37.0	-	-
6	-	-	41.8	24.9
10	66.6	39.7	48.5	28.9
15	-	-	51.8	30.8
20	65.9	39.2	53.6	31.8
30	58.8	34.9	59.0	35.1

initial activity of aqueous phase = 168 c.p.s.

FIGURE 7.6

(from Tables 5.6 and 7.6)

Effect of concentration on extraction of palladium with dithizone in carbon tetrachloride.

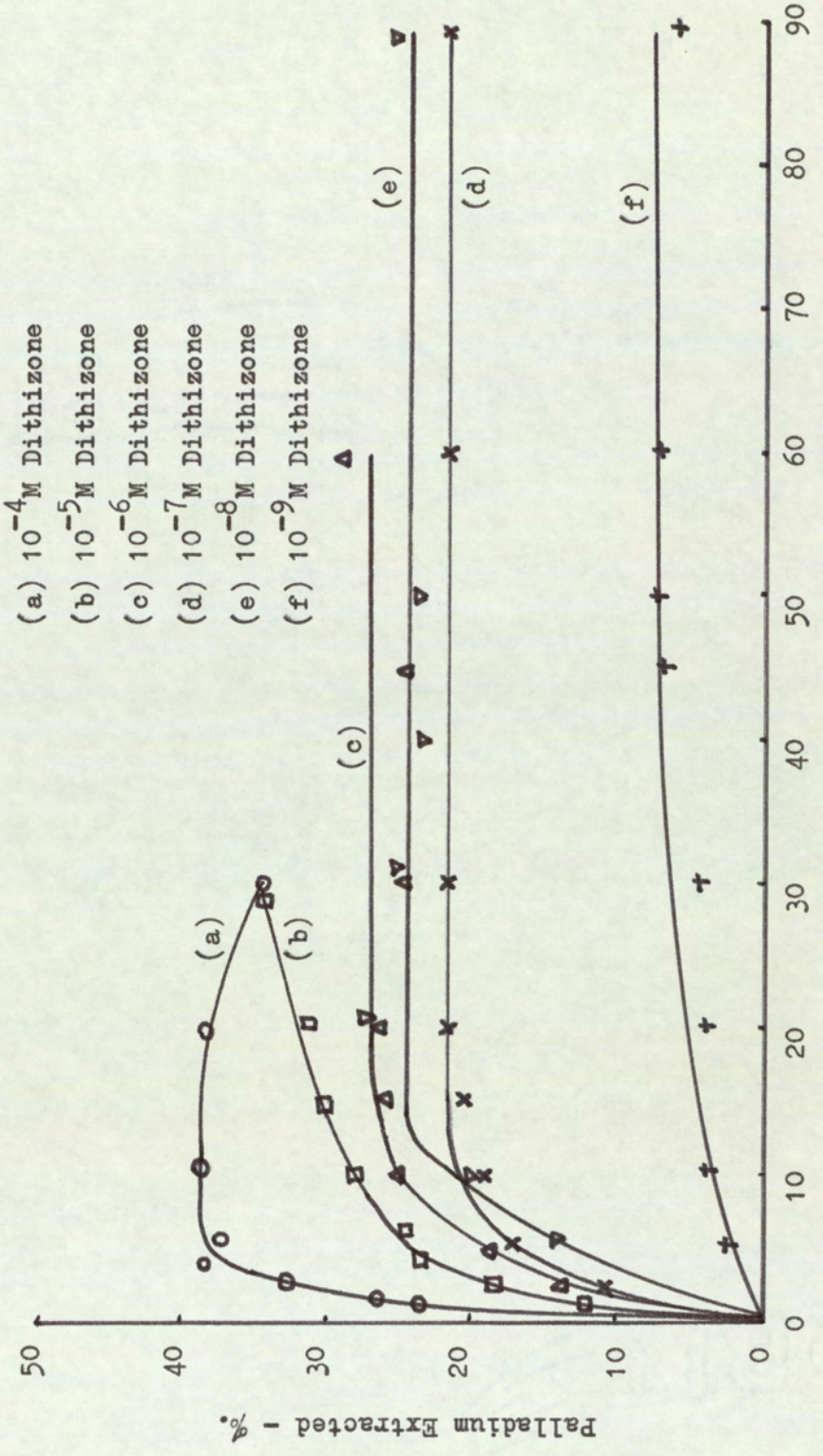
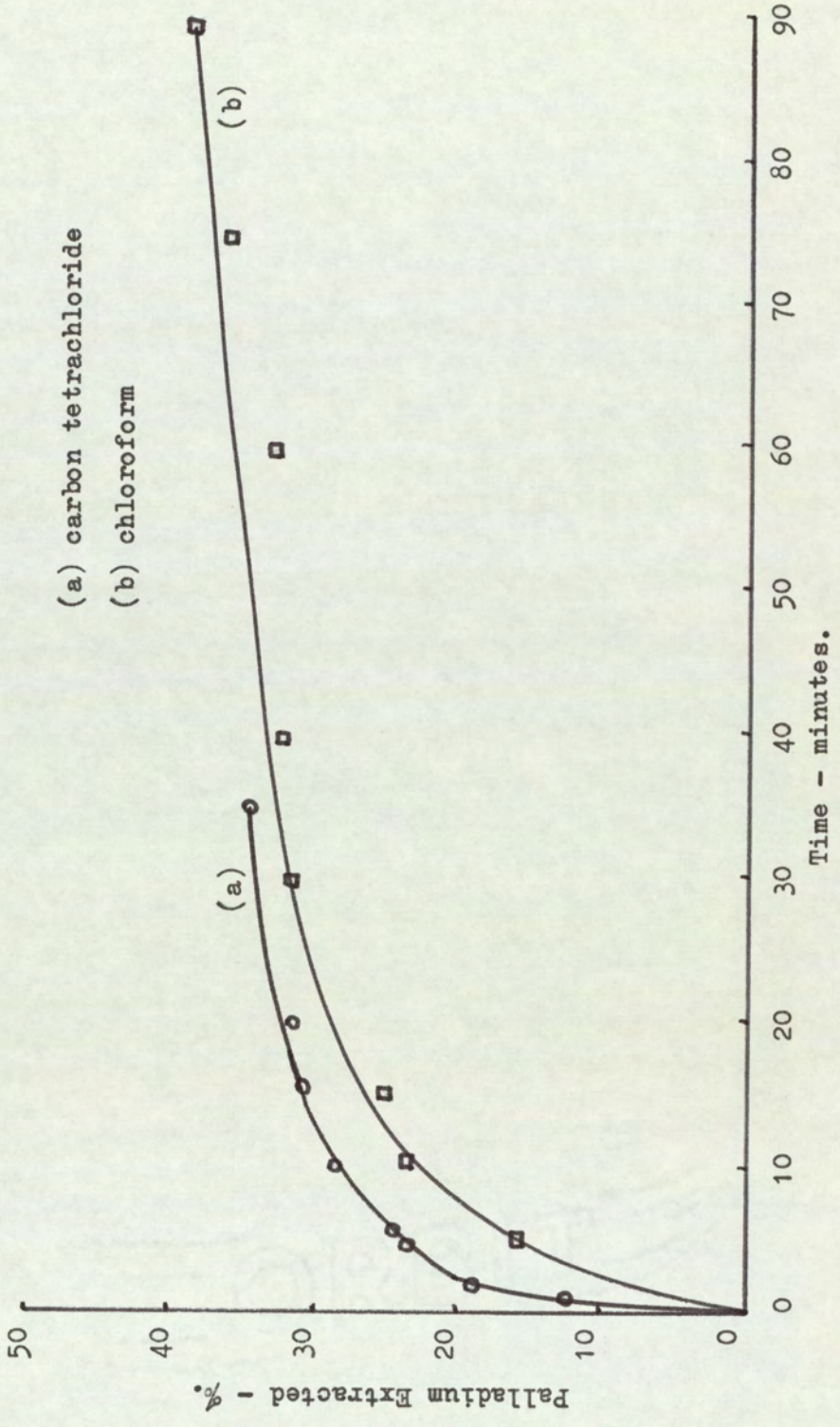


