SOME ASPECTS OF SUBSTOICHIOMETRY WITH SPECIAL REFERENCE TO GOLD

by

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Summary

The object of this research was to investigate the applicability of "Substoichiometry" to the development of very simple, selective radio-chemical methods for the determination of trace concentrations of gold in matrices that were considered to be of industrial significance.

Neutron activation (N.A.A.), and radio-active isotope-dilution analysis (I.D.A.) methods based on the solvent extraction of gold diethyldithiocarbamate from acidic solution using a substoichiometric amount of the copper (II) or zinc (II) salt of diethyldithiocarbamic acid in chloroform have been developed. The procedures have been applied to the determination of gold in high purity lead, the rock W1, and kale (N.A.A.), gold-bearing ores (I.D.A.), and gold-doped semi-conductor grade silicon (N.A.A. and I.D.A.). Amounts of gold down to 2×10^{-10}g (N.A.A.), and 5×10^{-7}g/20ml of solution (I.D.A.) were determined.

The composition of the gold diethyldithiocarbamate extracted into chloroform was found to be dependent on the experimental conditions of the extraction. From acidic solution with substoichiometric conditions (i.e. an excess of gold), a gold chelate of molar ratio gold to chlorine to diethyldithiocarbamate of 1:2:1 was extracted, and in the presence of a reductant, (ascorbic acid), as used in the I.D.A. method, a univalent gold diethyldithiocarbamate irrespective of whether an excess of gold, or chelating agent was used in the extraction. However in the presence of an excess of chelating agent, but in the absence of a reductant, a series of gold chelates

of molar ratio gold to diethyldithiocarbamate of 1:2 was found to be formed; the distribution ratio of the gold between the chloroform and aqueous phase being dependent on the hydrogen, and chloride ion concentrations of the latter phase.

Preliminary studies of the reaction of gold with dithizone in chloroform also revealed the existence of a series of gold dithizonates, the composition of which were dependent upon the experimental conditions.

Preface

The work described in this thesis was carried out at the University of Aston in Birmingham from January 1965 to October 1967 under the supervision of Dr. G.B. Briscoe, B.Sc., M.Sc., A.R.I.C., and Dr. M. Williams, B.Sc., F.R.I.C., to whom I would like to express my thanks for their encouragement and many helpful discussions.

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My sincere thanks are also due to Mrs. G.E. Chare, and Mr. P. Bill for their invaluable technical assistance, and to the University for appointing me as a Research Assistant, without which this research would not have been possible.

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Introduction

The research group was formed in January, 1965 to investigate the applicability of "Substoichiometry" to the development of very simple, selective radio-chemical methods for the determination of trace concentrations of a number of elements in matrices that were considered to be of industrial significance. The technique of substoichiometry was proposed by Starý and Růžička,[1,2] and the authors had demonstrated its application to the determination of a number of elements.[3]

On appointment as a Research Assistant of the University, the topic I was given to study was "The Substoichiometric Determination of Gold by Radio-chemical Methods." The findings of this research are presented in this thesis, and three papers concerned with the research have been published.[4,5,6] A paper was also presented at the Conference on the Application of Physico-Chemical Methods in Chemical Analysis held in Budapest in April, 1966 under the auspices of I.U.P.A.C.[7]

Chapter 1

Theory

I. Activation Analysis

The basic principles of activation analysis were laid by Hevesy and Levi[8] in 1936. After the Second World War, activation analysis became one of the most powerful tools in analytical chemistry. The monograph published by Koch[9] in 1960 contains about 600 references to original papers from the field of activation analysis, and that of Schulze[10] two years later, lists at least 1,000 such references. A number of excellent review papers have also been published[11-17] including substoichiometric methods for the determination of a number of elements (excluding gold).[3]

In this research thermal neutron irradiations were used, so the theory will be restricted to that for neutron activation analysis. Thermal neutrons have been more widely used for activation than any other particle for three main reasons. Firstly the absence of an energy threshold for neutron reactions allows neutrons of very low energy to react with nuclei. Secondly most nuclei have high thermal neutron activation cross sections, and thirdly experimental nuclear reactors are available for neutron irradiations.

Neutron activation analysis is based on the formation of active nuclides as a result of nuclear reaction between neutrons, and the stable isotopes of the element present in the sample. When an active nuclide is produced at a constant rate the overall rate of formation of the active nuclide is given by the difference between its constant rate of production, P, and the rate of its decay, λN, (λ, the decay constant, N, the number of active atoms).

$$\frac{dN}{dt} = P - \lambda N. \qquad \ldots \quad 1).$$

The solution of 1) gives

$$N = \frac{P}{\lambda}(1-e^{-\lambda t}) + N_o e^{-\lambda t} . \qquad \ldots \quad 2).$$

The term $(1-e^{-\lambda t})$ is known as the saturation factor.

Since the number of active atoms, N_o, initially present is zero,

$$N = \frac{P}{\lambda}(1-e^{-\lambda t}). \qquad \ldots \quad 3).$$

The rate of disintegration, A, of the active nuclei is given by

$$A = \lambda N \text{ d.p.s.} \qquad \ldots \quad 4).$$

Substituting 4) in 3) gives

$$A = P(1-e^{-\lambda t}) \text{ d.p.s.} \qquad \ldots \quad 5).$$

The rate of production, P, of active nuclei is directly proportional to the neutron flux, f, (neutrons, cm^{-2}, sec^{-1}), the neutron activation cross section for the reaction, σ, (barns x 10^{-24} = cm^2) the fractional isotopic abundance, ϕ, and the number of stable atoms of the element to be determined, N, i.e.

$$P = f\sigma\phi N \qquad \ldots \quad 6).$$

Substituting in 5):

$$A = f\sigma\phi N(1-e^{-\lambda t}) \text{ d.p.s.} \qquad \ldots \quad 7).$$

The number of stable atoms of the element can be obtained from the weight, y, and atomic weight, M, of the element, and the known value of Avogadro's number, N_A.

$$N = \frac{yN_A}{M} . \qquad \ldots \quad 8).$$

Therefore from 7)

$$A = f\sigma\phi \frac{yN_A}{M} (1-e^{-\lambda t}) \text{ d.p.s.} \quad \ldots 9).$$

If the activity of the active nuclide is not determined until a time, t_1, after the irradiation has ended, a decay term, $e^{-\lambda t_1}$, must be introduced.

Hence

$$A = f\sigma\phi \frac{yN_A}{M} (1-e^{-\lambda t}) e^{-\lambda t_1} \text{ d.p.s.} \quad \ldots 10).$$

The above relationship is valid provided:

a. The flux of neutrons does not change during irradiation.

b. The number of active atoms formed during irradiation is negligible when compared with the number of primary target atoms.

c. The active nuclide formed does not react with the neutrons, and

d. the self-shielding effect is negligible.

Rearranging 10) gives the weight, y, of element to be determined, as

$$y = \frac{AMe^{\lambda t_1}}{f\sigma\phi N_A(1-e^{-\lambda t})} \quad \ldots 11).$$

The values of the atomic weight, M, fractional isotopic abundance, ϕ, Avogadro's number, N_A, decay constant, λ, and times, t and t_1, are known to a high degree of precision. However the neutron flux, f, and neutron activation cross section, σ, are not so precisely known, and to determine the absolute disintegration rate, A, 4π counting techniques are necessary unless the decay characteristics of the active nuclide are very simple in which case it is often possible to use co-incidence methods.

Absolute methods have been used, but to overcome the difficulties most workers favour the comparison technique in which a known weight of the element to be determined, (standard), is simultaneously irradiated with a known weight of the matrix, (sample), in which the element is to be determined. The requirement of knowing the precise values of the terms in 11) is then overcome. The only assumptions made are that the neutron flux incident on the sample and standard is the same, and the degree of self-shielding is similar.

Using the comparison method the activity, A, of the active isotope of the element to be determined in the sample, and in the simultaneously irradiated standard, A_s, is directly proportional to the weight, y, of element present in the sample, and standard, y_s.

i.e. $y : y_s = A : A_s$,

or $$y = y_s \frac{A}{A_s} . \qquad \ldots 12).$$

To perform neutron activation analysis successfully the following factors must be considered.

a. Activation of the sample.

A suitable sample weight must be selected, which will be governed by the expected content of the element to be determined, the nuclear characteristics of the stable target nuclides, the available neutron flux, and the time necessary for the radio-chemical separation after irradiation. The main criteria is that after the irradiation and processing, sufficient of the required active isotope is present for an accurate determination by the counting technique selected.

For a given sample weight and neutron flux, the period of irradiation will also be governed by the nuclear characteristics of the stable target nuclides, and the time necessary for the radio-chemical separation after irradiation. The period of irradiation and sample weight are therefore inter-related.

Consideration must also be given to the possible formation of other active nuclides produced during the irradiation, as it may be necessary to allow the samples to "cool" prior to the radio-chemical separation.

b. Measurement of the activity of the isolated active element.

The efficiency of counting will depend upon the type of counter used, the geometry, and the nature of the radiation being detected. For example a Geiger-Müller counter has only a 1% efficiency for the detection of γ radiation.

An assessment of the expected counting efficiency is essential, as this will have to be taken into account when deciding upon a suitable period of sample irradiation which will produce sufficient activity for accurate determination by the counting technique selected.

The factors discussed under headings a and b, have been considered in detail in a number of papers.[9,10,18-20]

c. Radio-chemical separation technique.

To the irradiated sample is added a known weight, x, of the element to be determined in a stable state to act as a carrier, and isotopic exchange between the carrier and the active nuclide is expected to occur provided both are in the same valency state.

After dissolution the radio-chemical separation must result in the isolation of a radio-chemically and chemically pure active element having the correct decay characteristics of the particular active isotope concerned. Techniques such as precipitation, ion exchange and solvent extraction, are commonly used. The chemical purity of the separation is essential for an accurate determination of the chemical yield (see below), but need not be quantitative. Sufficient active element must however be separated for an accurate determination by some physico-chemical method of the weight, M. The criteria of radio-chemical purity will depend upon the counting technique to be employed. If a non-discriminating technique is to be used, such as Geiger-Müller counting, then radio-chemical purity is essential, but using gamma ray spectrometry in which it is possible to discriminate against the energies of the emitted radiation, radio-chemical purity is not essential.

From the activity, a, of the separated active element, the total activity, A, of the active element is given by:

$$A = \frac{ax}{M}. \qquad \ldots 13).$$

The term $\frac{x}{M}$ is the chemical yield of the separation.

By a similar procedure to the above, an analogous formula for the standard applies.

$$A_s = \frac{a_s x_s}{M_s}. \qquad \ldots 14).$$

Substituting 13) and 14) in 12) the weight, y, of the element determined is given by:

$$y = y_s \frac{axM_s}{a_s x_s M} \cdot \qquad \ldots 15).$$

Sensitivity of the method

If the irradiation is carried out for a sufficient number of half lives (about 6 or 7) so that the saturation factor becomes effectively unity, and if the activity is determined within a small fraction of a half life after the end of irradiation, 11) reduces to:

$$y = \frac{AM}{f\sigma \phi N_A} \cdot \qquad \ldots 16).$$

The sensitivity of the method will increase with increasing flux of bombarding particles, neutron activation cross section, fractional isotopic abundance, and to a more limited extent the detection efficiency, and decreasing atomic weight. Using a given set of counting equipment and neutron flux, the sensitivity of the determination of a given element by neutron activation analysis is fixed, as the neutron activation cross section, fractional isotopic abundance, and atomic weight are constants for a particular nuclide. It is not practicable to determine less than a certain level of activity with a given apparatus, and this activity level is usually taken as being equal to the background count rate. Increasing the detection efficiency could increase the background count rate and hence decrease the sensitivity.

Advantages of neutron activation analysis

The most outstanding advantage is the high sensitivity of the method for the determination of most elements.

Once the sample has been removed from the reactor, stable carrier of the element to be determined in the same valency state can be added, and the analysis can be carried out on the macro scale, provided isotopic exchange between the stable carrier and the active isotope of the element has occurred. Errors due to contamination by impurities in reagents during processing is eliminated as the method relies upon the measurement of the activity of the active isotope of the element being determined. The separation of the element need not be quantitative as a correction for the chemical yield can be made. A further advantage is the specificity, since the nuclear properties such as half life, beta and gamma ray energy, are uniquely characteristic of a particular nuclide, it is possible to measure these quantities to ensure that the activity of the active nuclide measured was that appropriate to the element being determined.

Disadvantages of neutron activation analysis

The main disadvantage is that a nuclear reactor is required for the highest sensitivity, and the technique only measures the total weight of element, taking no account of the different states of combination. Besides the above mentioned disadvantages certain precautions must be taken to avoid errors. These errors are due to such effects as flux inhomogenities, self-shielding, interfering nuclear reactions, and bad preparation of standard samples. A detailed account of such considerations have been given by Bowen and Gibbons.[21]

II. The Substoichiometric Principle Applied to Neutron Activation Analysis[2]

The expression for calculating the weight, y, of an element was given on p. 10, i.e.

$$y = y_s \frac{axM_s}{a_s x_s M} .$$

If the conditions are such that $x = x_s$ and $M = M_s$ then the above expression simplifies to:

$$y = y_s \frac{a}{a_s} . \qquad \ldots 17).$$

The weight of element determined in the sample can therefore be computed directly from the activities of the active element isolated from the sample, a, and the standard, a_s, knowing the weight, y_s, of element used as the standard.

In order that the above expression applies, two conditions must be fulfilled:

a. After irradiation and dissolution of the sample and standard, equal weights of stable carrier of the element to be determined must be added to both solutions (i.e. $x = x_s$).

b. For measuring the activity equal weights of the element to be determined must be isolated from the sample and standard solutions (i.e. $M = M_s$).

There are no difficulties in fulfilling the first condition. In most cases the weight, y, of element to be determined is far less than the weight, x, of stable carrier added. Generally y is of the order of 10^{-6}g and x, is of the order of 10^{-3}g, and therefore the weight of y, can be neglected in comparison to x.

The fulfilling of the second condition ($M = M_s$) is more difficult. It is necessary to isolate from different volumes of solution, of different concentration, always equal weights of the element to be determined. This type of isolation can be achieved substoichiometrically. If to the sample and standard solutions, exactly equal amounts of reagent, which is less than that required to react with all of the element present is added, then the condition $M = M_s$ can be satisfied. The reagent used must be consumed quantitatively in the reaction with the element to be determined, and the compound formed must be easily separable from the excess of unreacted element.

Consider the reaction of a metal ion, M^+, in aqueous solution with a ligand, L^-, (in the form of a weak acid, HL, in an organic phase) to form a complex, ML, extractable into the organic phase. If the weight of ligand, L^-, added is less than that required to react with all of the metal, M^+, then an extractable complex, ML, will be formed, and in the aqueous phase will be the unreacted metal ion, M^+. If the weight of the ligand, L^-, added is sufficient to react quantitatively with 50% of the metal, M^+, we will have 50% of the metal in the form of the complex, ML, and 50% unreacted in the form M^+. We denote such an extraction as one that has been performed at 50% STOICHIOMETRY OR 50% SUBSTOICHIOMETRY. If the weight of ligand added was sufficient to react with 75% of the metal, then this would be termed as an extraction at 75% stoichiometry or 25% substoichiometry. The former term % stoichiometry has been used in this research.

In fulfilling the conditions $x = x_s$, and $M = M_s$, the necessity of determining the chemical yield has been avoided which greatly simplifies the previous methods of neutron activation analysis.

III. Metal Chelate Solvent Extraction (I)[2,3,22]

The extraction of a metal in the form of a chelate by the addition of a substoichiometric amount of an organic chelating agent, HA, is one of the most suitable methods by which exactly the same weight of metal can always be separated from solutions of differing volume and concentration. The basic equation of the extraction can be written as:

$$M^{n+} + n\ HA_{org} \rightleftharpoons MA_{n\ org} + n\ H^{+},$$

where org denotes species in the organic phase.

The extraction constant, K, is given by:

$$K = \frac{[MA_n]_{org}[H^+]^n}{[M^{n+}]\ [HA]^n_{org}} . \qquad \ldots 18)$$

Knowing the equilibrium concentrations of the metal chelate, $[MA_n]_{org}$, and the chelating agent, $[HA]_{org}$, both in the organic phase, the equilibrium concentration of the metal, $[M^{n+}]$, in the aqueous phase, and the value of K, it is possible to calculate the threshold pH of the aqueous phase from which theoretically the same weight of metal can always be extracted.

The equilibrium concentration of the complex, $[MA_n]_{org}$, is derived from the assumption that greater than 99.9% of the organic reagent, HA, of initial concentration, C_{HA}, is consumed in forming the complex, MA_n.

$$\text{i.e. } [MA_n]_{org} V_{org} \geq 0.999 \frac{C_{HA}}{n} V_{org}, \quad \ldots 19)$$

where V_{org} is the volume of the organic phase.

If this condition is fulfilled then the same amount of metal is always isolated from solutions with an accuracy better than 0.1%.

The equilibrium concentration of the metal, $[M^{n+}]$, of original concentration, C_M, is given by:

$$[M^{n+}] V = C_M V - \frac{C_{HA}}{n} V_{org}, \quad \ldots 20)$$

where V is the volume of the aqueous phase, and that of the organic reagent by:

$$[HA]_{org} V_{org} \leq 0.001 C_{HA} V_{org}. \quad \ldots 21).$$

From 18), 19), 20) and 21) the threshold pH is given by:

$$pH \geq \frac{1}{n} \log \left(\frac{C_{HA}}{n}\right) - \frac{1}{n} \log \left(C_M - \frac{C_{HA} V_{org}}{n V}\right) - \frac{1}{n} \log K - \log (0.001 C_{HA}).$$

$$\ldots 22).$$

The above expression is only strictly valid when the degree of dissociation of the organic reagent in the aqueous phase is negligible.

$$\text{i.e. } [A^-] V < [HA]_{org} V_{org}. \quad \ldots 23).$$

This condition is fulfilled when the concentration of hydrogen ions is given by:

$$pH \leq pK_{HA} + \log q_{HA} + \log \frac{V_{org}}{V}, \quad \ldots 24)$$

where K_{HA} and q_{HA} are the dissociation constant, and partition coefficient of the organic reagent respectively.

An analysis of 22) indicates that the first two terms on the right hand side of the expression have a small effect on the value of the threshold pH. For example if the amount of reagent added is one half that required to react with all of the metal present, and the volumes of the organic and aqueous phases are the same, the sum of the first two terms is zero. If the quantity of reagent is one tenth that required to react with all of the metal the sum of the two terms is $-\frac{1}{n}$.

In activation analysis 1-10mg of stable carrier is generally added which corresponds to 10^{-2} to 10^{-3}M solution, if we assume an average atomic weight for the element of 100, and a volume of solution of 10ml. The concentration of organic reagent will be comparable, and so the value of -log 0.001 C_{HA} will be about 5 or 6. The expression for the threshold pH therefore simplifies to:

$$pH \geq 6 - \frac{1}{n} \log K, \qquad \ldots 25)$$

for the case where 10^{-3}M reagent is being considered.

From the known value of the extraction constant, K, the threshold pH of the aqueous phase necessary for determining a particular element can therefore be easily calculated.

The agreement of the theory with experimental findings can be demonstrated for the substoichiometric extraction of bismuth (III) with dithizone in carbon tetrachloride. The value of the extraction constant is $10^{9.98}$ [23] and therefore the threshold pH of the aqueous phase given by 25) must be greater than or equal to 2.7 when 10^{-3}M dithizone is used. In the alkaline region the maximum pH is

governed by 24). If the value of the dissociation constant of dithizone, K_{HA}, is taken as 2.8×10^{-5},[24] and the partition coefficient, q_{HA}, between carbon tetrachloride and an aqueous medium as 1.1×10^{4} [25] then the maximum suitable pH is given by:

$$pH \leq 8.59 + \log \frac{V_{org}}{V} \cdot \qquad \ldots 26).$$

The experimental findings indicated that a pH of the aqueous phase in the region 2.4-7 was suitable for a reproducible substoichiometric extraction of bismuth (III) with dithizone in carbon tetrachloride.[26] The ratio of $\frac{V_{org}}{V}$ was approximately 0.1, and therefore from 26) the maximum theoretical pH would be 7.6. As can be seen the agreement between the theoretical and experimentally determined values is very good.

Although 24) is used to calculate the maximum pH of the aqueous phase from which a reproducible separation can be performed, non-reproducibility of extraction often occurs at a lower pH due to the formation of insoluble hydroxides of the metal, or sometimes the formation of secondary complexes. Such effects can often be overcome by the addition of complexing agents, e.g. tartrate or cyanide. With these conditions the metal is present in the aqueous phase as a non-extractable complex, $MB_s^{(s-n)-}$, for example, which is in equilibrium with the free cations of the metal. With such conditions the following expression holds:

$$\frac{[MA_n]_{org}\,[H^+]^n}{([M^{n+}]+[MB_s^{(s-n)-}])[HA]_{org}^n} = \frac{K}{1+K_s[B^-]^s}, \qquad \ldots 27)$$

where s is greater than n, and K_s, is the stability constant of the complex, $MB_s^{(s-n)^-}$, in the aqueous phase, given by:

$$K_s = \frac{[MB_s^{(s-n)^-}]}{[M^{n+}][B^-]^s} \quad . \qquad \ldots 28).$$

From 27) the threshold pH of the aqueous phase in the presence of a complexing agent is governed by the expression:

$$pH \geq 6 - \frac{1}{n} \log K - \frac{1}{n} \log (1+K_s[B^-]^s). \qquad \ldots 29).$$

It is evident from 29) that the value of the threshold pH of the aqueous phase must increase in the presence of a complexing agent.

The conditions for a selective determination of a certain element can be derived from the theory even if the solution contains other metal ions which also react with the reagent, HA, to form extractable complexes. The ratio of the concentrations of two metals, M and M^*, in the organic phase in the form of the complex can be calculated from the individual extraction constants, K and K^*.

$$\frac{[MA_n]_{org}}{[M^*A_m]_{org}} = \frac{K[HA]^{n-m}[M^{n+}]}{K^*[H^+]^{n-m}[M^{*m+}]} \quad . \qquad \ldots 30).$$

Consider a simple case of the separation of two equally charged metal ions (n = m) whose original concentrations in the aqueous phase were equal. For a quantitative separation $\frac{[MA_n]_{org}}{[M^*A_n]_{org}}$ must be greater than 100, and $\frac{[M^{n+}]}{[M^{*n+}]}$ must be less than 0.01. If we substitute these terms in 30) then the ratio $\frac{K}{K^*}$ must be greater than 10^4 for a

quantitative separation using an excess of reagent.

If however a substoichiometric amount of the reagent is used, the ratio of $\frac{K}{K^*}$ does not have to be as large as 10^4. At 50% stoichiometry of reaction $\frac{[M^{n+}]}{[M^{*n+}]}$ will equal 0.5, and hence the ratio $\frac{K}{K^*}$ need only be greater than 200 for a quantitative separation. Therefore an increase in selectivity is achieved using a substoichiometric amount of the reagent.

If the solution contains simultaneously metal ions whose values of the extraction constant with a particular reagent do not differ sufficiently for a quantitative separation, then it is necessary to mask the interfering elements with a suitable reagent. In the presence of a masking agent, HB, the ratio of the concentrations of the element to be determined, and the interfering element both in the form of a complex in the organic phase is given by:

$$\frac{[MA_n]_{org}}{[M^*A_m]_{org}} = \frac{K[HA]^{n-m}C_M(1+K_s^*[B^-]^s)}{K^*[H^+]^{n-m}C_M^*(1+K_s[B^-]^s)} \quad , \qquad \ldots 31)$$

where C_M and C_M^* are the total concentrations of the metals M and M^* in the aqueous phase.

In the most simple case when the total concentrations of the metals, M and M^*, in the aqueous phase, and their charges, n and m, are equal, 31) simplifies to:

$$\frac{[MA_n]_{org}}{[M^*A_n]_{org}} = \frac{K(1+K_s^*[B^-]^s)}{K^*(1+K_s[B^-]^s)} \quad . \qquad \ldots 32).$$

Therefore in order to separate the metals, M and M^* the ratio

$\frac{1 + K_s^*[B^-]^s}{1 + K_s[B^-]^s}$ should be as large as possible. Knowing the values of stability constants, K_s and K_s^*, it is possible to select the most suitable masking agent, so that a selective substoichiometric determination of the element can be achieved. As an example the determination of copper (II) with dithizone can be given.[2,27] Mercury (II) interferes in the substoichiometric determination, but if 0.1M potassium iodide is added, it is possible to determine copper with dithizone in the presence of mercury. The extraction constant for copper (II) dithizonate is $10^{10.53}$,[24,28] that for mercury (II) dithizonate $10^{26.8}$,[29-31] and the stability constant of the mercury complex HgI_4^{2-} is $10^{30.5}$.[32] If these values are substituted in 32) one obtains:

$$\frac{[Cu(HDz)_2]_{org}}{[Hg(HDz)_2]_{org}} = \frac{10^{10.53}(1+10^{30.5}\times10^{-4})}{10^{26.8}\times1} = 10^{10.3}, \quad \ldots 33).$$

assuming that the concentration of cupric ions bound in the iodide complex can be neglected. The ratio of the concentrations of copper and mercury as the dithizonates in the organic phase is greater than 100 so a quantitative separation of the elements is possible.

IV. Exchange Reactions

Consider the following hypothetical reaction:

$$nM^{*m+} + m(ML_n)_{org} \rightleftharpoons mM^{n+} + n(M^*L_m)_{org},$$

where, L, denotes the anion of a ligand capable of reacting with the metals, M and M^*.

An example of such a reaction may be a solution of copper (II) dithiocarbamate in chloroform being shaken with a mercury (II) salt in an aqueous phase, with the resultant formation of mercury (II) dithiocarbamate and the liberation of copper (II) ions.

The exchange constant for the reaction is given by:

$$K^{**} = \frac{[M^{n+}]^m [M^*L_m]^n_{org}}{[M^{*m+}]^n [ML_n]^m_{org}} . \qquad \ldots 34).$$

If we consider the case of two equally charged metal ions (n = m) the above expression simplifies to:

$$K^{**} = \frac{[M^{n+}]^n [M^*L_n]^n_{org}}{[M^{*n+}]^n [ML_n]^n_{org}} . \qquad \ldots 35).$$

For a quantitative displacement of the metal, M, from the complex, ML_n, by the metal, M^*, $\frac{[M^*L_n]_{org}}{[ML_n]_{org}}$ must be greater than 100.

$$\text{i.e. } \frac{K^{**}[M^{*n+}]^n}{[M^{n+}]^n} > (100)^n . \qquad \ldots 36).$$

If the reaction is performed at 50% stoichiometry, then half of the original amount of metal, M^*, present is required to quantitatively displace all of the metal, M, from the complex, ML_n, and hence $\frac{[M^{*n+}]}{[M^{n+}]} = 1$.

Expression 36) therefore simplifies to:

$$K^{**} > 10^{2n} . \qquad \ldots 37).$$

The exchange constant K^{**} is also given by the ratio of the extraction constants, K and K^*, of the metal complexes, ML_n and

M^*L_n, respectively. Therefore $\frac{K^*}{K}$ must be greater than 10^{2n} for a quantitative exchange of metal, M, by metal, M^*, from the original complex, ML_n.

From the theory it can be seen that suitable conditions for a reproducible and selective substoichiometric separation of a metal as a chelate can be calculated from the known values of the extraction constants.

V. Radio-active Isotope-Dilution Analysis

The method of radio-active isotope-dilution was proposed independently by Hevesy[33] and Starik[34] about thirty years ago. Many review articles of the use of the technique applied to the determination of elements other than gold have been published,[14,35-38] and also several reviews concerned with the substoichiometric methods of radio-active isotope-dilution analysis.[3,39-41]

There are two approaches:

a. Direct isotope-dilution by which the stable element can be determined with the aid of an active isotope.

b. Reverse isotope-dilution by which the content of stable isotopic carrier in the solution of the active isotope can be determined.

Both approaches are based upon the determination of the change in specific activity (activity per unit weight) caused by the mixing of active and stable isotopes of the element to be determined. Direct isotope-dilution techniques were used in this research.

If the standard active element has a specific activity, S_s, given

by $\frac{a_s}{y_s}$ where, a_s, is the activity of a weight, y_s, of the active element, and a weight, y_s, is mixed with a known weight of sample containing a weight, y, of the element to be determined in a stable form, then the specific activity will be reduced to a value S, where:

$$S = \frac{a_s}{y+y_s} = \frac{S_s y_s}{y+y_s} . \qquad \ldots 38).$$

From 38)

$$Sy = y_s (S_s - S)$$

i.e.
$$y = y_s \left(\frac{S_s}{S} - 1\right), \qquad \ldots 39)$$

and hence the weight, y, of element in the sample can be calculated. Provided the active and stable element are in the same chemical form, and isotopic exchange has occurred, the specific activity, S, is independent of the weight of the element isolated for the determination of the specific activity. The weight separated, M, must be in a pure state, and its activity, a, must be measured since S is equal to $\frac{a}{M}$.

VI. The Substoichiometric Principle Applied to Radio-active Isotope-Dilution Analysis[1]

The necessity of determining the specific activity of the isolated active element limits the application of isotope-dilution for trace analysis, as the weight of isolated element must be sufficient to be determined either by weighing or some physico-chemical method.

If from the solution of original specific activity, S_s, and from the solution formed by isotope-dilution exactly equal weights of the element are isolated ($M = M_s$), then 39) simplifies to:

$$y = y_s \left\{ \frac{a_s}{a} - 1 \right\}, \qquad \ldots 40)$$

i.e. the weight, y, of the element in the sample can be computed from the activity measurements provided the weight, y_s, of active element is known.

This modification can be achieved using a substoichiometric amount of reagent, and direct isotope-dilution can then be applied for the determination of trace amounts of an element. The major limiting factor in the sensitivity of the method is the value of the specific activity, S_s, of the standard active element, and not the determination of the weight of the isolated active element as was the case in the "classical" method. The value of the blank must be a minimum, and therefore this necessitates the use of high purity reagents.

In isotope-dilution analysis the weight of element being determined is of the order of 10^{-6}g or less. The most suitable techniques for such determinations is that of metal chelate solvent extraction, other techniques such as ion exchange have been proposed.[3]

VII. Metal Chelate Solvent Extraction (II)[1,3,22]

The weight of element isolated from solution as previously stated is of the order 10^{-6}g or less. If we assume a lower limit of 10^{-9}g, and a solution volume of 10ml, this corresponds to about

10^{-6} to 10^{-9}M solutions (based on average atomic weight of 100), and the substoichiometric amount of organic reagent will correspond to 10^{-5} to 10^{-8}M solution, assuming the volume of the organic phase used is ten times smaller than the volume of the aqueous phase.

If more than 99.9% of the organic reagent, HA, of initial concentration, C_{HA}, is to react with the metal, M, to form the extractable chelate, the value of the threshold pH of the aqueous phase must satisfy the criteria:

$$pH \geq -\log 0.001\, C_{HA} - \frac{1}{n} \log K \quad \text{(p. 16)}.$$

It is apparent from the above expression when compared with 25) that the value of the threshold pH will have a higher value, than that with the neutron activation analysis conditions.

The number of suitable organic chelating agents for use in isotope-dilution analysis is more limited compared to those for neutron activation analysis for the reasons discussed in the next chapter.

Chapter 2

The Selection of the Chelating Agent for this Research

I. Introduction

The object of this research was given on p. 2; namely to develop very simple, selective methods for the determination of traces of gold by neutron activation, and radio-active isotope-dilution analysis. The substoichiometric principle as proposed by Růžička and Starý[1,2] was to be used, the theory of which was given in Chapter 1. Using this modification of the "classical" neutron activation analysis (N.A.A.), and radio-active isotope-dilution analysis (I.D.A.) methods, the determination of the chemical yield (N.A.A.), or the specific activity of the separated active element (I.D.A.), would be avoided.

It is apparent from the review of neutron activation analysis methods for the determination of gold published by Beamish and co-workers,[11] that the most favoured separation procedures for the element are those of extraction into an organic solvent, followed by a reduction of the gold to the metal, using hydroquinone as the reductant. The approach is an obvious one, when the chemical yield of the separation has to be determined. However using the substoichiometric technique this complication is avoided, and hence more favourable methods of separation are available, not involving the reduction of the gold to the metal.

In this research it was decided to attempt to achieve the desired simplicity, and selectivity, for the determination of gold by reacting the element with an organic chelating agent to form a neutral gold chelate, extractable into an organic phase. The technique of metal chelate solvent extraction has been used by

Starý, Růžička and co-workers[3] for the substoichiometric determination of a number of elements.

From the theory of metal chelate solvent extraction given in Chapter 1 it can be seen that an increase in selectivity is also achieved, by use of a substoichiometric amount of chelating agent, rather than an excess as is the normal procedure in analytical chemistry. However from the theory it is also apparent that the chelating agent selected, must satisfy a number of criteria in order to be applicable for the substoichiometric determination of an element.

a. It must react quantitatively with the element to be determined, (greater than 99.9% consumed) to form an extractable complex.

b. The complex once formed must be readily extractable from the excess of unreacted element.

c. The value of the extraction constant, K, of the metal chelate must be sufficiently high, so that the determination need not be carried out in such a basic medium that hydrolysis, and sorption of the metal ion, interferes with the determination.

d. The organic chelating agent being a weak acid, will at high pH values pass into the aqueous phase due to dissociation. The extraction must therefore be capable of being carried out from a medium whose pH value satisfies the criteria given in Chapter 1.

e. The chelating agent must not be easily decomposed by light, oxidising agents, etc. This criteria is most difficult to fulfil in the case of isotope-dilution analysis when the concentration of

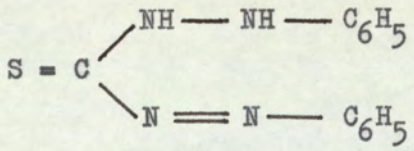
reagent is about 10^{-5}-10^{-8}M, compared to neutron activation analysis 10^{-2}-10^{-3}M.

f. The higher the value of the extraction constant, K, of the metal chelate formed, the more selective a particular reagent is likely to be (p. 19), and therefore the reagent selected should have as high a value of K as possible, provided the above criteria are met.

A book entitled "The Solvent Extraction of Metal Chelates" by Stary[22] has been published, which discusses the various types of chelating agents commonly used, together with their applicability for the determination of a particular element. A study of the appropriate chapters of this book and other relevant literature, revealed that the following reagents, dithizone, and diethyldithiocarbamic acid, were most promising for further investigation, in the hope of determining gold by simple selective methods. The published findings concerned with the reaction of gold with these reagents is reviewed below.

II. Dithizone

Diphenylthiocarbazone, or dithizone



was prepared by Emil Fischer,[42] who noted its reaction with heavy metals, giving brilliantly coloured products. It was not until 1925, some fifty years later, that Hellmut Fischer[43] realised the great potential of this reagent for the detection, and determination

of traces of many heavy metals. The findings of Fischer and co-workers have been published in an extensive series of papers,[44-58] and today the literature concerned with the use of dithizone as an analytical reagent is very extensive. The paper by Wickmann,[59] and books by Iwantscheff,[60] Sandell,[61] and Welcher[62] are examples.

The reagent is known to react with twenty metals,[60] and the order of extractability of metal dithizonates into carbon tetrachloride has been found to be; palladium (II), gold (III), mercury (II), silver (I), copper (II), bismuth (III), platinum (II), indium (III), zinc (II), cadmium (II), cobalt (II), lead (II), nickel (II), tin (II) and thallium (I)[60] (in decreasing order). Dithizone is therefore not a specific reagent, but the extraction of a particular metal may be made more specific by use of various masking agents.

The known extraction constants of metal dithizonates have been given by Sandell,[61] and selective separation conditions for the reacting elements by Stary.[22] The extraction constant for gold dithizonate is unknown, but an assessment can be made from the order of extractability of metal dithizonates into carbon tetrachloride, and the known value of the extraction constant of mercury (II) primary dithizonate $Hg(HDz)_2$ in the same solvent (p. 46).

A survey of the literature relevant to the reaction of gold with dithizone indicated that the composition of the complex formed was not fully understood. According to Fischer[50] gold (III) reacts with dithizone in carbon tetrachloride to give a golden-yellow primary complex, and also a red-brown secondary complex in accordance with the following reactions:

$$Au^{3+} + 3H_2Dz_{org} \rightleftharpoons Au(HDz)_{3org} + 3H^+,$$

$$2Au^{3+} + 3H_2Dz_{org} \rightleftharpoons Au_2Dz_{3org} + 6H^+$$

where org denotes species in the organic phase. The primary complex was formed in dilute mineral acid solution, and its solubility in carbon tetrachloride was reported as being about 10^{-5}M, whereas the secondary complex was formed in alkaline solution being only soluble in organic solvents with difficulty.[50,53] The author also stated that the kinetics and equilibrium composition of the reaction was not fully understood, and the possibility of gold (I) complexes existing was also mentioned.[53, 57,63]

In a paper entitled "Mikrobestimmung des Goldes," Erdey and Rady,[64] studied the reaction in considerable detail. A gold (III) chloride solution of known strength, was reacted with an excess of dithizone in carbon tetrachloride, using 0.1N sulphuric acid as the aqueous phase. After a 1-2min extraction the excess of dithizone was removed by washing the organic phase with dilute (1:1000) ammonia solution, and the extinction of the yellow-brown carbon tetrachloride solution, was measured. The spectra was found to be similar to that of diphenylcarbodiazone, i.e. the oxidation product of dithizone, and the authors considered that possibly the tervalent gold was oxidising the dithizone solution which would account for the similarity in the absorption curves. To prove or disprove this assumption, the extraction of the gold (III) with an excess of dithizone was repeated, and it was found that 70-95% of the gold was in the organic phase. The authors considered that the gold

could be present in this phase in three possible forms.

a. As free gold chloride.

b. As metallic gold in colloidal dispersion, as a result of reduction of the gold by dithizone, or

c. as the gold dithizonate complex.

The first possibility was disproved by shaking a gold (III) solution with carbon tetrachloride in the absence of dithizone, and examining the organic phase spectrographically. No gold was found to be present in the organic phase. The second possibility was eliminated by carrying out a chromatographic study. The behaviour of metal free dithizone, dithizone free carbon tetrachloride, a carbon tetrachloride solution obtained from the extraction of gold (III) in the presence of an excess of dithizone, and a carbon tetrachloride solution of dithizone and diphenylcarbodiazone on a chromatographic column previously washed free of water with anhydrous sodium sulphate, was studied. With the carbon tetrachloride phase obtained by the extraction of gold with an excess of dithizone, two coloured zones, a yellow-brown and a green resulted, and it was found that the gold was present in the former zone. The authors considered that if colloidal gold was present it would be strongly absorbed on the column, and not weakly as was the case with dithizone.

Further support for the third alternative, i.e. the formation of a gold dithizonate was obtained from the fact that when the yellow-brown zone was reacted with a 1% solution of potassium cyanide the colour was discharged, and dithizone remained in the

alkaline aqueous phase. The yellow-brown zone was also found to be unstable, gradually changing to green followed by a gradual reversion to yellow due to oxidation of the dithizone. During these changes a gold rich precipitate was formed. The effect of adding a slightly alkaline solution of a zinc salt to the original organic extracts was also studied. There was no reaction with diphenylcarbodiazone as was to be expected, but with the yellow-brown extract the red colour of zinc dithizonate was formed. The authors therefore concluded that zinc could replace gold from the complex.

The authors finally reacted fixed amounts of dithizone with an excess of copper, silver, and gold solutions, and the amount of metal extracted was found to be in equivalent ratios to one another. If one assumes one molecule of dithizone reacts with one silver ion, and two molecules with a copper ion, then three molecules must be reacting with one gold ion.

Erdey and Rady therefore concluded that the reaction of gold with dithizone was that to form gold dithizone $Au(HDz)_3$, and not diphenylcarbodiazone and colloidal gold. The authors as a result of this study, have developed a monocolour method for the determination of gold, the extinction of the gold dithizonate being measured at 450mμ. An extractive titration procedure in which the gold or dithizone could be used as the titrant, was also developed, and was found to be more rapid, and more accurate than the spectrophotometric method. Using dithizone as the titrant a number of samples were analysed, with an accuracy of 5%.

Erdey and Rady, did not investigate the secondary complex, but their findings for the primary gold dithizonate agreed with those of Fischer.[50]

Titley[65] has also developed an extractive titration procedure for the determination of milligram amounts of gold using dithizone as the titrant. The conditions used, a medium of 0.5N sulphuric acid, with the minimum concentration of chloride ions (less than 0.02M), was very similar to that used by Erdey and Rady.[64] With dithizone in carbon tetrachloride, a precipitate of gold dithizonate was found at the interface between the two phases; 1mg of gold as the dithizonate was not completely soluble in 30ml of the organic solvent, however if chloroform was used this effect was eliminated due to the greater solubility of the complex in the latter solvent. This finding was in agreement with that found by Fischer.[50]

An investigation of the molar ratio gold to dithizone in the complex, showed that with chloroform as the solvent, a molar ratio of approximately 1:1 was obtained, and with carbon tetrachloride 1:2, in disagreement with that found by Erdey and Rady.[64] The necessity of controlling the concentrations of hydrochloric, and nitric acids present during the extractive titration was stressed by the authors. If this criteria was not met high results for the determination of gold were obtained, the presence of hydrochloric acid having a more pronounced effect than that of nitric acid. The concentration of sulphuric acid present was not so critical, any normality between the values 0.3-1.0N was considered to be satisfactory.

Unlike Erdey and Rady,[64] Titley[65] did not purify the dithizone to remove oxidation products prior to its use, as this was considered unnecessary provided the reagent was standardised against a standard gold (III) solution. Mercury (II), silver (I) and platinum (II), but not copper (II) interfered in the method. The interference of mercury (II) was overcome by volatilisation of the mercury, silver (I) by precipitation of the chloride, and platinum (II) by removing the gold from solution by reduction with sulphur dioxide. The non-interference of copper (II) was considered to be due to the slow rate of extraction of the copper dithizonate from mineral acid solution.

For the determination of 0.2-1.5mg of gold in 10-25ml of solution, results reproducible to $\pm$1% of the weight of gold present were obtained, and the author applied the method to the determination of gold in a number of ores.

Several other spectrophotometric,[66-68] and extractive titration methods[69,70] for the determination of gold, using dithizone have been proposed, but no attempt had been made to find the composition of the gold dithizonate formed.

The use of dithizone as the analytical reagent for the substoichiometric determination of gold has been proposed by Stary and Růžička.[71] It is apparent from the findings of Erdey and Rady,[64] and Titley,[65] that a strict control of the hydrochloric acid concentration will be necessary if any measure of success in the use of this reagent is to be achieved. Although the composition of the primary gold dithizonate is in dispute between the authors, the use

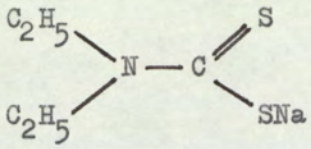
of dithizone in extractive titration procedures for the determination of gold is widely established. The extraction constant of the primary gold dithizonate is very high (p.46) and so a selective determination of the element should be possible.

One of the criteria for the development of a substoichiometric method for the determination of an element, is that the complex once formed must be easily separable from the excess of unreacted element (p. 28). Therefore in this research, chloroform rather than carbon tetrachloride was used as the solvent for the dithizone, as the gold dithizonate has a greater solubility in this solvent.

Another criterion of the substoichiometric method is that the reagent must not be easily decomposed by light, oxidising agents, etc. (p. 28). Dithizone is sensitive to light and oxidising agents, so difficulty may be encountered due to instability of reagent solutions, especially at concentrations 10^{-5}-10^{-8}M, which are required for isotope-dilution analysis. Regular standardisation of the solutions will therefore be required. Erdey and Rady[64] also observed that primary gold dithizonate was sensitive to light. This observation is very important when developing a spectrophotometric method. However, provided the effect is insignificant during the time necessary for the separation and transfer of an aliquot of the complex to a counting jar, this will not effect the substoichiometric method. The weight of gold present in the organic phase, will be determined from the activity of the active nuclide present, and not from the degree of absorbance of the incident light.

III. Diethyldithiocarbamic Acid

Diethyldithiocarbamic acid is generally used in the form of its sodium salt,



and was first applied to the determination of copper and iron in 1908.[72] It is not a specific reagent and it reacts with more metals than does dithizone, but by the use of masking agents it is possible to make the reagent more selective than dithizone.

Eckert[73] has shown that in spite of the lack of specificity separations are possible on the basis of one of three schemes.

a. By means of "positive selection", involving precipitation, or solvent extraction, of the required metal as the diethyldithiocarbamate, interfering metals being masked by other complexing agents.

b. By "negative selection", involving precipitation, or solvent extraction, of interfering metals as diethyldithiocarbamate complexes, the required metal being masked if necessary.

c. By means of differing stabilities, and distribution ratios of the diethyldithiocarbamate complexes.

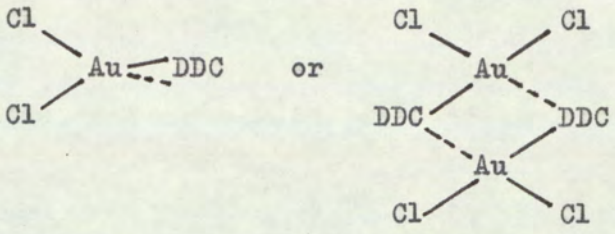
All three schemes are dependent on the relative stabilities, and solubilities of the diethyldithiocarbamate salt of the required metal, and of any other metal which is present in the system under the chosen conditions. The order of extractability of metal diethyldithiocarbamates into carbon tetrachloride,[73-78] and the order

of water solubility[79,80] has been determined by a number of authors. Selective separation procedures for the determination of a number of elements using one of the three schemes proposed by Eckert have also been published.[73,80,81]

The reaction of gold (III) with diethyldithiocarbamic acid has been studied by Bode.[77] The extraction of gold chelate into carbon tetrachloride from an aqueous solution of pH 4-11, was incomplete, and during the formation of the complex there was also some reduction of the gold to the metal which gave a cloudiness at the boundary between the two phases. In alkaline solution the proportion of reduced gold was smaller than that from acid solution, where occasionally no extraction of the gold was found to occur. An excess of reagent was always found, and this effect was more pronounced the more dilute the gold (III) solution. The presence of a solution of the disodium salt of ethylenediamintetraacetic acid (about 0.006M) did not interfere with the extraction, but the addition of a solution of potassium cyanide (about 0.03M) to a solution of pH 8-11 resulted in the complete masking of the gold. Since the extraction of the gold as the diethyldithiocarbamate was incomplete it was impossible to obtain a formula for the complex formed. The complex in carbon tetrachloride absorbed in the region 300-800mμ with absorption peaks at 410mμ and at 474 mμ.