FIGURE 7.7

(from Tables 7.5 and 7.6)

Comparison of chloroform and carbon tetrachloride.

(10^{-5}M dithizone)



IV. Determination of the Partition Coefficients of the Palladium Dithizonate Complexes.

Primary palladium dithizonate in chloroform was prepared by shaking 10.0ml of a 10^{-2}M palladium nitrate solution (^{103}Pd) in 100ml 5N sulphuric acid for 5 minutes with 50ml of a 10^{-3}M solution of dithizone in chloroform.

Primary palladium dithizonate in carbon tetrachloride was prepared as above using a 5×10^{-4}M solution of dithizone in carbon tetrachloride.

Palladium chloride dithizonate in chloroform was prepared by shaking 10.0ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 100ml 5N sulphuric and 0.01N hydrochloric acids for 30 minutes with 50ml of a 10^{-3}M solution of dithizone in chloroform.

Palladium chloride dithizonate in carbon tetrachloride was prepared as above using a 10^{-3}M palladium chloride solution and a 10^{-4}M solution of dithizone in carbon tetrachloride.

Secondary palladium dithizonate in chloroform was prepared by shaking the above solution of palladium chloride dithizonate in chloroform with 10 ml 1N sodium hydroxide solution for 2 - 3 minutes.

Secondary palladium dithizonate in carbon tetrachloride was prepared by shaking the above solution of palladium chloride dithizonate in carbon tetrachloride for 2 - 3 minutes with 10 ml of a 1N sodium hydroxide solution.

A 10 ml portion of each of the above solutions was shaken for about 5 minutes with 500 ml distilled water. The organic layer was separated, filtered and 3.0 ml evaporated for counting. The aqueous layer was filtered through a Whatman No. 42 filter paper and then shaken for a further 5 minutes with 10 ml of the pure solvent. The organic layer was separated for counting as before. Alternatively, the absorbance of the two organic layers was measured at a wavelength suitable for the complex under investigation. The value of the partition

coefficient, P, was calculated using equation 2.38 (Ch.2.II.6b) and the results are given in Tables 7.7 to 7.12.

Table 7.7

Primary palladium dithizonate in chloroform.

Absorbance of first organic layer at 450 nm.	Absorbance of second organic layer at 450 nm.	Ratio of concs. of organic layers	P
25.0	0.034	740	37,000
24.0	0.027	890	44,500
24.6	0.040	615	30,650
Activity of first organic layer, c.p.s.	Activity of second organic layer, c.p.s.		
478	0.63	760	38,000
453	0.64	710	35,500
565	0.75	755	37,750
			mean P = 37,230

Table 7.8

Primary palladium dithizonate in carbon tetrachloride.

Absorbance of first organic layer at 450 nm.	Absorbance of second organic layer at 450 nm.	Ratio of concs. of organic layers	P
10.4	0.066	158	7,900
11.4	0.074	154	7,700
11.4	0.068	168	8,400
Activity of first organic layer, c.p.s.	Activity of second organic layer, c.p.s.		
17.4	0.12	145	7,250
17.4	0.11	158	7,900
15.0	0.10	150	7,500
			mean P = 7,775

Table 7.9

Palladium chloride dithizonate in chloroform.

Absorbance of first organic layer at 490 nm.	Absorbance of second organic layer at 490 nm.	Ratio of concs. of organic layers	P
19.9	0.130	153	7,650
19.0	0.108	176	8,800
22.0	0.140	157	7,850
Activity of first organic layer, c.p.s.	Activity of second layer, c.p.s.		
52.2	0.28	186	9,300
55.2	0.37	149	7,450
57.6	0.37	156	7,800
			mean P = 8,140

Table 7.10

Palladium chloride dithizonate in carbon tetrachloride.

Absorbance of first organic layer at 490 nm.	Absorbance of second organic layer at 490 nm.	Ratio of concs. of organic layers	P
1.64	0.045	36	1,800
1.64	0.035	47	2,350
Activity of first organic layer, c.p.s.	Activity of second organic layer, c.p.s.		
24.0	0.70	34	1,700
24.0	0.80	30	1,500
21.1	0.50	42	2,100
45.0	0.10	45	2,250
45.0	0.10	45	2,250
			mean P = 1,990

Table 7.11

Secondary palladium dithizonate in chloroform.

Absorbance of first organic layer at 550 nm.	Absorbance of second organic layer at 550 nm.	Ratio of concs. of organic layers	P
5.70	0.030	190	9,500
5.85	0.032	183	9,150
5.56	0.032	177	8,850
Activity of first organic layer, c.p.s.	**Activity of second organic layer, c.p.s.**		
62.3	0.28	222	11,100
62.2	0.32	194	9,700
62.6	0.30	207	10,350
			mean P = 9,775

Table 7.12

Secondary palladium dithizonate in carbon tetrachloride.

Absorbance of first organic layer at 500 nm.	Absorbance of second organic layer at 500 nm.	Ratio of concs. of organic layers	P
0.548	0.017	32	1,600
0.548	0.017	32	1,600
0.519	0.017	30	1,500
Activity of first organic layer, c.p.s.	**Activity of second organic layer, c.p.s.**		
28.0	1.5	21	1,050
30.0	1.2	25	1,250
29.0	1.0	29	1,450
			mean P = 1,410

The partition coefficients are summarised in Table 7.13.