Bobtelsky and Eisenstadter have also studied the reaction of gold (III) with sodium diethyldithiocarbamate using a heterometric technique. In a heterometric titration in a medium of hydrochloric or nitric acid, a yellow precipitate of molar ratio gold (III) to

diethyldithiocarbamate of 1:1 was obtained. The complex was found to be easily soluble in chloroform, dioxan, acetone and methyl or ethyl alcohol, but insoluble in carbon tetrachloride. The authors postulated the following structures for the complex.



where DDC represents the diethyldithiocarbamate anion.

If the titration was performed from an acetic acid solution critical points in the heterometric curve corresponding to molar ratios of gold (III) to diethyldithiocarbamate of 1:1, and 1:1.5 were obtained. The authors considered the latter complex to be $(Au_2(DDC)_3)^{3+}$, which is present in the aqueous medium. In neutral or alkaline solution evidence for the formation of a complex $(Au(DDC)_2)^{+}$ soluble in the aqueous phase, was also found.

Vanngard and Akerstrom[83] have carried out electron spin resonance studies of the gold diethyldithiocarbamates and have claimed the existence of a gold (II) complex. Gold (I) and (III) complexes are dia-magnetic having electronic configurations, $5d^{10}$ and $5d^{8}$ respectively, and therefore the electron resonance absorption found was considered to be associated with a gold (II) complex which would have an electronic configuration of $5d^{9}$, i.e. paramagnetic.

A systematic study of the extraction of many metals as the diethylammonium diethyldithiocarbamates into carbon tetrachloride has been made by Bode and Neumann.[84] The reagent reacts with the

same metals as sodium diethyldithiocarbamate, but has the great advantage of being able to extract metals even from very acid medium.

The gold complex formed with the reagent had a strong colour in the visible region, and by measuring the extinction of the complex, it was possible to estimate the extent of the extraction. The extraction of gold (III) was always incomplete from solutions of pH 1-12 using the reagent in carbon tetrachloride, and the maximum acid concentration of the aqueous phase from which any gold could be extracted was 0.1N. However palladium (II), platinum (II), copper (II), mercury (II) and silver (I), could be extracted from 10N sulphuric acid.

Handley and Dean[85] claim that the relative order of extraction of metals with di-n-butylphosphorodithioc acid into carbon tetrachloride is: palladium (II), gold (III), copper (I), mercury (II), silver (I), copper (II), antimony (III), bismuth (III), lead (II), cadmium (II), nickel (II) and zinc (II) (in decreasing order of extractability). This reagent contains the reactive thiol group (-SH) similar to that of the dithiocarbamates, and therefore one would expect a similarity between the relative order of extraction of metals with the two reagents; this was so with one exception, the extraction of gold (III). According to Handley and Dean,[85] gold (III) is one of the most extractable metals with di-n-butylphosphorodithioc acid, whereas according to Bode and co-workers[77,84] the extraction of gold (III) as the diethyldithiocarbamate, or diethylammonium diethyldithiocarbamate, is incomplete. In all cases the solvent used was carbon tetrachloride. A direct comparison between

the two types of reagent is not fully justified, both reagents contain the thiol group (-SH), but in the case of di-n-butylphosphorodithioates the thiol group is joined to a phosphorous atom, and in the diethyldithiocarbamates it is joined to a carbon atom. The order of metal extractability found by Handley and Dean was very similar to that with dithizone in carbon tetrachloride as the reagent (p. 30).

The solubility of metal chelates is generally higher in chloroform than in carbon tetrachloride. Sedivic and Fleck[86] have studied the solubility of some metal dithiocarbamates in the following solvents, acetone, ethanol, pyridine, ethyl and isoamylacetate, ethyl ether, benzene, chloroform and carbon tetrachloride, and concluded that the highest solubilities were obtained using chloroform or pyridine as the solvent. It was therefore considered that the findings of Bode[77] and Bode and Neumann,[84] namely that gold was not completely extracted as the diethyldithiocarbamate or diethylammonium diethyldithiocarbamate, was due to the poor solubility of the gold chelates in carbon tetrachloride. If chloroform had been used as the solvent it was considered that the gold chelate would probably be one of the most stable in the series, having a high extraction constant similar to that of mercury (II), palladium (II) and silver (I) diethyldithiocarbamates. Support for this argument is given by Bobtelsky and Eisenstadter[82] who found that the gold chelate formed in acid solution was insoluble in carbon tetrachloride, but soluble in chloroform.

In this research it was decided to use a chloroform solution

of a metal salt of diethyldithiocarbamic acid as the chelating agent in the hope of being able to extract the gold as the diethyldithiocarbamate by an exchange reaction.

The metal salt chosen for this research was copper diethyldithiocarbamate for three reasons.

a. Unlike the sodium salt, the reagent in chloroform should be stable when in contact with acidic aqueous solutions. This conclusion was based upon the findings of Usatenko and Tulyupa,[81] who found that copper could only be displaced from the diethyldithiocarbamate complex in ethyl acetate, by the addition of concentrated hydrochloric acid.

b. The ratio of the values of the extraction constants of gold and copper diethyldithiocarbamates in chloroform, was thought to be large enough for complete exchange of the copper (II) by gold (III), from the copper diethyldithiocarbamate. The theory of such exchange reactions has been given in Chapter 1, and it is known that the complete exchange of copper (II) by silver (I) occurs.[87]

c. Copper diethyldithiocarbamate in chloroform is easily standardised by extinction measurements at 436mμ, or by an extractive titration procedure using a standardised silver (I) salt solution.[87]

If the use of copper diethyldithiocarbamate in chloroform was not found to be suitable for the development of substoichiometric methods for the determination of gold, then an alternative metal salt of diethyldithiocarbamic acid could be used. The metal salt selected as an alternative, would be one whose extraction constant

is lower than that of copper diethyldithiocarbamate in chloroform, as then the ratio of the extraction constants of gold and the metal as the diethyldithiocarbamates in chloroform will have a larger value and exchange will be more likely to occur. The most suitable metal is probably zinc in the form of its diethyldithiocarbamate

A third alternative reagent if no success was achieved using metal salts of diethyldithiocarbamic acid was the use of diethyl-ammonium diethyldithiocarbamate in chloroform. Prior to the use of dithiocarbamates the applicability of dithizone in chloroform as the chelating agent for the substoichiometric determination of gold was considered.

Chapter 3

The Substoichiometric Determination of Gold by Neutron Activation Analysis

I. Introduction

An excellent review of the previously published neutron activation analysis methods for the determination of gold has been given by Beamish and co-workers.[11]

The object of this investigation was to develop a substoichiometric separation procedure for gold, which from its generally higher selectivity and the avoidance of determining the chemical yield, would permit a considerable simplification over the radiochemical procedures commonly used.

Gold is a monoisotopic element and by its activation with thermal neutrons the following nuclear reaction occurs:[9,88]

$$^{197}Au\ (n, \gamma)\ ^{198}Au$$

($t_{\frac{1}{2}}$ = 2.70d σ = 98 barns β^- 0.29(1.2%), 0.96(98.8%), 1.37(0.025%)MeV; γ 0.412(95.8%), 0.68(1.0%), 1.09(0.2%)MeV).

From the above data it can be calculated that under suitable conditions; irradiation in a flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, to saturation activity, followed by a radio-chemical separation, it is theoretically possible to determine down to 5×10^{-12}g of gold. This value quoted by Jenkins and Smales[12] assumed a two hour decay period after irradiation, followed by the counting of the gold-198 β^- activity. A similar calculation of the sensitivity using expression 16) (p. 10) with the conditions used in this research, γ counting with a NaI(Tl) scintillation counter, and a low energy discrimination (0.07MeV), gave a value of 10^{-11}g of gold.

The separation procedure for the gold, was one of metal chelate solvent extraction. The choice of suitable chelating

agents was discussed in Chapter 2; dithizone, and copper diethyldithiocarbamate in chloroform, being selected as most promising.

II. Discussion

A. Development of the Method

i. Preliminary experiments.

a. Using dithizone in chloroform as the chelating agent.

If the extraction constant, K, for the formation of gold dithizonate in chloroform was known, it would be possible to calculate the threshold pH of the aqueous phase from which to extract the gold as the dithizonate (p. 16). The constant has not been determined, but the order of extractability of metal dithizonates in carbon tetrachloride is known.[60] Only palladium (II) is more extractable than gold (III), which is more extractable than mercury (II). The extraction constant for the formation of primary mercury (II) dithizonate, $Hg(HDz)_2$, is 6×10^{26} with carbon tetrachloride as the solvent,[89] and therefore the extraction constant for the gold (III) dithizonate in the same solvent must be greater than this value.

According to Sandell[90] for a given metal the value of the extraction constant, K, of metal dithizonates is larger using carbon tetrachloride (CCl_4) than chloroform ($CHCl_3$) as the solvent. The difference in extraction constants is determined by the ratio of the partition coefficients of dithizone, P_d, and the dithizonate, P_{pm}, for the two solvents.

For a tervalent metal:

$$\frac{K_{CCl_4}}{K_{CHCl_3}} = \frac{(P_d)^3_{CHCl_3}}{(P_d)^3_{CCl_4}} \times \frac{(P_{pm})_{CCl_4}}{(P_{pm})_{CHCl_3}} .$$

Dithizone (H_2Dz) is about fifty times more soluble in chloroform, than in carbon tetrachloride,[90] and therefore:

$$\frac{K_{CCl_4}}{K_{CHCl_3}} = 1.25 \times 10^5 \frac{(P_{pm})_{CCl_4}}{(P_{pm})_{CHCl_3}} .$$

If the ratios of the solubility of dithizone, and the dithizonate, are the same in the two solvents, the difference in extraction constants will be about 2.5×10^3. On this basis there is considerable justification for assuming that the extraction constant for the primary gold (III) dithizonate in chloroform will be at least 10^{21}.

If this value is substituted in the equation for calculating the threshold pH of the aqueous phase from which the extraction of the gold as the dithizonate can be performed,

i.e.

$$pH \geq 6 - \frac{1}{n} \log K$$

where n is the valency of the metal, and the concentration of the dithizone is 10^{-3}M (p. 16), a value for the threshold pH of -1 is obtained. Therefore theoretically the substoichiometric extraction of gold (III) as the dithizonate into chloroform can be performed from an acid solution.

An extraction titration of 1.03mg of gold (III) from a medium of 0.5N sulphuric acid, with dithizone in chloroform gave an end point, which corresponded to the reaction of 1 mole of gold with

1 mole of dithizone (Table 3.1). The chloride ion concentration was kept to a minimum, so as to keep the conditions similar to those used by Titley[65] (0.3-1.0N sulphuric acid, minimum chloride ion concentration), who observed a similar molar ratio gold to dithizone with chloroform as the organic solvent. The author also noted that at higher chloride ion concentrations, (0.1M and greater), high results for the extractive titrations were obtained, and the colours of the organic extracts were modified (p. 34). A similar conclusion was made in this research (Table 3.1).

Table 3.1.

Aqueous phase H^+ conc.^{n} (M)	Aqueous phase Cl^- conc.^{n} (M)	Vol. of stable Au sol.^{n} added (1.05×10^{-2}M) (ml)	Vol. of H_2Dz in $CHCl_3$ used (5.08×10^{-4}M) (ml)	Molar ratio Au:H_2Dz in organic phase
0.5	0.02	0.5	10.4	1.0:1.0
0.5	0.5	0.5	11.6	1.0:1.1
0.5	2.5	0.5	19.2	1.0:1.9

In order to understand the influence of chloride ions on the formation of the gold dithizonate a series of 3min extractions of the gold chelate were performed using a fixed weight of stable gold, 1.03mg, and a fixed hydrogen ion concentration of the aqueous phase, but varying chloride ion concentrations and substoichiometric amounts of the chelating agent (p. 86). After the extractions, the organic phases were removed, and the weight of unreacted gold in the aqueous phases was determined by the Bromoaurate Method.[91] A series of extractions were also performed keeping the chloride and hydrogen ion concentrations of the aqueous phase constant but varying the

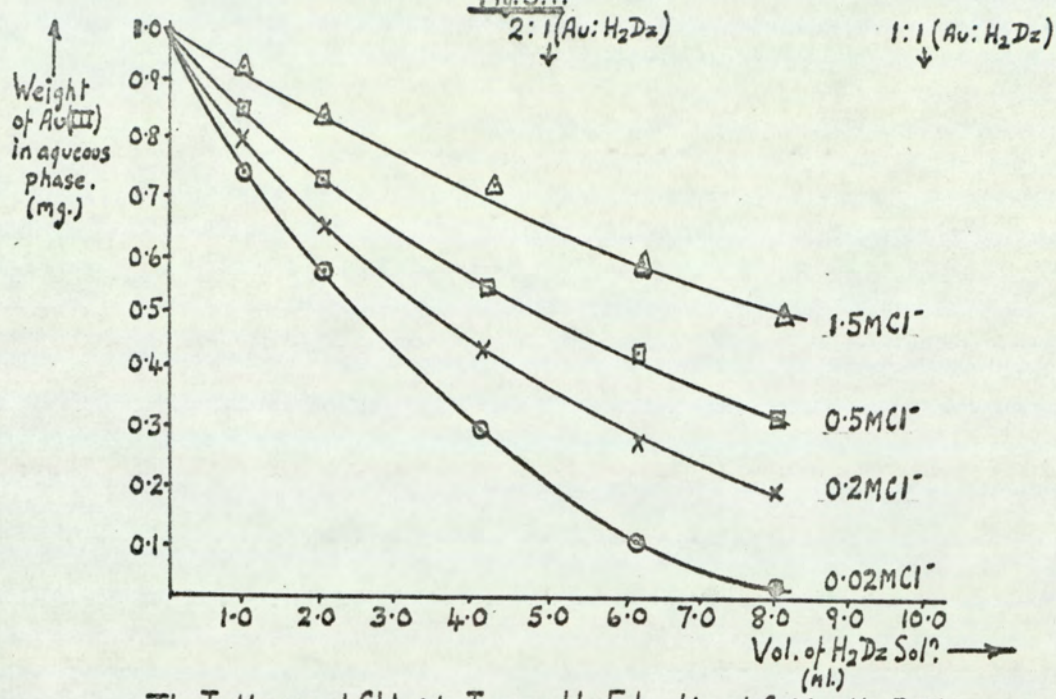
extraction times and amounts of chelating agent. The results of the investigations are given in Figs. 3.1 and 3.2.

The results given in Fig. 3.1 show that for a given stoichiometry of reaction and extraction time, the lower the chloride ion concentration of the aqueous phase the greater the tendency to form a complex in the organic phase of molar ratio gold to dithizone of 2:1. Chloride ions were therefore acting as a competing specie in the reaction to form the gold dithizonate.

From Fig. 3.2 it can be seen that as the extraction time of the separation was increased so the amount of gold extracted into the organic phase increased, and the molar ratio of gold to dithizone in the organic phase tended towards a value of 2:1. It was also observed that the colour of the organic phases changed from a red-brown to yellow as the period of extraction was increased. The organic phases obtained from the series of 3min extractions were found to contain free dithizone, but not those from the 10 or 30min extractions. At a stoichiometry of reaction of 40% or less with a 30min extraction the molar ratio of gold to dithizone in the organic phase was found to be 2:1, whereas at higher stoichiometry of reaction the molar ratio tended towards a value of 1:1.

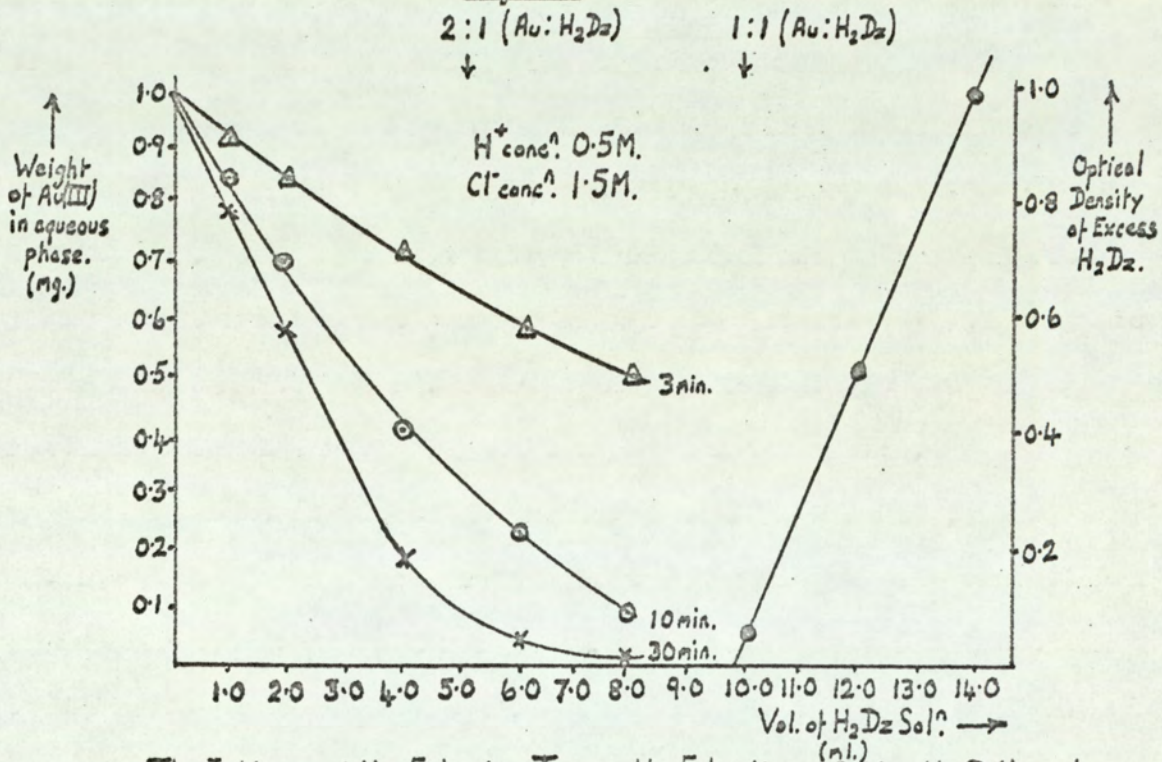
If a volume of dithizone greater than 10ml was used, free dithizone was found to be present in the organic phases even after a 30min extraction, and a straight line relationship existed between the amount of excess dithizone, determined spectrophotometrically at 605mμ, and the added volume of dithizone (Fig. 3.2). From the intercept of the graph corresponding to the complete reaction of the

Fig. 3.1.



The Influence of Chloride Ions on the Extraction of Gold as the Dithizonate into Chloroform.

Fig. 3.2.



The Influence of the Extraction Time on the Extraction of Gold as the Dithizonate into Chloroform.

(△, ○, × Left hand axis
• Right hand axis.)

added dithizone the molar ratio of gold to dithizone in the organic phase was found to be 1:1. It was therefore considered that the reaction to form the gold dithizonate of molar ratio gold to dithizone of 2:1, proceeded via the 1:1 chelate, i.e. 1:1 chelate + Au (III) $\rightleftharpoons$ 2:1 chelate. The formation of the 2:1 chelate would therefore be favoured by a low stoichiometry of reaction in agreement with the findings.

If the organic phase containing the gold dithizonate of molar ratio 1:1 was separated from the aqueous phase, and equilibrated with fresh dithizone solution in the presence of water, dithizone was consumed and the aqueous phase became acidic. If sodium chloride was now added to the aqueous phase and the extraction again performed, dithizone was found to be released. This was considered to indicate that the gold dithizonate of molar ratio gold to dithizone of 1:1 was probably a chloro-complex. This being the case, removing the aqueous phase containing chloride would disturb the equilibrium resulting in the consumption of dithizone, and the liberation of chloride to the aqueous phase.

The influence of the pH of the aqueous phase on the molar ratio of gold to dithizone in the organic phase was studied by carrying out a series of substoichiometric extractions of active gold as the dithizonate from aqueous solutions of differing pH, but all having a fixed low concentration of chloride ions (0.02M). The calculated molar ratios of gold to dithizone in the organic phases are given in Table 3.2.

Table 3.2.

Normality of H_2SO_4, or pH of aqueous phase	Activity of Au in organic phase (c/sec)	Molar ratio of Au:H_2Dz in organic phase
6N	1214	1.7(5):1.0
4N	1321	1.9(1):1.0
2N	1247	1.8(1):1.0
1N	1299	1.8(8):1.0
0.1N	1203	1.7(4):1.0
pH2.4	1167	1.6(7):1.0
pH3.8	1012	1.4(6):1.0
pH4.1	1008	1.4(6):1.0
pH4.5	1001	1.4(5):1.0
pH7.9	673	0.9(7):1.0
pH8.5	624	0.9(0):1.0
pH9.3	700	1.0(1):1.0
Activity of 0.5ml of Au solution (c/sec)	2302	

The radiometric results for the composition of the yellow coloured gold chelate extracted from acidic solution approximate to a molar ratio of gold to dithizone of 2:1 in agreement with the previous findings. The results do not give precisely 2:1 as was expected as there will always be a small contribution of the 1:1 gold chelate. In alkaline solution (pH of about 8 or higher), a red-brown complex of molar ratio gold to dithizone in the organic phase of approximately 1:1 was found, and at intermediate pH values (1-8) the molar ratio was found to have intermediate values between 2:1 and 1:1, gold to dithizone.

From the above discussion it is apparent that the proportions

of the various gold dithizonates extracted into the organic phase were dependent upon the pH and chloride ion concentration of the aqueous phase, the stoichiometry of the separation, and the period of extraction. The formation of the stable 2:1 complex being favoured by a low stoichiometry of reaction, with a prolonged period of extraction from an acidic medium of low chloride ion concentration. The study was far from complete, but sufficient evidence had been found to make it apparent that the use of dithizone for the substoichiometric determination of gold would have very serious limitations due to the strict control of experimental conditions that would have to be employed. The proposed method of Starý and Růžička[71] for the substoichiometric determination of traces of gold by neutron activation analysis using dithizone was therefore rejected. Further research to investigate the composition of the gold dithizonates formed would be of great interest, but was not pursued at this stage as the object of the research was to attempt to develop an analytical method for the substoichiometric determination of gold.

b. Using copper diethyldithiocarbamate as the chelating agent.

The reasons for the selection of copper diethyldithiocarbamate in chloroform as a possible chelating agent for the substoichiometric determination of gold were discussed in Chapter 2.

The extraction constant of gold (III) diethyldithiocarbamate, or the exchange constant for the reaction of gold (III) with copper (II) diethyldithiocarbamate in chloroform, or carbon tetrachloride are unknown. Only one extraction constant for metal diethyldithiocarbamates that of copper (II) in a medium of 75% ethanol is known,[92]

and therefore it was not possible to make even a qualitative assessment of the value expected for gold (III) diethyldithiocarbamate in chloroform.

As was discussed in Chapter 2, copper diethyldithiocarbamate is stable in acid solution, the metal being removed only by concentrated hydrochloric acid. This finding was confirmed by experiments in this laboratory using copper diethyldithiocarbamate in chloroform. No decrease in the extinction of a copper diethyldithiocarbamate solution (4.83×10^{-4}M) at 436mμ was observed during a 1hr extraction of the reagent in the presence of hydrochloric acid (0.1-8M) and sulphuric acid (0.1-10N).

An extractive titration of 1.03mg of gold (III) from a medium of 1M hydrochloric acid, with copper diethyldithiocarbamate in chloroform, resulted in the complete extraction of the gold to give a yellow complex in the organic phase of molar ratio gold to diethyldithiocarbamate of 1:1. A similar result was found when the extractive titration was performed from strong mineral acid solution (Table 3.3).

Table 3.3.

Aqueous phase HCl conc.^{n} (M)	Vol. of stable Au sol.^{n} added (1.05×10^{-2}M) (ml)	Vol. of $Cu(DDC)_2^*$ in $CHCl_3$ used (4.83×10^{-4}M) (ml)	Molar ratio of Au:DDC* in organic phase
1.0	0.5	5.2	1.0:1.0
2.0	0.5	5.1	1.0:0.9
5.0	0.5	5.2	1.0:1.0

*DDC represents the diethyldithiocarbamate anion.

The observed molar ratio gold to diethyldithiocarbamate for the gold chelate was in agreement with that found by Bobtelsky and Eisenstadter[82] using a heterometric technique, and the implication of this will be discussed in Chapter 5.

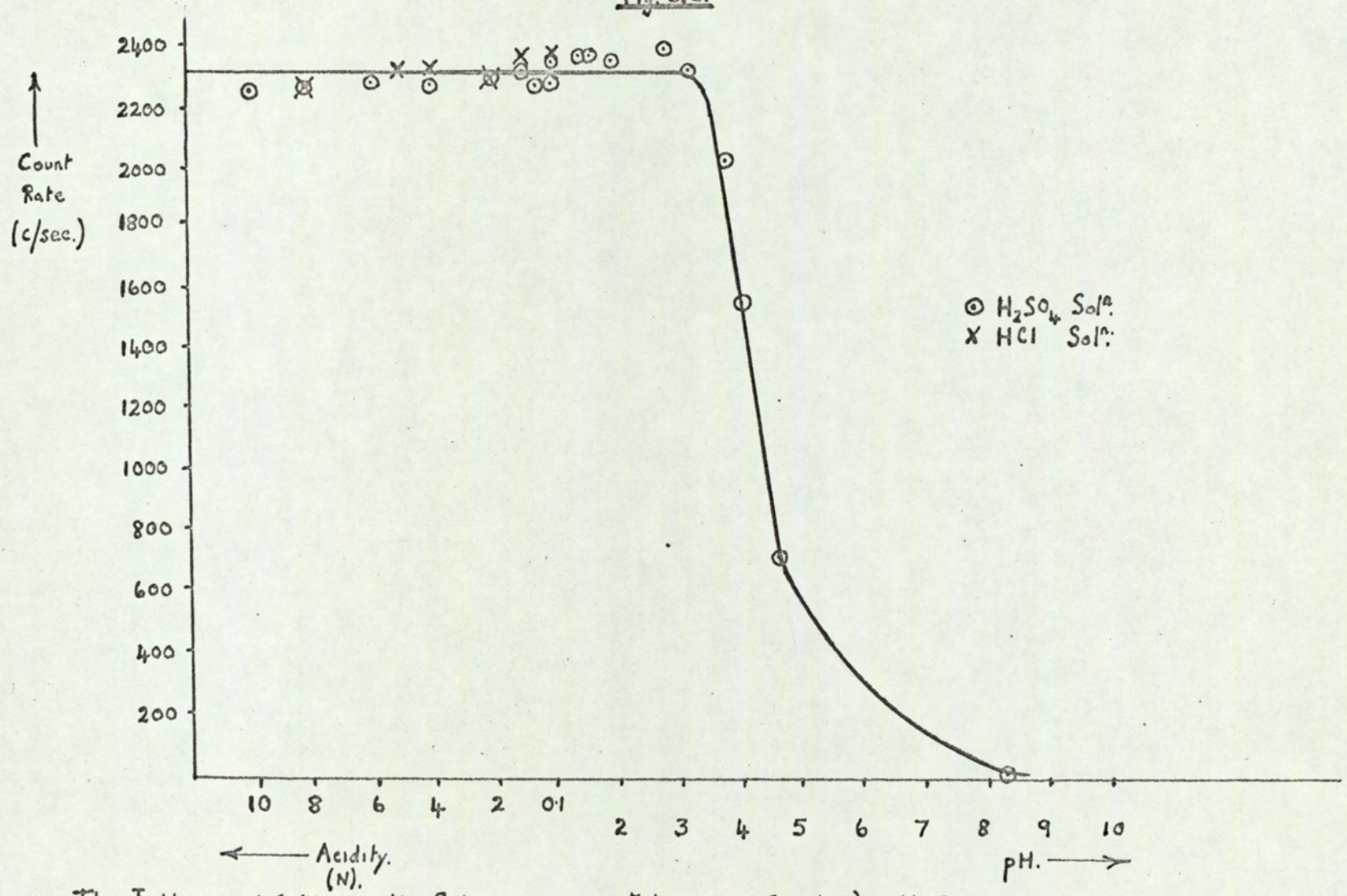
Copper diethyldithiocarbamate in chloroform was therefore considered to be a promising reagent for the substoichiometric determination of gold, and warranted further investigation.

ii. Influence of the pH of the aqueous phase.

An investigation to ascertain the optimum pH for the substoichiometric extraction of gold as the diethyldithiocarbamate showed that the extraction could be carried out over a wide range of acid concentration; 0.01-10N sulphuric, and 0.01-8M hydrochloric acid. The activity of the gold extracted (directly proportioned to the weight extracted) as a function of the pH of the aqueous phase is given in Fig. 3.3.

It can be seen that at a pH greater than 2, the weight of gold extracted decreased with increasing pH. This was considered to be due to one of two reasons, either the formation of hydroxy complexes of the type $AuCl_3OH^-$ in the aqueous phase, or possibly the formation of hydroxydiethyldithiocarbamates having a low partition coefficient between chloroform and an aqueous solution. Support for the former argument rather than the latter was found in the fact that the colour of the organic extracts changed from yellow to a greenish-brown which indicated the presence of unreacted copper diethyldithiocarbamate.

Fig. 3.3.



The Influence of Acidity on the Substoichiometric Extraction of Gold (III) as the Diethyldithiocarbamate into Chloroform.

For all future experiments a medium of 1.5±1M hydrochloric acid was selected.

iii. Time to reach extraction equilibrium.

The time to reach extraction equilibrium will depend upon the stoichiometry of the reaction in agreement with the Law of Mass Action, and at a stoichiometry of 80%, equilibrium in the extraction was reached in 20sec (Fig. 3.4). The stoichiometry of the extraction was selected as 80% as this was considered to be the maximum that was likely to be used. Wherever possible a stoichiometry of 50% was selected, and in such cases the time to reach extraction equilibrium will be less than 20sec.

If a prolonged period of extraction (up to 15min) was used, no change in the weight of gold extracted was observed. It was, therefore, concluded that no breakdown of the complex occurred on prolonged extraction.

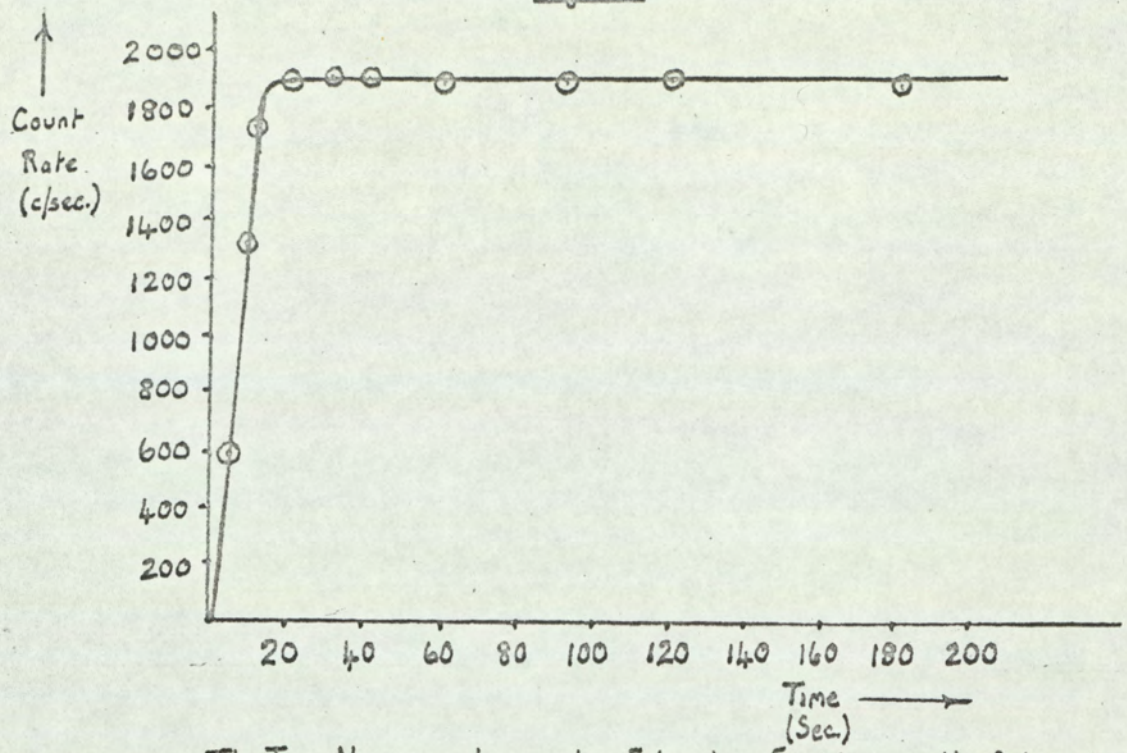
For all future experiments an extraction time of 1min was selected.

iv. Reproducibility.

The conditions under which the chelating agent reacts quantitatively with the gold has been established. The final condition to be satisfied was that the substoichiometric extraction could be carried out reproducibly independent of the stoichiometry of the reaction.

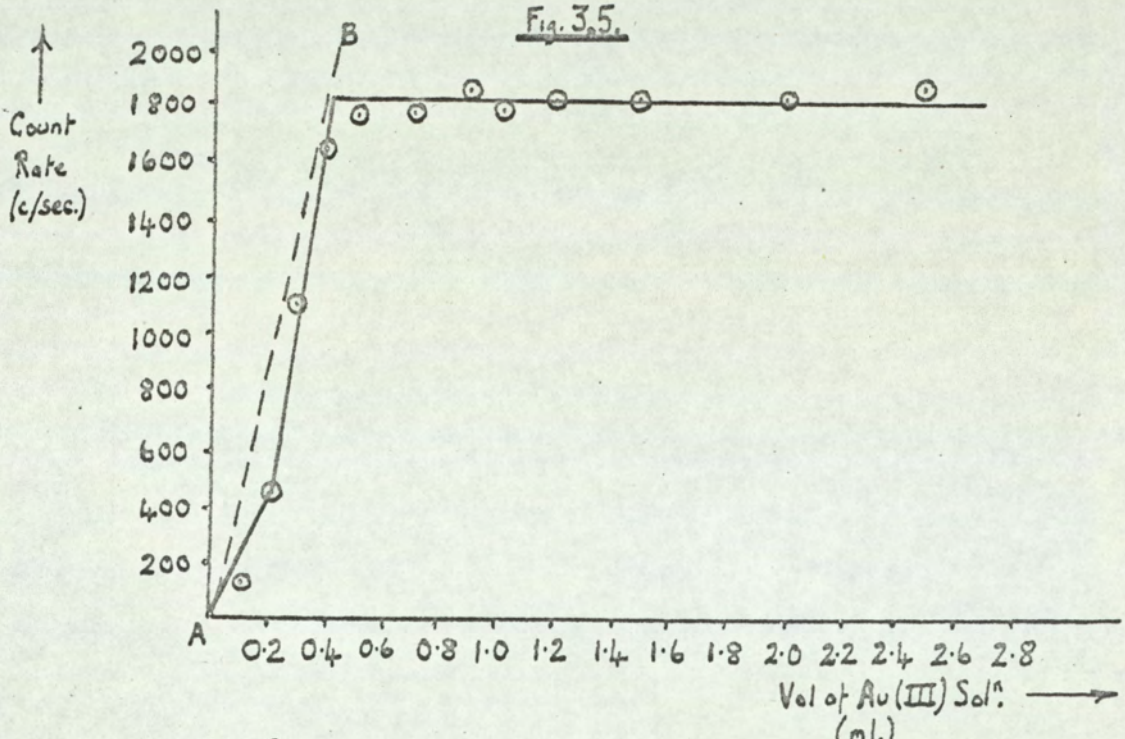
Fig. 3.5 shows that once all the chelating agent has been consumed the reproducibility of the substoichiometric separation is very good; coefficient of variation ±1.0% for the extractions made

Fig. 3.4.



The Time Necessary for reaching Extraction Equilibrium in the Substoichiometric Extraction of Gold (III) as the Diethyldithiocarbamate into Chloroform.

Fig. 3.5.



The Reproducibility of the Substoichiometric Extraction of Gold (III) as the Diethyldithiocarbamate into Chloroform.

in the presence of an excess of gold, i.e. the substoichiometric condition.

v. Partition coefficient of the gold diethyldithiocarbamate.

The partition coefficient of the gold chelate between chloroform, and an aqueous phase of 1.5M hydrochloric acid, using the substoichiometric conditions, i.e. in the presence of unreacted gold (III) was measured, using the method proposed by Duncan and Thomas.[93] Geiger and Sandell[24] had earlier proposed a spectrophotometric method, which was adapted to a radio-chemical technique by Duncan and Thomas. The procedure used is given in the experimental section (p. 92), and the equation necessary to calculate the partition coefficient is derived as follows:

Let, O_1 and O_2, represent the concentrations of the gold chelate in the first and second organic phases respectively.

A_1 and A_2, represent the concentrations of the gold chelate in the first and second aqueous phases respectively.

V_{O1} and V_{O2}, represent the volumes of the first and second organic phases respectively.

V_{A1} and V_{A2}, represent the volumes of the first and second aqueous phases respectively.

The partition coefficient, P, is then given by: $P = \frac{C_{org}}{C_{aq}}$ where, C_{org} and C_{aq}, represent the concentration of the gold chelate in the organic and aqueous phases respectively.

Therefore $\frac{C_{org}}{C_{aq}} = \frac{O_1}{A_1} = \frac{O_2}{A_2}$.

$$A_1V_{A1} = A_2V_{A2} + O_2V_{O2}, \text{ and since } V_{A1} = V_{A2}$$

$$A_1 = A_2 + \frac{O_2V_{O2}}{V_{A1}} .$$

Therefore

$$P = \frac{O_2}{A_2} = \frac{O_1}{A_2 + \frac{O_2V_{O2}}{V_{A1}}} \text{ , and if we let } \frac{V_{O2}}{V_{A1}} = V \text{ then}$$

$$O_1A_2 = O_2A_2 + O_2^2V, \text{ which reduces to}$$

$$A_2 = \frac{O_2^2V}{(O_1-O_2)} .$$

Therefore

$$P = \frac{O_2(O_1-O_2)}{O_2^2V} = \frac{(O_1-O_2)}{O_2V}$$

$$= \left(\frac{O_1}{O_2} - 1\right) \frac{1}{V}$$

$$= \left(\frac{O_1}{O_2} - 1\right) \frac{V_{A2}}{V_{O2}} .$$

Since, O_1 and O_2, are proportional to the specific activity of the respective organic phases, and provided the activity of equal volumes of the organic phases are measured, i.e. $V_{O1} = V_{O2}$ the above expression reduces to:

$$P = \left(\frac{Act_{org_1}}{Act_{org_2}} - 1\right) \frac{V_{A2}}{V_{O2}} .$$

The results for the determination of the partition coefficient of the complex at $20 \pm 1^{\circ}C$ are given in Table 3.14. The mean value was found to be 1259, the standard deviation of a single result ± 134, and the coefficient of variation $\pm 10.6\%$.

The gold was therefore forming with copper diethyldithiocarbamate in chloroform under substoichiometric conditions, a chelate which obeyed all the requirements laid down in the theory of substoichiometry.

vi. Selectivity.

For the method to be of analytical significance the separation procedure must be as selective as possible. From the theory of substoichiometry the higher the extraction constant of the metal complex, the more selective a particular reagent is likely to be. Also under substoichiometric conditions a quantitative separation of one metal from another is obtained if the ratio of the respective extraction constants with a particular reagent is greater than 200, (at 50% stoichiometry, with two equally charged ions initially at the same concentration, p. 19).

The selectivity study was therefore limited to the study of the effect of foreign metal ions which are likely to have extraction constants which do not satisfy the above criteria, and to other ions which may interfere by some other mechanism, e.g. reduction of the gold (III) to the metal. The effect of reagents likely to be used during the sample dissolution procedures were also examined.
Two approaches to the study were taken:

a. Indirect method.

This was based upon the detection of any depression of the activity of the gold extracted as diethyldithiocarbamate, caused by the presence of various stable foreign ions in the original aqueous solution. The weight of the ions introduced was of the same order

as that of the gold present. This was considered to be a very stringent test of the selectivity, as in most matrices the weight of the foreign ions will be far less than 1mg, (i.e. 0.1% in a 1g sample), unless the element is a major constituent.

The criteria of an interference.

The problem was to assess the magnitude of the differences between the mean value of the weight of gold extracted as the diethyldithiocarbamate in the absence of foreign ions, with that in the presence of foreign ions under the same conditions.

The method used was that of calculating the difference between the two observed means, and the standard error of the difference.[94] These values were then used to calculate the confidence limits for the true difference.

Suppose we have, n_1, observations in the absence of, and, n_2, observations in the presence of, a particular foreign ion, with corresponding means of the measured activities of, $\bar{a}_1$ and $\bar{a}_2$. Then the standard error of the difference in mean $(\bar{a}_1-\bar{a}_2)$, is:

$$SE\ (\bar{a}_1-\bar{a}_2) = \left(\frac{\sigma_1^2}{n_1} + \frac{\sigma_2^2}{n_2}\right)^{\frac{1}{2}},$$

where σ_1^2 and σ_2^2 are the true variances of the observations in the absence of, and in the presence of, a particular foreign ion respectively.

If we assume that the variances are the same in the absence or presence of foreign ions,

$$SE\ (\bar{a}_1-\bar{a}_2) = \sigma\left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}.$$

The true variance σ^2 is unknown but an estimate s^2 is known. The assumption is made that the estimated and true variance are the same.

Therefore

$$SE\ (\bar{a}_1-\bar{a}_2) = s \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}} .$$

The confidence limits for the difference in means is then given by:

$$(\bar{a}_1-\bar{a}_2) \pm ts \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}} ,$$

where t denotes the Student's test.

The 95% confidence limits of the difference are:

$$(\bar{a}_1-\bar{a}_2) \pm 2.365\ s \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}} .$$

The value of $t_{95\%}$ was based upon the results given under the heading Reproducibility (Table 3.13), where the number of observations was 8, and the coefficient of variation was $\pm$1.0%.

The null hypothesis is that $(\bar{a}_1-\bar{a}_2) = 0$ for no interference.

If $\left|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right| > \frac{2.365s}{\bar{x}_1} \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}$ or

$100 \left|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right| > 2.365C \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}\%,$

where C is the coefficient of variation, and is equal to 1% for this particular case, then the null hypothesis was rejected, and the particular foreign ion was considered to interfere.

Using this criteria only two elements were found to interfere, (Table 3.4) namely palladium (II) and tin (II).

Table 3.4.

Element or other specie added	Activity of 2.0ml of org. phase (c/sec)	Number of observations (n_1)	(n_2)	$100\frac{\lvert(\bar{a}_1-\bar{a}_2)\rvert}{\bar{a}_1}$ (%)	$2.365\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$ (%)
-	2382	2			
As(III)2.0mg*	2420		1	1.6	2.9
As(III)2.0mg	2411		1	1.2	2.9
As (V) 1.0mg	2442		1	2.5	2.9
In(III)2.0mg*	2335		1	2.0	2.9
In(III)2.0mg	2447		1	2.7	2.9
Mo(VI) 4.0mg*	2418		1	1.5	2.9
Mo(VI) 4.0mg	2411		1	1.2	2.9
Pd(II) 1.0mg	1972		1	17.2	2.9
Pd(II) 2.0mg	1239		1	48.0	2.9
Pt(IV) 2.0mg*	2354		1	1.2	2.9
Pt(IV) 2.0mg	2318		1	2.7	2.9
Sb(III)2.0mg*	2390		1	0.4	2.9
Sb(III)2.0mg	2348		1	1.4	2.9
Sb (V) 1.0mg	2390		1	0.4	2.9
Sn(II) 2.0mg*	30		1	98.7	2.9
Sn(II) 1.0mg	2442		1	2.5	2.9
Pb(II) 3g in 1N HNO_3	2382		1	0.04	2.9
-	2298	2			
5vol H_2O_2 0.1ml	2318		1	0.9	2.9
5vol H_2O_2 1.0ml	2332		1	1.5	2.9
1.5N HNO_3 (no HCl present)	2284		1	0.6	2.9
40%HF 1.0ml	2295		1	0.1	2.9
70%$HClO_4$ 0.5ml	2241		1	2.5	2.9
70%$HClO_4$ 1.0ml	2274		1	1.1	2.9

* No H_2O_2 present

The interference of tin (II), which was due to the reduction of gold (III) to the metal, could be overcome by the addition of hydrogen peroxide to the aqueous phase, prior to the extraction, this oxidised the tin from the bivalent to the tervalent state, in which it did not interfere. The addition of hydrogen peroxide to the other solutions containing the foreign ions prior to extraction, did not affect the result obtained. For all future experiments the addition of hydrogen peroxide was included.

The interference of palladium (II) was due to the metal competing with the gold (III) for complexation, palladium (II) being one of the most extractable elements as the diethyldithiocarbamate.[73-78] The results show that the ratio of the values of the extraction constants of gold and palladium (II) as the diethyldithiocarbamates is insufficient for the substoichiometric estimation of gold without interference from palladium (II).

The acids, and hydrogen peroxide, in the stated concentration had no interference (Table 3.4).

b. Direct method.

This method was based upon the addition of active isotopes of the foreign element (100-200μg), to the aqueous phase prior to the substoichiometric extraction of the stable gold.

Good agreement with the indirect study was obtained with one exception, the extraction in the presence of platinum (IV) (Table 3.5). The implication was that the platinum (IV) must interfere by some mechanism other than metal chelate formation. If the extraction

was carried out using only pure chloroform as the organic phase, the same amount of platinum (IV) was extracted (about 23%). Platinum (IV) was therefore interfering by extraction into pure solvent.

The method can be criticised as the weight of foreign element used in the direct study was not the same as that in the indirect. The prime reason for this was that it was very difficult to activate all the elements to produce similar specific activities, due to the variable thermal neutron cross sections and isotopic abundances. It was therefore decided to try to keep the weights of the foreign ions used as similar as possible, without the level of activity being too low or high for counting.

The two interfering ions in the method were therefore palladium (II) and platinum (IV). Fortunately both these elements are far less activated by thermal neutrons than gold, and the half lives of the active nuclides formed by (n,γ) reactions are shorter than that of gold-198 (Table 3.6). If the discriminator level of the scintillation counter was set to a value corresponding to 0.25MeV, and sufficient time (about 14hr) was allowed for the activity of the platinum-197^{m} ($t_{\frac{1}{2}}$ 80min) and 199 ($t_{\frac{1}{2}}$ 30min) to decay, the sensitivity of the determination of the gold-198 activity was only slightly reduced, and the interference of the platinum was almost avoided. There was a small contribution from the 0.28MeV γ ray of the 20hr platinum-197; 1µg of platinum irradiated for 24hr in a thermal neutron flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, followed by a 14hr decay, would have an absolute disintegration rate of 2d.p.s. of platinum-197. If one considers the irradiation of a theoretical

Table 3.5.

Results of the Selectivity Study (Direct Method)

Active nuclide		^{110m}Ag	^{76}As	^{64}Cu	^{203}Hg	^{99}Mo	^{109}Pd	^{197}Pt	$^{122+124}Sb$
Volume added	(ml)	10	10	10	2	1	2	2	6
Weight added	(µg)	111	110	83	100	167	100	116	104
Total activity added	(c/sec)	828	3190	6252	4526	28825	4514+	23404	4566
Activity of sub.^{c} extract	(c/sec)	0.3	0.6	0.7	2.5	5.9	380*	5455	6.3
Degree of extraction	(%)	0.03	0.02	0.01	0.06	0.02	8.4	23.2	0.14

+ One twentieth of stated activity actually measured.

* One sixth of stated activity actually measured.

Table 3.6.[95]

Nuclear Data

Stable isotope	Product of (n,γ) reaction	Half life	Principal γ energies (MeV)
^{108}Pd	^{109}Pd	14hr	-
^{110}Pd	^{111m}Pd	5.5hr	0.17
^{110}Pd	^{111}Pd	22min	-
^{196}Pt	^{197m}Pt	80min	0.337
^{196}Pt	^{197}Pt	20hr	0.077(19%), 0.19(2.5%), 0.28(0.6%).
^{198}Pt	^{199}Pt	30min	0.074, 0.197, 0.318, 0.540.

matrix of 1g of platinum containing 1μg of gold for a period of 24hr in a thermal neutron flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, followed by a 14hr decay, the absolute disintegration rate of the platinum-197 would be about 2×10^{6} d.p.s., and that of the gold-198 about 6×10^{4} d.p.s. Therefore when a platinum matrix is being considered the interference of platinum-197 activity would be severe. If however the discriminator level of the counter was set to a value corresponding to 0.30MeV, the nuclear interference of the platinum-197 would be overcome, with very little loss of sensitivity of the counting of the 0.41MeV gold-198 activity. A procedure for the determination of gold in platinum has been proposed by Morris and Killick.[96]

vii. Nuclear interference.

The following possible nuclear interference reactions[9]

$$^{198}Hg\ (n,p)\ ^{198}Au, \text{ and}$$

$$^{198}Pt\ (n,\gamma)\ ^{199}Pt \xrightarrow{\beta^-} {}^{199}Au$$

must be considered in the case of a mercury or platinum matrix.

In the thermal region of the neutron flux of a reactor there will always be present some fast neutrons, average energy about 2MeV, and so the possibility of the (n,p) reaction of mercury-198 to gold-198 must be considered. If a value of the cross section for the reaction with 2MeV neutrons is taken as 1millibarn, then the irradiation of 1g of mercury for 24hr in a neutron flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, would produce an absolute disintegration rate of about 7×10^{4} d.p.s. of gold-198.

The irradiation of 1g of a platinum matrix for 24hr in a thermal neutron flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, would produce

an absolute disintegration rate of about 1.7×10^8d.p.s. of gold-199, and if the matrix contained 1µg of gold then under the same conditions about 6.8×10^4d.p.s. of gold-198 would be produced. With a setting of the discriminator voltage corresponding to 0.25MeV however, the interference of the gold-199 would be overcome (γ 0.16, 0.21, 0.05MeV).

Also the reaction[9,88]

$$^{198}\text{Au}\ (n,\gamma)\ ^{199}\text{Au}$$

($t_{\frac{1}{2}}$ = 3.15d σ = 26,000 barns β- 0.30(70%), 0.25(23%), 0.46(7%)MeV; γ 0.16(38.2%), 0.21(9.4%), 0.05(0.04%) MeV),

must be considered in the case of a prolonged irradiation.

If one considers the irradiation of 1µg of gold-197 for a period of 24hr, in a thermal neutron flux of 10^{12} neutrons, cm^{-2}, sec^{-1}, then using the Bateman equation[97] a calculated absolute disintegration rate of about 2×10^3d.p.s. of gold-199, and about 6.8×10^4d.p.s. of gold-198 would be obtained, i.e. about 3% of the radio-active disintegration occur in gold-199.

However if, as was the case in sample analysis, a gold standard was irradiated simultaneously with the sample for the same period in the same thermal neutron flux (assuming degree of self-shielding identical), the ratio of gold-199 to gold-198 produced will be a constant. Therefore provided after irradiation there is no decay of one isotope to the other, (as was the case for gold-198 and 199), and the activity of both standard and sample are measured at the same time, the presence of gold-199 will not affect the final result.

It is also possible to discriminate against the gold-199 activity as was previously described, by setting the discriminator level to a value corresponding to 0.25MeV.

The irradiation times selected for the research were chosen, wherever possible, to be such that the above possibility need not be considered.

B. Sample Analysis

The samples selected for analysis were chosen so as to represent as wide a cross section of likely matrices in which gold may be determined as possible.

i. Weight of standard and samples.

The weight of the gold standard used for irradiation was in all cases about 10µg. This weight was selected in view of the findings of Vincent and Crocket,[98] who stated that with a weight of gold greater than 10µg, self-shielding errors become very pronounced. The sample weights were governed by the criteria discussed in Chapter 1.

Vincent and Crocket[98] assumed that in rocks and mineral samples, the traces of gold would be so uniformly distributed that self-shielding errors were inappreciable. The precision of the attained results by the authors gave some justification to this assumption. In this research the same assumption was made for all the samples analysed.

ii. Dissolution procedures.

The losses of gold which were likely to be incurred during sample dissolution were established by adding to the non-irradiated

matrix, a known weight of active gold (2.06mg), and ascertaining the recovery after the dissolution procedure. The weight of matrix examined was similar to that actually used in sample analysis (Table 3.7).

Table 3.7.

Matrix	Weight (g)	Activity of gold added (c/sec)	Activity of gold recovered (c/sec)	Recovery (%)
Silicon	1	6437	6088	94
Lead	3	1629	1570	96*
Kale	1	3015	1923	64

* After extraction with diethyl ether.

In all cases the recovery of the gold was greater than 94% with one exception, that of kale. Hillebrand[99] has shown that gold is lost from solution if evaporated to fumes with sulphuric acid, and therefore it was considered that most of the losses of gold occurred at this stage in the dissolution (p. 99). If the gold carrier was added prior to sample dissolution, the losses of gold would not affect the final result provided isotopic exchange had occurred.

The dissolution procedure for the silicon and rock samples involved the removal of the silicon as the volatile tetrafluoride. This method rather than the removal of the silicon as the dioxide, was preferred as considerable losses of gold were considered likely to occur using the latter method, due to co-precipitation of the gold. Bailey and Schuler,[100] using the former method for removing the silicon noted that poor precision of the results was obtained,

and considered this was due to a number of reasons, including co-precipitation of the gold by the silicon dioxide.

The lead samples were dissolved in a mixture of glacial acetic acid, and hydrogen peroxide as proposed by Hamilton,[101] followed by repeated evaporation of the solution almost to dryness in the presence of hydrochloric acid. The lead was finally allowed to precipitate out of the solution as the chloride, and the gold was extracted into ether (p.98).

iii. Extraction procedure.

The samples after dissolution finally in a medium of 1.5 ± 1M hydrochloric acid were extracted with a substoichiometric amount of copper diethyldithiocarbamate in chloroform, by the previously developed method. By knowing the % recovery of the gold after dissolution of the sample, it was always possible to carry out the final extraction under substoichiometric conditions. Without this prior knowledge, it was easy to add an excess of the reagent, especially if the recovery after dissolution was low.

The standards were extracted in a similar manner, using the same volume of chelating agent as was used for the samples (p. 100).

iv. Results.

The results obtained for the various samples are given in Table 3.8. The reproducibility of the results was good in the case of the silicon, lead and kale samples. The result of 1.1×10^{-3}ppm, for the kale sample of weight 0.2g, was that obtained from a test of the feasibility of the method for the determination of gold in this particular matrix. A recovery of 59% of the gold

was found, compared with the previous value of 64% (Table 3.7).

The results for the analysis of the rock Wl differ rather more, but this variation could not be explained on the basis of the presence of active nuclides other than gold; the decay measurements of these extracts confirmed their radio-chemical purity (Fig. 3.6). The discrepancies were probably due to inhomogenity of the sample, indication of this is given by the wide range of values found by other authors (Table 3.8).[98,102,103]

Fig. 3.7 shows that present with the kale sample extract of gold diethyldithiocarbamate was an active nuclide of an element other than gold. An estimation of the half life of the foreign active nuclide gave a value of about 45d, but unfortunately due to the low level of activity of the organic extract, it was impossible to obtain a suitable gamma ray spectrum, from which to estimate the γ ray energy.

Two active nuclides that could be produced by n, γ reaction, mercury-203, and iron-59, had similar half lives, 47d and 45d respectively, to that found by resolution of the decay curves (Fig. 3.7), and both of these elements were known to be present in the sample from the published data of Bowen.[104] The concentration of mercury, and iron found in the kale sample being about 0.15ppm and 119.5ppm respectively. The interference study (Table 3.5) shows that 100μg of mercury does not interfere with the method under the substoichiometric conditions used. Therefore the interference in the kale analysis was considered not to be due to mercury. Furthermore, mercury would be lost from the system by volatalisation

during the dissolution of the kale sample,[99] and therefore the concentration of mercury present in the solution prior to the extraction of the gold as the diethyldithiocarbamate would be less than 0.15ppm.

Iron (III) does form a diethyldithiocarbamate, but it is one of the lower members in the order of extractability of metal diethyldithiocarbamates.[73-78] Antimony (III) which is more extractable as the chelate than iron (III),[73-78] does not interfere by forming a diethyldithiocarbamate in opposition to the gold (III) (Table 3.4), and therefore iron (III) was considered unlikely to interfere. However, the concentration of iron in the kale about 119.5ppm was sufficiently high to give a solution having a considerable activity due to iron-59. If the organic phase was slightly contaminated by the aqueous phase then the activity from iron-59 (γ 1.10 (57%), 1.29 (43%)MeV)[9,88] would be detected by the scintillation counter which was only set at a low discriminator level corresponding to 0.07MeV. It was therefore concluded that the interference in the kale analysis, was probably due to the presence of traces of the aqueous phase containing iron-59, contaminating the organic phase. In the case of the rock W1 samples which were known to contain a large concentration of iron (p. 81), the organic phases after the extraction of the gold as the diethyldithiocarbamate were washed with 1M hydrochloric acid to remove any traces of the aqueous phase. In so doing, the possibility of any contamination due to an active foreign nuclide was eliminated, as was shown from the decay curves of the samples (Fig. 3.6). It was therefore apparent that the

separation of the organic and aqueous phases was not complete in the case of the kale samples, and a similar procedure to that employed in the case of the rock W1 samples should have been used.

If a correction for the presence of this foreign element was made, the results for the kale samples were modified to:

2.4×10^{-3}ppm of gold (previously 2.5×10^{-3}ppm), and

2.6×10^{-3}ppm of gold (previously 2.7×10^{-3}ppm), and

were in excellent agreement with those of Morris and Gupter[105] obtained by a "classical" neutron activation analysis, employing a chemical separation technique (Table 3.8).

The concentration of gold in the gold-doped semiconductor-grade silicon, calculated on the basis of the equilibrium segregation coefficient for gold in silicon was about 4×10^{-2}ppm. If this estimate was corrected for the Burton-Slichter layer,[106] because of the rather high crystal pulling speed employed in the preparation of the particular crystal examined, then a figure similar to that found by neutron-activation analysis would be obtained. There was little doubt the latter result was more correct.

The results for the high purity lead sample are in good agreement with those of Hoste,[107] and it was therefore concluded that the dissolution technique developed in this laboratory was fully satisfactory, and isotopic exchange between the stable carrier and active gold, formed by the neutron activation had been complete.

Table 3.8.

Results of Sample Analyses

Sample		Gold-doped semiconductor-grade silicon (1153)				
Weight	(g)	0.4472	0.5904	0.8949	1.0984	1.1429
Au standard	(μg)	1.04×10^{-1}	1.04×10^{-1}	1.04×10^{-1}	1.04×10^{-1}	1.04×10^{-1}
Activity from Au standard	(c/10sec)*	14613	14613	14613	14613	14613
Activity from sample	(c/10sec)	6149	9297	10985	14016	14625
Au found	(μg)	4.4×10^{-2}	6.6×10^{-2}	7.8×10^{-2}	9.9×10^{-2}	10.4×10^{-2}
	(ppm)	9.6×10^{-2}	11.0×10^{-2}	8.7×10^{-2}	9.1×10^{-2}	9.1×10^{-2}
Mean value	(ppm)			9.5×10^{-2}		
Standard deviation	(ppm)			$\pm 0.9 \times 10^{-2}$		
Coeff. of variation	(%)			± 9.5		
Results of other authors	(ppm)			-		

Table 3.8. (cont.)

Sample		High-purity lead (VM_3)				
Weight	(g)	1.6350	2.0500	2.5120	3.2270	3.6130
Au standard	(μg)	2.08×10^{-2}	2.08×10^{-2}	2.08×10^{-2}	2.08×10^{-2}	2.08×10^{-2}
Activity from Au standard	(c/10sec)*	6932	6932	6932	6932	6932
Activity from sample	(c/10sec)	680	773	1315	1093	1673
Au found	(μg)	2.0×10^{-3}	2.3×10^{-3}	4.0×10^{-3}	3.3×10^{-3}	5.0×10^{-3}
	(ppm)	1.3×10^{-3}	1.1×10^{-3}	1.6×10^{-3}	1.0×10^{-3}	1.4×10^{-3}
Mean value	(ppm)			1.3×10^{-3}		
Standard deviation	(ppm)			$\pm0.2\times10^{-3}$		
Coeff. of variation	(%)			±15.4		
Results of other authors	(ppm)			$1.0\pm0.4\times10^{-3}$ (ref. 107)		

Table 3.8. (cont.)

Sample		Rock W1			Leaves of kale (Brassica oleracea)+		
Weight	(g)	1.0000	0.5000**	0.5000**	0.2000	1.0006	1.0023
Au standard	(μg)	4.0×10^{-2}	4.0×10^{-2}	4.0×10^{-2}	4.16×10^{-2}	4.16×10^{-2}	4.16×10^{-2}
Activity from Au standard	(c/10sec)*	15237	15237	15237	15237	11609	11609
Activity from sample	(c/10sec)	1940	3269	3288	82	720	794
Au found	(μg)	5.1×10^{-3}	8.6×10^{-3}	8.6×10^{-3}	2.1×10^{-4}	2.5×10^{-3}	2.7×10^{-3}
	(ppm)	0.5×10^{-2}	1.7×10^{-2}	1.7×10^{-2}	1.1×10^{-3}	2.5×10^{-3}	2.7×10^{-3}
Mean value	(ppm)		1.1×10^{-2}			2.1×10^{-3}	
Standard deviation	(ppm)		$\pm 0.7 \times 10^{-2}$			$\pm 0.9 \times 10^{-3}$	
Coeff. of variation	(%)		±63.6			±42.9	
Results of other authors	(ppm)	1.1×10^{-2} (ref.102)	8.4×10^{-3} (ref.98)	4.9×10^{-3} (ref.103)		2.2×10^{-3}*** (ref.105)	

*The stated activities are the mean of two standards.

**Two equal aliquots from a 1g sample after dissolution.

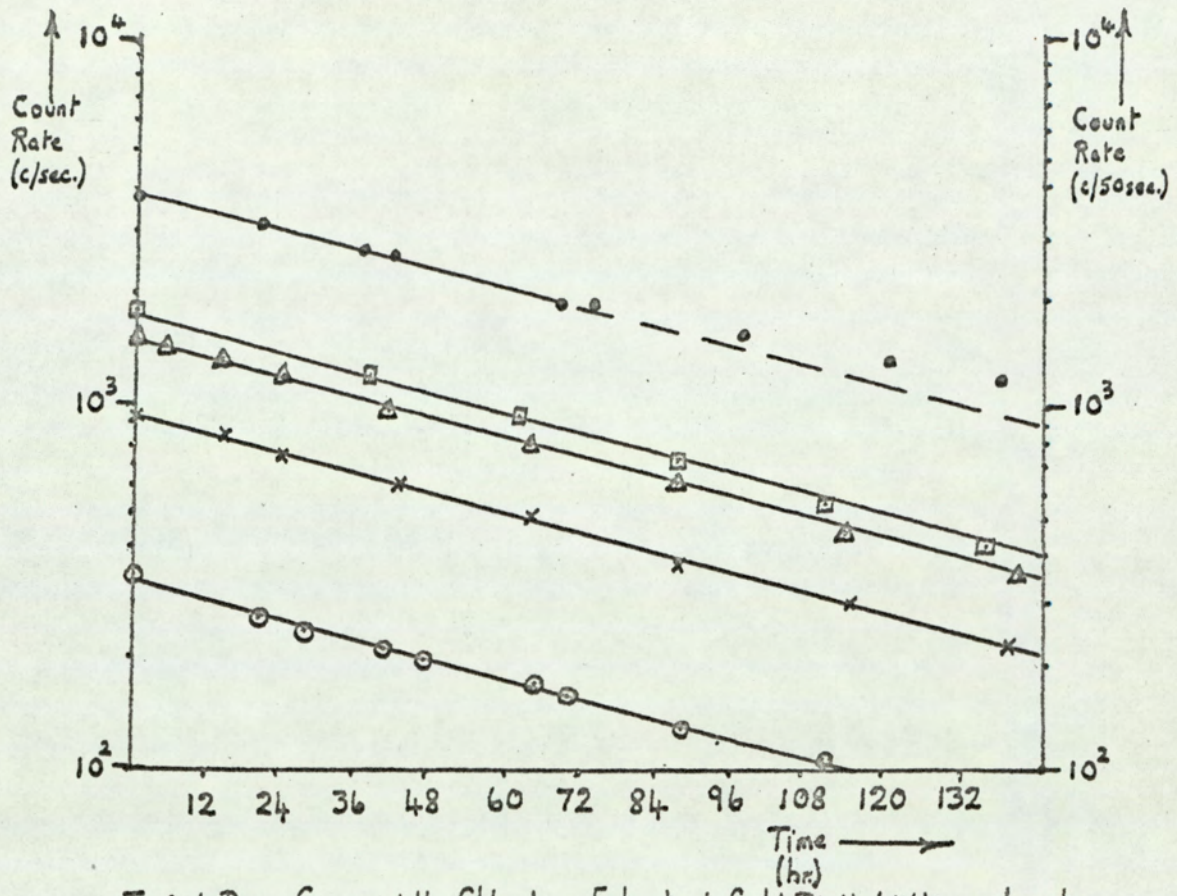
***Average of 2.1×10^{-3}, 2.0×10^{-3}, 2.4×10^{-3}, and 2.4×10^{-3} ppm (ref.105). Samples heated at 80°C for about 4hr before being weighed for analysis.

+Samples weighed without drying, material reported to have water content of 3-5%.

Standard deviation is that of a single result = $\pm \sqrt{\frac{\Sigma \Delta^2}{n-1}}$ where Δ is the deviation from the mean, ($\bar{x}$), and n is the number of observations.

Coefficient of variation = $\pm \frac{s}{\bar{x}} \times 100\%$.

Fig. 3.6.

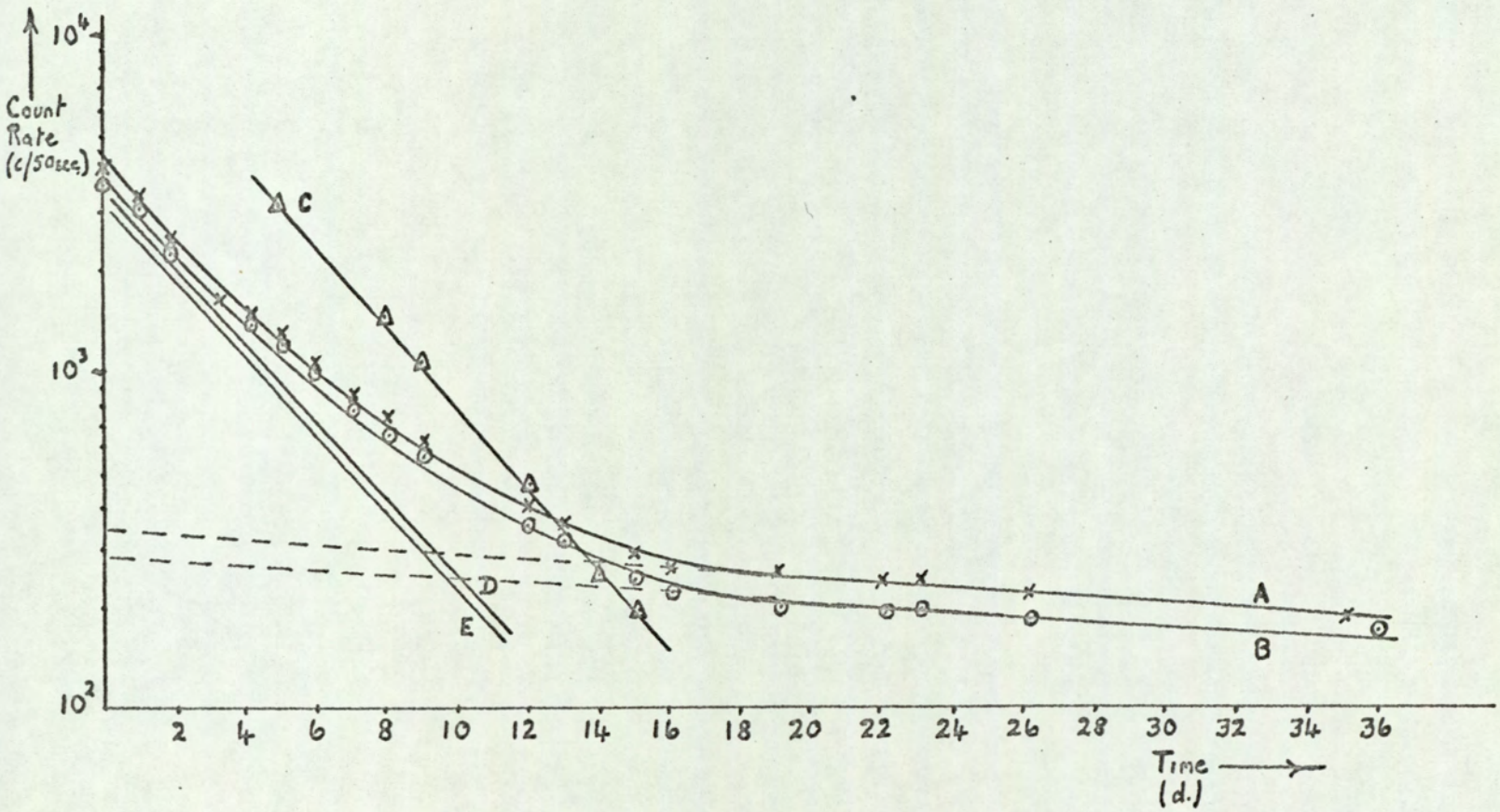


Typical Decay Curves of the Chloroform Extracts of Gold Diethyldithiocarbamate obtained from the various Irradiated Samples.

• Biological material (kale), ⊡ High purity lead, △ Gold-doped semiconductor grade silicon, × Gold standard, ⊙ Rock W-1.

(×, △, ⊙. Left hand axis, •, ⊡ Right hand axis.)

Fig. 3.7.



The Analysis of the Decay Curves of the Chloroform Extracts of Gold Diethyldithiocarbanate obtained from the Irradiated Kale Samples. (A, and B, are the observed decay data of two samples, C is the observed decay data of a Gold Standard, and D, and E, are the decay curves corrected for the longer lived component.)

III. Conclusion

The method developed has proved to be very simple, and very selective, only palladium (II) and platinum (IV) interfering. It has also been demonstrated that the method can be applied to the analysis of gold in many industrially important matrices.

It is interesting to note that the high purity lead sample was known to contain Ag, As, Cu, Hg, Sb and Tl in trace amounts (determined by neutron activation analysis),[107] and the rock Wl. Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, F, Ga, Ge, In, La, Li, Mo, Nb, Nd, Ni, Pb, Pd (0.02ppm) Rb, Re, Sb, Sc, Sm, Sn, Sr, Ta, Th, Tl, U, V, W, Y, Yb, Zn and Zr at trace levels (0.001 to 300ppm) and large amounts of Fe, Mg, Ca, Na, K, Ti, P and Mn, the main constituents being SiO_2 and Al_2O_3.[108]

Unfortunately quantitative extraction data of metal diethyldithiocarbamates is still not available, and for this reason, it was not possible to calculate the theoretical optimum conditions for the separation and selectivity of the method which has been developed, and to compare them with those which have been found experimentally.

In 1965 Alimarin and Perezhogin[109] also published a simple substoichiometric procedure for the determination of gold by neutron activation analysis. The gold was extracted into chloroform using tetraphenylarsonium chloride as the reagent, and was the first published substoichiometric separation procedure based on the extraction of an ion-association compound. The method however had the disadvantage of being dependent on the hydrochloric acid concentration of the aqueous phase; not greater than 0.5N could be used.

IV. Experimental

A. Apparatus

Scintillation counter. The detector was a 1.75in. diameter x 2in. NaI (Tl) well type crystal. Well volume 5ml. This was associated with a single channel gamma-ray spectrometer. In all experiments a setting of the discriminator voltage corresponding to 0.07MeV was used. This ensured only low selectivity, but high sensitivity of counting of the gold-198 activity.

For each experiment the samples for counting were:

1. All of fixed volume to keep a constant geometry of counting.

2. Counted for a period sufficient to yield a total of at least 10,000 counts, which ensured a counting ~~accuracy~~ precision of 1%, and the activities were corrected for background.

B. Reagents

All the reagents were prepared from analytical reagent grade chemicals, and the water used was doubly distilled from a glass still. The purification and standardisation procedures are given in the Appendix.

i. Stable gold carrier solution 2.06mg/ml (1.05×10^{-2}M)

0.1030g of metallic gold was dissolved in 10ml of aqua regia, and the resulting solution was evaporated almost to dryness. 5ml of hydrochloric acid was then added, and the evaporation repeated. The solution was then diluted to 50ml in a volumetric flask with 1M hydrochloric acid.

ii. Active gold carrier solution 2.06mg/ml (1.05×10^{-2}M).

To the above stable solution one or two drops of the active isotope solution of gold-198 was added. The amount of isotopic carrier introduced was negligible.

iii. Dithizone solution (5.08×10^{-4}M).

0.1282g of purified dithizone was dissolved in 200ml of chloroform. The solution was then filtered into a 1000ml volumetric flask, and diluted to the mark with the same solvent. The chloroform used was that suitable for use with dithizone.

iv. Copper diethyldithiocarbamate solution (4.83×10^{-4}M).

0.2253g of sodium diethyldithiocarbamate was dissolved in 250ml of water, to this was added 25ml of a copper (II) sulphate solution containing 2.5g of the pentahydrate. The precipitate formed was extracted by two 250ml portions of chloroform, and the combined extracts were diluted to 1000ml in a volumetric flask, with the same solvent.

v. Stable foreign metal ion solutions 1.0mg of metal/ml.

The solutions were prepared by dissolving the appropriate weight of the element (oxide, chloride or sulphate) by the method given in Table 3.9, and diluting the resulting solution to 100ml in a volumetric flask.

vi. Active nuclide solutions.

a. Gold-198.

The active isotope solution was obtained from the Radiochemical Centre, Amersham.

1mg of gold in 2.0ml of approximately 3M hydrochloric acid, 12.6mc ^{198}Au.

b. Antimony-122 and 124, Arsenic-76, Copper-64, Molybdenum-99, Platinum-197 and Silver-110m.

All the above active nuclides were prepared by irradiation of the corresponding elements or compounds in a flux of 6×10^{11} neutrons, cm^{-2}, sec^{-1}, for 6hr (Universities of Manchester and Liverpool Research Reactor). The preparation of the solutions is given in Table 3.10.

The mercury-203 and palladium-109 isotope solutions were available in the laboratory at the time of this research.

Table 3.9.

Element	Compound used	Weight taken (g)	Solvent
As (III)	As_2O_3	0.1322	Min. vol. of KOH followed by neutralisation with HCl.
As (V)	As_2O_5	0.1572	As for As_2O_3.
In (III)	$InCl_3$	0.1928	Water.
Mo (VI)	$(NH_4)_6Mo_7O_{24}4H_2O$	0.1843	Water.
Pd (II)	$PdCl_2 2H_2O$	0.2010	1M HCl.
Pt (IV)	H_2PtCl_6	0.2100	1M HCl.
Sb (III)	$SbCl_3$	0.1870	1M HCl.
Sb (V)	Sb_2O_3	0.1240	HCl, oxidise with $NaNO_2$, diluted with water. Excess NO_2 destroyed with urea.
Sn (II)	$SnCl_2 2H_2O$	0.1903	Min. vol. of 10M HCl followed by dilution with water.

Table 3.10.

Preparation of Active Element Solutions

Compound irradiated	Weight (mg)	Isotope produced	Principal γ ray energies[88] (MeV)	Solvent	Final vol. of sol^{n}. (ml)	Conc^{n}. of element (μg/ml)
$AgNO_3$	1.742	^{110m}Ag	0.66, 0.89	Water.	100	11.1
As_2O_3	0.365	^{76}As	0.56	Min. vol. of KOH followed by neutralisation with HCl.	25	11.0
$CuSO_4 5H_2O$	0.342	^{64}Cu	0.51	1M HCl.	10	8.25
$HgCl_2$		^{203}Hg	0.279	Water.	25	50.0
H_2PtCl_6	12.264	^{197}Pt	0.077 0.19	1M HCl.	100	58.3
MoO_3	25.104	^{99}Mo	0.74	5N NH_4OH.	100	167.2
Pd (elemental)		^{109}Pd	None (pure β^- 1.03 MeV)	Aqua regia followed by repeated evap^{n}. with HCl.	25	50.0
Sb (elemental)	0.432	$^{122+124}Sb$	0.57 0.60	5N H_2SO_4+5N HCl+ a few drops of HNO_3.	25	17.3

C. Development of the Method

All the experiments described in this section were carried out using the gold carrier solution, active or stable (1.05×10^{-2}M), dithizone solution in chloroform (5.08×10^{-4}M) and the copper diethyldithiocarbamate solution in chloroform (4.83×10^{-4}M).

i. Extractive titration of gold with dithizone.

To a 100ml separatory funnel containing 25ml of 0.5N sulphuric acid, 0.5ml of the stable gold carrier solution was added. The dithizone solution was then added in 0.5ml portions from a 10ml burette and after each addition, the extraction was carried out for 3min. The phases were then allowed to separate, and the organic phase was removed. The end point of the titration occurred when the yellow colour of the gold dithizonate no longer predominated, and the green colour of unreacted dithizone appeared. Once the approximate end point had been established the titration was repeated, reducing the addition of dithizone to 0.1ml portions in the region of the end point.

For the extractions at higher chloride ion concentration, the aqueous phase consisted of 12.5ml of 1N sulphuric acid, together with xml of 5M sodium chloride solution, and (12.5-x)ml of water. The results are given in Table 3.1.

ii. Influence of chloride ions on the reaction of gold with dithizone.

To a series of 100ml separatory funnels each containing 10.0ml of 1.0N sulphuric acid and 0.5ml of stable gold carrier solution, suitable volumes of 5M sodium chloride solution and water were

added, keeping the total volume of solution constant at 20.0ml. The hydrogen ion concentration of the aqueous phases was 0.5M and the chloride ion concentrations that given in Fig. 3.1, and for each set of conditions a series of 3min extractions were carried out in the presence of increasing substoichiometric amounts of dithizone in chloroform solution. After the extractions the organic phases were removed, and the aqueous phases washed with 5ml of chloroform. To the aqueous phases was added 1ml of concentrated hydrochloric, and 5ml of hydrobromic acids, and the solutions diluted to 50ml in volumetric flasks. The extinction of the solutions at 380mμ was then measured in 1cm cells, and the weight of gold remaining in the aqueous phases was obtained from the calibration graph (p. 237). This value was plotted as a function of the added volume of dithizone solution for the different chloride ion concentrations of the aqueous phase studied (Fig. 3.1).

iii. Influence of the extraction time on the reaction of gold with dithizone.

A similar procedure to that described in the previous experiment was used except a fixed hydrogen, and chloride ion concentration of the aqueous phase of 0.5, and 1.5M respectively were used, with a variable extraction time. The results are given in Fig. 3.2. With the study using an extraction time of 30min, extractions were also performed with greater than 10.0ml of dithizone (i.e. excess), and after the extractions the organic phases were diluted to 15.0ml with chloroform and the extinctions of the excess dithizone at 605mμ

in 0.5cm cells measured. The values as a function of the added volume dithizone were also plotted (Fig. 3.2). In all the extractions using 10.0ml or greater of dithizone no gold was found to be present in the aqueous phases using the Bromoaurate Method.[91]

iv. The composition of the organic phase containing gold and dithizone.

To establish the molar ratio of gold to dithizone in the organic phase a series of 3min extractions were performed using 0.5ml of active gold carrier solution in a medium of 20ml of the stated normality of sulphuric acid, or pH of solution, and 3.0ml of dithizone solution (5.25×10^{-4}M). After the extractions the activity of the gold in 1.0ml of the organic phase was determined, and from the known activity of 0.5ml of the gold solution, the weight of gold extracted into the organic phase was determined, and hence, the molar ratio of gold to dithizone (knowing the strength of the dithizone solution used). The results are given in Table 3.2.

v. Extractive titration of gold with copper diethyldithiocarbamate.

The extractive titration procedure was as previously described (p. 86). The aqueous phase consisted of 25ml of hydrochloric acid of the stated molarity (Table 3.3), and the end point of the titration was a change from the yellow colour of the gold diethyldithiocarbamate, to the dark brown colour of the unreacted copper diethyldithiocarbamate.

vi. Influence of the pH of the aqueous phase.

To a series of 100ml separatory funnels each containing 25ml of

different concentrations of sulphuric, or hydrochloric acid, or water alone, 0.5ml of the active gold carrier solution was added. The pH of the resulting solutions was then adjusted to reach the different values in the pH range 0-8.5 by adding dilute aqueous ammonia and/or small volumes (1-2ml) of 0.1M acetate, or borate buffer solutions (Table 3.11). 3.0ml of the copper diethyldithiocarbamate solution was added, and the extractions were carried out for 3min, after which the organic phases were filtered through Whatman 540 filter papers placed in the stems of the separatory funnels. 2.0ml of each organic phase was then pipetted into a series of counting jars, and their activities measured using the scintillation counter. The results are given in Table 3.11. The recorded pH values are those measured after the substoichiometric extraction.

Table 3.11.

N of acid (H_2SO_4)	Activity of 2.0ml of organic phase (c/sec)	pH	Activity of 2.0ml of organic phase (c/sec)
10	2233	1.0	2353
8	2243	1.6	2346
6	2269	1.7	2327
4	2267	2.0	2300
2	2284	2.8	2351
1	2273	3.2	2315
0.5	2239	3.8	2006
0.2	2228	4.0	1548
0.1	2328	4.5	682
		8.3	18

Table 3.11. (cont.)

N of acid (HCl)	Activity of 2.0ml of organic phase (c/sec)
8	2245
5	2315
4	2296
2	2297
1	2329
0.1	2340
Activity of 0.5ml of Au solution (c/sec)	5751

See also Fig. 3.3.

The stoichiometry of the extraction was calculated from the known activity of 0.5ml of the gold solution as follows:

Mean activity of gold extracted by 2.0ml of reagent = 2300c/sec.

Mean activity of gold extracted by 3.0ml of reagent = 3450c/sec.

Activity of 0.5ml of gold solution = 5751c/sec.

Therefore stoichiometry of extraction = $\frac{3450}{5751} \times 100 = 60\%$.

vii. Time to reach extraction equilibrium.

0.5ml of the active gold carrier solution in a medium of 25ml of 1.5 ± 1M hydrochloric acid was extracted for the stated time period (Table 3.12), with 4.0ml of the copper diethyldithiocarbamate, employing the same experimental technique as previously described. 2.0ml of each organic phase was counted.

The results are given in Table 3.12.

Table 3.12.

Extraction time (sec)	Activity of 2.0ml of organic phase (c/sec)
2	598
5	1300
10	1746
20	1907
30	1914
40	1905
60	1909
90	1913
120	1916
180	1907
900(15min)	1910
Activity of 0.5ml of Au solution (c/sec)	4760

Stoichiometry 80%.

See also Fig. 3.4.

viii. Reproducibility.

The method was as described in the previous experiment except all the extractions were carried out simultaneously for a period of 1min, in the presence of increasing amounts of active gold solution. The results are given in Table 3.13.

Table 3.13.

Vol. of active Au solution added (ml)	Activity of 2.0ml of organic phase (c/sec)
0.1	169
0.2	430
0.3	1091
0.4	1665

Table 3.13. (cont.)

Vol. of active Au solution added (ml)	Activity of 2.0ml of organic phase (c/sec)	
0.5	1794	
0.7	1799	$\bar{x}$ = 1820(c/sec)
0.9	1838	n = 8
1.0	1801	s = $\pm$18(c/sec)
1.2	1828	Coeff. of variation
1.5	1837	= $\pm$1.0%
2.0	1835	
2.5	1828	
Activity of 0.5ml of Au solution (c/sec)	4504	

$\bar{x}$ is the mean value of the observations in the presence of an excess of gold.

s is the standard deviation of a single result = $\pm\sqrt{\frac{\Sigma\Delta^2}{n-1}}$ where Δ is the deviation from the mean, and n is the number of observations.

The coefficient of variation is given by $\pm\frac{s}{\bar{x}}$ x 100%.

See also Fig. 3.5.

ix. Partition coefficient of the gold diethyldithiocarbamate.

To a series of 100ml separatory funnels each containing 25.0ml of 1.5M hydrochloric acid, the stated volume of active gold carrier solution was added (Table 3.14). 4.0ml of the copper diethyldithiocarbamate in chloroform was added, and the extraction carried out for 1min. The organic phases were then filtered, through Whatman 540 filter papers placed in the stems of the separatory funnels and 3.0ml of each was introduced into counting jars. The aqueous phases were centrifuged to remove any traces

of organic phase, and carefully transferred to a series of beakers using transfer pipettes. 15.0ml of each aqueous phase was then introduced into a series of clean dry 100ml separatory funnels, and 4.0ml of chloroform was added. A 1min extraction was carried out, followed by filtration of the organic phases as previously described. 3.0ml of the organic phases were then introduced into counting jars, and the activities were measured. The scintillation counter was used in a differential mode, setting a threshold voltage, and a channel width, suitable for counting the 0.41MeV photopeak of the gold-198 activity. This setting was preferred to the normal discriminator setting corresponding to 0.07MeV, which was used in all other experiments, as a lower background, and a better $\frac{(\text{sample count rate})^2}{(\text{background count rate})}$ value was obtained.[110] This criteria was particularly desirable in this experiment, as the activity of the second organic phase was very low, about 1 count/sec. The volumes of solutions used were all delivered from bulb pipettes, which were thoroughly cleaned, and dried, between each operation. The results are given in Table 3.14.

x. Selectivity.

a. Indirect.

0.5ml of the active gold solution in a medium of 25ml of 1.5 ± 1M hydrochloric acid, was mixed with the stated weights (Table 3.4), of the foreign metal ion solutions (or volume of acids or hydrogen peroxide), and then the extractions were carried out for 1min, using 4.0ml of the copper diethyldithiocarbamate

Table 3.14.

The Partition Coefficient of the Gold Diethyldithiocarbamate between Chloroform and 1.5M Hydrochloric Acid

Vol. of active Au solution added (ml)	Activity of 3.0ml of 1st organic phase (c/sec)	Activity of 3.0ml of 2nd organic phase (c/sec)	Vol. of 2nd aqueous phase (ml)	Partition Coefficient (p)	
0.5	248.5	0.9	15.0	1376	$\bar{x}$ = 1259
0.5	248.7	1.0	15.0	1239	n = 6
0.5	247.4	1.2	15.0	1026	s = ±134
1.0	246.0	0.9	15.0	1362	Coeff. of variation
2.0	246.2	1.0	15.0	1226	= ±10.6%
2.5	239.4	0.9	15.0	1325	

$\bar{x}$ is the mean value of the observations.

s is the standard deviation of a single result = $\pm \sqrt{\frac{\Sigma\Delta^2}{n-1}}$ where Δ is the deviation from the mean, and n is the number of observations.

The coefficient of variation is given by $\pm \frac{s}{\bar{x}} \times 100\%$.

solution. The separation and counting techniques employed were as previously described, 2.0ml of the organic phases being counted.

The extractions were repeated in the presence of 1ml of 5vol hydrogen peroxide in the aqueous phase prior to the extraction.

b. Direct.

The direct study was made under exactly the same conditions as for the indirect (1ml of 5vol H_2O_2 present) except 0.5ml of stable gold solution was used, together with the stated weight of active foreign metal ion solutions (Table 3.5). The counting technique employed was exactly the same as for gold-198 except in the case of palladium-109. Palladium-109 is a pure β^- emitter (1.03MeV), so it was therefore necessary to evaporate the organic phase after the extraction on a planchette, and count the activity using an end window Geiger-Müller tube. The activity measurements stated in Table 3.5 for the palladium-109 extraction have been corrected for the dead time, 400μsec and background, approximately 10 counts/min of the counter.

The weight of foreign metal ion introduced was kept within the range 100-200μg.

D. Sample Analysis

i. Weight of standard and samples.

The criteria governing the weight of gold to be irradiated as the standard was given on p. 70. A weight of about 10μg of gold was selected. 0.10400g of metallic gold was dissolved by the method previously described (p. 82), and the resulting solution was diluted to 100ml in a volumetric flask with 1M hydrochloric acid.

2.5ml of this solution was then diluted to 250ml in a volumetric flask, using 1M hydrochloric acid. This solution contained 10.40µg of Au/ml. For the standard used in the rock W1 analysis, 0.10000g of metallic gold was used, and the solution prepared in exactly the same manner as above. The resulting solution in this case had a gold content of 10.00µg/ml. The concentration of the solutions was checked using the methods given on p.235, which are themselves dependent upon the original weight of gold used. In all cases the concentrations were found to be as expected, 1.0ml of the solution of gold (10.40 or 10.00µg/ml) was introduced into a clean dry quartz ampoule, and very carefully evaporated to dryness under an infra red lamp. The ampoule was then sealed in the normal manner. Prior to use all the ampoules were cleaned by emmersing in a dilute aqua regia solution, followed by thorough washing with water, then alcohol and finally dried.

The samples, the weight of which were governed by the criteria given on p. 7 , were weighed into clean dry ampoules (rocks), or wrapped in spectrographically tested analytical grade aluminimum foil (lead, kale and silicon). The actual weights used are given in Table 3.8.

The sample of gold-doped semi-conductor grade silicon (1153) was obtained from Mullard's of Southampton, the lead from Hoste of the University of Ghent, Belgium, the rock W1 from the U.S. Geological Survey, Washington, and the kale from Bowen of the University of Reading.

ii. Irradiation procedure.

The samples together with a standard were all placed together in the same standard Al irradiation can. This ensured that the neutron flux incident on the samples and standard was as similar as possible. The time of irradiation (lead 3d, rock W1 4.75d, kale 5d and silicon 1d), reactor flux (6×10^{11} to 6×10^{12} neutrons, cm^{-2}, sec^{-1}), and time of cooling (usually about 1d) were chosen according to the expected content of gold. For the irradiations the Harwell reactors, BEPO, and DIDO, and the University of Manchester and Liverpool Research Reactor were used.

iii. Dissolution procedures.

To determine the losses of gold which can occur during dissolution of the samples, the dissolution procedures detailed below were investigated using a non-irradiated matrix, and a known weight of active gold solution (2.06mg). The activity of the gold added, and that of the gold recovered was measured, under identical counting conditions, and the recoveries obtained are given in Table 3.7.

The ampoules containing the samples after irradiation, were opened inside a glove box using a diamond tipped cutting wheel driven by an electric motor, and the samples wrapped in aluminium foil were carefully opened, again inside a glove box, using tweezers. Extreme care was necessary in the case of the kale samples, which were in the form of a fine powder.

Before dissolution of the irradiated samples, the lead and silicon samples were carefully leached to remove any surface

contamination. For the lead samples dilute nitric acid was used, and for the silicon samples dilute hydrofluoric and nitric acid mixture. The kale and rock W1 samples could not be treated in this way as they were in the form of a fine powder.

a. Silicon and rocks.

To the matrix, placed in a 50ml Teflon beaker, 1.0ml of stable gold carrier solution was added, and the matrix dissolved in a mixture of 10ml of concentrated hydrofluoric, 2ml of hydrochloric and 10ml of nitric acids. After the silicon had been fumed off, two evaporations were carried out with 5ml portions of hydrochloric acid to a volume of about 1-2ml in order to remove oxides of nitrogen.

b. Lead.