Table 7.13

Complex	P in chloroform	P in carbon tetrachloride
$Pd(HDz)_2$	37,230	7,775
Pd.Cl(HDz)	8,140	1,990
PdDz	9,775	1,410

V. The Solubilities of the Palladium Dithizonate Complexes.

1. Primary Palladium Dithizonate in Carbon Tetrachloride.

A sample of solid primary palladium dithizonate (^{103}Pd) was prepared by evaporation of its chloroform solution. This was shaken with carbon tetrachloride for 1 hour and then allowed to stand with occasional stirring for several hours. The activity of 3.0 ml of the filtered solution was measured.

Activity of 3.0 ml saturated primary palladium dithizonate solution = 17.4, 17.4, 15.0 c.p.s.

mean = 16.6 c.p.s.

Activity of 1.0 ml 0.88×10^{-2}M palladium chloride solution = 171.1 c.p.s.

Hence, solubility of primary palladium dithizonate = 2.8×10^{-4}M.

2. Palladium Chloride Dithizonate in Carbon Tetrachloride.

A 5 ml portion of 10^{-4}M dithizone in carbon tetrachloride was shaken for 30 minutes with 1.0 ml of a 10^{-3}M palladium chloride solution (^{103}Pd) in 10 ml 0.1N sulphuric acid. At this concentration precipitation occurs. The organic layer was separated, filtered and 3.0 ml evaporated for counting.

Activity of 3.0 ml organic phase = 621, 666, 659, 688 c.p.s.

mean = 659 c.p.s.

Activity of 1.0 ml 1.02×10^{-3}M palladium chloride solution = 2739 c.p.s.

Hence, solubility of palladium chloride dithizonate = 8.2×10^{-5}M.

3. Palladium Chloride Dithizonate in Chloroform.

A 5 ml portion of 10^{-3}M dithizone in chloroform was shaken for 30 minutes with 1.0 ml of a 10^{-2}M palladium chloride solution (^{103}Pd) in 10 ml 5N sulphuric acid. At this concentration precipitation occurs. The organic layer was separated, filtered and 3.0 ml evaporated for counting.

Activity of 3.0 ml organic phase = 119.5, 124.2, 121.1, 122.8 c.p.s.

mean = 121.9 c.p.s.

Activity of 1.0 ml 0.88×10^{-2}M palladium chloride solution

= 633 c.p.s.

Hence, solubility of palladium chloride dithizonate = 5.5×10^{-4}M.

4. Secondary Palladium Dithizonate in Carbon Tetrachloride.

A sample of solid secondary palladium dithizonate was prepared by evaporation of its chloroform solution and shaken with carbontetrachloride as in 1.

Activity of 3.0 ml saturated secondary palladium dithizonate solution

= 2.7, 3.0, 2.9 c.p.s.

mean = 2.87 c.p.s.

Activity of 1.0 ml 0.88×10^{-2}M palladium chloride solution

= 167 c.p.s.

Hence, solubility of secondary palladium dithizonate = 5.1×10^{-5}M.

Knowing the solubilities of the complexes in carbon tetrachloride and the partition coefficients between this solvent and water, and between chloroform and water, it is possible to calculate the solubilities in water and chloroform from the equations:

$$S_{H_2O} = \frac{S_{CCl_4}}{P_{CCl_4}} \qquad \text{and} \qquad S_{CHCl_3} = S_{H_2O} \times P_{CHCl_3}.$$

As the solubility of palladium chloride dithizonate is also known in chloroform it is possible to calculate its solubility in water from the equation:

$$S_{H_2O} = \frac{S_{CHCl_3}}{P_{CHCl_3}}.$$

Using these calculated values, Table 7.14 was compiled. The solubilities of the primary and secondary complexes in chloroform agreed with previous observations.

Table 7.14

Complex	Solvent		
	Chloroform	Carbon tetrachloride	Water
$Pd(HDz)_2$	1.3×10^{-3}M	2.8×10^{-4}M	3.6×10^{-8}M
Pd.Cl(HDz)	5.5×10^{-4}M	8.2×10^{-5}M	4.1×10^{-8}M (CCl_4) 6.9×10^{-8}M ($CHCl_3$)
Pd.Dz	3.5×10^{-4}M	5.1×10^{-5}M	3.6×10^{-8}M

VI. The Ultraviolet and Visible Spectra of the Palladium Dithizonate Complexes.

Solutions of the three complexes in both chloroform and carbon tetrachloride were prepared as in section IV, using inactive palladium solutions. The spectra of each of the above solutions were measured, after dilution, in a 10 mm cell against the constituent solvent. The results are given in Figures 7.9 to 7.11. The spectra of dithizone in the two solvents are given in Figure 7.8. The extinction coefficients of the complexes are summarised in Table 7.15. The solutions of the complexes in chloroform were visibly different from those in carbon tetrachloride, the colours being clearer and more attractive.