To the matrix, placed in a 500ml conical flask, 1.0ml of stable gold carrier solution was added, and the matrix dissolved in a mixture of 5ml of glacial acetic acid and 15ml of 100vol. hydrogen peroxide, which was added in 0.5ml portions with gentle warming between the additions. The resulting solution was evaporated almost to dryness, and the evaporation repeated with 15ml of 50% v/v hydrochloric acid plus 2 drops of concentrated nitric acid, then with 15ml of 50% v/v hydrochloric acid alone. The residue was dissolved in the minimum volume of hot concentrated hydrochloric acid (3g of lead requires about 150ml of acid) to obtained a perfectly clear solution. This solution was diluted to twice its volume with water and allowed to stand in an ice-bath, whereupon lead chloride precipitated. The supernatant liquid was decanted

into a 500ml separatory funnel, the lead chloride being washed with two 10ml portions of 25% v/v hydrochloric acid, and the washings also added to the separatory funnel. The gold was then extracted, as the chloride, by two 50ml portions of diethyl ether, and finally the combined ether extracts were evaporated to dryness, and the residue dissolved in 20-30ml of $1.5^{+}_{-}1$M hydrochloric acid.

c. Biological material (kale).[111]

To the matrix, placed in a 250ml beaker, 1.0ml of stable gold carrier solution was added, followed by 2ml of 100vol. hydrogen peroxide. The beaker was covered with a clock glass and 5ml of concentrated sulphuric acid carefully added via the beaker lip, the beaker contents being swirled gently until effervescence ceased. Next 5ml of concentrated nitric acid was added, the beaker again swirled gently, and finally 2ml of 70% perchloric acid added. The covered beaker was heated until white fumes appeared, then allowed to cool appreciably before adding 20ml of aqua regia. Heating was resumed, and evaporation continued to the appearance of white fumes of sulphuric acid. The resulting clear solution, after cooling, was diluted to about 30ml with $1.5^{+}_{-}1$M hydrochloric acid.

The kale sample giving a result of 1.1×10^{-3}ppm of gold on a 0.2g sample (Table 3.8), constituted a preliminary test of the method for this particular matrix. The sample was irradiated in a quartz ampoule, and half quantities of the reagents detailed above were used in the dissolution.

d. Standard.

After opening the ampoule the gold was removed by careful

leaching with a solution of 2.5M hydrochloric acid. The solution was then diluted with 2.5M hydrochloric acid by the following procedure.

Using the standard of weight 10.40µg.

a. Solution diluted to 100ml - 1.04×10^{-1}µg Au/ml - used for gold-doped semi-conductor grade silicon analysis.

b. Solution diluted to 100ml. 5.0ml of this solution diluted to 25ml - 2.08×10^{-2}µg Au/ml - used for lead analysis.

c. Solution diluted to 100ml. 10.0ml of this solution diluted to 25ml - 4.16×10^{-2}µg Au/ml - used for kale analysis.

Using the standard of weight 10.00µg.

a. Solution diluted to 100ml. 10.0ml of this solution diluted to 25ml - 4.00×10^{-2}µg Au/ml - used for rock W1.

All the above listed dilutions were made using bulb pipettes, and volumetric flasks, and the weight of gold used to represent the standard in the final substoichiometric extraction was selected so as to be of a similar order to that expected in the sample.

iv. Extraction procedure.

The dissolved samples were diluted to 20-50ml with water or acid, so as to obtain a medium of 1.5 ± 1M hydrochloric acid, then transferred to 100ml separatory funnels. After adding 0.5ml of 5vol. hydrogen peroxide, the extractions were carried out using 7.0ml of copper diethyldithiocarbamate in chloroform solution for 1min. In the case of the biological material (kale) where only 64% recovery of gold was obtained after dissolution (Table 3.7) a volume of 5.0ml of extractant was used, so as to be below the stoichiometric

requirements. To 1.0ml of the appropriate irradiated gold standard solution containing a weight y_s of gold, 1.0ml of stable gold carrier solution was added, and the gold extracted in exactly the same way as described above for the sample solutions.

In the case of the rock W1, the organic extracts obtained were washed with 1M hydrochloric acid to remove any traces of the aqueous phase. This precaution was necessary as the aqueous phase contained a large number of foreign active nuclides. All the organic phases were filtered through Whatman 540 filter papers, placed in the stems of the separatory funnels, and the activity of exactly the same volumes of separated organic phases from the sample a, and the standard a_s, were measured using the scintillation counter.

The weight, y, of gold present in the test sample, was then calculated from the equation:

$$y = y_s \frac{a}{a_s} \quad \text{(p. 12)},$$

and the results are given in Table 3.8.

v. Decay measurements.

In order to establish the radio-chemical purity of the extracted gold the activity of the organic extracts were counted at regular intervals (about every 12hr) together with a gold standard organic extract. The scintillation counter settings were kept constant, and by reference to the decay characteristics of the standard organic extract it was possible to observe any drift in the count rate due to electrical instability. The results are given in Figs. 3.6 and 3.7.

Chapter 4

The Substoichiometric Determination of Gold by Radio-active Isotope-Dilution Analysis

I. Introduction

The success achieved in the development of a neutron activation analysis method for the determination of traces of gold, suggested the study of a radio-active isotope-dilution method, involving the use of the same chelating agent.

The technique of radio-active isotope-dilution analysis has been applied to the determination of a number of elements,[3,14,35-41] but no reference could be found to its application to gold.

II. Discussion

A. Development of the Method

i. Preliminary experiments.

The extraction constant of gold diethyldithiocarbamate in chloroform is unknown, and therefore it was not possible to calculate the threshold pH of the aqueous phase from which to extract the gold as the chelate. The nature of the expression however (p. 25) indicates that the threshold pH will have a higher value than in the neutron activation method, due to the lower concentration of chelating agent used in isotope-dilution analysis. In the former method, a medium of 0.01-10N sulphuric, or 0.01-8M hydrochloric acid, was found to be suitable from which to extract the gold as the diethyldithiocarbamate into chloroform (Fig. 3.3).

For the preliminary experiments it was decided to use a medium of 1M hydrochloric acid. A 3min substoichiometric extraction in the presence of 1.00µg of gold (III) resulted in only a 5.9% consumption of the chelating agent (Table 4.10); this was considered to be due to chloride ions acting as a competing specie

for the gold. It must be remembered that in the neutron activation analysis method, milligram amounts of gold (where stable isotopic carrier had been added) were being extracted, whereas in isotope-dilution, microgram or less quantities are being considered. Any competing specie for the gold will therefore have a more pronounced effect.

Repeating the experiment in a medium of 1N sulphuric acid did not lead to the complete reaction of the substoichiometric amount of chelating agent, 10.9% of the reagent was consumed, and in a medium of 0.1N sulphuric acid, with a 10min rather than a 3min extraction, no marked increase in the value was observed, 17.9% (Table 4.10). It was concluded that the competition of chloride ions was not the only factor involved.

The reaction of gold with copper (II) diethyldithiocarbamate occurs by an exchange reaction, the theory of which was given in Chapter 1. If a metal salt of diethyldithiocarbamic acid is used which has a larger difference in extraction constant in relation to gold than has copper diethyldithiocarbamate, then from a kinetic point of view, gold may replace this metal more rapidly than copper from the chelating agent. Using the zinc (II) salt of the same concentration as the copper salt, it was found that the rate of reaction under identical conditions was more rapid. After a 10min extraction 71.4% of the substoichiometric amount of reagent had been consumed, compared with 17.9% using the copper salt (Table 4.10). Even so complete consumption of the substoichiometric amount of reagent had still not been achieved. The rate determining step was

therefore probably some other mechanism, then the formation of the gold chelate.

It was found in the developed neutron activation analysis method, that gold (III) reacted with copper (II) diethyldithiocarbamate in chloroform to form a chelate having a gold to diethyldithiocarbamate molar ratio of 1:1 (p.54). This was considered to indicate the formation of either a ternary complex involving tervalent gold, or a univalent gold diethyldithiocarbamate. The formation of the latter gold chelate if it exists, would be assisted by the presence of a reducing agent capable of reducing the gold from the tervalent to the univalent state. The reagent must not however reduce the gold to the metal. According to Erdey and Rady,[112] ascorbic acid reduces gold (III) to the metal at a temperature of about 50°C, but the rate of reduction at room temperature is very slow, and an elevated temperature of 80-90°C was recommended by Stathis and Gatos[113] for the reduction. Many authors have also reported that the oxidation of ascorbic acid is strongly inhibited by the presence of diethyldithiocarbamates.[114-119] For these reasons, the use of ascorbic acid at room temperature was selected as possibly being a suitable reductant for the gold (III), with the conditions being studied in this research. Using 1ml of a 1% aqueous solution of ascorbic acid in the presence of an 0.5N sulphuric acid medium, complete consumption of the substoichiometric amount of zinc diethyldithiocarbamate in chloroform was achieved during a 3min extraction (Table 4.10). It was therefore concluded that the rate determining step was probably the reduction of the gold from the

tervalent to the univalent state, and not the exchange reaction to form the gold chelate.

At this stage in the research it was necessary to decide whether to firstly attempt to develop an isotope-dilution method based on these findings, or whether to investigate the composition of the complexes formed using the substoichiometric conditions, i.e. an excess of gold (III) in the presence, and absence of ascorbic acid. It was decided to attempt to develop the analytical method first, and then study the composition of the complexes formed. The findings of the latter study are given in Chapter 5.

ii. Influence of the pH of the aqueous phase.

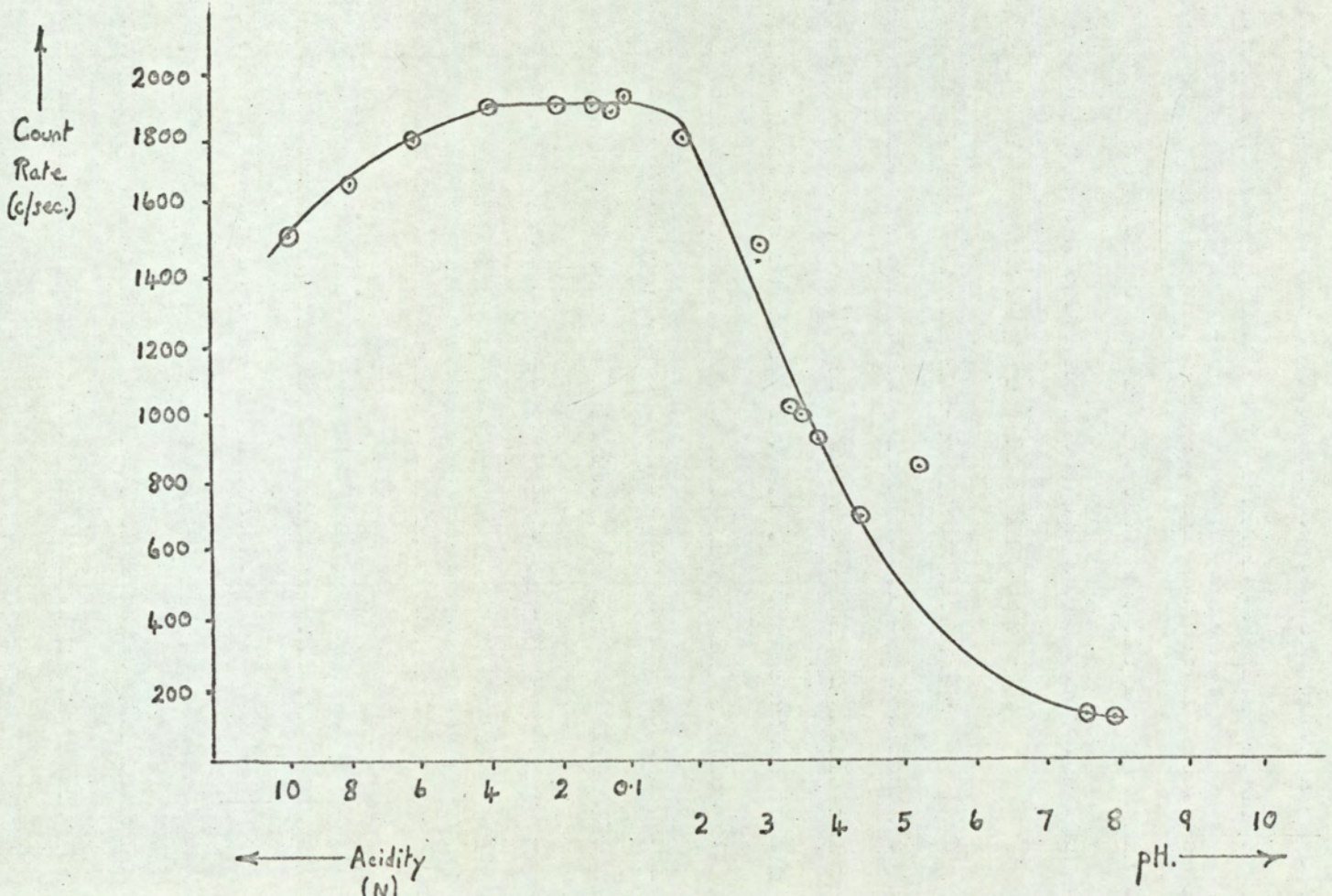
Any normality of sulphuric acid from 0.1N-4N was found to be a suitable medium from which to extract the gold substoichiometrically as the diethyldithiocarbamate (Fig. 4.1). The decrease in the weight of gold extracted as the chelate from acid solution of normality greater than 4, was considered to be due to the partial destruction of the zinc diethyldithiocarbamate. Qualitative tests in the laboratory confirmed this finding. Also at a pH of the aqueous phase greater than 1, a decrease in the weight of gold extracted as the chelate occurred, the reasons for this have been previously given (p. 55).

For all further experiments a medium of 0.5N sulphuric acid, in the presence of ascorbic acid was selected.

iii. Time to reach extraction equilibrium.

At a fixed stoichiometry of 66%, extraction equilibrium was reached in 1.5min, using an active gold solution 1.25µg/ml, and in

Fig. 4.1.



The Influence of Acidity on the Substoichiometric Extraction of Gold as the Diethyldithiocarbamate into Chloroform in the Presence of Ascorbic Acid.

2min using an active gold solution 0.10µg/ml, i.e. 1.25, or 0.10µg of gold in 20ml of 0.5N sulphuric acid medium (Fig. 4.2). If a prolonged period of extraction (up to 15min) was used, no change in the weight of gold extracted was observed, and it was therefore concluded that no breakdown of the complex occurred. For all future experiments an extraction time of 5min was selected, when using gold solutions of either concentration.

iv. Influence of the concentration of ascorbic acid.

The selection of 1ml of a 1% aqueous solution of ascorbic acid added to the aqueous phase prior to the substoichiometric extraction was an arbitary one. It was therefore decided to investigate the effect of differing concentrations of the acid upon the time necessary to reach extraction equilibrium. At a fixed stoichiometry of extraction of 66% as previous, it was found that as the concentration of added ascorbic acid decreased, so the time to reach extraction equilibrium increased (Table 4.14). In the absence of ascorbic acid, extraction equilibrium was not reached in 1.5hr. In view of these findings it was decided to maintain the addition of 1ml of a 1% solution of ascorbic acid to the aqueous phase, so as to keep the extraction time necessary to form the gold chelate in chloroform, as short as possible.

v. Reproducibility.

The reproducibility of the substoichiometric extraction using an active gold solution 1.00µg/ml is shown in Fig. 4.3. The coefficient of variation was found to be $\pm$1.4% for the extractions made in the presence of an excess of gold (i.e. the substoichiometric condition).

When the concentration of gold was reduced by one order, the reproducibility of the separation was found to be poor (Table 4.15). This was found to be due to the instability of both the active gold (III) solution, and the zinc diethyldithiocarbamate solution in in chloroform (5×10^{-8}M). The instability of the former solution was considered to be due to the adsorption of gold on the walls of the containing vessel, or possibly by a base exchange reaction. Papers by Leutwein,[120] Benes,[121] and Sonstadt[122] are of particular interest with reference to the instability of dilute gold (III) solutions.

The stability of both the active gold (III), and the chelating agent solutions, at different concentrations was studied (p.149).

Using a freshly prepared active gold (III) solution, 0.10µg/ml, and fresh reagent solution, prepared from recrystallised sodium diethyldithiocarbamate,[122] good reproducibility of the substoichiometric extraction of gold as the diethyldithiocarbamate was achieved (Fig. 4.3), and the coefficient of variation being $\pm$1.8% for the extractions made in the presence of an excess of gold.

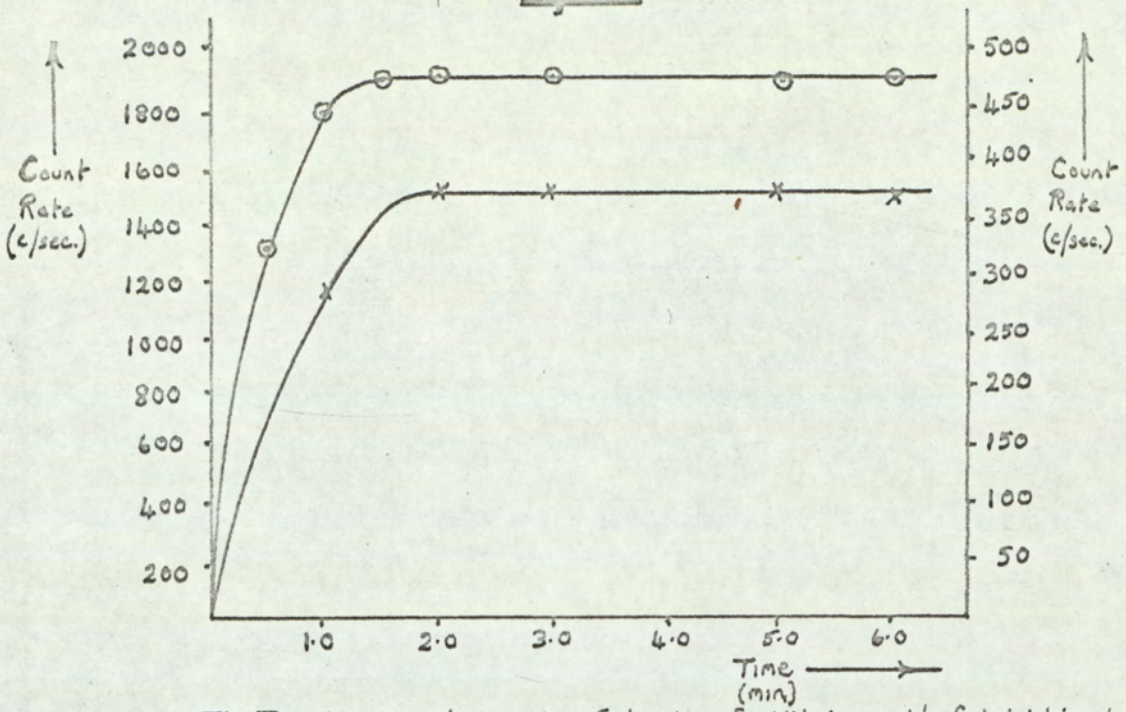
For gold solutions of lower concentration, i.e. less than 0.10µg/ml, poor reproducibility of the substoichiometric extraction of gold as the diethyldithiocarbamate was obtained.

The lower limit at which an acceptable reproducibility of the separation could be achieved was therefore 0.10µg of gold in 20ml of solution.

vi. Stability of solutions.

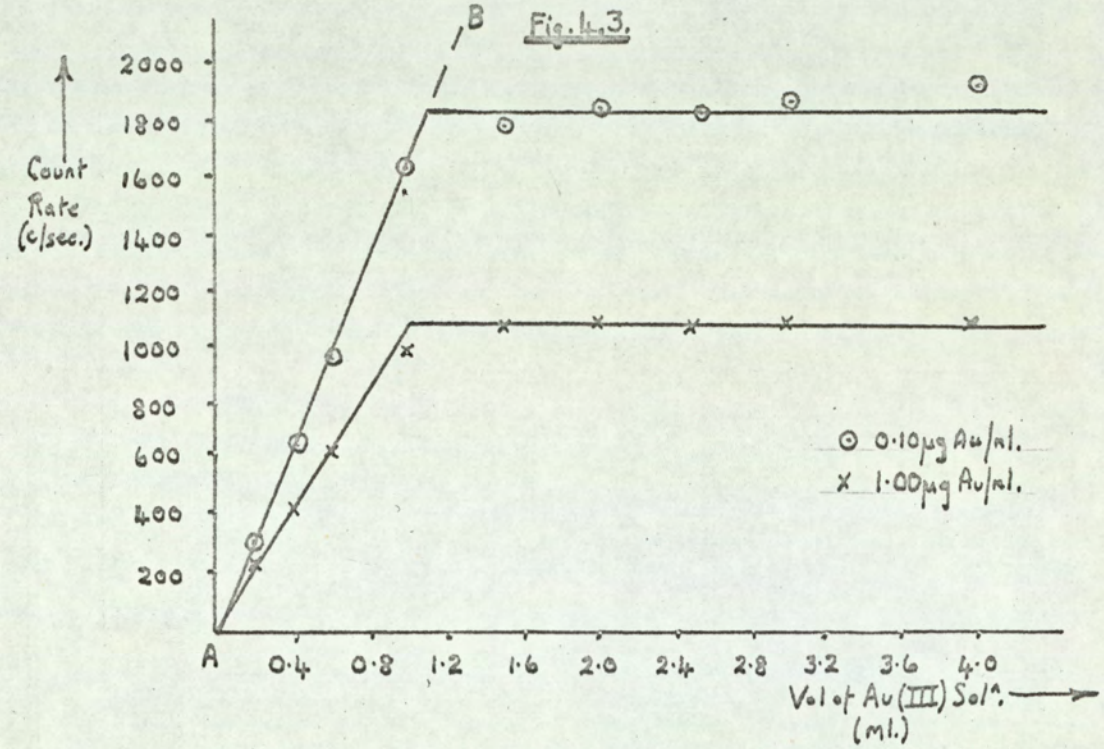
The maximum period during which different concentrations of

Fig. 4.2.



The Time Necessary for reaching Extraction Equilibrium in the Substoichiometric Extraction of Gold as the Diethyldithiocarbamate into Chloroform in the Presence of Ascorbic Acid. (⊙ Left hand axis 1·25μg Au. × Right hand axis 0·10μg Au.)

Fig. 4.3.



The Reproducibility of the Substoichiometric Extraction of Gold as the Diethyldithiocarbamate into Chloroform in the Presence of Ascorbic Acid.

solutions of gold (III), and zinc (II) diethyldithiocarbamate, were found to be stable (not more than a 10% change from the initial concentration), are summarised in Table 4.1, and the experimental results are given in Tables 4.16 and 4.17. If the sodium diethyldithiocarbamate was purified to remove oxidation products,[123] the zinc diethyldithiocarbamate solution prepared from it was more stable (2.5×10^{-7}M solution stable for at least 3hr) and its use is therefore recommended.

Table 4.1.

Solution	Concentration (µg/ml)	Concentration (M)	Maximum period of stability (hr)
Gold in 2.5M HCl	5.40		504 (21d)
	1.06		53
	0.12		24
$Zn(DDC)_2$ in $CHCl_3$		1.0×10^{-6}	4
		1.0×10^{-7}	1.5
		5.0×10^{-8}	0.5
		1.0×10^{-8}	0.25
		2.5×10^{-7}*	at least 3

*Prepared from recrystallised NaDDC.

vii. Partition coefficient of the gold diethyldithiocarbamate.

The partition coefficient of the gold chelate between chloroform and an aqueous phase of 0.5N sulphuric acid, using substoichiometric conditions, was measured by the method discussed in Chapter 3, (p. 92) and the results are given in Table 4.18. The mean value was found to be 512 at $20 \pm 1^{\circ}$C, the standard deviation of a single result ± 65, and the coefficient of variation $\pm 12.7\%$.

viii. The role of chloride ions.

Very dilute solutions of gold (III) as the chloride, are known to decrease in strength with time. Chloride ions in sufficient quantity can retard the rate of the effect, as was found by Benes.[121] If the losses of gold do occur by adsorption onto the glass walls of the containing vessel, then the adsorbed specie cannot be the chloroaurate $AuCl_4^-$ as one would expect a constant or increasing extent of adsorption with increasing chloride ion concentration. The adsorbed species are therefore more likely to be hydrolysed forms of $AuCl_4^-$, e.g. $AuCl_3OH^-$ the concentration of which can be expected to increase with decreasing chloride ion concentration.

Besides retarding the rate of loss of gold from solution, chloride ions in sufficient concentration can also compete with the chelating agent for the gold, thus preventing the complete consumption of the substoichiometric amount of chelating agent. Therefore the concentration of chloride ions in the aqueous phase is very critical, and that permissible will depend upon the gold concentration. The maximum concentration that can be tolerated for different concentrations of gold is summarised in Table 4.2, and the experimental results are given in Table 4.19.

Table 4.2.

Weight of gold in 20ml of solution (µg)	Maximum concentration of chloride ions (M)
1.00	0.36
0.50	0.18
0.20	0.06
0.10	0.05

Wherever possible it was advisable to prepare the active gold (III) solutions in a medium of 2.5M hydrochloric acid. If the amount of chloride ions introduced into the aqueous phase by the addition of the active gold (III), was more than could be tolerated according to the data given in the above table, it was often more beneficial to prepare a solution of higher concentration in 2.5M hydrochloric acid, and to dilute this with water to the desired concentration as required.

ix. Accuracy and precision.

In order to establish the accuracy and precision of the developed method a number of repetitive 1:1 dilutions, i.e. 1 part active to 1 part stable gold by weight, were performed, followed by identical substoichiometric extractions of the gold. Knowing the activity, a, of a fixed volume of the organic phase after the extraction, and the activity, a_s, of an equal volume of organic phase obtained from a similar substoichiometric extraction of the active gold in the absence of the stable gold, (referred to as the standard), the weight, y, of stable gold determined was calculated assuming the weight, y_s, of gold present in the active solution was known, using the substoichiometric formula:

$$y = y_s \left(\frac{a_s}{a} - 1 \right) , \text{ (p. 24).}$$

The weight of the stable gold determined, y, was then compared with the actual weight, y^*, added.

The results of the investigation are given in Table 4.3.

Table 4.3.

Weight of stable Au added (μg) y^*	Weight of active Au added (μg) y_s	Activity of 3.0ml of organic phase (c/sec) a_s	a	Weight of stable Au found (μg) y	
1.00	1.06	1647	863	0.96	
		"	804	1.10	
		"	806	1.10	
		"	834	1.03	
		"	810	1.09	
		"	840	1.02	$\bar{y}$ = 1.03μg
		1584	822	0.99	n = 15
		"	833	0.94	s = $\pm$0.057μg
		2465	1293	0.96	Coeff. of
		"	1250	1.03	Variation
		"	1237	1.05	= $\pm$5.5%
		"	1225	1.07	
		"	1252	1.03	
		"	1270	1.00	
		"	1245	1.03	
0.10	0.11	258	129	0.11	
		"	135	0.10	
		"	120	0.12	
		"	123	0.12	
		"	132	0.10	
		"	124	0.12	
		159	104	0.12	
		"	115	0.08	
		"	110	0.10	$\bar{y}$ = 0.10μg
		"	111	0.10	n = 15

Table 4.3. (cont.)

Weight of stable Au added (μg) y^*	Weight of active Au added (μg) y_s	Activity of 3.0ml of organic phase (c/sec) a_s	a	Weight of stable Au found (μg) y	
0.10	0.11	169	122	0.08	$s = \pm 0.016 \mu g$
		"	116	0.10	Coeff. of
		"	127	0.07	Variation
		"	119	0.09	$= \pm 16.0\%$
		"	117	0.10	
0.05	0.05	178	93	0.05	
		"	94	0.05	
		"	78	0.07	$\bar{y} = 0.06 \mu g$
		"	81	0.06	$n = 10$
		"	82	0.06	$s = \pm 0.013 \mu g$
		169	94	0.04	Coeff. of
		"	76	0.06	Variation
		"	93	0.04	$= \pm 21.7\%$
		232	120	0.05	
		"	127	0.04	
0.01	0.02	55	41	0.007	$\bar{y} = 0.01 \mu g$
		"	41	0.007	$n = 6$
		"	39	0.008	$s = \pm 0.003 \mu g$
		54	32	0.014	Coeff. of
		"	32	0.014	Variation
		"	30	0.009	$= \pm 30.0\%$

$\bar{y}$ is the mean weight of stable gold found.

s is the standard deviation of a single result $= \pm \sqrt{\frac{\Sigma \Delta^2}{n-1}}$, where Δ is the deviation from the mean, and n is the number of observations.

The coefficient of variation, which is a measure of the precision of the results, increases as the concentration of active and stable gold decreases as was to be expected. The value, $\pm$5.5%, using an active gold (III) solution of 1.06µg/ml was very acceptable, and those for active gold solutions of 0.11 and 0.05µg/ml, ($\pm$6.0% and $\pm$21.7% respectively), reasonable when one considers the concentration of gold being determined. It must be remembered in this method no stable gold carrier was added as was the case in the neutron activation analysis method. The precision of the results using an active gold solution 0.02µg/ml was poor, (coefficient of variation $\pm$30.0%). This was to be expected, as the total weight of gold present, 0.03µg, was below that for which a satisfactory reproducibility of separation could be obtained (p. 109).

x. Selectivity.

From the theory of substoichiometry, the higher the extraction constant of the metal chelate, the more selective a particular reagent is likely to be. The constant for gold (III) diethyldithiocarbamate in chloroform is unknown, and the situation is even more complicated by the fact that possibly a univalent gold diethyldithiocarbamate is being formed with the conditions used in this research. However, the order of extractability of metal diethyldithiocarbamates into carbon tetrachloride is known.[73-78] If the assumptions are made that the order will be very similar using chloroform as the solvent, and also that the gold diethyldithiocarbamate has a relatively high extraction constant since it can be formed from acid solution, a qualitative assessment of the metal ions likely to interfere could

be made. The effect of these ions together with those which may cause interference by some other mechanism, e.g. reduction of the gold to the metal, or oxidation of the chelating agent were studied. The experiments were carried out using 1.00µg of active gold together with 100 or 1000µg of the foreign ion to be examined, followed by a substoichiometric separation of the gold as the chelate (p.156). Ideally since no stable gold was added, a result of $y = o$ should be obtained when the results are substituted in the substoichiometric formula:

$$y = y_s\left(\frac{a_1}{a_2} - 1\right).$$

The criteria of an interference.

The same argument can be applied in this study as was used in the selectivity study in the developed neutron activation analysis method (p. 62). The confidence limits for the difference in means is then given by:

$$(\bar{a}_1 - \bar{a}_2) \pm ts \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}},$$

where the definition of the symbols is the same as that previously given (p. 62).

The 95% confidence limit of this difference is:

$$(\bar{a}_1 - \bar{a}_2) \pm 2.776s \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}.$$

The value of $t_{95\%}$ was based on the results of the Reproducibility experiments using an active gold solution 1.00µg/ml (Table 4.15), where the number of observations was 5, and the coefficient of variation ±1.4%.

The null hypothesis is that $(\bar{a}_1 - \bar{a}_2) = 0$ for no interference.

If $\left|\frac{(\bar{a}_1 - \bar{a}_2)}{\bar{a}_1}\right| > \frac{2.776s}{\bar{a}_1}\left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}$ or

$100\left|\frac{(\bar{a}_1 - \bar{a}_2)}{\bar{a}_1}\right| > 2.776C\left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}\%$,

where C is the coefficient of variation and is equal to $\pm 1.4\%$, then the null hypothesis was rejected, and the particular foreign ion was considered to interfere.

Using this criteria, the foreign ions found to interfere are summarised in Table 4.4, and the experimental results are given in Table 4.20.

Table 4.4.

Interfering foreign ion	
1000 fold excess	100 fold excess
Ag(I), Bi(III), Cr(VI), Cu(II), Hg(II), Pd(II), Pt(IV), Se(IV), Sb(III), Sn(II), Te(IV).	Ag(I), Cu(II), Hg(II), Pd(II), Se(IV), Sb(III), Sn(II), Te(IV).
2ml of 10M HNO_3.	
1ml of 2M HBr.	
Cl^- (Table 4.19).	

The valency state of the metal ions in Tables 4.4 and 4.20, are that on addition to the aqueous phase, and no necessarily their final valency state due to the presence of ascorbic acid. The redox potential of ascorbic acid has been found to vary from -0.012 volts at pH 8.7 to +0.326 volts at pH 1.05.[124] If the value with the conditions used in this experiment, (pH approximately 0.3), is taken as being very similar to the value found by Rao and Rao[124] at

pH 1.05, then from the known redox potentials,[32] one would expect that the following interfering ions, silver (I), copper (II), mercury (II), palladium (II), platinum (IV), selenium (IV) and tellurium (IV) would be reduced to their elemental state by ascorbic acid. Selenium (IV) and tellurium (IV) were found to be reduced to the metal, and their interference was considered to be due to co-precipitation of the gold during their reduction. The rate of reduction of all the other metal ions listed above either to their lower valency, or elemental state, with the exception of palladium (II), had been reported to be very slow or negligible at room temperature, in acid solution with ascorbic acid as the reductant.[124-132] These metal ions were therefore probably present in their original valency state, in which case their interference was due to their competition with gold to form the diethyldithiocarbamate. This can be expected from the order of extractability of the metals as diethyldithiocarbamates.[73-78] In the case of palladium (II), no reduction to the metal was observed, and it was therefore considered to interfere by a similar mechanism. The same mechanism of interference applied to bismuth (III) and antimony (III), which are not expected to be reduced by the ascorbic acid. However, antimony (V) is expected to be reduced to the tervalent state, but no interference from antimony (V) was found, and hence the rate of reduction of the element from the pentavalent to the tervalent state must therefore be too slow to cause any interference in the substoichiometric determination of the gold as the diethyldithiocarbamate with the conditions used in this experiment.

Chromium (VI) was reduced to the tervalent state by the ascorbic acid in which condition it does not easily form a diethyldithiocarbamate. A calculation of the amount of ascorbic acid oxidised to dehydroascorbic acid in the reaction showed that in the presence of 100µg of chromium (VI) about 5% of the added ascorbic acid would be consumed, and therefore about 50% in the presence of 1000µg of the element. No interference was found in the presence of 100µg of chromium (VI), but a serious interference in the presence of 1000µg (Table 4.4 and 4.20). As the excess of ascorbic acid in the presence of 1000µg of chromium (VI) was only about one twentieth that when only 100µg of the element was present, the reduction of the chromium (VI) to the tervalent state was considered to be incomplete in the former case. This being so, any unreduced chromium (VI) would oxidise the zinc diethyldithiocarbamate, and hence cause an interference in the substoichiometric determination of the gold.

Tin (II) interfered by reducing the gold (III) to the metal. The element in the tervalent state is expected to be reduced to the divalent state in the presence of ascorbic acid, but no interference was found. Again it was concluded that the rate of reduction under the experimental conditions used must be too slow for sufficient tin (II) to be formed to cause an interference.

The selectivity of the method is poor when compared to that found in the neutron activation analysis method (p. 61), but it must be remembered that the ratio of foreign metal to gold was 100 or 1000:1 by weight, whereas in the neutron activation analysis method where stable gold carrier had been added, the ratio was 1:1 by weight.

The inferior selectivity can be predicted from the theory.

Let us consider two equally charged metal ions present in solution in a 1000:1 ratio by weight, both of which are capable of forming an extractable complex with the same reagent. If a reaction is performed at 50% stoichiometry relative to the metal ion of lesser weight, then from the theory of substoichiometry (p. 19) for a quantitative separation of the metal as the chelate without interference from the other metal, the ratio of extraction constants must be greater than 2×10^5, whereas if both the metal ions were originally present in a 1:1 ratio by weight the value need only be greater than 200. It is therefore apparent that the selectivity of the separation must be inferior to that found with the neutron activation analysis conditions.

xi. Elimination of interfering ions.

Three methods were investigated:

1. Preliminary ether extraction of the gold from either a) hydrochloric acid or b) hydrobromic acid solution, followed by either a) evaporation of the ether phase in the presence of an acid, or b) the back extraction of the gold by water.

2. The addition of EDTA prior to the substoichiometric separation.

3. The addition of sodium dimethylglyoximate prior to the substoichiometric separation.

1. The extraction of gold from hydrochloric, or hydrobromic acid solution, as $HAuCl_4$, or $HAuBr_4$ into diethyl ether is well known,[91,133-138] and some authors prefer the use of isopropyl ether,[91] or ethyl acetate.[134]

According to Mylius,[137,138] and Schweitzer[135] and co-workers, gold can be quantitatively extracted into diethyl ether from 1.5-3M hydrochloric acid solution.

A 3min extraction of gold (III) from a medium of 2M hydrochloric acid into 20ml of diethyl ether resulted in about an 80% extraction. Using two or three 20ml portions of the extractant the percentage extraction was found to be about 86 and 90, and with ethyl acetate similar results were obtained (Table 4.21). As diethyl ether is a more volatile solvent than ethyl acetate, and therefore more easily removed on a water bath, the former solvent was preferred, and as a quantitative separation is not necessary, the increase in the degree of extraction of the gold using more than 20ml of extractant did not justify its use.

After the extraction of the gold into the ether, the ether was removed by evaporating the solution in the presence of hydrochloric acid. The amount of hydrochloric acid that could be used was governed by the criteria given on p. 112. If the acid strength was below 3M, it was found that not all of the gold was in a form extractable by the chelating agent (Table 4.22). This was considered to be due to the formation of hydrolysed species of gold (III) produced at the elevated temperature of about 50°C used for the evaporation of the ether phase. This effect was also observed using 3N sulphuric or nitric acids (Table 4.22). Furthermore if the latter acids were used, losses of gold from solution occurred, probably due to adsorption of the hydrolysed species on the walls of the containing vessels. If after such an experiment the

beaker was rinsed with water and monitored, considerable activity of gold-198 was observed, which supported this argument. The presence of chloride ions was therefore essential during the evaporation of the ether phase, and in order to keep their amount to a minimum, the evaporations were performed using 0.5ml of 3M hydrochloric acid. The lowest weight of gold for which 0.5ml of 3M hydrochloric acid would not interfere in the final substoichiometric separation was 0.50µg (Table 4.2).

The possibility of eliminating the interference of some of the foreign metal ions using this preliminary extraction method was examined. The results are given in Table 4.23. Half of the metal ions interfering at a 1000 fold weight excess were overcome, and are summarised in Table 4.6. A preliminary ether extraction of the gold was therefore a profitable stage in the separation.

Experiments designed to back extract the gold from the ether phase met with moderate success. From 20ml of an ether phase containing 0.7-0.8µg of gold about a 50% back extraction of the gold into two 20ml portions of water was obtained (Table 4.24). Initial attempts to carry out a reproducible substoichiometric separation of the recovered gold as the diethyldithiocarbamate failed, due to dissolved ether in the aqueous phase. By a preliminary chloroform extraction of the aqueous phase prior to the substoichiometric separation, the ether was removed, and a reproducible separation of the gold chelate was achieved. The method was considered to be inferior to the evaporation method, as after the back extraction only

about 0.4µg from the original 1.00µg of gold added was present in the 40ml of solution prior to the substoichiometric separation. The concentration of gold in solution was therefore not far removed from the lower limit of the method, 0.10µg in 20ml of solution, whereas the evaporation procedure resulted in a final solution of 20ml containing about 0.8µg of gold.

The extraction of gold from 2M hydrobromic acid solution was examined using diethylether, and isopropyl ether as the extractants, and it was found that the gold was more efficiently extracted by the former solvent, about 80%, than by the latter, about 70% under similar conditions (Table 4.21). The degree of back extraction of the gold into two 20ml portions of water was similar from either ether phase, about 80% (Table 4.24). The re-extractability of the gold as the bromide into water from diethyl ether was therefore more efficient than as the chloride. Even so, neither the evaporation nor back extraction method could be used as traces of bromide in the final solution caused a serious interference in the final substoichiometric separation of the gold as the diethyldithiocarbamate (Table 4.20).

2. The prevention of the interference of copper (II), mercury (II) and bismuth (III), by the addition of EDTA to an 0.5N, or 0.1N sulphuric acid solution prior to the substoichiometric separation of the gold as the diethyldithiocarbamate was studied (p.167). The results are given in Table 4.25.

If, with the experimental conditions used, gold is forming a univalent diethyldithiocarbamate, then the following reaction having

an extraction constant, K, can be written:

$$2AuCl_4^- + 2C_6H_8O_6 + Zn(DDC)_2 \rightleftharpoons 2AuDDC + 2C_6H_6O_6 + Zn^{2+} + 4H^+ + 8Cl^-,$$

Ascorbic acid — Dehydro ascorbic acid

$$K_1 = \frac{[AuDDC]^2_{org}\,[C_6H_6O_6]^2\,[Zn^{2+}]\,[H^+]^4\,[Cl^-]^8}{[AuCl_4^-]^2\,[C_6H_8O_6]^2\,[Zn(DDC)_2]} \quad \ldots\ 1).$$

The valency state of copper (II), mercury (II), and bismuth (III) is not expected to change in the presence of the ascorbic acid as previously described (p. 118). If we take the interference of mercury (II) as an example, then a similar equation, and extraction constant, for the formation of mercury (II) diethyldithiocarbamate can be written:

$$Hg^{2+} + Zn(DDC)_2 \rightleftharpoons Hg(DDC)_2 + Zn^{2+},$$

$$K_2 = \frac{[Hg(DDC)_2]_{org}\,[Zn^{2+}]}{[Zn(DDC)_2]_{org}\,[Hg^{2+}]} \quad \ldots\ 2).$$

From 1) and 2)

$$K = \frac{K_1}{K_2} = \frac{[AuDDC]^2_{org}\,[Hg^{2+}]\,[C_6H_6O_6]^2\,[H^+]^4\,[Cl^-]^8}{[AuCl_4^-]^2\,[Hg(DDC)_2]_{org}\,[C_6H_8O_6]^2}, \quad \ldots\ 3)$$

and represents the reaction:

$$2AuCl_4^- + Hg(DDC)_2 + 2C_6H_8O_6 \rightleftharpoons 2AuDDC + Hg^{2+} + 2C_6H_6O_6 + 4H^+ + 8Cl^-.$$

If we assume that the volume of the organic and aqueous phases are equal, the equilibrium concentration of dehydroascorbic acid $[C_6H_6O_6]$ will be equal to the equilibrium concentration of the univalent gold diethyldithiocarbamate $[AuDDC]$, and if the reaction to form the gold chelate is performed at 50% stoichiometry, the ratio $\frac{[AuDDC]}{[AuCl_4^-]}$ will be equal to 1.

Then 3) can be written as:

$$K = \frac{[C_6H_6O_6]}{[Hg(DDC)_2]_{org}} \times \frac{[AuDDC]^2_{org}}{[AuCl_4^-]^2} \times \frac{[Cl^-]^8}{[C_6H_8O_6]^2} \times [H^+]^4 [AuDDC]_{org} [Hg^{2+}],$$

which reduces to:

$$K = \frac{[AuDDC]_{org}}{[Hg(DDC)_2]_{org}} \times \frac{[Cl^-]^8}{[C_6H_8O_6]^2} \times [H^+]^4 [AuDDC]_{org} [Hg^{2+}]. \quad \ldots \quad 4).$$

Rearranging 4) gives:

$$\frac{[Hg(DDC)_2]_{org}}{[AuDDC]_{org}} = \frac{1}{K} \times \frac{[Cl^-]^8}{[C_6H_8O_6]^2} \times [H^+]^4 [AuDDC]_{org} [Hg^{2+}]. \quad \ldots \quad 5).$$

The criteria for an interference was given on p. 117.

$$\text{If } 100 \left| \frac{(\bar{a}_1 - \bar{a}_2)}{\bar{a}_1} \right| > t C \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}\%, \quad \ldots \quad 6)$$

the element was considered to interfere.

The term $\left|\frac{(\bar{a}_1 - \bar{a}_2)}{\bar{a}_1}\right|$ can be written as $\left|\frac{\Delta c}{c}\right|$ where c is the equilibrium concentration of the gold chelate in the absence of interfering ions. The decrease in the equilibrium concentration of the gold chelate Δc in the presence of mercury (II) as an interfering ion must be equal to one half the concentration of mercury (II) diethyldithiocarbamate. The criteria for no interference now becomes:

$$\frac{[Hg(DDC)_2]_{org}}{[AuDDC]_{org}} \leq \frac{\Delta c}{2c} \leq \frac{t C}{200} \left(\frac{1}{n_1} + \frac{1}{n_2}\right)^{\frac{1}{2}}. \quad \ldots \quad 7).$$

The value of the second term in 7) is equal to 4.7% when the number of observations, n_1 and n_2, are 2 and 1 respectively, as was the case

in the experiment (p. 167). Therefore for no interference, the ratio $\frac{[Hg(DDC)_2]_{org}}{[AuDDC]_{org}}$ must be equal to, or less than, 0.024.

EDTA, Y^{4-}, has been added, so the mercury (II) will be involved in the following side reactions in the organic phase, each reaction having a corresponding stability constant.

$$Hg^{2+} + Y^{4-} \rightleftharpoons HgY^{2-},$$

$$K_{HgY^{2-}} = \frac{[HgY^{2-}]}{[Hg^{2+}]\,[Y^{4-}]}, \qquad \ldots 8)$$

and $$HgY^{2-} + H^{+} \rightleftharpoons HgHY^{-},$$

$$K_{HgHY^{-}} = \frac{[HgHY^{-}]}{[HgY^{2-}]\,[H^{+}]}. \qquad \ldots 9).$$

If we use α coefficients as a measure of the extent of the side reactions of the various species in the aqueous phase,[139] then a coefficient α_{Hg} equal to $\frac{[Hg']}{[Hg^{2+}]}$ can be introduced, where $[Hg']$ is the total equilibrium concentration of all forms of mercury present in the aqueous phase.

If the term α_{Hg} is substituted in 5) then:

$$\frac{[Hg(DDC)_2]_{org}}{[AuDDC]_{org}} = \frac{1}{K} \frac{[Cl^{-}]^8}{[C_6H_8O_6]^2} \times \frac{[H^{+}]^4\,[AuDDC]_{org}\,[Hg']}{\alpha_{Hg}} \qquad \ldots 10).$$

The equilibrium concentration of ascorbic acid, $[C_6H_8O_6]$, will approximately be equal to the concentration added, as the acid is present in a large excess over that required to reduce gold (III) to the univalent state, and the equilibrium chloride ion concentration,

$[Cl^-]$, is fixed in the design of the experiment. Also if there is no significant interference from mercury (II) the equilibrium concentration of the gold chelate, [AuDDC], and the total concentration of mercury in the aqueous phase, $[Hg']$, will not vary over the pH range studied. These terms together with the exchange constant, K, can be grouped together in the form of a constant term, C'.

Expression 10) now becomes:

$$\frac{[Hg(DDC)_2]_{org}}{[AuDDC]_{org}} = \frac{[H^+]^4}{\alpha_{Hg}} \times C' \qquad \ldots 11),$$

where

$$C' = \frac{1}{K} \cdot \frac{[Cl^-]^8 \, [AuDDC]_{org} \, [Hg']}{[C_6H_8O_6]^2}$$

To calculate α_{Hg} the following method is used. A conditional constant, K' can be written as:

$$K' = \frac{[HgY']}{[Hg^{2+}] \, [Y']} . \qquad \ldots 12).$$

From 8)

$$K' = \frac{K_{HgY^{2-}} \; \alpha_{HgY(H)}}{\alpha_{Y(H)}} . \qquad \ldots 13).$$

$\alpha_{HgY(H)}$ is a measure of the extent of the side reaction of the mercury EDTA complex, and is given by:

$$\alpha_{HgY(H)} = \frac{[HgY^{2-}] + [HgHY^-]}{[HgY^{2-}]} . \qquad \ldots 14).$$

From 9)

$$\alpha_{HgY(H)} = 1 + [H] \, K^H_{HgHY} . \qquad \ldots 15).$$

$\alpha_{Y(H)}$ is a measure of the extent of the side reaction of the EDTA, and is given by:

$$\alpha_{Y(H)} = \frac{[Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]}{[Y^{4-}]} . \quad \ldots 16).$$

The extent of the side reaction of the mercury (II) in the aqueous phase is given by:

$$\alpha_{Hg(Y)} = \frac{[Hg']}{[Hg^{2+}]} = \frac{[Hg^{2+}] + [HgY']}{[Hg^{2+}]} . \quad \ldots 17).$$

From 12)

$$\alpha_{Hg(Y)} = 1 + K'[Y'], \quad \ldots 18)$$

and from 13)

$$\alpha_{Hg(Y)} = 1 + K_{HgY^{2-}} \frac{\alpha_{HgY(H)}}{\alpha_{Y(H)}} [Y'] . \quad \ldots 19).$$

From the known values of the formation constant of the EDTA complexes, the α coefficients at the investigated pH,[140] and the total concentration of added EDTA $[Y']$, the value of $\alpha_{M(Y)}$ for the three metal ions studied can be calculated. The results are given in Table 4.5. Increasing the pH of the solution decreases the values of $\alpha_{Y(H)}$ and $\alpha_{HgY(H)}$, but the former term changes more rapidly than the latter, and hence from 19) the value of $\alpha_{Hg(Y)}$ will increase. Therefore at a higher pH, more of the metal ion will be complexed by the EDTA. From 3), increasing the pH will decrease the extent of the mercury (II) interference, and increasing the mercury (II) concentration will increase the extent of interference. If the term $\frac{[H^+]^4}{\alpha_{M(Y)}}$ is calculated, then from 11) the influence of the

pH of the aqueous phase on the ratio of the equilibrium concentration of mercury (II) and gold (I) diethyldithiocarbamate can be demonstrated. The results are given in Table 4.5.

Table 4.5.

Foreign metal ion present	$\alpha_{M(Y)}$		$\frac{[H^+]^4}{\alpha_{M(Y)}}$	
	pH 0.3	pH 0.7	pH 0.3	pH 0.7
Mercury (II)	$10^{2.3}$	$10^{3.4}$	$10^{-3.4}$	$10^{-6.2}$
Copper (II)	$10^{-0.8}$	$10^{0.3}$	$10^{-0.3}$	$10^{-3.1}$
Bismuth (III)	$10^{1.1}$	$10^{2.4}$	$10^{-2.2}$	$10^{-5.2}$

The values of $\alpha_{M(Y)}$ and $\frac{[H^+]^4}{\alpha_{M(Y)}}$ given in the table demonstrate that increasing the pH of the aqueous phase results in a decrease in the extent of the mercury (II) interference. From 11) if the extraction constant for the gold (I) and mercury (II) diethyldithiocarbamate were known, it would be possible to calculate the concentration of mercury (II) that must be present to cause an interference.

The experimental results given in Table 4.25, which are summarised in Table 4.6, indicate that the interference of 1000µg of bismuth (III), and 100µg of copper (II) and mercury (II) was overcome in the presence of EDTA in an 0.1N sulphuric acid solution, and none of the metal ions when the normality of the acid was 0.5. If the pH of the aqueous phase could be increased, then the interference of 1000ug of copper (II) and mercury (II) would be overcome, however this was not possible as at higher pH values, the gold chelate is not completely formed (p. 106).

3. The separation of palladium (II) as the dimethylglyoximate into chloroform has been used by a number of authors.[69,141,142] Gold (III) does form a dimethylglyoximate,[143,144] but in the presence of hydrochloric acid its formation is prevented. Young[69] separated the palladium complex into chloroform from a solution of 0.5N sulphuric acid, 0.2N with respect to hydrochloric acid, and observed no interference from gold or platinum. The reaction proceeds slowly to form the complex, and is favoured by a considerable excess of reagent. Using an excess of reagent, and allowing the solution to stand for 30min prior to the extraction of the dimethylglyoximate into three 10ml portions of chloroform, the interference of palladium (II) was overcome (Table 4.26), but using three 5ml portions of solvent, incomplete extraction of the complex occurred.

The interfering ions overcome by the three methods are summarised in Table 4.6.

Table 4.6.

Method	Interfering foreign ions overcome	
	1000 fold excess	100 fold excess
Ether extraction	Ag(I), Bi(III), Cr(VI), Cu(II), Sn(II).	Ag(I), Cu(II), Sn(II).
Addition of EDTA (0.1N H_2SO_4 sol^n.)	Bi(III).	Cu(II), Hg(II).
Addition of DMG	Pd(II).	Pd(II).

B. Sample Analysis

i. Sample weight.

The sample weight was selected according to the expected content of gold, and was such that the weight of stable gold was

approximately equal to the weight of active gold added. The active gold was always added to the sample prior to the dissolution. Using this approach if any gold was lost during dissolution, the ratio of active to stable gold would be unaltered, provided the gold is not preferentially lost from either the active gold solution, or from the sample, and isotopic exchange has occurred.

ii. Dissolution procedure.

The concentration of chloride ions in the final aqueous phase prior to the substoichiometric separation of the gold chelate is very critical for the reasons previously discussed (p. 112). With this criteria in mind attempts were made to dissolve a sample of gold-doped semi-conductor grade silicon in a mixture of nitric and hydrofluoric acids by the procedure given on p. 170. Complete dissolution of the sample occurred, but a considerable loss of gold was incurred (about 80%), due to adsorption of hydrolysed species of the gold on the walls of the containing vessel. As an alternative approach the sample was dissolved using nitric and hydrofluoric acids, together with hydrochloric acid, and in this case about a 98% recovery of the gold was achieved. Using a similar dissolution procedure for the rock samples comparable recoveries of the gold were obtained (Table 4.7). The silicon was removed by volatilisation as the tetrafluoride, for the reasons previously discussed (p. 71).

Using the latter dissolution procedure, the chloride ion concentration of the resulting solution was too high for a direct substoichiometric separation of the gold chelate. In order to reduce the concentration of chloride ions, the gold was extracted

into diethyl ether using the method described for the removal of interferences (p. 160). Besides reducing the amount of chloride ions, the extraction also served to separate the gold from a number of interfering ions if present in the sample (Table 4.6).

Table 4.7.

Matrix	Weight (g)	Activity of gold added (c/sec)	Activity of gold recovered (c/sec)	Recovery (%)
Silicon*	1.0601	689	279	40.4
Silicon	1.2031	688	679	98.1
Rock RSM25	1.0020	3374	3283	97.5
Rock RSM349	1.0090	3374	3362	99.6

*In the absence of hydrochloric acid.

iii. Extraction procedure.

The extraction procedure is described on p. 172. A spectrographic examination of the samples to be analysed indicated either the absence of, or the presence of a concentration of copper (II), mercury (II), bismuth (III) or palladium (II) which would not interfere in the method. The preliminary addition of EDTA, or sodium dimethylglyoximate was therefore omitted.

iv. Results.

The results are given in Table 4.8. The coefficient of variation, $\pm$9.1%, and the mean result, 0.11ppm, for the analysis of the gold-doped semi-conductor grade silicon, was very similar to that found by the neutron activation analysis method previously developed, $\pm$9.5%, 0.095ppm. In the case of the rocks RSM25 and 349, the results were in reasonable agreement with those obtained by a fire

assay technique when one considers the large difference in sample weights taken for the two methods; about 1g compared to a factor weight sample of 32.67g for the latter method.[145] Sample RSM25 contained about 12ppm and RSM349 about 11ppm of silver,[145] interference from which was eliminated during the extraction with diethyl ether.

III. Conclusion

The method is capable of determining gold down to 0.10µg/20ml of solution, but the need to have chloride ions present during the sample dissolution, raises this limit to 0.50µg/20ml of solution. The smallest weight of gold that was determined by the method was 1.45×10^{-7}g compared with 2.1×10^{-10}g by the neutron activation analysis method.

Antimony (III), selenium (IV) and tellurium (IV) interfered if present in a 100 fold weight excess compared to that of the gold, and mercury (II) and platinum (IV), if present in a 1000 fold excess.

If the weight of gold to be determined is greater than about 10^{-6}g the use of active nuclides was not considered to be justified, as many suitable spectrophotometric methods are available. A review of such methods has been presented by Beamish and co-workers.[146,147]

Table 4.8.

Results of Sample Analyses

Sample		Gold-bearing ore RSM25				
Weight	(g)	1.0061	0.9857	0.9830	0.9941	0.9872
Au standard	(µg)	1.07	1.07	1.07	1.07	1.07
Activity from Au standard	(c/sec)	255	255	255	637	637
Activity from sample	(c/sec)	71	68	63	147	184
Au found	(ppm)	2.78	3.00	3.32	3.58	2.66
Mean value	(ppm)			3.07		
Standard deviation	(ppm)			±0.38		
Coeff. of variation	(%)			±12.3		
Results of other authors	(ppm)			3.7 (ref. 145)		

Sample		Gold-bearing ore RSM349				
Weight	(g)	1.0073	1.0133	0.9798	0.9760	0.9908
Au standard	(µg)	1.07	1.07	1.07	1.07	1.07
Activity from Au standard	(c/sec)	1098	1098	1098	637	637
Activity from sample	(c/sec)	204	193	231	125	107
Au found	(ppm)	4.70	4.98	4.10	4.48	5.36
Mean value	(ppm)			4.72		
Standard deviation	(ppm)			±0.48		
Coeff. of variation	(%)			±10.2		
Results of other authors	(ppm)			3.7 (ref. 145)		

Table 4.8. (cont.)

Sample		Gold-doped semiconductor-grade silicon 1153		
Weight	(g)	1.2787	1.2196	1.8894
Au standard	(μg)	0.49	0.49	0.49
Activity from Au standard	(c/sec)	206	206	206
Activity from sample	(c/sec)	159	158	154
Au found	(ppm)	0.11	0.12	0.09
Mean value	(ppm)		0.11	
Standard deviation	(ppm)		±0.01	
Coeff. of variation	(%)		±9.1	
Results of other authors	(ppm)		0.095 (by the developed NAA method, see Table 3.8.)	

Standard deviation is that of a single result = $\pm\sqrt{\frac{\Sigma\Delta^2}{n-1}}$ where Δ is the deviation from the mean, $(\bar{x})$, and n is the number of observations.

Coefficient of variation = $\frac{\pm s}{\bar{x}} \times 100\%$.

IV. Experimental

A. Apparatus

The scintillation counter and counting techniques used were as previously described (p. 82).

B. Reagents

All the reagents were prepared from analytical grade chemicals unless otherwise stated. Electronic grade nitric, and hydrochloric acids, and micro analytical grade sulphuric acid were used. The purification and standardisation procedures are given in the Appendix.

i. Distilled water

The water used must be as pure as possible, and in this research double distilled water as obtained from a Scorah Type 4 glass distillation unit was found to be satisfactory. To check the purity a sample was extracted with dithizone (5×10^{-6}M in chloroform). No change in the green colour of the reagent was taken as the criterion of purity.

ii. Active gold solution 1.00µg/ml (5.08×10^{-6}M)

0.01000g of metallic gold was irradiated in a flux of 6×10^{11} neutrons, cm^{-2}, sec^{-1}, for 6hr, using the Universities of Manchester and Liverpool Research Reactor. The amount of gold-198 produced by the nuclear reaction[9,88]

$$^{197}Au\ (n, \gamma)\ ^{198}Au$$

($t_{\frac{1}{2}}$ = 2.70d σ = 98 barns β^- 0.29(1.2%), 0.96(98.8%), 1.37(0.025%)MeV; γ 0.412(95.8%), 0.68(1.0%), 1.09(0.2%)MeV), was sufficient for experiments over a period of about 17d.

After irradiation the gold was dissolved by the previously described procedure (p. 82), and the solution was diluted appropriately with 2.5M hydrochloric acid.

iii. Stable gold solution 1.00µg/ml (5.08×10^{-6}M).

0.01000g of metallic gold was dissolved by the method previously described, and diluted appropriately with 2.5M hydrochloric acid.

Gold solutions of lower concentrations were prepared by dilution of the above listed solutions, using either water, or 2.5M hydrochloric acid.

iv. Copper diethyldithiocarbamate solution (1.0×10^{-4}).

0.0225g of sodium diethyldithiocarbamate and 0.5g of copper (II) sulphate pentahydrate was used to prepare the solution by the previously described method (p. 83), the final volume of the solution being 500ml.

v. Zinc diethyldithiocarbamate solution (1.0×10^{-4}M).

0.0225g of sodium diethyldithiocarbamate was dissolved in 125ml of water containing 5ml of 0.2M sodium acetate-acetic acid buffer (pH 4.7), to this was added 25ml of zinc (II) sulphate solution containing 0.0285g of the heptahydrate. The precipitate formed was extracted by two 200ml portions of chloroform, and the combined extracts were diluted to 500ml in a volumetric flask using the same solvent. The use of recrystallised sodium diethyldithiocarbamate is recommended for the reasons discussed in this chapter (p. 111).

vi. Stable foreign metal ion solutions 1.0mg of metal/ml.

The solutions were prepared by dissolving the appropriate

weight of the element, or a suitable compound of the element, by the method given in Table 4.9, and diluting the resultant solutions to 100ml in a volumetric flask. Solutions of lower concentrations were prepared by dilution of these solutions as required.

Table 4.9.

Element	Compound used	Weight taken (g)	Solvent
Ag (I)	$AgNO_3$	0.1585	Water.
Bi (III)	$Bi(NO_3)_3 5H_2O$	0.2328	HCl, followed by dilution with water.
Cd (II)	$CdSO_4 8H_2O$	0.6846	Water.
Co (II)	$Co(NO_3)_2 6H_2O$	0.4942	Water.
Cr (VI)	K_2CrO_4	0.3733	Water.
Cu (II)	$CuSO_4 5H_2O$	0.3930	Water.
Fe (II)	$FeSO_4 7H_2O$	0.4985	Water.
Fe (III)	$FeCl_3 6H_2O$	0.4840	Dilute HCl.
Hg (II)	$Hg(NO_3)_2 H_2O$	0.1708	Water.
Ni (II)	$Ni(NO_3)_2 6H_2O$	0.4880	Water.
Pb (II)	$Pb(NO_3)_2$	0.1600	Water.
Se (IV)	SeO_2	0.1523	Min. vol. HCl, followed by dilution with water.
Sn (IV)	$SnCl_2 2H_2O$	0.1903	As for Sn (II)*, oxidised with H_2O_2.
Te (IV)	TeO_2	0.1250	KOH, followed by acidification with HCl.
Tl (I)	$TlNO_3$	0.1064	Water.
Zn (II)	$ZnSO_4 7H_2O$	0.4393	Water.

* As (III), As (V), In (III), Mo (VI), Pd (II), Pt (IV), Sb (III), Sb (V) and Sn (II) solutions were prepared by the procedure given in Table 3.9.

C. Development of the Method

i. Preliminary experiments.

a. Using copper diethyldithiocarbamate solution.

To a 100ml separatory funnel containing 20ml of the stated acid (Table 4.10), 2.0ml of the active gold solution 1.00µg/ml (5.08×10^{-6}M) was added. 5.0ml of 5.0×10^{-7}M copper diethyldithiocarbamate in chloroform was added, and the extraction carried out for the stated time. The organic phase was separated, and 3.0ml introduced into a counting jar. The activity of this aliquot and 1.0ml of the active gold solution diluted to 3.0ml with water, to keep a constant geometry, was then determined.

It was assumed that a 1:1 chelate would be formed (p. 105), i.e. 1 mole of gold to 1 mole of diethyldithiocarbamate. This being so, then 5.0ml of 5.0×10^{-7}M copper diethyldithiocarbamate should react with 1.0ml of the active gold solution (5.08×10^{-6}M). From the activity measurements, the percentage gold extracted as a function of that expected was calculated, and the results are given in Table 4.10.

The copper diethyldithiocarbamate solution was prepared by dilution of the stock 1.0×10^{-4}M solution using chloroform.

b. Using zinc diethyldithiocarbamate solution.

The procedure used was the same as that previously described, except zinc rather than copper diethyldithiocarbamate of the same strength, 5.0×10^{-7}M, was used, and the aqueous phase was 0.1N sulphuric acid. The results are given in Table 4.10.

c. Using zinc diethyldithiocarbamate solution in the presence of ascorbic acid in the aqueous phase.

The method used was similar to that described above, except prior to the addition of the chelating agent 1ml of 1% ascorbic acid was introduced into the aqueous phase, and the extraction was carried out for 3min. The results are given in Table 4.10.

Table 4.10.

Aqueous phase Acid	Normality	Extraction time (min.)	Activity of 1.0ml of Au solution (5.08×10^{-6}M) (c/sec)	Activity of 3.0ml of organic phase. (c/sec)	Gold extracted (%)
A)					
HCl	1.0	3	8528	303	5.9
H_2SO_4	1.0	3	7233	480	10.9
H_2SO_4	0.1	10	6983	749	17.9
B)					
H_2SO_4	0.1	10	5700	2454	71.4
H_2SO_4+ Ascorbic acid	0.1	3	3591	2157	100.0

The results under heading A) are those using $Cu(DDC)_2$ 5.0×10^{-7}M.
The results under heading B) are those using $Zn(DDC)_2$ 5.0×10^{-7}M.

ii-vi and viii-x.

These experiments were all carried out using the same basic technique given below. The conditions used for each experiment are given in Table 4.11, and each experiment is considered individually following this table.

Table 4.11.

The Experimental Conditions used for Experiments ii-x (excluding vii)

Exp.t No.	Aqueous phase	Amount of active Au solution added ——M (——ml)	Amount of stable Au solution added ——M (——ml)	Amount of foreign specie added g or ——M (——ml)	Amount of ascorbic acid sol.n added 1ml of ——%	Amount of $Zn(DDC)_2$ in $CHCl_3$ added ——M (——ml)	Ext. time ——min	Vol. of organic phase counted ——ml
	20ml of -							
ii	Variable acidity or pH	5.08×10^{-6} (1.0)	-	-	1.0	5.0×10^{-7}	5	2.0
iii								
a)	0.5N H_2SO_4	6.34×10^{-6} (1.0)	-	-	1.0	5.0×10^{-7} (4.0)	Variable	2.0
b)	0.5N H_2SO_4	5.08×10^{-7} (1.0)	-	-	1.0	5.0×10^{-8} (3.0)	Variable	2.0
iv	0.5N H_2SO_4	6.34×10^{-6} (1.0)	-	-	Variable	5.0×10^{-7} (4.0)	Variable	2.0

Table 4.11. (cont.)

Exp.t No.	Aqueous phase	Amount of active Au solution added —M (—ml)	Amount of stable Au solution added —M (—ml)	Amount of foreign specie added g or —M (—ml)	Amount of ascorbic acid sol.n added 1ml of —%	Amount of $Zn(DDC)_2$ in $CHCl_3$ added —M (—ml)	Ext. time —min	Vol. of organic phase counted —ml
	20ml of -							
v								
a)	0.5N H_2SO_4	5.08×10^{-6} (Variable)	-	-	1.0	5.0×10^{-7} (5.0)	5	3.0
b) & c)	0.5N H_2SO_4	5.08×10^{-7} (Variable)	-	-	1.0	5.0×10^{-8} (5.0)	5	3.0
vi								
a)	0.5N H_2SO_4	Variable (1.0)	-	-	1.0	1.0×10^{-4} (5.0)	5	3.0
b)	0.5N	Variable (1.0)	-	-	1.0	Variable (5.0)	5	3.0
viii	0.5N H_2SO_4	Variable (1.0)	-	Variable NaCl (1.0)	1.0	Variable (5.0)	5	3.0

Table 4.11. (cont.)

Exp.t No.	Aqueous phase	Amount of active Au solution added	Amount of stable Au solution added	Amount of foreign specie added	Amount of ascorbic acid sol.n added	Amount of $Zn(DDC)_2$ in $CHCl_3$ added	Ext. time	Vol. of organic phase counted
	20ml of -	——M (——ml)	——M (——ml)	g or ——M (——ml)	1ml of ——%	——M (——ml)	——min	——ml
ix	0.5N H_2SO_4	Variable (1.0)	Variable (1.0)	-	1.0	Variable (5.0)	5	3.0
x	0.5N H_2SO_4	5.08×10^{-6} (1.0)	-	100 or 1000ug	1.0	2.5×10^{-7} (5.0)	5	3.0

Basic experimental technique.

To a series of 100ml separatory funnels each containing 20ml of an aqueous phase, the stated amount of active and stable, or active gold solution was added, followed by the stated amount of a foreign specie (e.g. metal ion solution other than gold). 1ml of ascorbic acid of the stated concentration was added, followed by the stated amount of zinc diethyldithiocarbamate in chloroform solution. The extractions were then carried out for the stated time period, after which the organic phase was filtered through Whatman 540 filter papers placed in the stems of the separatory funnels. The stated volume of each organic phase was finally pipetted into a series of counting jars, and the activity of the gold-198 measured.

ii. Influence of the pH of the aqueous phase.

The experiment was carried out using the experimental technique given above, with the conditions given in Table 4.11.

In order to obtain an aqueous phase having a pH value in the range 1.5-7.9, the aqueous phase consisted initially of 20ml of water, to which was added dilute aqueous ammonia and/or a small volume (1-2ml) of 0.1N acetate, or borate buffer solutions. The pH values stated in the table of results (Table 4.12), were measured after the substoichiometric extraction.

iii. Time to reach extraction equilibrium.

The conditions used for the experiment are given in Table 4.11. The stoichiometry of the separation using an active gold solution 1.25µg/ml (6.34×10^{-6}M) was 64%, and that using an active gold solution 0.10µg/ml (5.08×10^{-7}M) 60%.

The results are given in Table 4.13.

Table 4.12.

N of acid (H_2SO_4)	Activity of 2.0ml of organic phase (c/sec)	pH	Activity of 2.0ml of organic phase (c/sec)
10	1505	1.5	1800
8	1651	2.7	1401
6	1793	3.0	1096
4	1887	3.2	1067
2	1878	3.6	925
1	1876	4.3	703
0.5	1858	5.2	822
0.1	1871	7.5	126
		7.9	110
Activity of 1.0ml of Au solution (c/sec)	4631		

See also Fig. 4.1.

Table 4.13.

Extraction time (min)	Activity of 2.0ml of organic phase (c/sec) a	b
0.5	1304	
1	1739	293
1.5	1919	
2	1916	374
3	1910	373
5	1918	375
6	1917	369
15	1911	370
Activity of 1.0ml of Au solution (c/sec)	6010	932
Stoichiometry (%)	64	60

Table 4.13. (cont.)

The results in columns a and b are for active gold solutions 1.25µg/ml (6.34×10^{-6}M), and 0.10µg/ml (5.08×10^{-7}M) respectively.

See also Fig. 4.2.

iv. Influence of the concentration of ascorbic acid.

The effect of varying the concentration of ascorbic acid in the aqueous phase, on the time to reach extraction equilibrium at a fixed stoichiometry of about 64% was investigated using the conditions given in Table 4.11.

The results are given in Table 4.14.

Table 4.14.

Extraction time (min)	Activity of 2.0ml of organic phase (c/sec)					
	I	II	III	IV	V	VI
0.5	1304	670	428	568	68	
1	1739	902	668	714	320	
2	1919	1143	1024	894	685	
3	1910	1256	1061	907	701	
5	1918	1320	1255	1227	867	
8		1320	1289	1255	950	
10		1316	1286	1373	1002	
15	1911		1285	1369	1042	215
25				1371	1139	268
30					1142	348
40					1142	383
50					1141	448
60						518
90						587

The figures given in columns I-V are the results using 1ml of a 1.0%, 0.1%, 0.01%, 0.001%, 0.0005% ascorbic acid solution respectively, and those in column VI are in the absence of ascorbic acid.

The underlined values in Table 4.14 signify the stage at which equilibrium was considered to have been reached.

v. Reproducibility.

The reproducibility of the substoichiometric separation of gold as the diethyldithiocarbamate in chloroform was investigated using the conditions given in Table 4.11. The reproducibility of the separation using an active gold solution 0.10µg/ml (5.08×10^{-7}M) was poor. The reasons for this are discussed on p. 109. The experiment was repeated using freshly prepared active gold and chelating agent solutions.

The results are given in Table 4.15.

Table 4.15.

Vol. of active Au solution added (ml)	Activity of 3.0ml of organic phase (c/sec)		
	a	b	c
0.2	224	183	255
0.4	429		650
0.5		373	
0.6	610		960
1.0	993	667	1610
1.5	1063	1171	1794
2.0	1077	1455	1810
2.5	1050	1228	1785
3.0	1057	1153	1850
4.0	1038	1370	1890
Activity of 1.0ml of Au solution (c/sec)	1784	1528	2683

Table 4.15. (cont.)

	a	b	c
$\bar{x}$ (c/sec)	1057	1275	1826
n	5	5	5
s (c/sec)	±15	±132	±33
Coeff. of variation (%)	±1.4	±10.4	±1.8

The figures given in columns a and b are the results using active gold solutions, 1.00µg/ml (5.08×10^{-6}M) and 0.10µg/ml (5.08×10^{-7}M), and those in column c using a freshly prepared active gold solution 0.10µg/ml (5.08×10^{-7}M) and chelating agent solution.

$\bar{x}$ is the mean of the activity measurements for the observations with substoichiometric conditions (i.e. greater than 1.0ml of added active gold solution).

s is the standard deviation of a single result = $\pm\sqrt{\frac{\Sigma\Delta^2}{n-1}}$, where Δ is the deviation from the mean, and n is the number of observations.

The coefficient of variation = $\frac{\pm s}{\bar{x}} \times 100$.

See also Fig. 4.3.

vi. Stability of solutions.

a. Gold solutions.

Two 1.0ml aliquots of the active gold solution were sampled at regular intervals (about every 12hr). The first aliquot was extracted with an excess of chelating agent using the conditions given in Table 4.11, and the second was diluted to 3.0ml with distilled water and its activity measured. From the measurements the percentage extraction of the gold with an excess of chelating agent was calculated (Table 4.16).

In order to avoid correcting the results for the decay of the gold-198 activity all the previous samples were recounted when the activity of the most recent was being determined.

Table 4.16.

Age of active Au solution (hr)	Activity of 1.0ml of Au solution (c/sec)			Activity of 3.0ml of organic phase (c/sec)			% extracted as Au chelate		
	I	II	III	I	II	III	I	II	III
0	1763	1048	1250	1044	646	753	99	103	100
12	1773	1046		1016	646		96	103	
24	1777	1047	1249	980	642	752	92	101	100
36	1730	1030		920	636		89	103	
42		1019	1242		629	756		103	101
53	1630	970		834	540		85	93	
60	1529	968		779	510		85	88	
80			1240			749			100
120		880	1238		440	746		83	100
161	1508		1238	678		743	75		100
205			1226			722			98
306			1210			710			98
360			1210			711			98
404			1204			703			97
480			1200			693			96
504			1198			680			94
526			1196			643			89
600			1180			622			88

The figures in columns I, II and III are the results using active gold solutions 0.12µg/ml (6.08×10^{-7}M), 1.06µg/ml (5.36×10^{-6}M) and 5.40µg/ml (2.74×10^{-5}M) respectively.

b. Zinc diethyldithiocarbamate in chloroform solutions.

The stability of the chelating agent solutions was determined using the conditions given in Table 4.11, i.e. an extraction in the presence of a ten-fold excess of active gold solution (substoichiometric conditions). For the extractions using 5.0ml of 5×10^{-8}M chelating agent this corresponded to 1µg of active gold solutions, and therefore the weight of gold necessary for all the concentrations of chelating agent could easily be computed. In order to avoid decay corrections the same counting technique as previous described was used, and the results are given in Table 4.17.

Table 4.17.

Age of $Zn(DDC)_2$ solution in $CHCl_3$ (hr)	Activity of 3.0ml of organic phase (c/sec)				
	I	II	III	IV	V
0	709	1155	1084	8350	2991
0.25	665	1125	1053		
0.5	610	1060	1022	8100	2934
1	580	1002	1002	8065	3035
1.5			991		2996
2			943	7960	2986
3				7580	2938
4				7560	
5				7501	
6				7380	

The figures in columns I to IV are the results for $Zn(DDC)_2$ solutions 1.0×10^{-8}M, 5.0×10^{-8}M, 1.0×10^{-7}M and 1.0×10^{-6}M respectively. Those in column V are for 2.5×10^{-7}M chelating agent prepared from recrystallised NaDDC.

The solutions of both reagent and active gold were considered to be stable until such time that the activity of the organic phase had decreased by more than 10% of their original value.

A summary of the results given in Tables 4.16 and 4.17 is given in Table 4.1.

vii. Partition coefficient of the gold diethyldithiocarbamate.

The method used was the same as that given in Chapter 3 (p. 92) except an active gold solution 1.00µg/ml (5.08×10^{-6}M)was used in a medium of 20ml of 0.5N sulphuric acid containing 1ml of 1% ascorbic acid. The extractions were carried out for 5min using 4.0ml of 5.0×10^{-7}M zinc diethyldithiocarbamate, 3.0ml of the organic phases being separated for counting. The second extraction was performed using 20.0ml of the aqueous phase and 4.0ml of chloroform.

The results of the investigation are given in Table 4.18.

viii. The role of chloride ions.

The maximum concentration of chloride ions in the aqueous phase that could be tolerated for a given concentration of gold was established using the conditions given in Table 4.11. A similar extraction was then performed without the addition of sodium chloride to serve as the reference standard. The concentration of chelating agent used was dependent upon the gold concentration, and that used is given below:

Weight of active gold (µg)	Concentration of $Zn(DDC)_2$ in chloroform (M)
1.00	2.5×10^{-7}
0.50	1.25×10^{-7}
0.20	0.5×10^{-7}
0.10	2.5×10^{-8}

Table 4.18.

The Partition Coefficient of the Gold Diethyldithiocarbamate between Chloroform and 0.5N sulphuric Acid

Vol. of active Au solution added (ml)	Activity of 3.0ml of 1st organic phase (c/sec)	Activity of 3.0ml of 2nd organic phase (c/sec)	Vol. of 2nd aqueous phase (ml)	Partition Coefficient (p)	
1.0	2255	28	20.0	530	$\bar{x}$ = 512
1.0	2307	34	20.0	453	n = 6
1.0	2321	34	20.0	456	s = ±65
2.0	1880	25	20.0	495	Coeff. of
4.0	1910	20	20.0	631	Variation
5.0	1934	25	20.0	508	= ±12.7%

$\bar{x}$ is the mean value of the observations.

s is the standard deviation of a single result = $\pm\sqrt{\frac{\Sigma\Delta^2}{n-1}}$, where Δ is the deviation from the mean, and n is the number of observations.

The coefficient of variation is given by $\pm \frac{s}{\bar{x}} \times 100\%$.

The results are given in Table 4.19, and are summarised in Table 4.2.

Table 4.19.

Conc^{n}. and vol. of NaCl added ——M(—ml)	Total Cl^{-} conc^{n}. present (M)	Activity of 3.0ml of organic phase (c/sec)
A)		
-	0.11	103
1.0 (1.0)	0.15	103
2.0 (1.0)	0.20	104
3.0 (1.0)	0.25	103
4.0 (1.0)	0.29	102
5.0 (1.0)	0.34	101
3.0 (2.0)	0.36	98
4.0 (2.0)	0.38	92
5.0 (2.0)	0.49	90
B)		
-	0.06	102
1.0 (1.0)	0.10	103
2.0 (1.0)	0.16	102
2.5 (1.0)	0.18	97
3.0 (1.0)	0.20	91
4.0 (1.0)	0.24	90
5.0 (1.0)	0.29	88
C)		
-	0.02	70
1.0 (1.0)	0.06	70
1.5 (1.0)	0.09	58
2.0 (1.0)	0.12	49
3.0 (1.0)	0.16	55

Table 4.19. (cont.)

Conc^{n}. and vol. of NaCl added ——M(——ml)	Total Cl^{-} conc^{n}. present (M)	Activity of 3.0ml of organic phase (c/sec)
D)		
-	0.01	436
0.5 (1.0)	0.03	431
1.0 (1.0)	0.05	430
1.5 (1.0)	0.08	383
2.0 (1.0)	0.11	318
3.0 (1.0)	0.15	294

The figures given under headings A, B, C and D were the results obtained using active gold solutions 1.00µg/ml (5.08×10^{-6}M) in 2.5M HCl, 0.50µg/ml (2.54×10^{-6}M) in 1.25M HCl, 0.20µg/ml (1.01×10^{-6}M) in 0.5M HCl, and 0.10µg/ml (5.08×10^{-7}M) in 0.25M HCl respectively.

ix. Accuracy and precision.

The accuracy and precision of the isotope-dilution method was assessed by carrying out a series of repetitive 1:1 dilutions (i.e. 1 part active to 1 part stable gold by weight) at four different concentrations of active and stable gold solutions (Table 4.3). The conditions used are given in Table 4.11. Besides the separations in the presence of active and stable gold, a separation was carried out in the absence of stable gold under identical conditions using 2.0ml of the active gold solution. The activity, a_s, of 3.0ml of the separated organic phase was measured under the same conditions as those from the 1:1 dilutions - activity a. For the extractions in the presence of 1.00µg of active and 1.06µg of stable gold the concentration of chelating agent used was

5.0×10^{-7}M. The concentration required for all other concentrations of gold studied could therefore be calculated from this data. The weight of active and stable gold, y_s and y^*, respectively, stated in the table of results (Table 4.3) were calculated from the known weight of gold used to prepare the solutions.

The solutions of concentration about 1µg Au/ml were in a medium of 2.5M hydrochloric acid, and all the more dilute solutions were prepared by dilution with distilled water, so as to keep the chloride ion concentration of the aqueous phase below the maximum permitted concentration (Table 4.2).

x. Selectivity.

The effect of introducing 100 or 1000µg of a foreign ion into the aqueous phase prior to the substoichiometric separation of the gold as the diethyldithiocarbamate in chloroform was studied using the conditions given in Table 4.11. The activity, a_2 of a 3.0ml aliquot of the organic phase, and that of an equal volume of the organic phase after a similar extraction in the absence of foreign ions, activity a_1, were measured.

By substituting the results obtained in the substoichiometric formula applied to isotope-dilution, the apparent weight of stable gold determined could be calculated. Theoretically the result should be zero, as no stable gold was added. The results are given in Table 4.20, and are summarised in Table 4.4.

Table 4.20.

Foreign ion present 1000 fold	Foreign ion present 100 fold	Activity of 3.0ml of organic phase (c/sec) a_1	a_2	a_2^*	Mean of a_2 & a_2^* (c/sec) $\bar{a}_2$	Weight of stable gold found (µg) y	y^*	$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$ (%)	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$ (%)
Ag(I)		96	6	6	6	+15.0	+15.0	93.8	4.7
	Ag(I)	268	233	233	233	+ 0.15	+ 0.15	13.1	4.7
As(III)		96	92	92	92	+ 0.04	- 0.01	4.5	4.7
As(V)		159	164	162	163	- 0.03	- 0.02	2.5	4.7
Bi(III)		816	296	333	315	+ 1.76	+ 1.45	61.3	4.7
	Bi(III)	245	240	246	243	+ 0.02	0.0	0.8	4.7
Cd(II)		1309	1349	1375	1362	- 0.03	- 0.05	4.0	4.7
Co(II)		159	153	158	156	+ 0.04	0.0	1.9	4.7
Cr(VI)		1409	510	586	548	+ 1.76	+ 1.41	61.2	4.7
	Cr(VI)	268	270	271	270	- 0.01	- 0.01	0.7	4.7
Cu(II)		816	334	315	324	+ 1.44	+ 1.59	60.2	4.7
	Cu(II)	613	284	292	288	+ 1.18	+ 1.13	53.0	4.7
Fe(II)		494	490	502	496	+ 0.01	- 0.02	0.4	4.7
Fe(III)		494	488	503	495	+ 0.01	- 0.02	0.2	4.7
Hg(II)		816	190	186	188	+ 3.30	+ 3.38	76.9	4.7
	Hg(II)	613	262	271	266	+ 1.36	+ 1.30	56.7	4.7
In(III)		159	160	157	158	- 0.01	+ 0.01	0.6	4.7

Table 4.20. (cont.)

Foreign ion present		Activity of 3.0ml of organic phase			Mean of a_2 & a_2^*	Weight of stable gold found		$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$
1000 fold	100 fold	(c/sec)			(c/sec)	(µg)		(%)	(%)
		a_1	a_2	a_2^*	$\bar{a}_2$	y	y^*		
Mo(VI)		864	906	911	908	- 0.06	- 0.05	3.9	4.7
Ni(II)		494	495	506	500	0.0	- 0.02	1.2	4.7
Pb(II)		159	162	162	162	- 0.02	- 0.02	1.9	4.7
Pd(II)		864	76	75	75	+10.36	+10.51	92.4	4.7
	Pd(II)	626	63	80	71	+ 9.2	+ 7.1	88.6	4.7
Pt(IV)		816	735	712	724	+ 0.11	+ 0.15	11.3	4.7
	Pt(IV)	576	580	549	564	- 0.02	+ 0.04	2.1	4.7
Se(IV)		245	28	28	28	+ 7.97	+ 7.97	88.6	4.7
	Se(IV)	1309	378	441	410	+ 2.46	+ 1.97	68.7	4.7
Sb(III)		864	540	541	540	+ 0.60	+ 0.60	37.5	4.7
	Sb(III)	450	370	340	355	+ 0.21	+ 0.31	21.1	4.7
Sb(V)		450	460	430	445	- 0.02	+ 0.04	1.1	4.7
Sn(II)		613	237	246	242	+ 1.62	+ 1.54	60.6	4.7
	Sn(II)	494	449	471	460	+ 0.10	+ 0.05	6.9	4.7
Sn(IV)		450	460	460	460	- 0.02	- 0.02	2.2	4.7
Te(IV)		1409	217	185	201	+ 5.48	+ 6.60	85.7	4.7
	Te(IV)	450	340	350	345	+ 0.31	+ 0.28	23.3	4.7

Table 4.20. (cont.)

Foreign ion present 1000 fold 100 fold	Activity of 3.0ml of organic phase (c/sec) a_1	a_2	a_2^*	Mean of a_2 & a_2^* (c/sec) $\bar{a}_2$	Weight of stable gold found (µg) y	y^*	$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$ (%)	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$ (%)
Tl(I)	159	157	156	156	+ 0.01	+ 0.02	1.9	4.7
Zn(II)	159	151	156	154	+ 0.05	+ 0.02	3.1	4.7
1ml 6N nitric acid	100	100		100	0.0		0.0	5.5
1ml 8N nitric acid	100	99		99	+ 0.01		1.0	5.5
1ml 10N nitric acid	100	95		95	+ 0.05		5.0	5.5
2ml 10N nitric acid	100	91		91	+ 0.10		9.0	5.5
1ml 2M hydrobromic acid	123	77		77	+ 1.60		37.4	5.5
1ml 0.1M EDTA sol^{n}.	169	164		164	+ 0.03		3.0	5.5
1ml 1% dimethyl-glyoxime sol^{n}.	41	41		41	0.0		0.0	5.5
1ml 40% hydro-fluoric acid	41	41		41	0.0		0.0	5.5

Activity a_1 refers to the Standard, and activities a_2 and a_2^* refer to two separate trials in the presence of the same foreign ion. y and y^* are the calculated weights of gold from the corresponding activities a_2 and a_2^*.

xi. Elimination of interfering ions.

Three methods were studied as was discussed on p. 121.

1. Preliminary ether extractions.

a. From hydrochloric acid solution.

1.0ml of active gold solution 1.00µg/ml (5.08×10^{-6}M) in a medium of 10ml of 2M hydrochloric acid, contained in a 100ml separatory funnel, was extracted with 20ml of ether for 3min. The aqueous phase was then run off, and the ether phase was transferred to a 50ml beaker. 1ml of concentrated hydrochloric acid was added, and the solution evaporated over a water bath at a temperature of about 50°C to remove the ether. The resulting solution was transferred to a counting jar, and the volume made up to 5ml with water. The activity of the gold-198 was then measured, and this result was compared with the activity of 1.0ml of the active gold solution diluted to 5ml in a counting jar. A second series of extractions were carried out using two 20ml and also three 20ml portions of ether extracting with each for 3min. The combined ether phases were then evaporated, and counted as previously.

The results of this set of experiments together with those obtained with similar conditions using ethyl acetate as the extractant are given in Table 4.21. The only modification necessary using the latter solvent was that a higher temperature of the water bath of about 90°C was necessary to remove the ethyl acetate by volatilisation. This was due to the higher boiling point of this solvent (77°C) in comparison to that of diethyl ether (35°C).

Table 4.21.

Extractant	Volume of extractant (ml)	Activity of 1.0ml of Au solution (c/sec)	Activity of Au extracted (c/sec)	Recovery (%)
A)				
Diethyl	20	789	640	81.2
ether	20	789	643	81.4
	2x20	789	677	85.7
	3x20	789	702	88.9
Ethyl	20	851	680	79.9
acetate	20	851	690	81.2
	2x20	851	707	83.0
	3x20	851	747	87.7
B)				
Diethyl	20	2095	1798	85.8
ether	20	2095	1834	87.6
	2x20	2095	1841	87.8
	3x20	2095	1897	90.4
Iso-propyl	20	2131	1358	63.6
ether	2x20	2131	1420	66.7
	3x20	2131	1470	68.9

The results under heading A) are for extractions from a 2M hydrochloric acid solution, and those under B) from a 2M hydrobromic acid solution.

The extractant and volume to be used had been decided (p. 122), but it was necessary to establish the minimum concentration of hydrochloric acid that must be present during the evaporation of the ether, to avoid losses of gold. The lowest concentration of hydrochloric acid must be used for reasons discussed on p. 112. 1.00µg of active gold in 10ml of 2M hydrochloric acid was extracted with 20ml of diethyl ether using the method previously described.

To the separated organic phase contained in a 50ml beaker, was added the stated volume and concentration of hydrochloric, nitric or sulphuric acid (Table 4.22), and the ether phase volatilised over a water bath at about 50°C. After removal of the ether the solution was counted, then transfered to 100ml separatory funnel containing 20ml of 0.5N sulphuric acid and 1ml of 1% ascorbic acid. 5.0ml of 1.0×10^{-4}M zinc diethyldithiocarbamate in chloroform solution (excess) was added, and the extraction performed for 5min. The activity of 3.0ml of the separated organic phase was then measured, and the percentage gold complexed by the excess of chelating agent calculated. The results are given in Table 4.22.

Table 4.22.

Acid present during evap.^{n} of ether phase	Conc.^{n} and Vol. used	Activity of Au after ether ext.^{n} and evap.^{n}	Activity of Au ext.^{d} by 3.0ml of 1.0×10^{-4}M $Zn(DDC)_2$	Degree of ext.^{n} as metal chelate
	——M(—ml)	(c/sec)	(c/sec)	(%)
HCl	4.0 (1.0)	460	271	98.0
HCl	4.0 (0.5)	430	256	98.8
HCl	3.0 (1.0)	500	296	98.7
HCl	3.0 (0.5)	450	265	98.0
HCl	2.0 (1.0)	380	185	81.3
HCl	2.0 (0.5)	360	142	65.7
HNO_3	3.0 (1.0)	300	120	66.7
H_2SO_4	3.0 (1.0)	310	131	70.3
Activity of 1.0ml of Au solution (c/sec)		620		

The possibility of eliminating the interference of some of the

metal ions by a preliminary extraction of the gold into 20ml of diethyl ether was studied using the method previously described. The weight of active gold solution used was 1.00μg, and that of the interfering ions 100 or 1000μg. After the preliminary extraction, the ether phases were evaporated in the presence of 0.5ml of 3M hydrochloric acid, then transferred to counting jars, and the activity of gold-198 was measured. The solutions were then transferred to 100ml separatory funnels, and the gold was extracted from a medium of 0.5N sulphuric acid in the presence of ascorbic acid in the usual manner using 4.0ml of 2.5×10^{-7}M chelating agent. The activity, a_2, of 3.0ml of the separated organic phase was measured.

A similar extraction was carried out using 1.00μg of active gold and the same amount of chelating agent to act as a reference standard. The preliminary extraction of the gold into diethyl ether was omitted and the activity, a_1, of 3.0ml of the organic phase was again measured.