Table 7.15

Complex	ε_{max} in chloroform	ε_{max} in carbon tetrachloride
$Pd(HDz)_2$	$\varepsilon_{280} = 4.2 \times 10^4$ $\varepsilon_{450} = 3.9 \times 10^4$ $\varepsilon_{630} = 3.5 \times 10^4$	$\varepsilon_{300} = 2.2 \times 10^4$ $\varepsilon_{450} = 3.6 \times 10^4$ $\varepsilon_{650} = 2.8 \times 10^4$
Pd.Cl(HDz)	$\varepsilon_{260} = 2.9 \times 10^4$ $\varepsilon_{490} = 2.6 \times 10^4$	$\varepsilon_{290} = 2.6 \times 10^4$ $\varepsilon_{490} = 1.9 \times 10^4$
PdDz	$\varepsilon_{280} = 2.5 \times 10^4$ $\varepsilon_{550} = 2.0 \times 10^4$	$\varepsilon_{230} = 9.5 \times 10^3$ $\varepsilon_{500} = 1.8 \times 10^4$

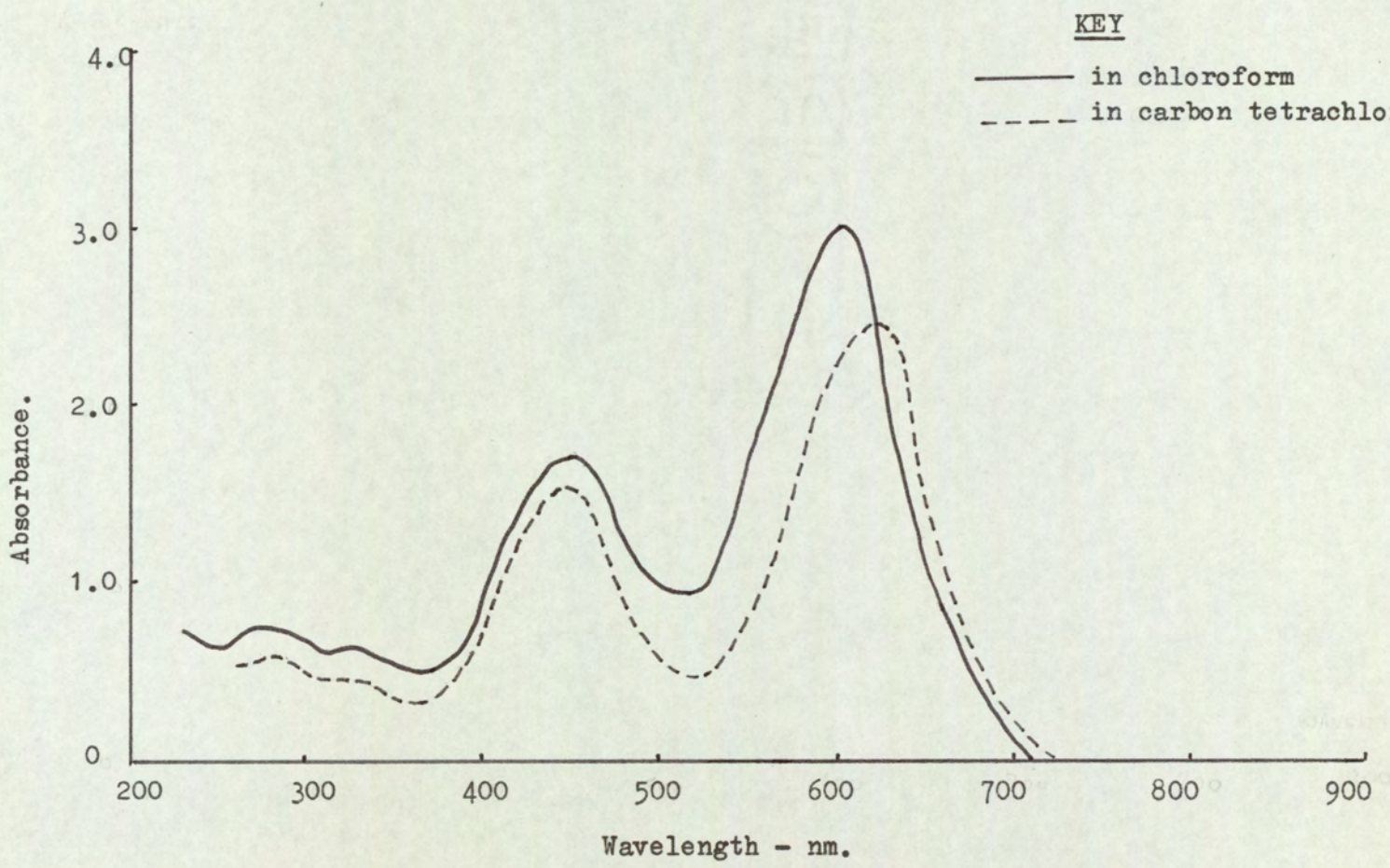


FIGURE 7.8

Spectrum of Dithizone.
(7.5×10^{-5} M)

FIGURE 7.9

Spectrum of Palladium dithizonate.