The activity of the solution after the preliminary ether extraction was measured so that the weight of gold present at this stage of the experiment could be calculated, from the known activity of gold added. By so doing, it was possible to ensure that the final separation of the gold as the chelate in chloroform was always carried out under substoichiometric conditions. The results are given in Table 4.23, a summary of which is given in Table 4.6.

Table 4.23.

Foreign ion present		Activity of 3.0ml of organic phase		$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$
1000 fold excess	100 fold excess				
		a_1	a_2	(%)	(%)
Ag(I)		264	258	2.3	4.7
	Ag(I)	612	588	3.9	4.7
Bi(III)		769	736	4.3	4.7
Cr(VI)		769	748	2.7	4.7
Cu(II)		654	641	2.0	4.7
	Cu(II)	264	258	2.3	4.7
	Hg(II)	2155	1746	19.0	4.7
	Pd(II)	612	505	17.5	4.7
Pt(IV)		769	458	40.4	4.7
	Sb(III)	2155	1749	18.8	4.7
	Se(IV)	2155	57	97.4	4.7
Sn(II)		769	771	0.4	4.7
	Sn(II)	2155	2134	1.0	4.7
	Te(IV)	2155	1806	19.3	4.7

The quoted values for a_1 are the mean of two results, i.e. $n_1 = 2$, and those for a_2 are a single result, i.e. $n_2 = 1$.

Back extraction of the gold from diethyl ether.

1.00µg of active gold of known activity was extracted into 20ml of diethyl ether using the method previously described (p.160). The separated ether phase was diluted to 20ml, and the activity of a 5.0ml aliquot was measured. After measurement, this aliquot was recombined with the remainder of the ether phase which was transferred to a 100ml separatory funnel. The gold was then re-extracted from the ether phase with two 20ml portions of water, using a 3min extraction after each addition. After each extraction,

the aqueous phase was separated and rediluted to 20ml, and the activity of a 5.0ml aliquot was measured. From the activity measurements the total activity of gold-198 present in the two 20ml solutions of water, and the original 20ml of ether could be calculated, and hence the percentage re-extraction of the gold. The results are given in Table 4.24.

If to the aqueous phases chloroform was added an increase in volume of the organic phase was observed, indicating the presence of traces of ether phase. In order to obtain a true determination of the degree of back extraction of the gold by water, the aqueous phases were washed with 5.0ml of chloroform and the activity of the chloroform extracts was measured.

The activity of the aqueous phases were then corrected, and the corrected results are given in parenthesis in Table 4.24.

To the combined aqueous phases was then added 0.5ml of concentrated sulphuric acid dropwise to give a resultant solution of about 0.5N with respect to sulphuric acid. 1ml of 1% ascorbic acid was added, and the substoichiometric extraction of the gold carried out for 5min using 5ml of 1.0×10^{-7}M zinc diethyldithiocarbamate solution. The activity of 3.0ml of the separated organic phase was determined. The result was compared with the activity of 3.0ml of the organic phase obtained after a similar substoichiometric separation of the gold, using the same amount of chelating agent. The results are given in Table 4.24.

b. From hydrobromic acid solution.

The efficiency of extraction of gold from 2M hydrobromic acid

Table 4.24.

Activity of 1.00µg of Au (c/sec)	Activity of ether phase (c/sec)	Activity of 1st aqueous phase (c/sec)	Activity of 2nd aqueous phase (c/sec)	Degree of back extraction (%)	Weight of Au back extracted (µg)	Activity of 3.0ml of organic phase after sub.^{c} extraction (c/sec)
A)						
2083	1614	704 (640)	158 (98)	53.4(45.7)	0.41(0.35)	249
2083	1657	742 (693)	136 (87)	53.0(47.1)	0.42(0.37)	255
						Std. 254
B)						
2098	1977	(1068)	(540)	(81.3)		171
2098	2047	(1044)	(564)	(81.3)		124
						Std. 246
C)						
2098	1533	(1160)	(48)	(78.7)		110
2098	1514	(1115)	(57)	(77.4)		100
						Std. 246

The results given under A) are for the back extraction of gold after a preliminary extraction into diethyl ether from 2M hydrochloric acid solution, and those under B) and C) are for the back extraction of gold after preliminary extraction into diethyl B) or isopropyl ether C) from 2M hydrobromic acid solution.

using diethyl or isopropyl ether was determined using the same experimental procedure as previously described for the extractions from 2M hydrochloric acid, except a water bath temperature of about 90°C was necessary for the evaporation of the isopropyl ether phases (B Pt 69°C). The results are given in Table 4.24.

Back extraction of the gold from ethyl or isopropyl ether.

The experimental procedure was the same as that previously described. The results are given in Table 4.24.

2. The addition of EDTA.

To a series of 100ml separatory funnels each containing 20ml of 0.5N sulphuric acid 1.0ml of active gold solution (1.00µg/ml 5.08×10^{-6}M) and 100 or 1000µg of interfering ions to be examined was added. 1ml of 0.1M EDTA solution was added, followed by 1ml of 1% ascorbic acid solution and 5.0ml of 2.5×10^{-7} chelating agent. After a 5min extraction the organic phase was separated in the usual manner, and the activity, a_2, of 3.0ml was measured. An extraction was also carried out in the absence of foreign ions under identical conditions to serve as a reference standard, 3.0ml of the separated organic phase again being counted, activity a_1.

The procedure was then repeated using 20ml of 0.1N sulphuric acid as the aqueous phase. The results are given in Table 4.25.

The concentration of EDTA used represented about a 20 fold excess of reagent based on the addition of 1mg of bismuth (III).

Table 4.25.

Foreign ion present 1000 fold excess	100 fold excess	Activity of 3.0ml of organic phase a_1	a_2	$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$ (%)	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$ (%)
A)					
Bi(III)		133	57	57.1	4.7
	Cu(II)	169	145	14.2	4.7
	Hg(II)	133	104	21.8	4.7
B)					
Bi(III)		1270	1250	1.6	4.7
	Cu(II)	130	127	2.3	4.7
Cu(II)		141	120	14.9	4.7
	Hg(II)	1270	1276	0.5	4.7
Hg(II)		1270	1008	20.6	4.7

The results under headings A) and B) are those using an aqueous medium of 0.5N and 0.1N sulphuric acid solutions respectively. The quoted values of a_1 are the mean of two results, i.e. $n_1 = 2$, and those for a_2 for a single result, i.e. $n_2 = 1$.

3. The addition of dimethylglyoxime.

To a series of 100ml separatory funnels each containing 20ml of 0.5N sulphuric acid, 1.0ml of active gold solution 1.00µg/ml (5.08×10^{-6}M), and 100 or 1000µg of palladium (II) was added. 3ml of a 1% aqueous solution of sodium dimethylglyoximate was added, and the solutions allowed to stand for 30min. The palladium dimethylglyoximate was then extracted using three 5ml portions of chloroform, extracting with each for 3min. To the solutions after the extraction of the palladium dimethylglyoximate was added 1ml of 1% ascorbic acid followed by 5.0ml of 2.5×10^{-7}M zinc diethyldithiocarbamate in chloroform. The extractions were then performed for 5min, after

which the organic phases were filtered, and the activity, a_2, of 3ml of each was measured. An extraction was also carried out simultaneously in the absence of palladium (II) using the same volume and concentration of chelating agent. The activity, a_1, of 3.0ml of the resulting organic phase was then measured to serve as a reference standard.

A second series of experiments was performed using the same experimental procedure except three 10ml portions of chloroform were used for the extraction of the palladium dimethylglyoximate.

The results of the experiments are given in Table 4.26.

Table 4.26.

Foreign ion present		Vol. of $CHCl_3$ used	Activity of 3.0ml of organic phase (c/sec)		$100\left\|\frac{(\bar{a}_1-\bar{a}_2)}{\bar{a}_1}\right\|$	$3.89\left(\frac{1}{n_1}+\frac{1}{n_2}\right)^{\frac{1}{2}}$
1000 fold excess	100 fold excess	(ml)	a_1	a_2	(%)	(%)
Pd(II)		3x5	87	72	17.3	3.15
	Pd(II)	3x5	87	87	0	3.15
Pd(II)		3x10	52	51	1.9	3.15
	Pd(II)	3x10	52	52	0	3.15

The stated value for a_1 are the mean of three results, i.e. $n_1 = 3$, and those for a_2 are also the mean of three results, i.e. $n_2 = 3$.

D. Sample Analysis

i. Weight of standard and samples.

The weight of standard used was computed from the known weight of gold metal irradiated (about 10mg) using the Universities of Manchester and Liverpool Research Reactor. All the dilutions of the

irradiated gold after dissolutions were made using 2.5M hydrochloric acid.

The sample weights were selected according to the expected gold content so as to give approximately a 1:1 dilution with the weight of active gold used as the standard.

The sample of gold-doped semi-conductor grade silicon (1153) was obtained from Mullards of Southampton, and the rock samples RSM25 and 349, from the Royal School of Mines, Imperial College, London.

ii. Dissolution procedure.

The main criteria necessary during the dissolution of the samples was to keep the concentration of chloride ions to a minimum for the reasons previously discussed (p. 112). The following procedure was used in an attempt to dissolve a sample of gold-doped semi-conductor grade silicon in the absence of hydrochloric acid: 1.0ml of active gold solution 0.49µg/ml (2.49×10^{-6}M) was added to about 1g of the sample contained in a 50ml Teflon beaker. 10ml of nitric acid was added followed by the dropwiwe addition of 10ml of hydrofluoric acid. The addition of the hydrofluoric acid must be carried out very cautiously, as a vigorous reaction occurs. Complete dissolution of the sample was found to occur, and the solution was then evaporated to about 1ml, transferred to a counting jar, and the activity of gold-198 was measured. The recovery of the gold after dissolution was computed by comparison with the activity of 1.0ml of the gold solution diluted to the same volume as the sample. From the results given in Table 4.7, it can be seen that the recovery of gold after dissolution was unsatisfactory. An alternative approach

was selected based upon the dissolution of the sample in a mixture of acids, including hydrochloric, and then to reduce the concentration of chloride to a suitable level by extracting the gold into diethyl ether. The procedure is given below, a discussion of which is given in p. 132.

To the sample in a 50ml Teflon beaker, a weight, y_s, of active gold approximately equal to the weight of gold expected in the sample was added. The sample was then dissolved initially at room temperature and finally with gentle heating, in a mixture of 10ml of nitric acid and 2ml of hydrochloric acid with the gradual addition of 10ml of hydrofluoric acid. The solution was evaporated to about 0.5ml, and the evaporation repeated twice, each time after the addition of 5ml of hydrochloric acid, and was then transferred to a counting jar and the activity of the gold-198 was measured. The recovery of the gold after dissolution of the sample was calculated, and the results are given in Table 4.7. The solution was then transferred to a 100ml separatory funnel, and diluted with water and 2M hydrochloric acid to give finally 10ml of 2M hydrochloric acid solution. 20ml of diethyl ether was added and a 3min extraction of the gold into the ether phase was performed, after which the ether phase was separated, washed with 5ml of 2M hydrochloric acid and transferred to a 50ml beaker. 0.5ml of 3M hydrochloric acid was added, and the solution was heated on a water bath at about 50°C to remove the ether.

The rock samples were dissolved by exactly the same procedure, and the recoveries of the gold after dissolution are given in Table 4.7.

iii. Extraction procedure.

The solutions after the removal of the ether were transferred to 100ml separatory funnels and diluted to 20ml with 0.5N sulphuric acid. At this stage EDTA or sodium dimethylglyoximate would be added if necessary. In the samples analysed this addition was not necessary as the foreign ions which could be masked by EDTA, or extracted as the dimethylglyoximate into chloroform were not present. Finally 1ml of 1% ascorbic acid solution was added and the gold extracted by a substoichiometric amount of zinc diethyldithiocarbamate solution in chloroform (4.0ml of 2.5×10^{-7}M for gold-bearing ores; 4.0ml of 5×10^{-8}M for gold-doped semi-conductor grade silicon). The extractions were carried out for 5min, and then a 3.0ml aliquot of the filtered organic phase was removed for counting, activity a .

For the standard (run simultaneously) the same weight, y_s, of active gold was taken as that added to the sample, and it was extracted under the same conditions as for the sample, and the same volume of organic phase was separated for counting, activity a_s. The weight, y, of gold in the sample was then calculated, using the substoichiometric equation:

$$y = y_s \left\{ \frac{a_s}{a} - 1 \right\}.$$

The results of the analyses are given in Table 4.8.

Chapter 5

The Diethyldithiocarbamates of Gold

I. Introduction

The relevant literature concerned with the formation of gold diethyldithiocarbamate complexes has been reviewed in Chapter 2.

In this research the reaction of gold initially in the tervalent state in acid solution, with a substoichiometric amount of a divalent metal salt of diethyldithiocarbamic acid in the presence, or absence, of ascorbic acid, has been found to result in the formation of a gold chelate having a molar ratio of gold to diethyldithiocarbamate (DDC) of 1:1 in chloroform (p. 54 and 105). The gold chelate formed in the absence of ascorbic acid was thought to be a ternary complex involving tervalent gold, whereas that formed in the presence of the reducing agent was considered more likely to be a univalent complex (p. 105).

A study of the reproducibility curve given in Chapter 3, Fig. 3.5, indicated that below the equivalence point not all of the gold was present as a chelate in the organic phase. The line A-B represents the expected activity of the gold chelate in the organic phase, and it can be seen that the experimental results showed a marked deviation from this line. Below the equivalence point, an excess of the chelating agent was present, and therefore it appeared that a different gold chelate was formed to that in the presence of an excess of gold (III). In the presence of ascorbic acid no deviation from the expected activity of gold in the organic phase below the equivalence point was observed (Fig. 4.3), and therefore it was most likely that the same gold chelate was formed as that in the presence of an excess of gold. The chelates formed with all the

above discussed conditions were examined.

II. Discussion

For simplicity the investigations will be discussed under four main headings.

A. The Gold Chelate formed in the Presence of an Excess of Gold (III).

The gold chelate being investigated was that formed with the conditions used in the developed neutron activation analysis method. If the gold was forming a ternary chelate the second ligand was most likely to be chlorine, as the extractions were performed from a medium of 1.5 ± 1M hydrochloric acid, and also the gold (III) solutions were in hydrochloric acid. To investigate the possibility, an active isotope of chlorine, chlorine-36 ($t_{\frac{1}{2}} = 3 \times 10^5$y β^- 0.714 (98.3%) MeV)[88] in the form of a sodium chloride solution was used.

Before any quantitative measurements could be made it was necessary to establish suitable conditions for the counting of the chlorine-36 activity using liquid scintillation counting techniques. The experiments designed to achieve this are given on p. 215. With a sample volume of 0.1ml it was found that 6-10ml of the organic scintillator was suitable to obtain the maximum efficiency of chlorine-36 counting(Table 5.9). A volume of 10ml of scintillator was selected for use, and the counting efficiency was not affected by the presence of up to 10% of water by volume (Table 5.10). Above this value the scintillator began to separate from solution leading to a turbidity of the solution, and hence a reduced counting efficiency.

Many organic solvents including chloroform are known to cause

severe quenching of the system,[148] and since the gold chelate will be in chloroform, it was necessary to investigate the quenching effect of the solvent.

The counting efficiency of a scintillating system decreases as an exponential function of the concentration of quenching agent.[148] If, N_o and N, are the number of counts in the absence and presence of a quenching agent in a time, t, respectively, then the following relationship can be written:

$$N = N_o e^{-qC},$$

where, q, is the quenching constant, and C is the concentration of quenching agent.

If a semi-log plot of N against C is drawn, a straight line should result, and from the graph the concentration of quenching agent necessary to reduce the counting efficiency by one half, $C_{\frac{1}{2}}$, can be found, and is equal to $\frac{0.693}{q}$.

If the change in the volume of the solution for counting due to the addition of chloroform is neglected, then the concentration of chloroform is directly proportional to the volume added. A graph of log N as a function of the added volume of chloroform for the results given in Table 5.11, is given in Fig. 5.1. An approximately straight line relationship was found, and the volume of chloroform necessary to reduce the counting efficiency by one half was found to be approximately 1.3ml. For the highest sensitivity it was desirable that the maximum volume of the chloroform phase containing the gold chelate was counted, and at the same time the degree of quenching must not be too severe. A volume of 1.0ml of the organic phase was

selected, which gave a counting efficiency of about 60%.

Coloured solutions can also cause a quenching effect,[148] so it was necessary to investigate the effect of the presence of the gold chelate in chloroform on the counting efficiency. The results given in Table 5.12, indicated that the gold chelate did not show any marked quenching effect, but the highly coloured copper (II) diethyldithiocarbamate did cause severe quenching. Fortunately using substoichiometric conditions all the chelating agent is consumed to form the gold chelate, so this problem does not arise. The optimum conditions for the counting of the chlorine-36 activity had therefore been established.

For the quantitative experiments to establish whether a ternary gold chelate containing chlorine was formed with the conditions used in the neutron activation analysis method, the specific activity of the active sodium chloride solution must be kept as high as possible. The extraction of the gold chelate could not therefore be performed from a medium of 1.5M hydrochloric acid as previously used. The pH study in the neutron activation analysis method indicated that any normality of sulphuric acid from 0.01-10 was a suitable medium from which to extract the gold substoichiometricaly as a diethyldithiocarbamate into chloroform (Fig. 3.3). On this basis a medium of 0.5N sulphuric acid was selected.

As a second refinement so as to keep the amount of stable chloride introduced to the solution prior to the extraction of the gold chelate to a minimum, attempts were made to prepare the stable gold solution in the absence of chloride ions. Metallic gold can

be dissolved in a mixture of nitric and sulphuric acids,[149] but it was found that the gold had a limited solubility, and the dissolved gold remained in solution only in concentrated sulphuric acid. If the solution was diluted, gold precipitated from solution and was therefore not suitable. As an alternative approach gold in the form of potassium gold chloride $KAuCl_4 2H_2O$ was used, so as to keep the stable chloride ion concentration to a minimum. The solution must be freshly prepared and used immediately for the reasons discussed on p. 112.

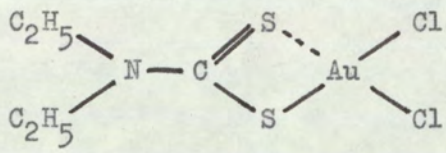
The extractions of the gold chelate were carried out by the method described on p. 218 and it was found that chlorine was present in the complex, the molar ratio of gold to chlorine being 1:2 (Table 5.1). The calculations were based upon the known molar ratio of gold to diethyldithiocarbamate of 1:1, i.e. from the known concentration of chelating agent used the weight of gold extracted could be calculated, and from the chlorine-36 activity of the organic phase the weight of chlorine, and hence the molar ratio of gold to chlorine. The results obtained with the low chloride ion concentration (0.09M) indicated that the specific activity of the chlorine-36 could be reduced by introducing stable sodium chloride solution into the aqueous phase prior to the extraction of the gold chelate into chloroform, and still produce sufficient chlorine-36 activity in the organic phase for detection. An extraction of the gold chelate was satisfactorily performed from a medium of 1.5M hydrochloric acid, i.e. similar conditions to that used in the neutron activation analysis method.

Table 5.1.

The Composition of the Gold Chelate Extracted into Chloroform from an Aqueous Phase containing an Excess of Gold (III) (Chlorine-36 Experimental Results)

Weight of Au added	Vol. of active NaCl added (0.1M)	Conc^{n}. and Vol. of stable NaCl added	H^{+} Conc^{n}.	Cl^{-} Conc^{n}.	Expected sample count rate (100% Eff.)	Observed count rates		Molar ratio Au:Cl in org. phase
						Sample	Ref.	
(mg)	(ml)	——M(——ml)	(M)	(M)	(c/sec)	(c/sec)	(c/sec)	
2.00	1.0	0.1 (17.0)	0.5	0.09	52	26	116	1.0:2.0(0)
2.00	1.0	0.1 (17.0)	0.5	0.09	52	25	118	1.0:1.9(1)
2.00	1.0	0.1 (17.0)	0.5	0.09	52	26	116	1.0:2.0(0)
2.00	1.0	0.1 (17.0)	0.5	0.09	52	24	115	1.0:1.9(1)
2.00	6.0	1.0 (12.0)	0.5	0.63	44	23	710	1.0:2.0(0)
2.00	6.0	2.5 (12.0)	0.5	1.53	18	10	720	1.0:2.0(6)

With all the conditions studied the molar ratio of gold to chlorine was found to be 1:2 in the gold chelate extracted into chloroform (Table 5.1). The partition coefficient of the gold chelate has been found to be 1259±134 at 20±1°C (p. 60), and therefore an empirical formula for the gold chelate in the organic phase of $AuDDCCl_2$ can be written. The most probable structure being:



,

i.e. a ternary chelate of tervalent gold having a co-ordination number of four which is the most favoured value for tervalent gold complexes. The spectrum of about a 1 x 10^{-4}M solution of the gold chelate in chloroform, measured in an 0.5cm cell is given in Fig. 5.5.

The reaction to form the gold chelate may be written as:

$$2AuCl_4^- + Cu(DDC)_2 \rightleftharpoons 2AuDDCCl_2 + Cu^{2+} + 4Cl^-,$$

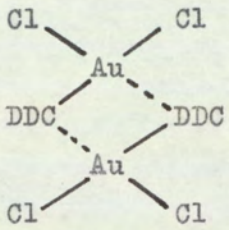
and the extraction constant, K, as:

$$K = \frac{[AuDDCCl_2]^2_{org}\ [Cu^{2+}]\ [Cl^-]^4}{[AuCl_4^-]^2\ [Cu(DDC)_2]_{org}}.$$

It can be seen from the above reaction that chloride ions tend to reverse the reaction, but it was found in the neutron activation analysis method that the gold chelate could be extracted using substoichiometric conditions from 8M hydrochloric acid, and therefore the extraction constant of the gold chelate must have a very high value.

The work of Bobtelsky and Eisenstadter[82] is of particular interest in relation to the above findings. In acid solution the

authors found a gold chelate was formed which was insoluble in the titration medium, but soluble in chloroform, with a molar ratio of gold to diethyldithiocarbamate of 1:1 (p. 38). The authors did not carry out an investigation to find the presence of chlorine in the complex, but predicted the same formula as that given above. The possibility of bi-nuclear complexes of the type $Au_2(DDC)_2Cl_4$ which would have a structure which may be represented as:



cannot be ignored. The determination of the molecular weight of the chelate would resolve this problem, but to achieve this the chelate must firstly be isolated in a pure form.

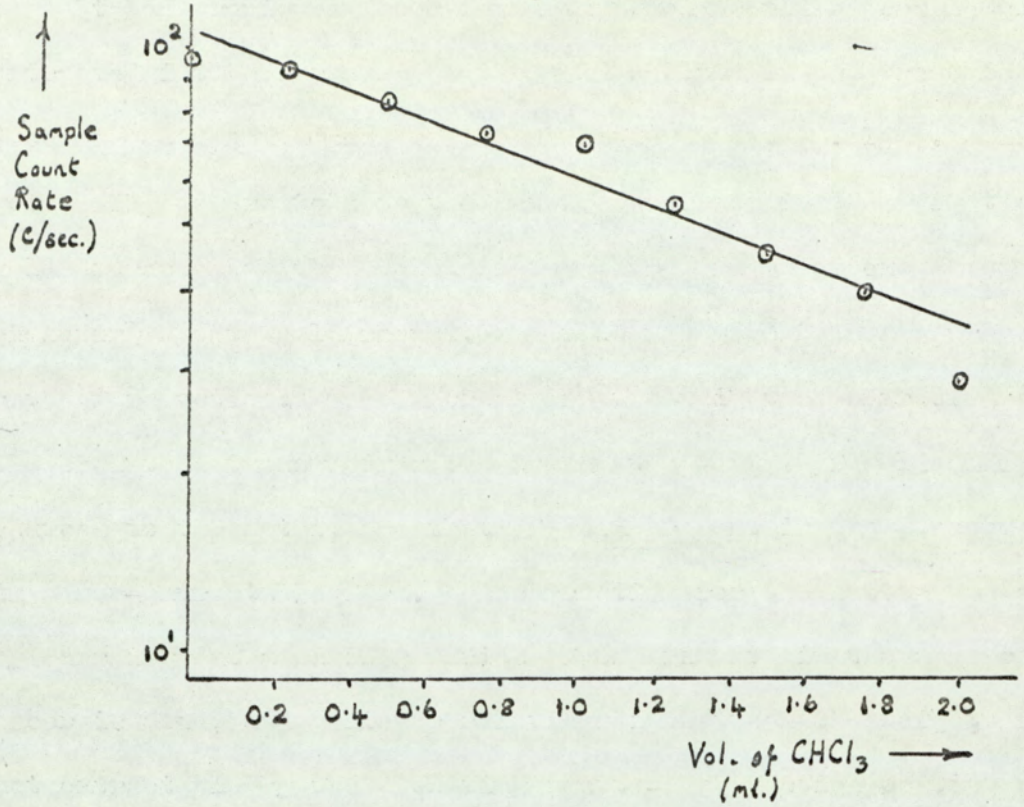
B. The Gold Chelate formed in the Presence of Ascorbic Acid, and an Excess of Gold.

The gold chelate to be studied was that formed with the conditions used in the radio-active isotope-dilution analysis method. As a reducing agent was present in the system it was considered most likely that a univalent gold diethyldithiocarbamate in chloroform was formed. The first criteria to confirm was that the rate of reduction of gold (III) to the metal was slow with the conditions used in the developed method. Chloride ions in sufficient concentration were found to have a serious interference in the method (p. 112), and the effect of their presence on the rate of reduction of the gold (III) to the metal was also studied.

It had previously been found that gold could be completely extracted into chloroform as the gold chelate in the presence of ascorbic acid and excess of the chelating agent (p. 149). If any gold (III) was reduced to the metal a decrease in the weight of gold extracted as the chelate into chloroform by an excess of the chelating agent would result, and this was used as a measure of the rate of reduction. The decrease in the weight of extracted gold as the chelate actually gives the sum of the weight of gold (III) reduced to the metal, and that of gold present in the aqueous phase in a non-extractable form. A correction for the latter was applied by carrying out a similar series of experiments in the absence of the ascorbic acid, and a linear relationship between the weight of gold not extractable by the chelating agent as a function of time was assumed. In most cases the correction was small, and the best fit to the experimental values was a straight line. The results of the experiments using active gold solutions 1.0, 10.0, and 100.0μg/ml are given in Figs. 5.2, 5.3 and 5.4, and have been corrected for the non-extractable component.

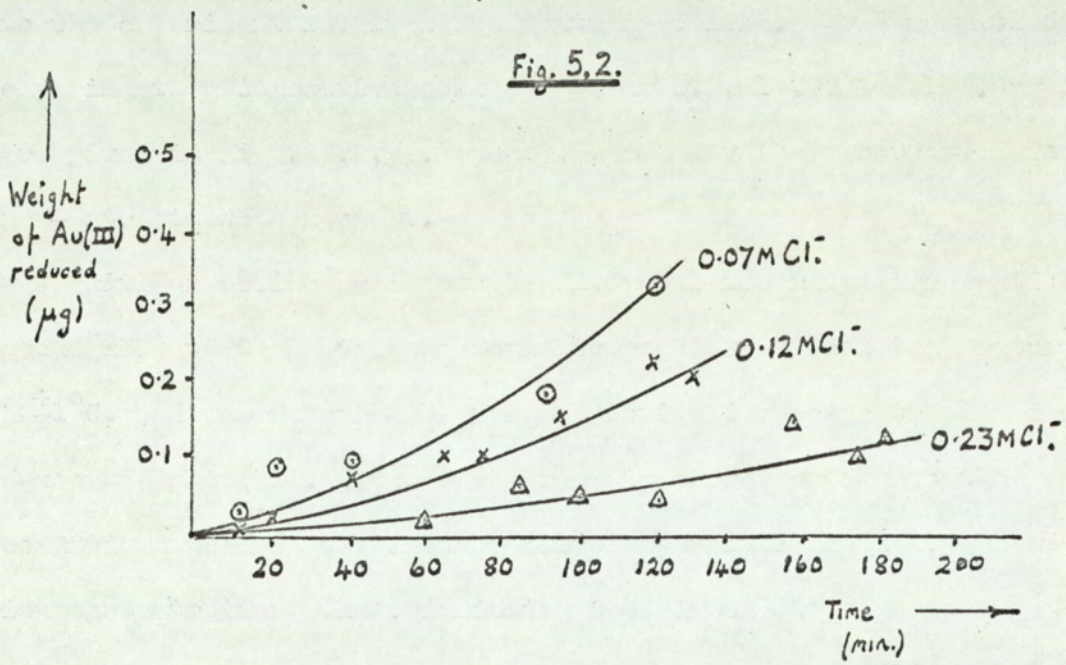
With an active gold solution 1.0μg/ml the rate of reduction of gold (III) to the metal was found to be slow at room temperature $20\pm1^{\circ}C$, and was favoured by a low chloride ion concentration in the aqueous phase (Fig. 5.2). The results corresponding to the conditions used in the isotope-dilution analysis method, chloride ion concentration 0.12M, indicated that in the time necessary to reach extraction equilibrium in the formation of a gold chelate, (1.5min at 80% stoichiometry), the weight of gold (III) reduced to

Fig. 5.1.



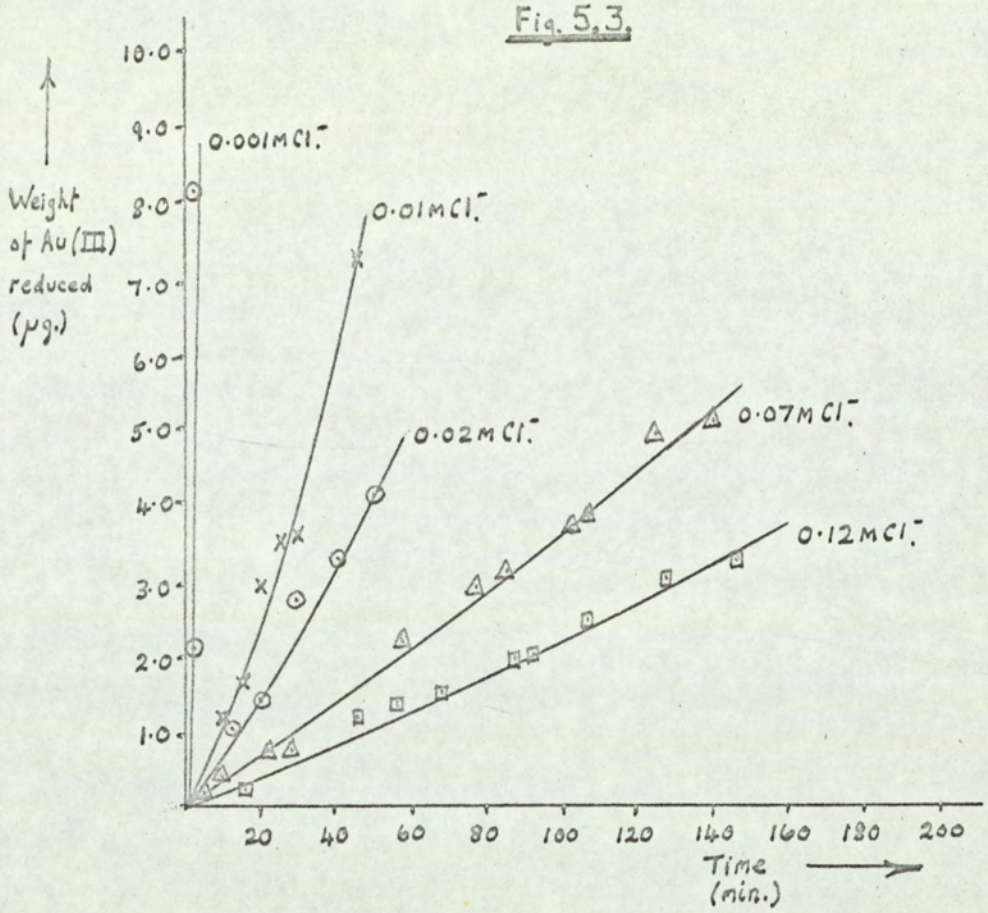
The Quenching Effect of Chloroform.
(Chlorine-36 Experimental Results)

Fig. 5.2.



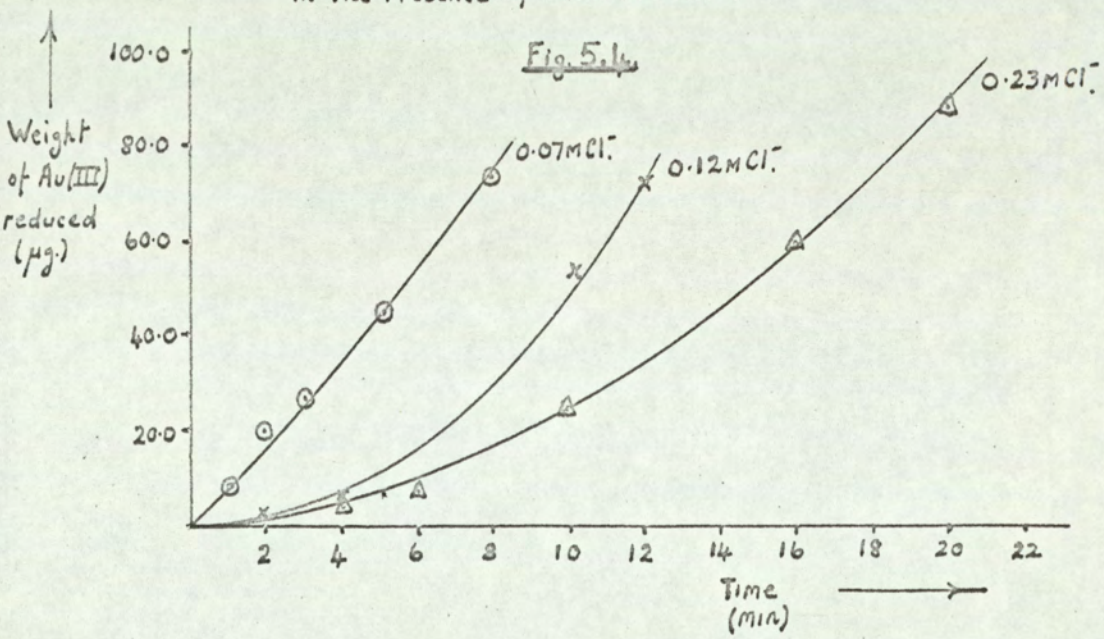
The Rate of Reduction of Gold(III) to the Elemental State in the Presence of Ascorbic Acid.

Fig. 5.3.



The Rate of Reduction of Gold (III) to the Elemental State in the Presence of Ascorbic Acid.

Fig. 5.4.



The Rate of Reduction of Gold (III) to the Elemental State in the Presence of Ascorbic Acid.

the metal was negligible. Using substoichiometric conditions, provided there is an excess of gold in a form capable of reacting with the chelating agent, then a reproducible separation of the gold chelate can be performed. On this basis the gold solution would have to stand for about 2hr before there would be insufficient gold in a form capable of reacting with all of the chelating agent at 80% stoichiometry of reaction.

As the concentration of the gold (III) in the aqueous phase was increased so the extent of reduction to the metal increased, as would be expected from the reaction which may be written as:

$$2AuCl_4^- + 3C_6H_8O_6 \rightleftharpoons 2Au + 3C_6H_6O_6 + 6H^+ + 8Cl^-.$$

ascorbic acid — dehydro ascorbic acid

A calculation of the order of the reaction with respect to the gold, or chloride concentration was not made, as the experiments were designed to give only an indication of the reduction rate. To find the order a more strict control of the temperature of the solutions would be necessary as the reduction process is known to be temperature dependent.[111]

The evidence so far indicated that the rate of reduction of 1.0µg of gold (III) to the metal at a temperature of $20\pm1^{\circ}C$ was slow. It did not give definite evidence about the rate of reduction of gold (III) to the univalent state, but it did indicate that the formation of a univalent diethyldithiocarbamate of gold was feasible. Rady and Erdey[150] have used ascorbic acid to reduce $AuBr_4^-$ to $AuBr_2^-$ which offers some support for the possible reduction of $AuCl_4^-$,

to $AuCl_2^-$, which would then react with the chelating agent by the following reactions:

$$2AuCl_2^- + Zn(DDC)_2 \rightleftharpoons 2AuDDC + Zn^{2+} + 4Cl^-.$$

For the reduction of gold (III) to the univalent state the molar ratio of gold (III) to ascorbic acid is 1:1, whereas for the reduction to the metal it is 1:1.5, and therefore it should be possible to distinguish between the reactions by determining the amount of ascorbic acid consumed. Calculations of the weight of ascorbic acid consumed when 1µg of gold (III) was reduced to the univalent, or metallic state, indicated that the change in the ascorbic acid concentration was too small to detect using the potassium iodate titration method.[151] In order to be able to distinguish between the two possible reactions 1mg of gold must be used. For the titration of 1.0ml of 1.0% ascorbic acid, 11.35ml of 10^{-2}M iodate was required, and for the reduction of 1.00mg of gold (III) to the univalent state, 1.34×10^{-3}g of ascorbic acid would be consumed, which was equivalent to 1.0ml of 10^{-2}M iodate. The rate of reduction of gold (III) to the metal in the presence of ascorbic acid will be moderately fast at room temperature, and therefore it may be difficult to carry out the extraction of the gold chelate and titration of the excess of ascorbic acid without a considerable error due to reduction of some of the gold (III) to the metal. It has been found however that the presence of diethyldithiocarbamate inhibits the rate of oxidation of ascorbic acid,[114-119] so it may be possible to conduct the experiment successfully. An excess of the chelating agent will have to be used so that all the gold is extracted into the organic

phase, and also to assist the rate of attaining extraction equilibrium. It was therefore assumed at this stage that the gold chelate formed with an excess of reagent was the same as that in the presence of an excess of gold. Evidence for this can be found from the reproducibility curve (Fig. 4.3) for the reason previously given (p.174). The validity of this assumption will be discussed later in this Chapter (p.192).

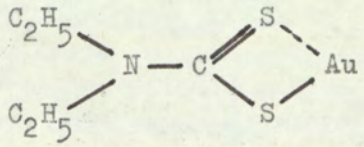
It was found that in the absence of the chelating agent, the gold (III) was reduced to the metal in 5min, in the presence of 1ml of 1.0% ascorbic acid (p.222), and that the molar ratio of gold (III) to ascorbic acid consumed in the reduction was 1:1.5 as expected (Table 5.2, part A). If, however, prior to the addition of the ascorbic acid, a 20 fold excess of zinc diethyldithiocarbamate was added, and a 5min extraction performed immediately after adding the ascorbic acid, it was found by titration of the excess ascorbic acid after removal of the organic phase that the molar ratio of gold (III) to ascorbic acid consumed was 1:1 (Table 5.2, part B). This finding was in agreement with the reduction of gold (III) to the univalent state, and therefore the presence of the diethyldithiocarbamate must be inhibiting the rate of reduction of the gold (III) to the metal. Finally the chelating agent was shaken with the aqueous phase containing ascorbic acid to test for any reaction between the reducing agent and the chelating agent. No reaction was found to occur (Table 5.2, part C), provided the organic phase was removed prior to the iodate titration of the ascorbic acid, this being necessary as the iodine can oxidise the chelating agent.[123]

Table 5.2.

Vol. of 0.01N IO_3^- required to titrate 1.0ml of 1.0% $C_6H_8O_6$ (ml)	Vol. of 0.01N IO_3^- required to titrate excess of $C_6H_8O_6$ (ml)	Weight of $C_6H_8O_6$ consumed in the reaction (mg)	Molar ratio Au (III): $C_6H_8O_6$
A)			
11.35	9.85	1.32	1.0:1.4(7)
11.40	9.90	1.32	1.0:1.4(7)
11.40	9.85	1.36	1.0:1.5(2)
11.35*	9.85	1.32	1.0:1.4(7)
B)			
11.40	10.40	0.88	1.0:0.9(8)
11.40	10.35	0.92	1.0:1.0(2)
11.35	10.35	0.88	1.0:0.9(8)
11.40	10.40	0.88	1.0:0.9(8)
C)			
11.40	11.40	0.00	
11.40	11.40	0.00	
11.35	11.35	0.00	

*After a period of 1hr.

The final evidence for the formation of a univalent diethyldithiocarbamate of gold was obtained by carrying out a series of extractions of the chelate in the presence of chlorine-36. The procedure used is given on p. 223 , and the results in Table 5.3. No evidence for the presence of chlorine in the gold chelate formed was found. All the evidence therefore predicted the formation of a univalent gold diethyldithiocarbamate, AuDDC, whose structure can be represented as:



with the gold having a co-ordination number of two, which is the most favoured value for univalent gold. The spectrum of about 1 x 10^{-5}M solution of the gold chelate measured in a 4cm cell is given in Fig. 5.6.

The overall reaction for the formation of the chelate can be written as:

$$2AuCl_4^- + 2C_6H_8O_6 + Zn(DDC)_2 \rightleftharpoons 2AuDDC + 2C_6H_6O_6 + Zn^{2+} + 4H^+ + 8Cl^-,$$

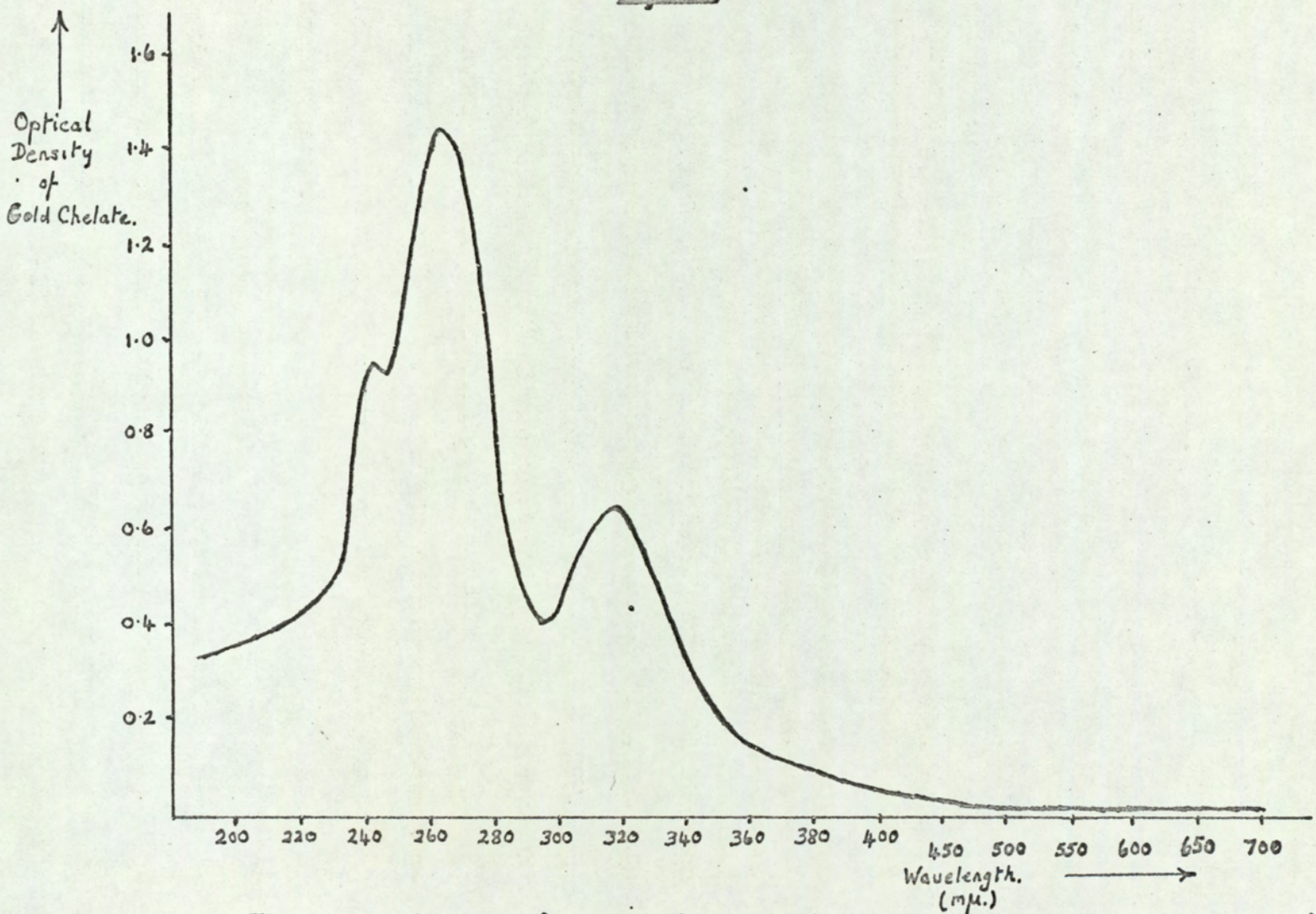
and the extraction constant, K, as:

$$K = \frac{[AuDDC]^2_{org}\,[C_6H_6O_6]^2\,[Zn^{2+}]\,[H^+]^4\,[Cl^-]^8}{[AuCl_{4-}]^2\,[C_6H_8O_6]^2\,[Zn(DDC)_2]_{org}}.$$

The critical dependence of the reaction of the chloride ion concentration can be predicted from the above reaction, and also from the fact that the rate of reduction of gold (III) was decreased by an increase in the chloride ion concentration of the aqueous phase. The latter dependancy was found for the reduction of gold (III) to the metal (Fig. 5.2), and it was considered reasonable to expect a similar dependance for the reduction of the gold (III) to the univalent state.

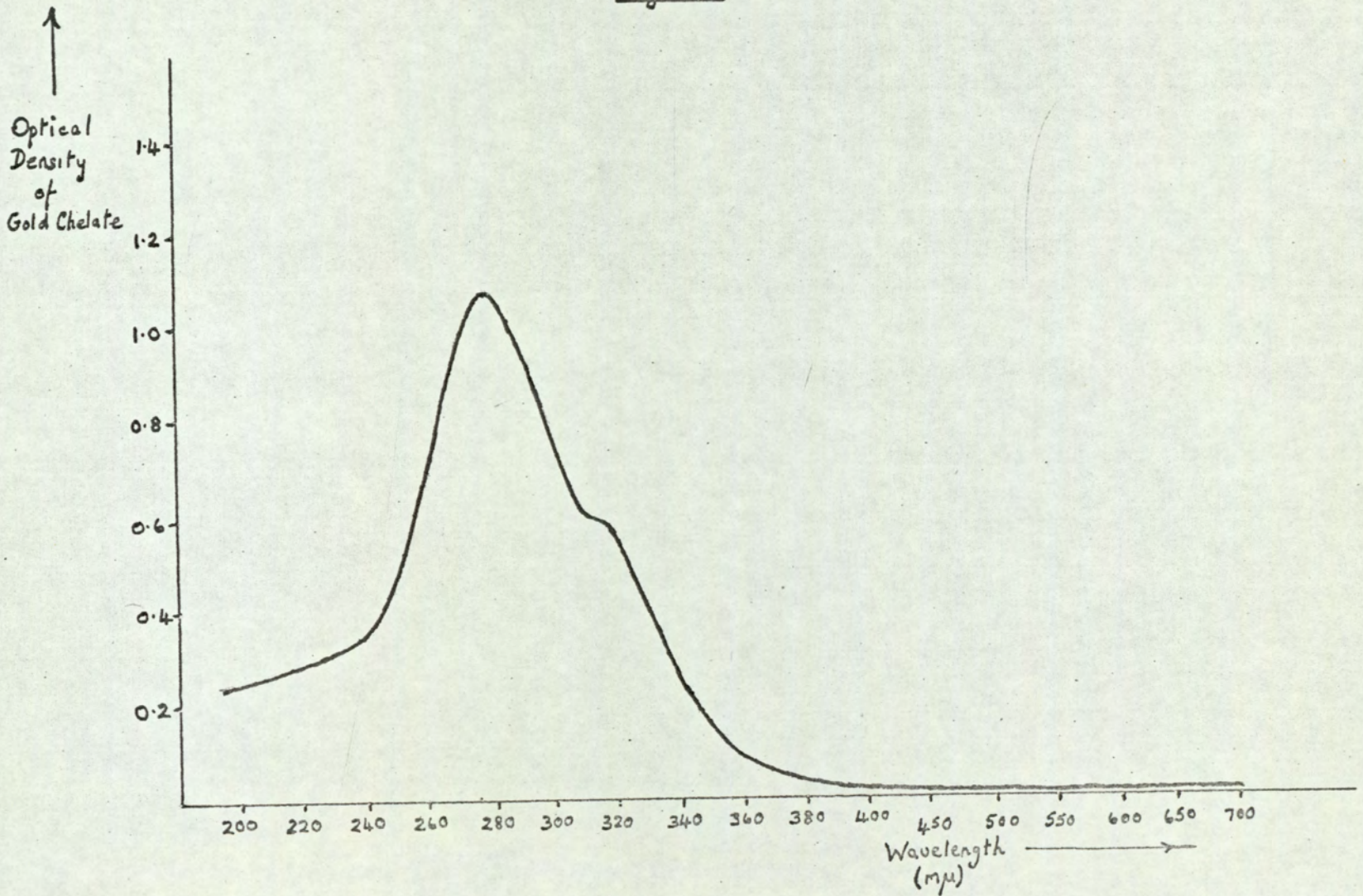
The possibility of the gold forming a ternary complex involving ascorbic acid was considered unlikely, as if this was the case then one would expect a molar ratio of gold (III) to ascorbic acid of 1:2 whereas a ratio of 1:1 was found. Final evidence could be obtained by the use of carbon-14 labelled ascorbic acid which can be prepared

Fig. 5.5.



The Spectral Absorption Curve of the Gold Chelate formed in the Presence of an Excess of Gold (III)

Fig. 5.6.



The Spectral Absorption Curve of the Gold Chelate formed in the Presence of Ascorbic Acid, and an Excess of Gold (III).

from xylose and labelled potassium cyanide, via the osone.[152,153]

C. The Gold Chelate formed in the Presence of Ascorbic Acid, and an Excess of Chelating Agent.

The gold chelate formed with the above conditions was considered to be the same as that formed in the presence of an excess of gold for the reasons given earlier in this Chapter (p. 174). To prove or disprove this assumption a fixed amount of zinc diethyldithiocarbamate in chloroform was used in a series of extractions in the presence of increasing amounts of stable gold, and a fixed amount of ascorbic acid. In every extraction an excess of chelating agent was present, and after the extractions, the organic phases were re-extracted in the presence of an excess of copper (II) solution when the excess of zinc diethyldithiocarbamate was converted to the copper chelate. The extinction of the excess of chelating agent was then measured, and the values were plotted against the added gold concentration (Fig. 5.7). The intercept of the graph corresponding to the complete reaction of the chelating agent to form the gold chelate gave a gold to diethyldithiocarbamate molar ratio of 1.0:0.9(5), i.e. 1:1.

In the isotope-dilution analysis method it was found that copper (II) when present in a 100 fold weight excess over that of the added gold (III) interfered (Table 4.3). It would therefore be expected that the gold chelate would be partially converted to the copper chelate as well as the excess zinc chelate, when the organic phase was extracted in the presence of copper (II) solution. If the gold chelate is unaffected by the presence of the copper (II)

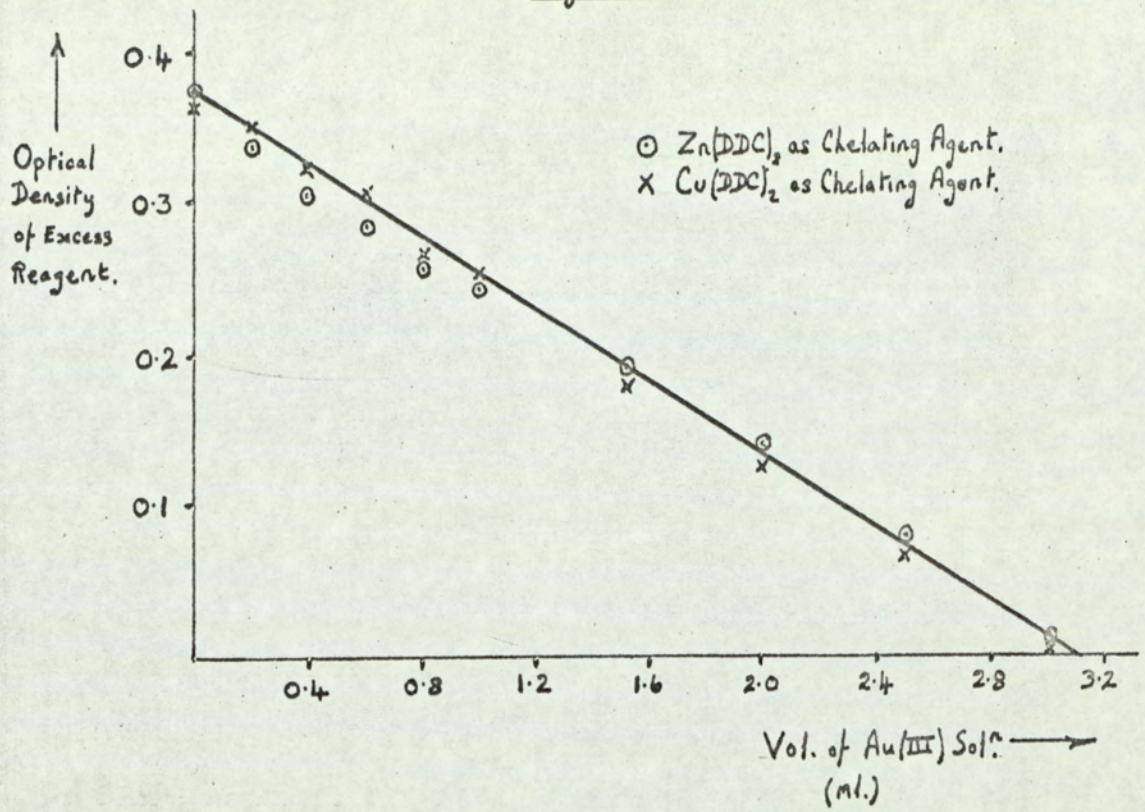
solution the explanation of this finding is as follows. In the study of the interference of copper (II) ions, a solution of copper (II) and gold (III) ions in the presence of ascorbic acid was extracted with a substoichiometric amount of zinc diethyldithiocarbamate. If the rate of the exchange reaction of copper (II) with the zinc chelate is very much faster than that of the gold, the copper chelate will be formed preferentially. The gold will then exchange with the copper chelate, but if the rate of the exchange is such that equilibrium is not reached during the 5min extraction period used in the method then copper (II) would be considered to interfere by competing with the gold for chelate formation. In the method used in this study however the gold chelate was completely formed prior to the addition of the copper (II) solution. The gold chelate will therefore not undergo an exchange reaction with the copper (II), if the ratio of the values of the extraction constants is not sufficiently large (p. 20). If the latter is true no interference from the copper (II) ions exchanging with the zinc chelate to form the copper chelate will be found.

To verify this argument the time necessary to reach extraction equilibrium in the formation of the gold chelate in chloroform using the diethyldithiocarbamates of copper and zinc was examined. It was found that using the copper chelating agent in the presence of ascorbic acid, and 1.0µg of active gold solution, extraction equilibrium was reached in 20min at 50% stoichiometry, and 1.5min using the zinc chelating agent of the same conditions. Similar extraction times were found using 10.0µg of active gold solution,

with the same conditions (Table 5.13). It was also known that during a 5min extraction period copper (II) completely exchanges with the zinc chelate forming the copper chelate, this being the basis of the standardisation of zinc diethyldithiocarbamate (p. 239). Support of the argument for the mechanism of interference of copper (II) ions in the isotope-dilution analysis method was therefore found. To verify the second argument, namely that no exchange reaction between the gold chelate and copper (II) ions occurs, the experiment to find the composition of the gold chelate in the presence of ascorbic acid and an excess of chelating agent was repeated using copper rather than zinc diethyldithiocarbamate. The same molar ratio of gold to diethyldithiocarbamate, i.e. 1:1 was found (Fig. 5.7). No exchange between the gold chelate and copper (II) ions was therefore occurring.

A series of chlorine-36 experiments were then carried out using an excess of zinc diethyldithiocarbamate and a similar procedure to that previously described (p. 188). The results given in Table 5.3, showed no evidence for the presence of chlorine in the gold chelate extracted into chloroform, and therefore it was concluded that the same gold chelate was formed in the presence of ascorbic acid, and an excess of gold or chelating agent, namely a univalent gold diethyldithiocarbamate.

Fig. 5.7.



Spectrophotometric Study of the Gold Chelate formed in the Presence of Ascorbic Acid, and an Excess of the Chelating Agent.

Table 5.3.

The Composition of the Gold Chelate Extracted into Chloroform from an Aqueous Phase containing Ascorbic Acid (Chlorine-36 Experimental Results)

Weight of Au added	Vol. of active NaCl solution added (1.37×10^{-2}M)	Vol. of stable NaCl solution added (4.0×10^{-1}M)	H^+ Conc.^{n}	Cl^- Conc.^{n}	Expected sample count rate (100% Eff.)	Observed count rates	
						Sample	Ref.
(µg)	(ml)	(ml)	(M)	(M)	(c/sec)	(c/sec)	(c/sec)
*100.0(0)	10.0	5.0	0.55	0.12	7	0.1	443
*100.0(0)	10.0	5.0	0.55	0.12	7	0.1	443
**100.0(0)	10.0	5.0	0.55	0.12	14	0.1	443
**100.0(0)	10.0	5.0	0.55	0.12	14	0.2	443

*Extractions performed in the presence of an excess of gold.

**Extractions performed in the presence of an excess of chelating agent.

D. The Gold Chelate formed in the Presence of an Excess of Chelating Agent.

As was previously discussed, the experimental points of the reproducibility curve (Fig. 3.5), below the equivalence point in the neutron activation analysis method showed a marked deviation from the expected values. This was considered to indicate the possibility of a different gold chelate being formed in the presence of an excess of chelating agent to that formed with the substoichiometric conditions used in the neutron activation analysis method.

To investigate this possibility a spectrophotometric study was carried out by a similar method to that used in studying the previous complex. From the intercept of the graph of the extinction of the excess of copper diethyldithiocarbamate as a function of the added volume of stable gold solution, the molar ratio of gold to diethyldithiocarbamate in the gold chelate was found to be 1:2, (Fig. 5.8). The indication was therefore that a different complex from that formed with substoichiometric conditions used in the neutron activation analysis method was being formed. Extraction equilibrium had been reached in this extraction, this was verified by the usual method using an active gold solution (p. 90). The spectrophotometric examination was repeated at various hydrogen ion and chloride ion concentrations of the aqueous phase, and in every case a molar ratio of gold to diethyldithiocarbamate of 1:2 was found (Table 5.4).

The possibility of a blank error due to light absorption by the gold chelate at the wavelength used to estimate the excess of copper diethyldithiocarbamage (436mμ) was examined by using a fixed

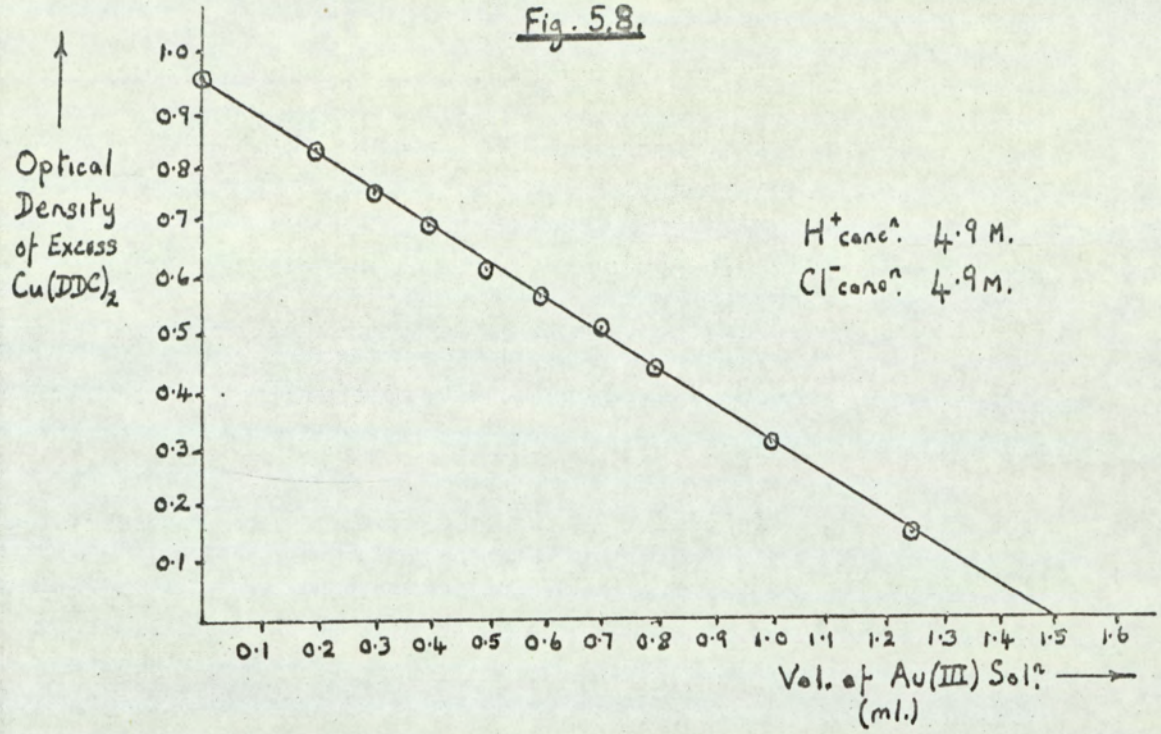
concentration of gold (III), chloride and hydrogen ions, in a series of extractions in the presence of a fixed volume, but varying concentration of the chelating agent. The extinction of the excess of chelating agent was measured spectrophotometrically as previously, and plotted against the original concentration of chelating agent (Fig. 5.9). A straight line relationship was obtained indicating the same complex was formed over the whole range of copper diethyldithiocarbamate concentration used, $0.1-1.0 \times 10^{-3}$, and the blank error due to the light absorption of the gold chelate at 436mμ was negligible.

Table 5.4.

Aqueous phase		Molar ratio of gold to diethyldithiocarbamate
H^+ conc.^{n} (M)	Cl^- conc.^{n} (M)	
0.01	0.21	1.0:1.9(4)
0.01	4.81	1.0:1.9(3)
4.90	4.90	1.0:1.9(4)

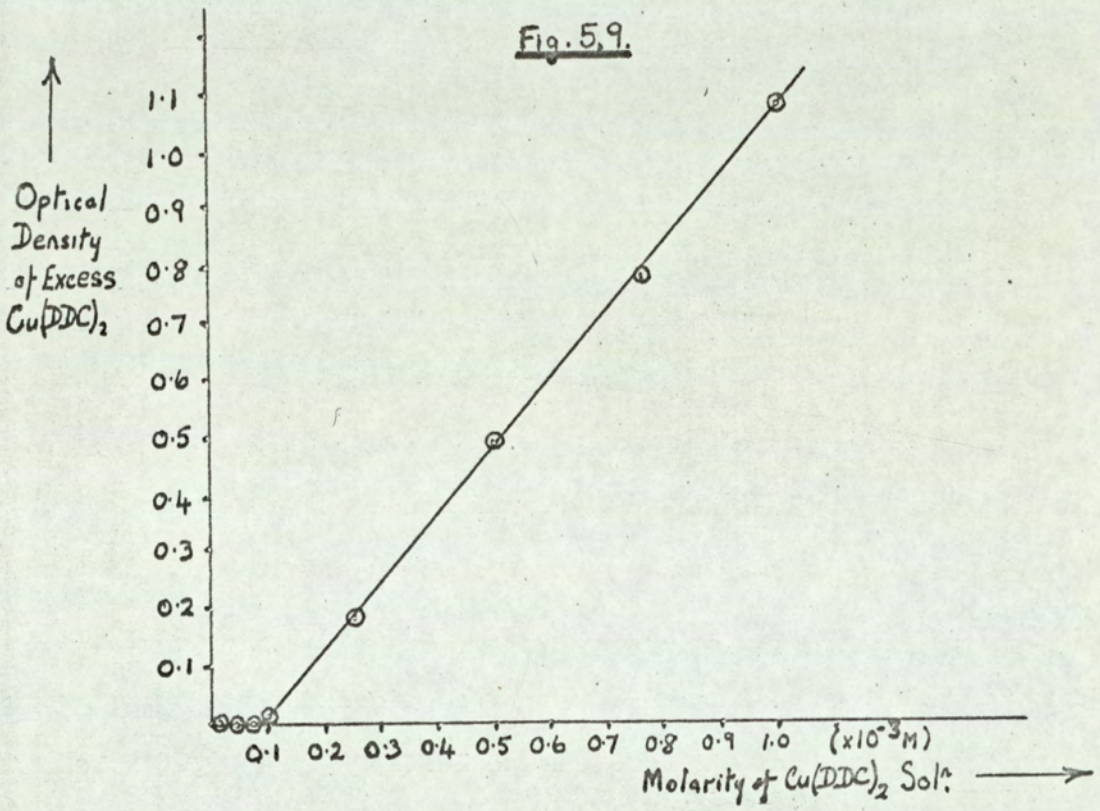
The experiments were then repeated with an active gold solution of the same concentration, 100.0(0)μg/ml, and the same hydrogen and chloride ion concentrations of the aqueous phase as used in the spectrophotometric examination. A variable amount of gold was found in the organic phase according to the chloride and hydrogen ion concentration of the aqueous phase (Table 5.14). It was therefore apparent that the gold chelate was not all present in the organic phase but was distributed between the organic and aqueous phases in a manner dependent upon the chloride and hydrogen ion concentration of the aqueous phase.

Fig. 5.8.



Spectrophotometric Study of the Gold Chelate formed in the Presence of an Excess of Chelating Agent.

Fig. 5.9.



An Investigation to find the Absorbance of the Gold Chelate. (See p197)

The distribution ratio of the gold between the organic and aqueous phase was studied at varying hydrogen ion concentrations of the aqueous phase, using a fixed chloride ion and gold concentration of the aqueous phase, and a fixed excess of chelating agent. The distribution ratio of the gold was also measured as a function of the chloride ion, gold (III), and chelating agent concentrations, keeping the other variables constant for each experiment. The results are given in Figs. 5.10 and 5.11 and Tables 5.5 and 5.6.

Table 5.5.

Weight of Au (III) solution used (µg)	Distribution ratio, q, of gold (III) between chloroform and an aqueous phase		
	I	II	III
20.0(0)	1.6	164	0.6
50.0(0)	1.8	159	0.7
80.0(0)	1.9	153	0.7
100.0(0)	1.7	158	0.6
200.(0)	1.6	159	0.5
500.(0)	1.4	164	0.6
800.(0)	1.5	160	0.6
1000.(0)	1.6	168	0.5

Table 5.6.

Concentration of chelating agent (M)	Distribution ratio, q, of gold (III) between chloroform and an aqueous phase		
	I	II	III
4.0×10^{-2}	1.6	179	0.6
4.0×10^{-3}	1.7	161	0.7
1.0×10^{-3}	1.6	159	0.7
4.0×10^{-4}	1.5	168	0.6

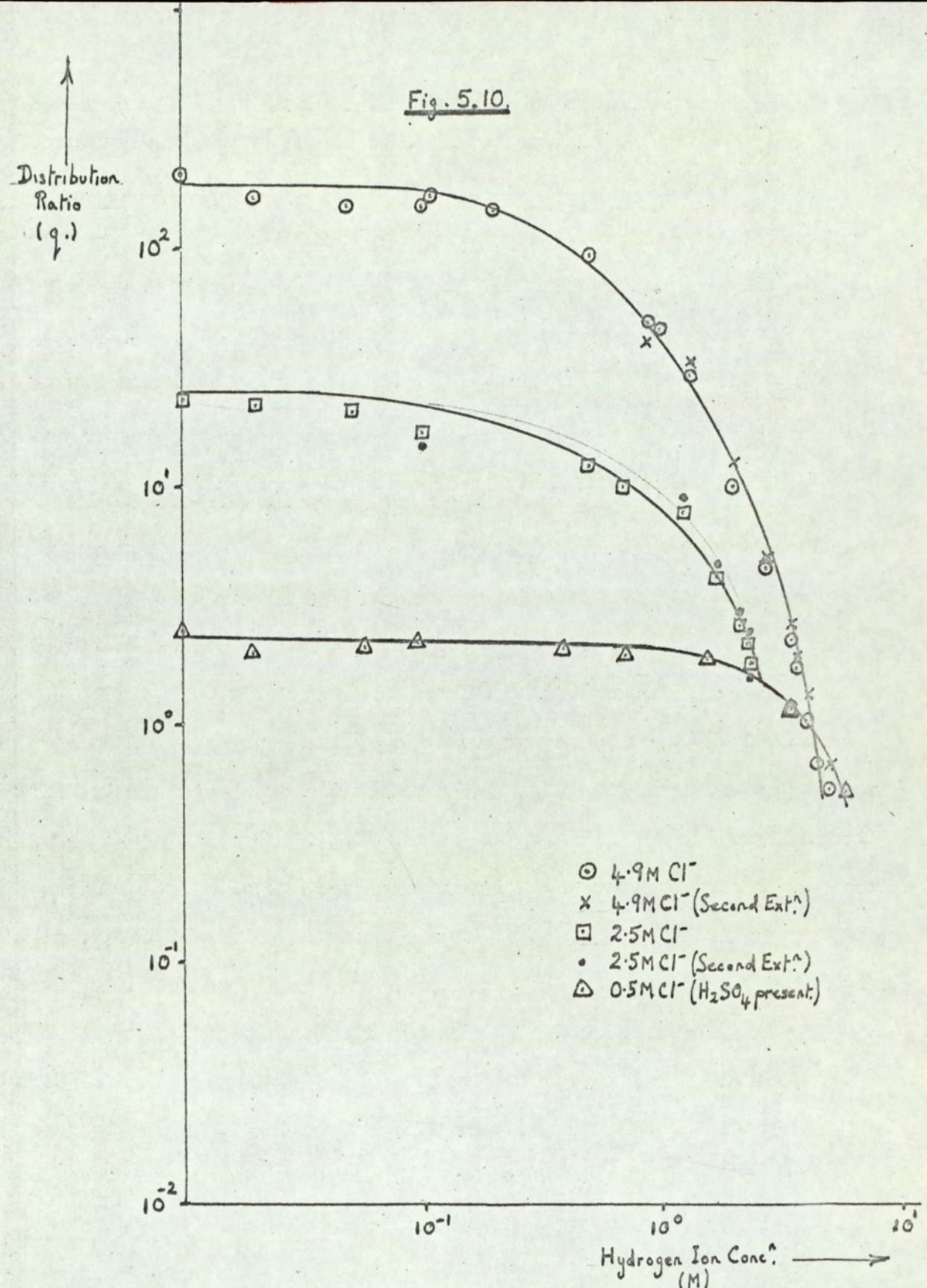
The figures in columns I to III of Tables 5.5 and 5.6 are the results for the experiments using an aqueous phase of hydrogen ion

concentrations of 0.01, 0.01, 4.90M respectively, and chloride ion concentrations of 0.21, 4.81,4.90M respectively.

The distribution ratio of the gold between the organic and aqueous phases for a given chloride and hydrogen ion concentration of the aqueous phase, was independent of the excess of gold (III) and chelating agent, and therefore it was impossible for the gold chelate to be polynuclear in one phase and not in the other (Tables 5.5 and 5.6). If the latter was true the distribution ratio, q, of the gold given by $\left(\frac{\text{concentration of gold in the organic phase}}{\text{concentration of gold in the aqueous phase}}\right)$ would not be a constant, but the possibility of the gold chelate being polynuclear to the same degree in both phases cannot be ignored as the above relationship for q would still be a constant.

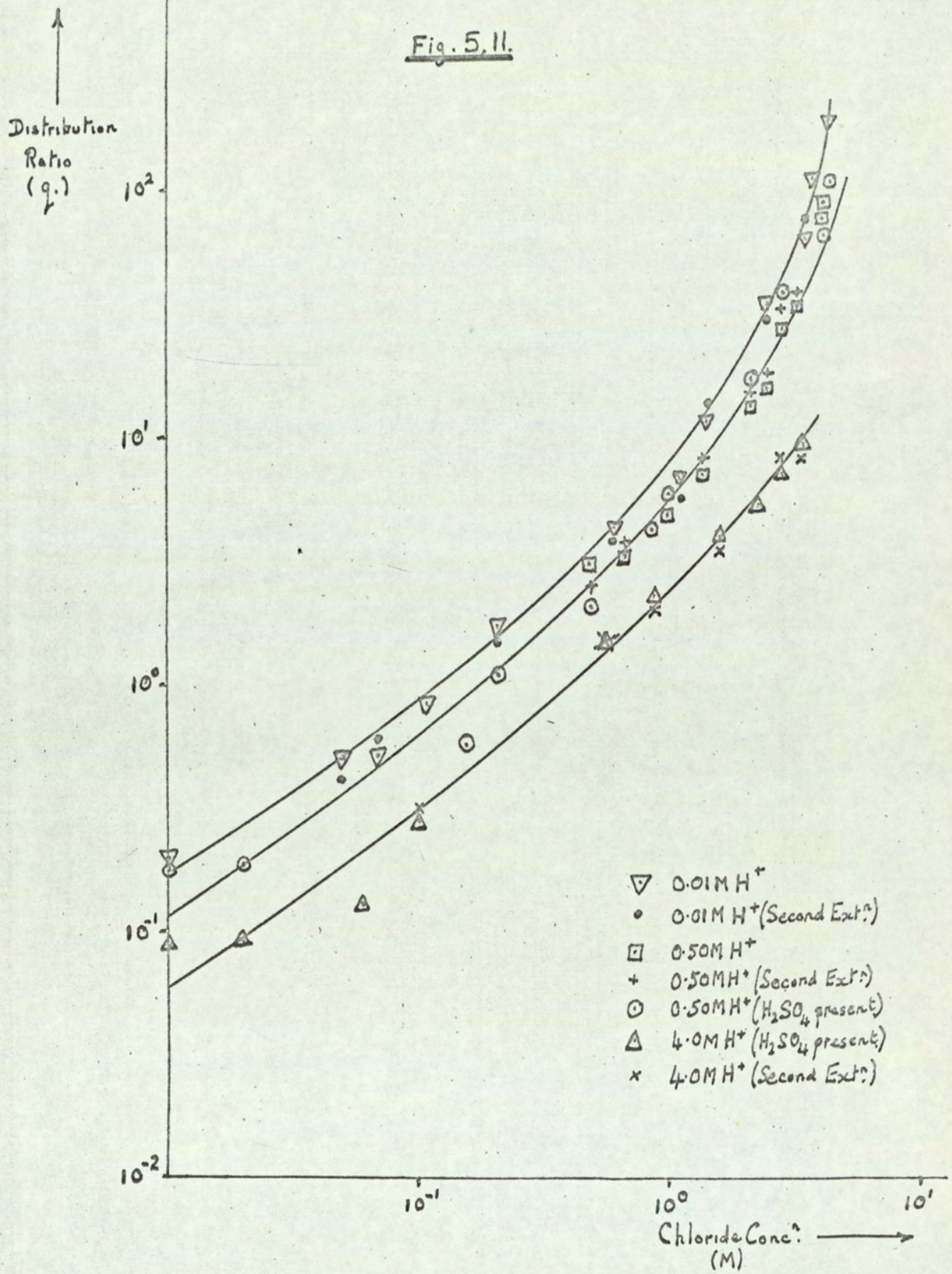
The hydrogen ion dependancy of the distribution ratio of the gold showed that for a given chloride ion concentration, increasing the hydrogen ion concentration reverted the gold from the organic to the aqueous phase (Fig. 5.10), whereas at a fixed hydrogen ion, but an increasing chloride ion concentration the reverse effect was found (Fig. 5.11). Using the zinc rather than copper chelating agent the same relationships were found, and also if after the first extraction the aqueous phase was equilibrated with chloroform the same q values were obtained as those for the first extraction using either chelating agent. The value of q was also found to be independent of the concentration of copper (II) and zinc (II) ions in the aqueous phase when all the other variables were kept constant (Table 5.7 and p. 232).

Fig. 5.10.



The Distribution Ratio of Gold (III) between Chloroform and an Aqueous Phase as a Function of the Hydrogen Ion Concentration (See p 228).

Fig. 5.11.



The Distribution Ratio of Gold (III) between Chloroform and an Aqueous Phase as a Function of the Chloride Concentration (See p. 230).

Table 5.7.

Concentration of copper (II) sulphate solution added (M)	Distribution ratio, q, of gold (III) between chloroform and an aqueous phase		
	I	II	III
0.0001	1.6	176	0.7
0.01	1.7	160	0.6
0.10	1.6	158	0.6

Footnote as per Tables 5.5 and 5.6.

The reaction to form the gold chelate of molar ratio gold to diethyldithiocarbamate of 1:2 must be complete otherwise the distribution ratio, q, of the gold between the organic and aqueous phase, for a given hydrogen and chloride ion concentration of the aqueous phase, would be dependent on the concentration of added gold (III), copper (II) or zinc (II) ions in the aqueous phase, and the concentration of the chelating agent. The reaction therefore being studied was the distribution of the gold chelate, $Au(DDC)_2$ XY, where X and Y are unknowns, between the organic and aqueous phase, as a function of the chloride and hydrogen ion concentration of the aqueous phase.

If we assume X and Y are hydrogen and chlorine atoms a reaction of the form:

$$H_{n+m}Au(DDC)_2Cl_y + zCl^- \rightleftharpoons H_nAu(DDC)_2Cl_{y+z}{}_{org} + mH^+$$

can be written, as it is known that with a fixed hydrogen ion concentration, increasing the chloride ion concentration favours the formation of gold chelate in the organic phase, whereas at a fixed

chloride and increasing hydrogen ion concentration the reverse applies.

A stability constant, K, for the above reaction can be written, and is given by:

$$K = \frac{[H_n Au(DDC)_2 Cl_{y+z}]_{org}\ [H^+]^m}{[H_{n+m} Au(DDC)_2 Cl_y]\ [Cl^-]^z} \ .$$

Taking logs:

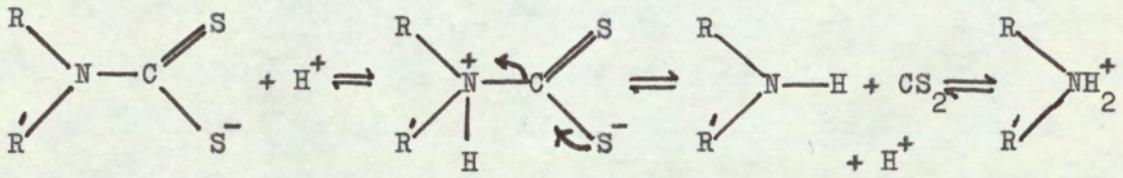
$$\log K = \frac{\log [H_n Au(DDC)_2 Cl_{y+z}]_{org}}{[H_{n+m} Au(DDC)_2 Cl_y]} + m \log [H^+] - z \log [Cl^-] \ ,$$

and reduces to:

$$\log K = \log q + m \log [H^+] - z \log [Cl^-] \ .$$

At a fixed chloride ion concentration of the aqueous phase, a graph of log q as a function of log $[H^+]$ should therefore have a slope of m. Fig. 5.10 is a plot of such a relationship, and it can be seen that the value of m is variable. By a similar argument a plot of log q as a function of log $[Cl^-]$ at a fixed hydrogen ion concentration of the aqueous phase should give a graph of slope -z. From Fig. 5.11 it can be seen that the value of z is also variable.

Zuman and Zahradrik[154,155] have explained the acid decomposition of dithiocarbamate by a proton addition mechanism according to the following equilibrium reactions:



If the nitrogen atom of the diethyldithiocarbamate group can be protonated, and the gold chelate still remains stable, then two hydrogen atoms can be accommodated in the chelate. Even so the slope of the relationship of log q with log $[H^+]$ predicts a value greater than two at high acidity of the aqueous phase (Fig. 5.10).

To study the possibility of the formation of a series of chloro-complexes of gold in the organic phase, experiments using chlorine-36 were performed by the procedure given on p.232 . The results given in Table 5.8 showed that as the chloride ion concentration of the aqueous phase was increased the molar ratio of gold to chlorine in the organic phase increased.

If the organic phase consisted of only a chloro-complex of gold, the lowest molar ratio of gold to chlorine in the gold chelate would be 1:1 corresponding to a gold chelate $Au(DDC)_2Cl$. At low chloride ion concentrations of the aqueous phase, about 1M or less, the molar ratio of gold to chlorine in the organic phase is less than 1:1, and therefore the organic phase must contain another complex of gold other than a chloro-complex. The specific activity of the supplied chlorine-36 was not high enough to investigate the molar ratio of gold to chlorine at a chloride ion concentration of the aqueous phase greater than about 3M. A study of the system at higher chloride ion concentrations could be performed using chlorine-38 ($t_{\frac{1}{2}}$ 38min β^- 1.11 (31.0%), 2.77 (16.0%), 4.81 (53.0%) MeV)[88] but this would require the experiments to be performed at the site of the nuclear reactor, due to the short half life of the isotope.

Table 5.8.

The Composition of the Gold Chelate Extracted into Chloroform from an Aqueous Phase using an Excess of Chelating Agent (Chlorine-36 Experimental Results)

Weight of Au added (mg)	Vol. of active NaCl added (0.1M) (ml)	Conc.^{n} and vol. of stable NaCl added —M (—ml)	H^{+} Conc.^{n} (M)	Cl^{-} Conc.^{n} (M)	Dist.^{n} ratio q	Expected sample count rate (c/sec)	Observed count rates Sample (c/sec)	Observed count rates Ref. (c/sec)	Molar ratio Au:Cl in org. phase
1.00	3.0	0.1(6.0)	0.50	0.09	0.8	44	1.4	870	1.0:0.0(5)
1.00	7.0	5.0(2.0)	0.50	1.07	9.0	24	7.1	2456	1.0:0.3(8)
1.00	4.0	5.0(6.0)	0.46	2.76	20.0	5	4.3	1255	1.0:1.1(3)
1.00	2.0	0.1(7.0)	0.01	0.10	0.8	27	0.8	805	1.0:0.0(4)
1.00	7.0	5.0(2.0)	0.01	1.08	7.0	24	3.6	2337	1.0:0.2(1)
1.00	3.0	5.0(6.0)	0.01	3.04	46.0	5	1.5	1038	1.0:0.4(5)

The conclusion was therefore that a series of gold complexes are formed in both the organic and aqueous phases, the proportions of which are dependent upon the experimental conditions.

The nature of the reproducibility curve found in the neutron activation analysis method Fig. 3.5, can now be understood in more detail.

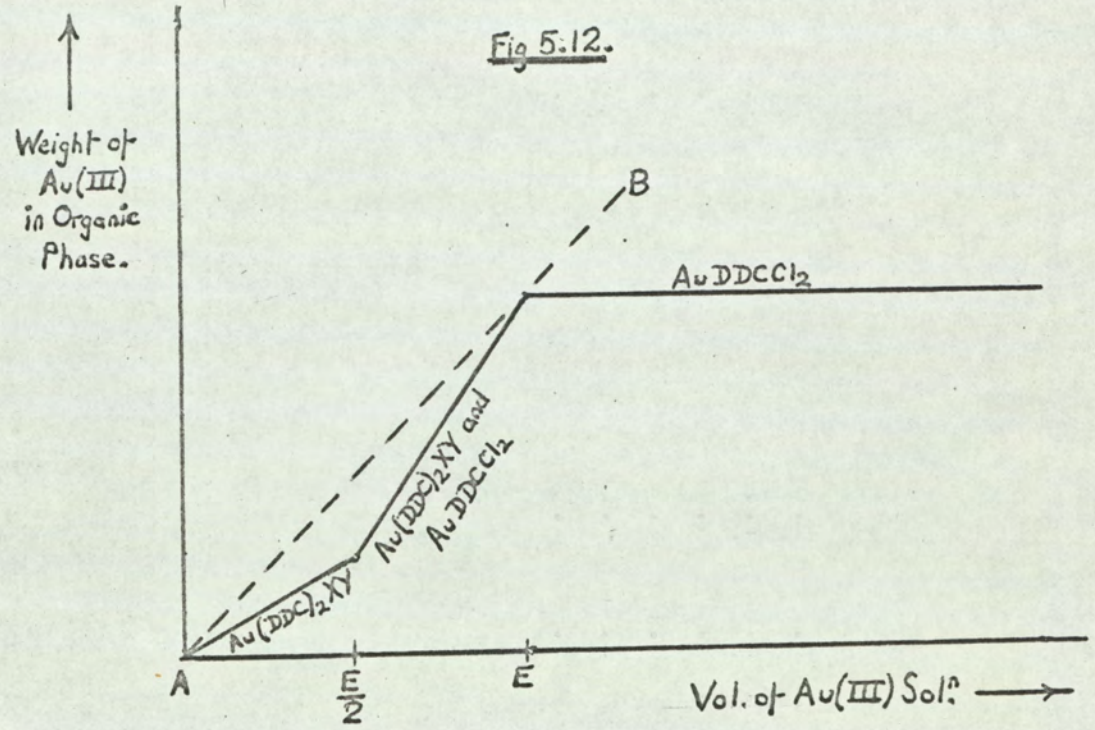


Fig 5.12.

If the equivalence point of the separation is given by E (Fig. 5.12) then below the point, $\frac{E}{2}$, (i.e. half equivalence) where an excess of chelating agent is present, a gold chelate of molar ratio gold to diethyldithiocarbamate of 1:2 is formed, and the deviation of the results from the theoretical line, AB, (corresponding to all of the gold in the organic phase) will be governed by the distribution ratio of the gold between the organic and aqueous phases,

which itself is dependent upon the hydrogen and chloride ion concentrations of the aqueous phase. In the region between $\frac{E}{2}$ and E, the gold chelate of molar ratio gold to diethyldithiocarbamate of 1:2 is being converted to the 1:1 chelate (i.e. $AuDDCCl_2$) in the presence of the increasing amounts of added gold (III) solution. Beyond the equivalence point, E, where an excess of gold (III) is present in the aqueous phase, the chloro-complex $AuDDCCl_2$ is formed, which is completely present in the organic phase.

Bobtelsky and Eisenstadter[82] using a heterometric technique have also found evidence for the formation of a gold diethyldithiocarbamate of molar ratio gold to diethyldithiocarbamate of 1:2, the chelate being stable in the aqueous phase (p. 39). The gold chelate was formed in neutral or alkaline solution, whereas in this research the gold chelate of the same molar ratio gold to diethyldithiocarbamate was formed in acid solution.

The arguments as to the composition of the gold chelate have been based upon the assumption that gold in the tervalent state was involved, however Vanngard and Akerstrom[83] have claimed the formation of a gold (II) diethyldithiocarbamate based on electron spin resonance studies (p. 39). In view of this finding a similar study of the gold chelate, or chelates, formed with the conditions used in this research would be profitable, but before such studies could be made pure gold chelates would have to be separated.

III. Conclusion

The conclusion to the study was that the composition of the gold diethyldithiocarbamate formed between the reaction of gold with zinc

or copper diethyldithiocarbamate in chloroform, was dependent upon the condition of the aqueous phase from which the extraction was made. In acid solution, a gold chelate soluble in chloroform of empirical formula $AuDDCCl_2$ was formed in the presence of an excess of gold (III), whereas in the presence of an excess of chelating agent, a mixture of gold chelates both in the organic and aqueous phases were found according to the hydrogen and chloride ion concentration of the aqueous phase. The molar ratio of gold to diethyldithiocarbamate in the latter chelate was always 1:2. In acid solution and in the presence of a reducing agent, (ascorbic acid), however the same gold chelate was formed with an excess of gold or chelating agent, and the evidence supported the composition of the chelate as being AuDDC, i.e. a univalent gold diethyldithiocarbamate.

Since the completion of this research, and the drafting of this chapter, a paper has been received from Kukula and Krivanek[156] which without exception supports the findings of this research.

The authors using the zinc, copper or mercury salt of diethyldithiocarbamic acid have reported the formation of a gold diethyldithiocarbamate of molar ratio 1:1; the gold chelate being completely soluble in chloroform, and formed in acid solution, only with substoichiometric conditions (i.e. an excess of gold (III)). The same composition of the gold chelate as that predicted in this research (p. 180) was proposed, but work had not been carried out to prove the presence of chlorine in the chelate.

In acid solution in the presence of an excess of the chelating agent the authors also supported the formation of a gold chelate of

molar ratio gold to diethyldithiocarbamate of 1:2, the chelate being only partially soluble in chloroform. The effect of the chloride and hydrogen ion concentrations in the aqueous phase on the distribution ratio, q, of the gold between the organic and aqueous phases was not studied, but evidence for dependancy of q on the hydrochloric acid concentration of the aqueous phase was found. The value of q was also found to be independent of the excess of chelating agent, and of the particular metal salt of diethyldithiocarbamic acid used. The gold chelate was found to be insoluble in benzene, but soluble in chloroform which is a more polar solvent, and for this reason the authors suggested the formula of the chelate as being $Au(DDC)_2^+Cl^-$, but again experimental work to support the presence of chlorine in the chelate had not been carried out.

In acid solution and in the presence of a reducing agent the authors also reported the formation of a univalent gold diethyldithiocarbamate soluble in chloroform, in agreement with the findings of this research.

IV. Experimental

A. Apparatus

i. Scintillation counter. The detector used was a 2in diameter x 2in NaI(Tl) well type crystal: well volume 10ml. This was associated with the Nuclear Enterprises (N.E.) single channel gamma ray spectrometer comprised of "Edinburgh Series" units. A setting of the discriminator voltage corresponding to 0.05MeV, with an EHT of 1205 volts, and an amplifier gain of 70 was used. This ensured only low selectivity, but high sensitivity of counting of the

gold-198 activity. The instrument was calibrated using a mercury-203 source, and the Laben 400 channel analyser-spectroscope model 400. For samples of low activity, the gold-198 0.41MeV photopeak was measured using the instrument in a differential mode with a bias voltage corresponding to 0.32MeV, and a channel width corresponding to 0.18MeV. Using this setting a lower background count rate, and a better $\frac{(\text{source count rate})^2}{(\text{background count rate})}$ value[110] was obtained.

ii. NE 8651 Dual channel Gamma-matric Scintillation Spectrometer.

This instrument which is fitted with a 3in diameter x 3in NaI(Tl) well type crystal: well volume 10ml, was used for the detection of the gold-198 activity when a large number of samples were to be counted. The instrument was set with a discriminator voltage corresponding to 0.05MeV.

iii. NE8305 Triple channel automatic Liquid Scintillation Spectrometer fitted with a refrigeration unit.

This instrument was used for the counting of chlorine-36 activity. The settings of the instrument are discussed later in this Chapter (p.215).

All the samples for counting whether for gold-198 or chlorine-36 activity were counted using the previously described conditions (p. 82).

Prior to counting the chlorine-36 containing samples, nitrogen was bubbled through the solutions to reduce the concentration of oxygen to a minimum. This was necessary as oxygen has a severe quenching effect.[148]

UNICAM SP 600 Spectrophotometer

This instrument was used for the measurement of the extinction of solutions at a particular wavelength.

Perkin-Elmer Model 137-UV Spectrophotometer

This instrument was used to record the spectra of the various complexes studied.

B. Reagents

All the reagents were prepared from analytical grade chemicals unless otherwiwe stated. The purification and standardisation procedures are given in the Appendix.

i. Distilled water.

The distilled water used was that obtained by double distillation (p. 137).

ii. Active gold solution 1.00mg/ml (5.08×10^{-3}M).

0.01000g of metallic gold was irradiated, and dissolved by the procedures previously given (p. 82). To the solution was added a solution containing 0.09000g of stable gold, and the resulting solution was diluted with 2.5M hydrochloric acid solution to a volume of 100ml.

iii. Stable gold solution 1.0mg/ml (5.08×10^{-3}M).

0.10000g of metallic gold was dissolved by the procedure previously given (p. 82), and diluted with 2.5M hydrochloric acid to a volume of 100ml.