(3.7×10^{-5} M)

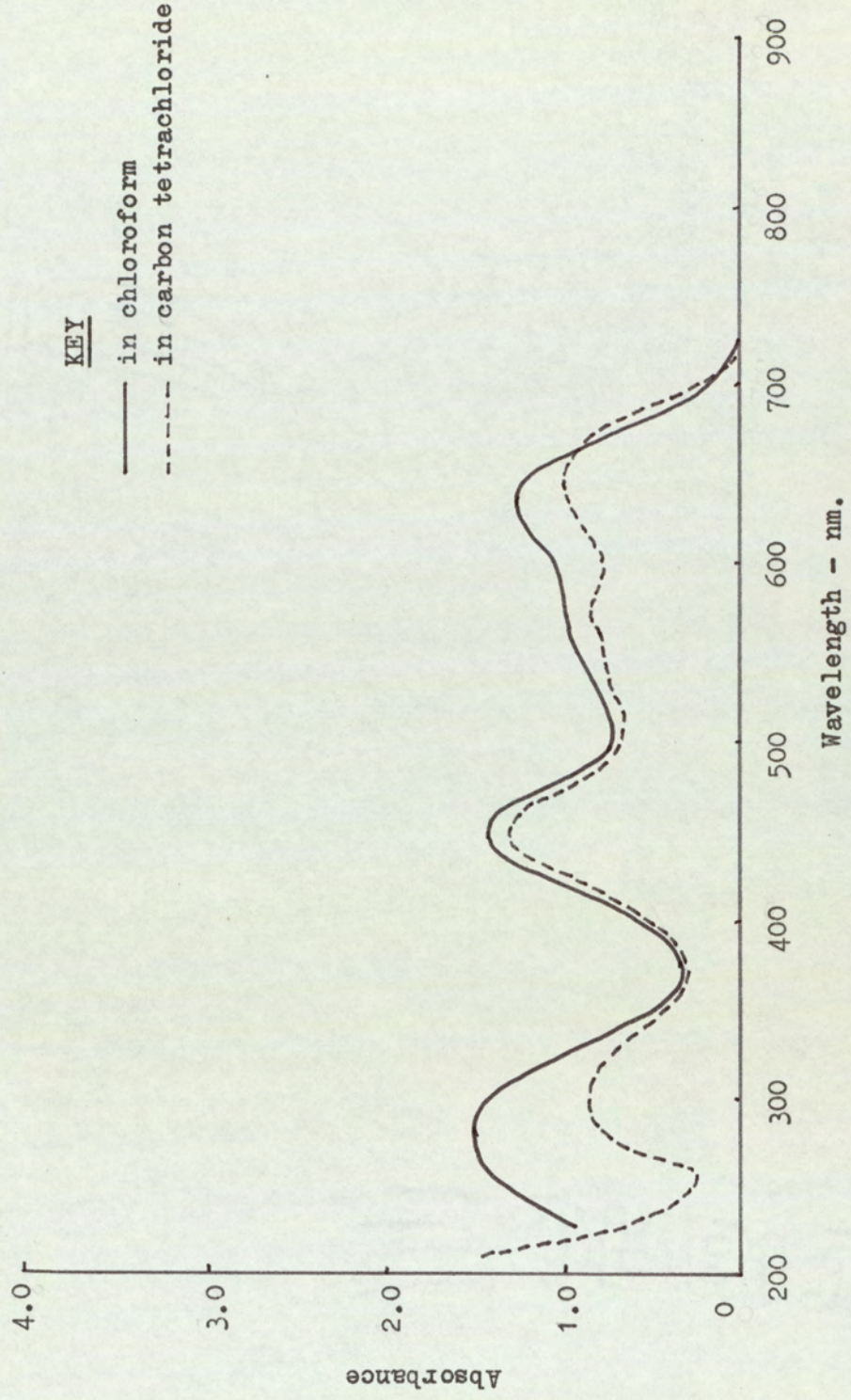


FIGURE 7.10

Spectrum of palladium chloride dithizonate.

(3.7×10^{-5}M)

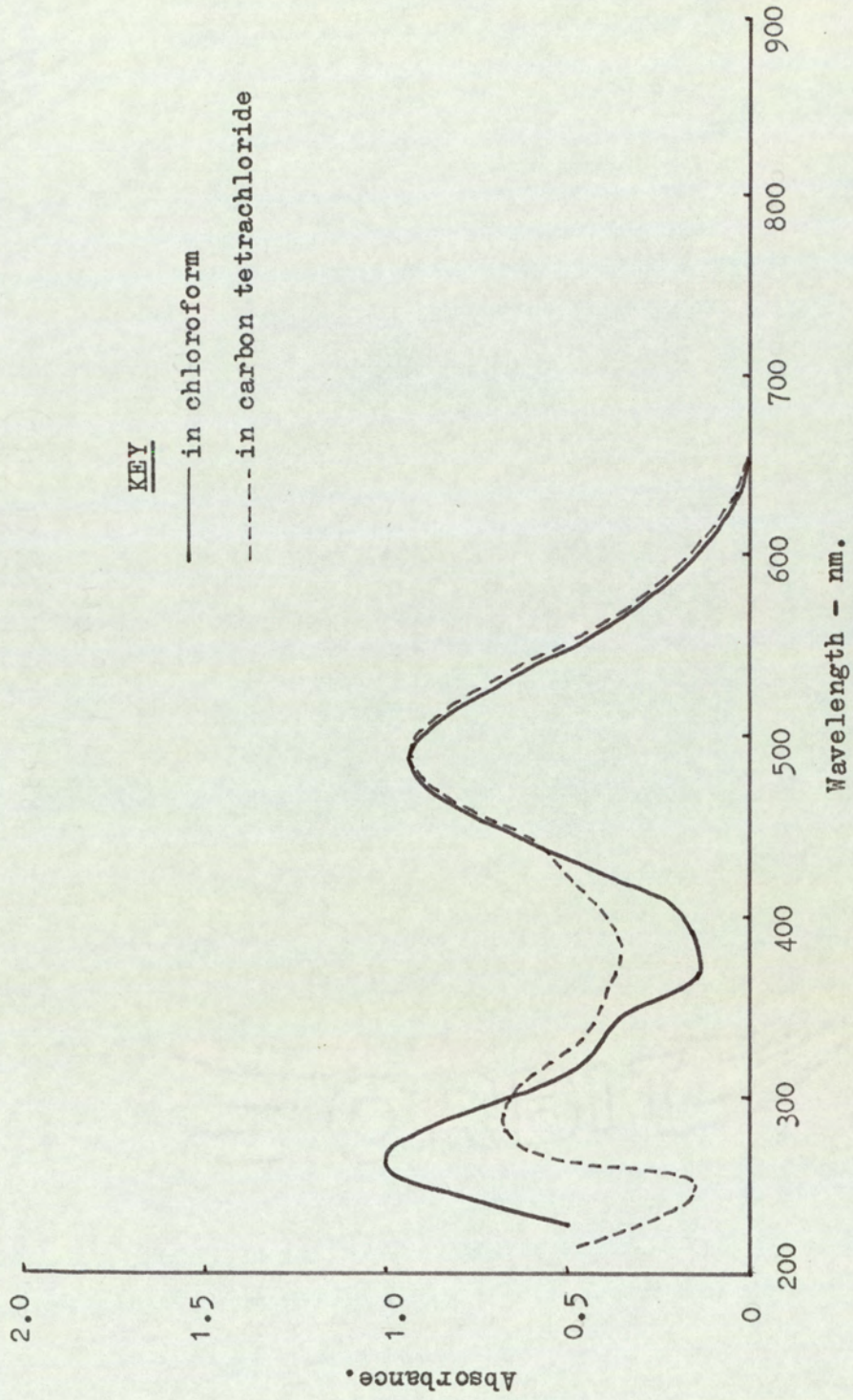
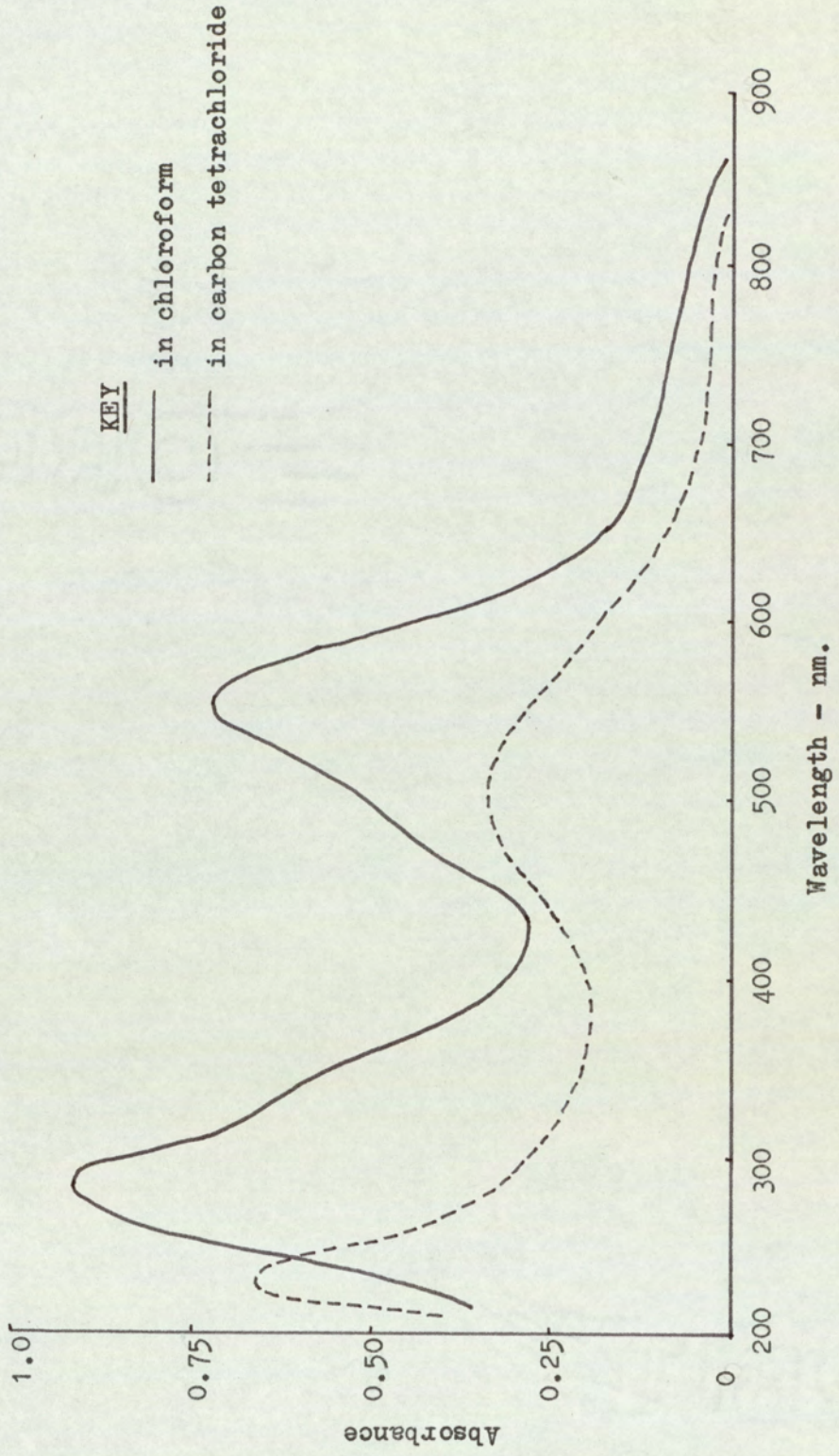


FIGURE 7.11

Spectrum of secondary palladium dithizonate.

(3.7×10^{-5}M)



VII. Analysis of the Palladium Dithizonate Complexes.

Samples of the three complexes in solid form, prepared by evaporation of their chloroform solutions, were submitted to elemental analysis as in Chapter 3, section XII. The results are given in Table 7.16.

Table 7.16

Complex	C %	H %	N %	S %	Cl %
$Pd(HDz)_2$:					
found:	51.04	3.26	19.95	10.52	0
calculated for $Pd(HDz)_2$:	50.5	3.57	18.2	10.3	0
Pd.Cl(HDz):					
found:	36.56	3.10	12.31	9.46	7.45
calc. for Pd.Cl(HDz):	39.4	2.80	14.1	8.05	8.90
calc. for $Pd.Cl(HDz).H_2O$:	37.6	3.13	13.5	7.70	8.55
PdDz:					
found:	40.45	3.82	14.19	-	-
calc. for PdDz:	43.4	2.80	15.5	-	-
calc. for $PdDz.H_2O$:	41.3	3.18	14.8	-	-
calc. for $PdDz.2H_2O$:	39.4	3.54	14.15	-	-

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