Gold solutions of lower concentration were prepared by dilution of the above listed solutions using 2.5M hydrochloric acid.

iv. Stable gold solution 1.00mg/ml (5.08×10^{-3}M) for use in the chlorine-36 experiments.

0.21010g of $KAuCl_4 2H_2O$ was dissolved in 5.0N sulphuric acid solution, and diluted to 10ml with the same solvent. 2.5ml of this solution was then diluted to 25ml with 5.0N sulphuric acid solution.

Solutions of lower gold concentrations were prepared by dilution of the above solution.

v. Active sodium chloride solution (0.10M).

50μc of active sodium chloride solution of specific activity 346μc/g Cl^- was obtained from the Radiochemical Centre, Amersham. The solution was transferred to a preweighed porcelain crucible and placed in an oven set at 140° for 24hr. The crucible containing the evaporated sodium chloride was then weighed, and the procedure repeated until a constant weight was achieved. The weight of sodium chloride was found to be 0.2367g. This was dissolved in water and diluted to 40.0ml giving a solution 0.10M.

vi. Active sodium chloride solution (1.37×10^{-2}M).

This solution was available in the laboratory at the time of the investigation, and had a specific activity of 809μc/g Cl^-. The solution 1.1×10^{-3}M was prepared by dilution of the above solution with water.

vii. Copper diethyldithiocarbamate solution (1.0×10^{-3}M).

0.2253g of sodium diethyldithiocarbamate and 5g of copper (II) sulphate pentahydrate was used to prepare the solution by the previously described procedure (p. 83), the final volume of the solution being 500ml.

viii. Zinc diethyldithiocarbamate solution (1.0×10^{-2}M).

2.2530g of sodium diethyldithiocarbamate and 2.85g of zinc (II) sulphate heptahydrate was used to prepare the solution by the previously described procedure (p. 138), the final volume of the solution being 500ml.

ix. Liquid Scintillator for chlorine-36 experiments.

The liquid scintillator used was NE220 supplied by Nuclear Enterprises which is suitable for internal counting of aqueous solutions.

C. Preliminary Experiments to find the Optimum Conditions for the Counting of Chlorine-36 Activity

i. The optimum amplifier gain for a fixed EHT.

The source of chlorine-36 for this experiment was 0.1ml of 1.37×10^{-2}M sodium chloride solution in 10.0ml of scintillator contained in a counting jar, and for the background determination 0.1ml of stable 1.37×10^{-2}M sodium chloride solution together with 10.0ml of scintillator.

Keeping the EHT, and discriminator voltage settings of the liquid scintillation equipment constant at 950 volts and 1 volt respectively, the gain of the amplifier was varied, and at each setting the source and background count rates were determined. A graph of $\log \frac{(\text{source count rate})^2}{(\text{background count rate})}$ as a function of the amplifier gain was constructed and from the graph where the relationship was a maximum[110] the optimum amplifier gain was found to be 50.

ii. The optimum volume of scintillator.

0.1ml of a 1.1×10^{-3}M active sodium chloride solution was

introduced into a series of counting jars using an Emil pipette having a constriction in the bore. The stated volume of scintillator (Table 5.9) was then introduced into the counting jars followed by sufficient dioxan to make all the volumes of organic phases to 10.0ml. The samples were counted, and the activities corrected for background. For the background determination 0.1ml of a 1.1×10^{-3}M stable sodium chloride solution, together with a similar volume of scintillator and dioxan as the sample was used. The results are given in Table 5.9. The efficiency was calculated from the known specific activity of the chlorine-36 solution.

Table 5.9.

Vol. of scintillator added (ml)	Vol. of dioxan added (ml)	Sample count rate -x (c/sec)	Efficiency = $\frac{x}{117} \times 100$ (%)
1.0	9.0	45.5	39.0
2.0	8.0	74.5	63.8
3.0	7.0	84.3	72.2
4.0	6.0	84.3	72.2
5.0	5.0	89.4	76.6
6.0	4.0	90.0	77.9
8.0	2.0	93.0	79.7
9.0	1.0	90.3	77.4
10.0	0.0	94.5	81.0

iii. The influence of sample volume.

The procedure used was as described in the previous experiment, except 10.0ml of scintillator, and increasing volumes of water were used, and the addition of dioxan was omitted. The results are given in Table 5.10.

Table 5.10.

Vol. of water added (ml)	Sample count rate -x (c/sec)	Efficiency = $\frac{x}{117}$ x 100 (%)
0.0	96.5	82.7
0.2	96.5	82.7
0.4	95.3	81.6
0.7	95.4	81.6
0.9	94.7	81.3
1.2	72.9	62.5

iv. The influence of chloroform.

The experiment was carried out as described in the previous experiment, except increasing volumes of chloroform rather than water was used. The results are given in Table 5.11. A graph of log of the count rate as a function of the volume of chloroform was constructed (Fig. 5.1), and the implication of this was discussed on p. 176.

Table 5.11.

Vol. of $CHCl_3$ added (ml)	Sample count rate -N (c/sec)	Efficiency = $\frac{N}{117}$ x 100 (%)
0.0	96.6	82.7
0.25	92.9	79.6
0.50	81.1	69.5
0.75	74.3	63.7
1.00	70.5	60.4
1.25	55.9	47.9
1.50	45.6	39.1
1.75	41.0	35.1
2.00	28.4	24.3

v. The influence of the gold chelate in chloroform.

The experiment was carried out as described in the previous experiments except 1.0ml of a chloroform solution containing the gold chelate formed by the extraction procedure given in Table 5.12, was added. As a comparison the quenching effect of 1.0ml of the chelating agent of the same strength as that used to form the gold chelate was examined. The results are given in Table 5.12.

Table 5.12.

Present in 1.0ml of $CHCl_3$ added	Sample count rate -x (c/sec)	Efficiency = $\frac{x}{117}$ x 100 (%)
1.01×10^{-3}M Au chelate formed in the presence of an excess $Zn(DDC)_2$ 2.5×10^{-2}M.	55.2	47.4
2.5×10^{-2}M $Zn(DDC)_2$	65.4	55.0
5.08×10^{-4}M Au chelate (Sub.^{c} conditions)	65.3	55.0
2.5×10^{-4}M $Zn(DDC)_2$ used in the above ext.^{n}	69.5	59.7
1.0×10^{-3}M $Cu(DDC)_2$	0.2	0.2
1.5×10^{-4}M $Cu(DDC)_2$	8.7	7.5
5.0×10^{-5}M $Cu(DDC)_2$	53.3	45.7

D. The Gold Chelate formed in the Presence of an Excess of Gold (III)

i. Chlorine-36 experiments.

2.0ml of the stable gold solution 1.00mg/ml (5.08×10^{-3}M) in 5.0N sulphuric acid was introduced into a 100ml separatory funnel followed by the stated volume of active 0.1M sodium chloride

solution, and the stated amount of stable sodium chloride solution (Table 5.1). 0.1ml of the resulting solution was then transferred to a counting jar followed by 10.0ml of scintillator - (Reference). The remainder of the solution was used in a substoichiometric separation of the gold chelate using 5.0ml of 1.0×10^{-4}M copper diethyldithiocarbamate in chloroform, with a 2min extraction time. After the extraction the organic phase was filtered through a Whatman 540 filter paper placed in the stem of the separatory funnel, and 1.0ml of the filtered solution was transferred to a counting jar followed by 10.0ml of the scintillator - (Sample).

The procedure was then repeated using 2.0ml of stable gold solution as before, and the same volume and concentration of sodium chloride solution, but in this case both solutions were stable (i.e. no chlorine-36 present). 0.1ml of the resulting solution was transferred to the Sample solution in the counting jar, and the remainder of the solution was used in a substoichiometric separation of the gold chelate using identical conditions to that previously described. 1.0ml of the filtered organic phase was then added to the Reference solution in the counting jar.

Using such a technique both the Reference and Sample solutions for counting contained the same weight of gold chelate and chlorine, and the same volume of aqueous phase, chloroform and scintillator, and therefore the counting efficiencies should be identical for the two solutions. The activity of the chlorine-36 was counted using the conditions previously selected (p. 175), and the results are given in Table 5.1. The expected sample count rate was based on

the assumptions that the efficiency of counting of the chlorine-36 activity was 100%, and that the gold to chlorine molar ratio in the chelate was 1:2.

The molar ratio of gold to chlorine for the experimental results was calculated from the prior knowledge that the molar ratio of gold to diethyldithiocarbamate in the chelate formed was 1:1 (p. 54). The concentration of the chelating agent must therefore be determined with the maximum degree of accuracy. The method used for the standardisation is given on p.239 .

E. The Gold Chelate formed in the Presence of Ascorbic Acid and an Excess of Gold.

i. Reduction experiments.

The rate of reduction of gold (III) to the metal, as a function of the gold and chloride ion concentration of the aqueous phase was examined using the following procedure: to a series of 100ml separatory funnels each containing 20.0ml of 0.5N sulphuric acid, 0.1ml of active gold (III) solution in hydrochloric acid of known strength was added followed by 1.0ml of 1.0% ascorbic acid solution. The solutions were mixed, and allowed to stand for the stated time period, after which gold was extracted for 5min using 5.0ml of 5.0×10^{-4}M zinc diethyldithiocarbamate in chloroform solution (excess). The organic phases were then filtered using the previously described procedure, and the activity of 3.0ml of each was measured. From the known activity of the active gold solution the weight of gold extracted as the chelate, and hence the weight of gold not extracted could be calculated.

The experiments were repeated using the same procedure as previously described except no ascorbic acid solution was added. The difference in the weight of gold not extracted with identical conditions in the presence, and absence, of ascorbic acid, was then calculated, this being the weight of gold (III) reduced to the metal. The weight of gold (III) reduced to the metal as a function of time for a number of different initial gold (III), and chloride ion concentrations of the aqueous phase are given in Figs. 5.2, 5.3 and 5.4. The temperature of the solutions in all cases was $20 \pm 1^{\circ}C$.

ii. The titration of ascorbic acid with potassium iodate.

Ascorbic acid can be conveniently standardised against potassium iodate via potassium iodide to a starch end point.[150] This method was preferred to a direct titration with iodine, as potassium iodate unlike iodine is a primary standard, and therefore requires no standardisation. The reaction of potassium iodate with ascorbic acid can be written as:

$$IO_3^- + 5I^- + 6H^+ + 3C_6H_8O_6 \rightleftharpoons 3C_6H_6O_6 + 6HI + 3H_2O.$$

In an oxidation reaction the equivalent weight of potassium iodate is one sixth of the molecular weight,[157] and therefore from the above reaction 1 litre of a normal solution of iodate is equivalent to one half of the molecular weight of ascorbic acid.

The ascorbic acid was titrated in a medium of 20ml of 0.5N sulphuric acid in the presence of 1ml of 10% potassium iodide, the starch being added near the end point. The method was found to be successful and agreement with the theoretical titration figures was obtained, i.e. 1.0ml of 1.0% ascorbic acid solution was equivalent to

11.35ml of 0.01N iodate solution.

iii. The molar ratio of gold (III) to ascorbic acid in the reduction of gold (III) to the metal.

1.0ml of a stable gold (III) solution 1.00mg/ml (5.08×10^{-3}M) in 2.5M hydrochloric acid was added to 20ml of 0.5N sulphuric acid, followed by 1.0ml of 1.0% ascorbic acid. The solution was mixed and allowed to stand for 5min. The excess of ascorbic acid was then titrated with 0.01N iodate solution by the procedure previously described. The experiment was repeated allowing the solution to stand for 1hr prior to the titration of the excess of ascorbic acid. This was considered necessary to ensure that the reduction of the gold (III) to the metal was complete. From the known titre of 1.0ml of 1.0% ascorbic acid with potassium iodate, the weight of ascorbic acid consumed, and hence the molar ratio of gold (III) to ascorbic acid in the reaction could be calculated. The results are given in Table 5.2.

iv. The molar ratio of gold (III) to ascorbic acid in the presence of an excess of zinc diethyldithiocarbamate in chloroform.

The same procedure was used to that given above, except the excess of zinc diethyldithiocarbamate solution, 5.0ml of 1.0×10^{-2}M, was added to the solution of the gold in 0.5N sulphuric acid before the addition of the ascorbic acid. After the 5min extraction the organic phase was removed, and the aqueous phase was washed with two 5ml portions of chloroform to remove all traces of the gold and zinc diethyldithiocarbamates, which would react with iodine. The excess

of ascorbic acid in the aqueous phase was then titrated with potassium iodate by the previously described method (p. 221). The molar ratio of gold (III) to ascorbic acid in the reaction was calculated, and the results are given in Table 5.2.

v. The reaction of ascorbic acid with zinc diethyldithiocarbamate in chloroform.

1.0ml of 1.0% ascorbic acid in 20ml of 0.5N sulphuric acid was shaken with 5.0ml of 1.0×10^{-2}M zinc diethyldithiocarbamate solution for 5min. The organic phase was then removed, and the aqueous phase was washed with chloroform and the excess of ascorbic acid was titrated by the previously described procedure.

vi. Chlorine-36 experiments.

2.0ml of stable gold (III) solution 50.0(0)µg/ml (2.54×10^{-4}M) in 5.0N sulphuric acid was added to the stated volume of stable and active sodium chloride solutions (Table 5.3) contained in a 100ml separatory funnel. 1.0ml of 1% ascorbic acid solution was added, and 0.1ml of the resulting solution after mixing, was quickly removed and transferred to a counting jar containing 10.0ml of scintillator - (Reference). 5.0ml of 2.5×10^{-5}M zinc diethyldithiocarbamate in chloroform was added to the remainder of the solution, and the extraction performed immediately for 5min (50% stoichiometry). The extraction must be performed as rapidly as possible to keep the amount of gold (III) reduced to the metal, in the presence of the ascorbic acid to a minimum. The organic phase after the extraction was filtered using the previously described procedure, and 1.0ml transferred to a counting jar containing 10.0ml of scintillator - (Sample).

The experiment was repeated using the above conditions except both the sodium chloride solutions were stable (i.e. no chlorine-36 present), and were of the same concentrations as that previously used. Prior to the substoichiometric separation of the gold chelate 0.1ml of the aqueous phase was removed, and transferred to the Sample counting jar, and after the extraction 1.0ml of the filtered organic phase was transferred to the Reference counting jar. The activity of the chlorine-36 was then measured using the previously selected condition (p. 175). The expected sample count rate was calculated assuming a 100% efficiency of chlorine-36 counting, and the formation of a gold chelate of molar ratio gold to chlorine of 1:2. If a univalent gold chelate is formed the expected activity will be zero. The results are given in Table 5.3.

F. The Gold Chelate formed in the Presence of Ascorbic Acid, and an Excess of the Chelating Agent

i. Spectrophotometric study using zinc diethyldithiocarbamate in chloroform.

To a series of 100ml separatory funnels each containing 20ml of 0.5N sulphuric acid increasing amounts of stable gold (III) solution, 10.00µg/ml (5.08×10^{-5}M) in 2.5M hydrochloric acid solution was added. 1ml of 1% ascorbic acid followed by 5.0ml of 1.5×10^{-5}M chelating agent was added, and the extraction of the gold chelate performed for 5min. After the extraction 1ml of about 10^{-3}M copper sulphate solution was added and the solution extracted for a further 5min. The extinction of the filtered organic phase was measured at 436mµ in a 2cm cell, and a graph of the optical density of the copper

chelate as a function of the added volume of gold solution was constructed Fig. 5.7.

From the intercept of the graph corresponding to the complete reaction of all of the chelating agent the molar ratio of gold to diethyldithiocarbamate was found to be 1.0:0.9(5).

ii. Time to reach extraction equilibrium.

The procedure used was that previously given (p. 90). For the extractions using an active gold solution 1.0µg/ml (5.08×10^{-6}M) 5.0ml of the copper or zinc chelating agent 2.5×10^{-7}M was used, and for the active gold solution 10.0µg/ml (5.08×10^{-5}M) 5.0ml of 2.5×10^{-6}M chelating agent. The results are given in Table 5.13.

Table 5.13.

Weight of Au (µg)	Chelating agent	Time to reach ext.^{n} equil.^{n} (min)
1.0	$Zn(DDC)_2$	1.5
1.0	$Cu(DDC)_2$	2.0
10.0	$Zn(DDC)_2$	1.5
10.0	$Cu(DDC)_2$	20.0

iii. Spectrophotometric study using copper diethyldithiocarbamate in chloroform.

The method was the same as that previously given (p. 224) except the copper rather than zinc chelate of the same strength was used with a 30min extraction. The results are given in Fig. 5.7.

From the intercept of the graph corresponding to the complete reaction of all of the chelating agent the molar ratio of gold to diethyldithiocarbamate was found to be 1.0:0.9(5).

iv. Chlorine-36 experiments.

The same procedure as that for the study in the presence of an excess of gold was used (p. 223) except an excess of chelating agent, 5.0ml of 5.0 x 10^{-4}M zinc diethyldithiocarbamate in chloroform was employed. The results are given in Table 5.3.

G. The Gold Chelate formed in the Presence of an Excess of Chelating Agent.

i. Spectrophotometric study using copper diethyldithiocarbamate in chloroform.

The method used was similar to that given on p. 224. A fixed amount of the chelating agent, 5.0ml of 1.50 x 10^{-4}M copper diethyldithiocarbamate in chloroform was used in a series of 10min extractions in the presence of increasing volumes of stable gold solution, 100.0(0)µg/ml (5.08 x 10^{-4}M) in hydrochloric acid of known strength. The chloride ion concentration of the aqueous phase was governed by the volume of 5M sodium chloride solution added, and the study was carried out at a series of different hydrogen and chloride ion concentrations of the aqueous phase. The extinction of the excess of chelating agent at 436 mµ present in the filtered organic phase was measured in a 0.5cm cell, and a graph of the optical density as a function of the volume of added gold solution drawn. From the intercept of the plotted line corresponding to the complete reaction of all of the chelating agent, the molar ratio of gold to diethyldithiocarbamate was calculated. A typical graph is given in Fig. 5.8 and the calculated molar ratio of gold to diethyldithiocarbamate for each set of conditions are given in Table 5.4.

The possibility of a blank error due to the light absorption of the gold chelate at 436mμ was studied by extracting a fixed weight of gold, 100.0(0)μg for 10min, from an aqueous phase of fixed hydrogen and chloride ion concentration, using varying concentrations of chelating agent. The extinction of the excess of chelating agent at 436mμ in a 0.5cm cell was measured and plotted as a function of the added concentration of chelating agent. The study was made with the various conditions used in the previous experiment (p. 225). A typical graph is given in Fig. 5.9, and for all other conditions identical relationships were obtained.

ii. Time to reach extraction equilibrium.

In order to be certain that extraction equilibrium had been reached during the 10min extraction period used in the previous experiment, the time necessary to reach extraction equilibrium in the formation of the gold chelate was examined by the previously described procedure (p. 90). Using an active gold solution 100.0μg/ml (5.08×10^{-4}M), and an excess of chelating agent, 5.0ml of 1.5×10^{-4}M copper diethyldithiocarbamate in chloroform, with the conditions of the aqueous phase used in the previous experiment it was found that extraction equilibrium was reached in 2min with all the conditions studied.

iii. Repeat of (i) using an active gold solution 100.0(0)μg/ml (5.08×10^{-4}M).

The experiment described under i) was repeated using increasing volumes of an active gold solution 100.0(0)μg/ml (5.08×10^{-4}M) with the same fixed amount of chelating agent. After the extractions

the organic phases were filtered, and the activity of 3.0ml of each phase diluted to 5.0ml with chloroform was measured. The aqueous phases were then centrifuged, and the activity of a 5.0ml aliquot measured. From the measured activity of the 3.0ml of each original organic phase after the extraction, the activity of 5.0ml of the organic phase corresponding to the total weight of gold extracted as the gold chelate could be calculated. The distribution ratio, q, of the gold given by $\left(\frac{\text{concentration of gold in organic phase}}{\text{concentration of gold in aqueous phase}}\right)$ was calculated for each extraction and the results are given in Table 5.14.

Table 5.14.

Vol. of active Au solution added (ml)	Activity of 5.0ml of organic phase (c/sec)			Activity of 5.0ml of aqueous phase (c/sec)			Distribution ratio of gold(q)		
	I	II	III	I	II	III	I	II	III
0.1	25	132	43	16	0.8	48	1.6	165	0.9
0.3	78	205	60	38	1.2	62	2.1	171	1.0
0.4	95	277	80	51	1.5	90	1.9	185	0.9
0.5	118	331	95	66	2.0	110	1.8	165	0.9
0.6	153	403	117	85	2.5	130	1.8	161	0.9
0.7	164	456	117	95	3.0	140	1.7	152	0.8
0.8	164	545	142	112	3.0	170	1.5	182	0.8
1.0	222	688	156	143	4.0	180	1.6	172	0.9

The results in columns I, II and III are for aqueous phases $0.01MH^+$ $0.21MCl^-$, $0.01MH^+$ $4.81MCl^-$, $4.90MH^+$ $4.90MCl^-$ respectively.

iv. The distribution ratio of the gold between chloroform and the aqueous phase as a function of the hydrogen ion concentration of the latter phase.

The above relationship was studied at a series of different

hydrogen ion concentrations of the aqueous phase in the presence of a fixed weight of gold (III), 100.0(0)µg, and chloride ions in the aqueous phase, together with a fixed amount of chelating agent 5.0ml of 1.0×10^{-3}M copper diethyldithiocarbamate in chloroform (excess). By using varying volumes of sodium chloride, and hydrochloric acid solutions of the same strength, and keeping the total volume of the two solutions constant at 24.0ml, the chloride ion concentration and the ionic strength of the aqueous phase was kept constant. After the 10min extractions the organic phases were filtered using the previously described procedure, and the activity of 3.0ml of the organic phases diluted to 5.0ml with chloroform were measured. The aqueous phases were centrifuged and the activity of 5.0ml of each solution measured. The distribution ratio, q, of the gold between the two phases was then calculated. 10.0ml of the aqueous phase was transferred to a series of clean dry 100ml separatory funnels, and the extraction and separation procedure was repeated using 5.0ml of chloroform as the extractant. Again the distribution ratio of the gold was measured. The results are given in the form of a graph of log q as a function of the log of the hydrogen ion concentration of the aqueous phase (Fig. 5.10). In order to study the relationship at a fixed value of the chloride ion concentration below 2.5M it was necessary to vary the hydrogen ion concentration using sulphuric acid rather than hydrochloric acid. The procedure was the same as that previously described, except a fixed volume of sodium chloride solutions was used with varying volumes of sulphuric acid. Again the total volume was kept constant at 24.0ml by the addition of water.

The hydrogen ion concentration of the aqueous phase as a function of the normality of sulphuric acid was found from the data given by Hamer.[158] The results are given in Fig. 5.10.

v. The distribution ratio of the gold between chloroform and the aqueous phase as a function of the chloride ion concentration of the latter phase.

The above relationship was studied by a similar technique to that used in the previous experiment except the variable on this occasion was the chloride ion concentration of the aqueous phase, the concentration of which was varied using sodium chloride solution and water keeping the total volume of the two solutions constant at 24.0ml. The different values of the hydrogen ion concentration of the aqueous phases were obtained by use of an active gold solution in a suitable molarity of hydrochloric acid solution. The graph of log q as a function of log of the chloride ion concentration of the aqueous phase is given in Fig. 5.11. To study the relationship at a hydrogen ion concentration of 4.0M it was necessary to use sulphuric rather than hydrochloric acid solution. If the latter acid was used then the chloride ion concentration of the solution would be 4.0M, and therefore it would be impossible to study the distribution ratio of the gold between the two phases at a chloride ion concentration below this value. The chloride ion concentration of the aqueous phase was again varied using sodium chloride solution and water.

As a comparison the study at a hydrogen ion concentration 0.5M was repeated in the presence of sulphuric rather than hydrochloric

acid and the results are given in Fig. 5.16.

vi. The distribution of the gold between chloroform and the aqueous phase as a function of the initial gold (III) concentration of the latter phase.

The effect of the initial concentration of gold (III) in the aqueous phase on the value of the distribution ratio, q, of the gold between the two phases was examined with the same conditions of the aqueous phase as used in the spectrophotometric study, i.e.

H^+ conc.^{n} (M)	Cl^- conc.^{n} (M)
0.01	0.21
0.01	4.81
4.90	4.90

The procedure was the same as that previously described except in this experiment the variable was the initial gold (III) concentration. The results are given in Table 5.5.

vii. The distribution ratio of the gold (III) between chloroform and the aqueous phase as a function of the excess of chelating agent.

The experiment was performed in a similar manner to the previous, except a fixed weight of gold (III), 100.0(0)µg, was used, but increasing concentrations of chelating agent keeping the volume constant at 5.0ml. The obtained values of q as a function of the concentration of chelating agent are given in Table 5.6.

viii. The effect of adding copper (II) ions to the aqueous phase on the distribution ratio of the gold (III) between the chloroform and the aqueous phase.

The experiment was performed in a similar manner to the previous, except into the aqueous phase was introduced 1.0ml of 0.1, 0.01 or 0.001M copper (II) sulphate solution keeping all the other variables fixed. The concentration of the chelating agent was again fixed at 1.0×10^{-3}M. The study was made at the same hydrogen and chloride ion concentration as the aqueous phase as in the previous experiment, and the results are given in Table 5.7.

ix. The distribution ratio of gold (III) between chloroform and the aqueous phase as a function of the previously considered variables, using zinc rather than copper diethyldithiocarbamate in chloroform.

This study was carried out in the same manner as previously described in experiments i) to viii). For experiment i) after the extractions with the zinc chelate the excess of chelating agent was converted to the copper chelate and the extinction measured as previously described (p. 226). The molar ratio of gold to diethyldithiocarbamate was again found to be 1:2. The value of the distribution ratio, q, of the gold (III) between the organic and aqueous phases for a given set of conditions was found to be the same whether zinc or copper chelating agent was used. Experiment viii) was repeated studying the effect of the addition of zinc (II) rather than copper (II) ions to the aqueous phase on the value of q. It was found that the presence of zinc (II) in the aqueous phase had no effect on the value of q.

x. Chlorine-36 experiments.

The procedure used was the same as that previously given (p. 218)

and the conditions used in this study are given in Table 5.8 together with the results of the investigation. For the extractions performed at a hydrogen ion concentration of the aqueous phase of 0.5N, the stable gold solution 1.00mg/ml (5.08×10^{-3}M) was prepared from the potassium gold chloride salt dissolved in 5.0N sulphuric acid, and for those at hydrogen ion concentration of 0.01M the same gold salt was used but dissolved in 0.1M hydrochloric acid.

The chloride ion concentration, and the activity of chlorine-36 in the aqueous phase, was varied using a 0.1M solution of active, and suitable amounts of stable, sodium chloride solutions. The extractions were performed for 10min using 5.0ml of 1.0×10^{-2}M zinc diethyldithiocarbamate solution. The latter chelating agent rather than the copper salt must be used as an excess of the copper chelate would have a severe quenching effect (Table 5.12).

Making the assumptions that the gold chelate formed had a molar ratio of gold to chlorine of 1:1, and that the chlorine-36 activity was detected with a 100% efficiency, the expected activity in the organic phase was calculated from the known distribution ratio, q, of the gold (III) between the organic and aqueous phases, with the known conditions of the extraction.

Appendix

Purification and Standardisation Procedures

1. Purification Procedures

For all the purification procedures it was essential to use analytical grade reagents so as to keep any introduced contamination to a minimum.

i. Dithizone.

The reagent was purified by the following procedure:[22] about 0.5g was dissolved in 50ml of chloroform, transferred to a separatory funnel and extracted with four successive 50-75ml portions of 1:100 ammonia solution. The aqueous phase was filtered, and made slightly acidic by the addition of hydrochloric acid. The precipitated dithizone was then re-extracted into the minimum volume of chloroform, and the solution was washed with water, followed by evaporation on a water bath at 50°C to remove the chloroform. The product was finally dried in a desiccator, and stored in the dark.

ii. Sodium diethyldithiocarbamate.[123]

About 1g of the salt was dissolved in the minimum volume of absolute alcohol after which diethyl ether was added dropwise whereupon the sodium diethyldithiocarbamate recrystallised from solution. The solution was then filtered through a buchner funnel, washed with diethyl ether, and allowed to dry in a desiccator.

The water of crystallisation of the reagent is retained during the purification procedure.[123]

II. Standardisation Procedure

i. Gold solutions.

All the solutions of gold used in this research were prepared from metallic gold, except that for the chlorine-36 experiments,

which itself may be considered as a primary standard. As a check of the concentrations of the solutions the Bromoaurate Method[91] was used. The procedure to prepare the calibration graph was as follows: 0.5000g of metallic gold was dissolved by the method previously given (p. 82), and diluted to 100ml in a volumetric flask using 2.5M hydrochloric acid solution. 10.0ml of this solution was then diluted to 100ml in a volumetric flask by a similar procedure giving a solution 0.50mg Au/ml. Suitable aliquots of this solution (Fig. A.1) were pipetted into a series of 50ml volumetric flasks, followed by 5.0ml of hydrobromic acid (48%) and 1.0ml of concentrated hydrochloric acid. The solutions were then diluted to 50ml with water and after thoroughly mixing the extinction was measured at 380mμ in a suitable cell against a reference solution prepared in the same manner, but in the absence of gold (Fig. A.1).

The concentration of the gold solution used in the preparation of the calibration curve was also checked gravimetrically by taking a 25.0ml aliquot of the original solution 5.00mg Au/ml, and reducing the gold to the metal using sodium nitrite. The expected content of gold was confirmed.

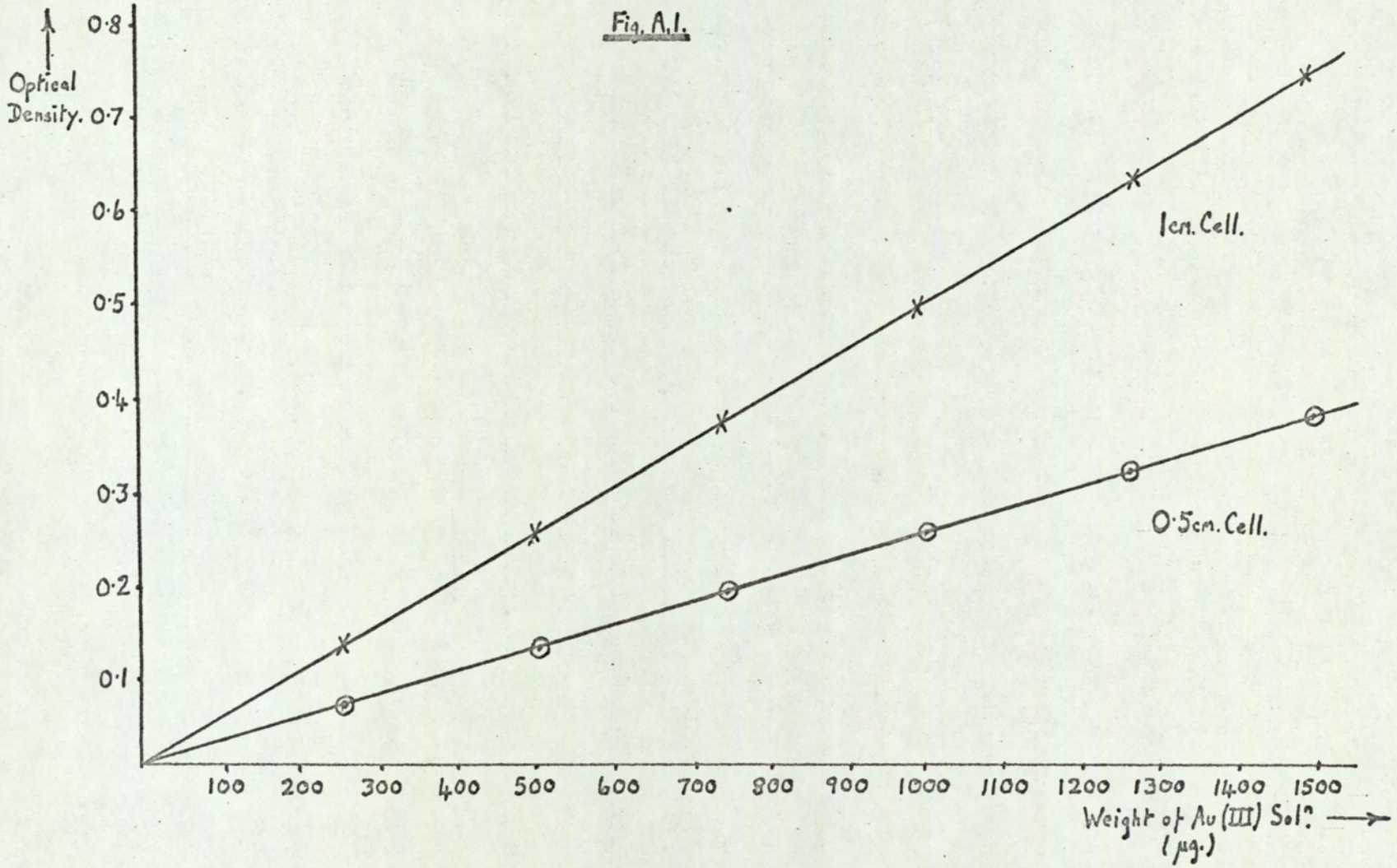
ii. Dithizone solutions.

Two procedures were used.

a. Spectrophotometric.

The extinction of the solution at 445mμ and 605mμ was measured,[60] and from the known extinction coefficients the concentration of the reagent could be calculated. Measurement at 605mμ was preferred as at this wavelength the absorption from any oxidised reagent would be

Fig. A.I.



The Calibration Curve for the Determination of Gold (III) as the Bromoaurate.

less than that at 445mμ.

b. Titrimetric.[51]

The second standardisation procedure used was an extractive titration of a known weight of silver in the form of a standard silver nitrate solution by a similar method to that previously described for gold (p. 86). The aqueous phase was 0.5N sulphuric acid, and the end point was given by a change of colour from the yellow of primary silver dithizonate to the green of excess dithizone.

iii. Copper diethyldithiocarbamate solutions.

The reagent was standardised spectrophotometrically using a calibration curve which was prepared by the following method: a 1.0×10^{-4}M copper (II) solution was prepared by dissolving 1.2485g of copper (II) sulphate pentahydrate in water, and diluting to 500ml in a volumetric flask, followed by the dilution of 5.0 of this solution to 500ml in a similar manner. The solution was then standardised iodometrically[157] and found to be of the expected concentration.

Suitable aliquots of the solution (Fig. A.2) were introduced into a series of separatory funnels each containing 10ml of 0.5N sulphuric acid. 5.0ml of 1.0×10^{-3}M zinc diethyldithiocarbamate in chloroform (excess) was added, and a 5min extraction was carried out during which the copper (II) exchanged with the zinc (II) to form the copper (II) chelate. The extinction of the copper diethyldithiocarbamate at 436mμ was measured in a suitable cell (Fig. A.2) using chloroform as the reference. The calibration

graph obtained is given in Fig. A.2. All the solutions of the chelating agent could now be standardised by use of the calibration graph after measuring their extinction at 436mμ.[77]

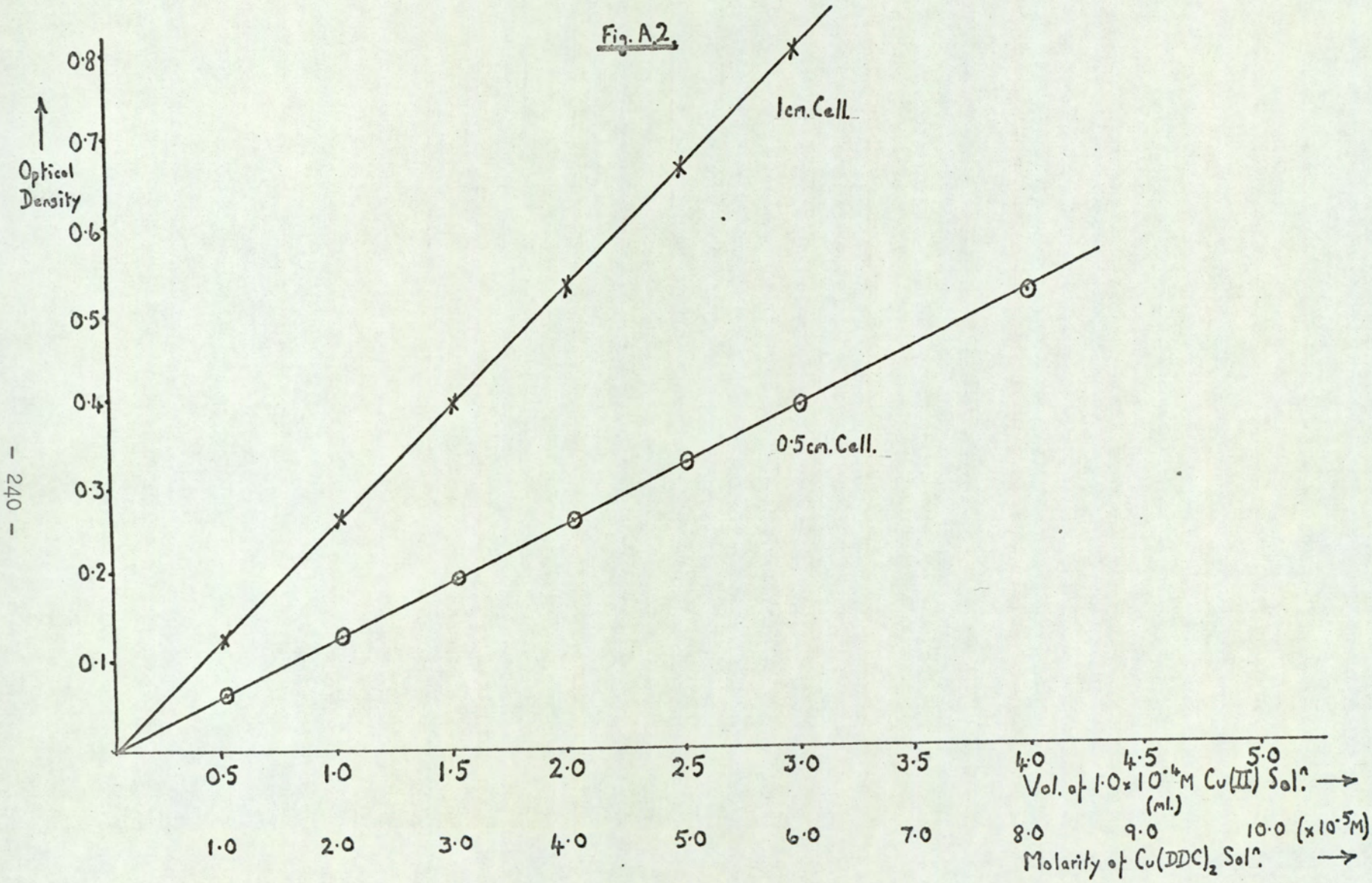
If the molar extinction coefficient of the copper chelate in chloroform was considered to be the same as that in carbon tetrachloride,[77] good agreement between the calculated concentration and that obtained from the calibration graph was obtained. The value of the extinction coefficients in the two solvents must therefore be very similar, and was found to be the case from the calibration curve, approximately 1.3×10^4.

iv. Zinc diethyldithiocarbamate solutions.

The reagent was standardised by the reverse procedure to that given above. 5.0ml of the solution to be standardised was used in a similar extraction, but in the presence of an excess of copper (II) solution. After the extraction the extinction of the copper diethyldithiocarbamate formed was measured at 436mμ in a suitable cell and the concentration of the chelating agent was found from the previously prepared calibration graph (Fig. A.2).

An iodometric titration procedure based upon the oxidation of the chelating agent to the thiuram disulphide can be used,[123] but it was found to be unsuitable for this research as the method is only applicable to the standardisation of chelating agent solutions of concentration 10^{-2}M or higher.

Fig. A2.



The Calibration Curve for the Standardisation of the Copper(II), or Zinc(II) Diethyldithiocarbamate Solutions.

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Dithizonates of gold and palladium

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DURING our studies on the substoichiometric separation of gold[1] and palladium,[2] we have tried to use dithizone as the chelating agent. With an amount of dithizone in an organic solvent which is smaller than that required to react with all of the gold (or palladium) present in the aqueous test solution, it was found that the composition and colours of the extracted gold dithizonates differ from those previously reported.[3] Subsequent studies using this smaller amount of dithizone as well as an excess (as is normal practice in analytical chemistry) confirmed our results and have led to their explanation. Because dithizone has been used for the determination of gold both by extractive titration[3–6] and by spectrophotometry,[7] our results seem to be of analytical importance and they are summarised below.

Gold has been reported[3] to react with dithizone (H_2Dz) according to the following equations:

$$Au^{3+} + 3[H_2Dz]_{org} \rightleftharpoons [Au(HDz)_3]_{org} + 3H^+$$

$$2Au^{3+} + 3[H_2Dz]_{org} \rightleftharpoons [Au_2Dz_3]_{org} + 6H^+.$$

The red-brown complex formed in an alkaline medium was reported to be Au_2Dz_3 and the yellow-brown complex formed in an acidic medium was supposed to be a mixture of $Au(HDz)_3$ and Au_2Dz_3. Also, the straight-forward formation of $Au(HDz)_3$ has been reported,[7] using chloroform as the organic solvent. On the other hand, gold to dithizone ratios of 1:1 (in chloroform) and 1:2 (in carbon tetrachloride) have been claimed.[6] All the above-mentioned extractive titrations[3–6] are carried out from an acidic medium in the presence of various amounts of chloride ion.

To establish the ratio of gold to dithizone in the complex extracted into chloroform, the following experiment was carried out. To a series of separatory funnels, each containing the same amount of aqueous gold solution (for acidity see Fig. 1), increasing amounts of dithizone in chloroform were added, then all the solutions were extracted simultaneously. (Judex analytical-grade chloroform "suitable for use with dithizone" was employed. The dithizone solution was standardised by extractive titration against silver nitrate and also by measurement of the absorbance of the dithizone at 445 mμ.[11]) After the organic extract had been separated, the amount of gold remaining in the aqueous phase was determined. From the results (Fig. 1) it follows that the amount of gold extracted by dithizone depends on the acidity of the original aqueous solution, the chloride ion concentration and the time of shaking. It is apparent that practically any ratio of gold to dithizone between 1:1 and 2:1 can be obtained according to the conditions of extraction; the colour of the extract changes correspondingly from red-brown to yellow. Formation of the yellow 2:1 complex is favoured by an excess of gold, a prolonged time of shaking and an absence of competing species for the gold, *e.g.*, chloride and hydroxyl ions. The red-brown complex (λ_{max} *ca.* 500 mμ) changes to a yellow complex (λ_{max} *ca.* 315 mμ) and the rate of change depends on the pH of the aqueous solution from which the extraction was made (a complex prepared in an alkaline medium is more stable). Sometimes a green colour appears, which turns to yellow (ref. 3, p. 121); it can be explained by oxidation of liberated dithizone. Further attempts to establish molar ratios of gold to dithizone in the organic extracts were carried out using the radioisotope ^{198}Au for labelling solutions of gold. The gold extracted for 3 min by a known amount of dithizone (less than that required to react with all of the gold) in chloroform was measured radiometrically. The composition of the yellow complex was found to vary from 1·74:1 to 1·91:1 (gold:dithizone) according to the acidity of the solution from which the extraction was made (0·1–6*N* sulphuric acid; in the absence of chloride ions), and that of the red-brown complex approached 1:1 (Table I).

The radiometric results are in good agreement with the results in Fig. 1, bearing in mind that some proportion of the 1:1 complex is always present in the organic extracts. It is concluded that the 1:1 complex and the 2:1 complex are probably formed by the reaction of dithizone with monovalent gold, because it is impossible to formulate complexes of dithizone and tervalent gold having these compositions. It appears that the red-brown complex changes to the yellow complex, liberating dithizone, which subsequently decomposes.

From the above it follows that the use of dithizone as an extractive titrant or a spectrophotometric reagent for the determination of gold cannot be recommended. It can be seen from Fig. 1 that the volume of titrant required for reaching the equivalence point depends rather critically on the acidity, the chloride ion concentration and the time of shaking; these factors were not strictly controlled in the proposed titration procedures.[3,4,6] Also, discarding the first portion(s) of the organic extract, as is commonly recommended in extractive titrations, can lead to errors, because the rate of formation of the complex extracted depends on the amount of gold present in the aqueous phase. The spectrophotometry of gold, based on an absorbance measurement at 450 mμ,[7] seems to be more reliable, but instability of the colour may lead to errors. Probably, it is best to use dithizone only for the separation of gold from a test solution, then to destroy the organic extract and determine

TABLE I—MOLE RATIOS OF GOLD:DITHIZONE IN CHLOROFORM FROM RADIOMETRIC MEASUREMENTS

Normality of H_2SO_4 or pH of aqueous phase	Activity of extract,* *counts*/100 *sec*	Calculated mole ratio of gold:dithizone
6*N*	121,395	1·75:1
4*N*	132,135	1·91:1
0·1*N*	120,315	1·74:1
pH 7·9	67,305	0·97:1
pH 8·5	62,415	0·90:1
pH 9·3	70,020	1·01:1

* $5{\cdot}25 \times 10^{-6}$ mole of labelled gold solution (230,230 counts/100 sec) extracted for 3 min by $1{\cdot}58 \times 10^{-6}$ mole of dithizone in chloroform.

the liberated gold by some other method, *e.g.*, spectrophotometry with *p*-dimethylaminobenzylidenerhodanine.[9] For the above reasons, the substoichiometric separation of gold by dithizone, suggested previously,[10] is unsatisfactory because the good reproducibility needed for this type of separation can only be reached by a very strict control of conditions.

Palladium has been reported to form dithizonates according to the following equations:[3]

$$Pd^{2+} + 2[H_2Dz]_{org} \rightleftharpoons [Pd(HDz)_2]_{org} + 2H^+ \quad (1)$$

$$Pd^{2+} + [H_2Dz]_{org} \rightleftharpoons PdDz\downarrow + 2H^+ \quad (2)$$

$$PdDz\downarrow + [H_2Dz]_{org} \rightleftharpoons [Pd(HDz)_2]_{org} \quad (3)$$

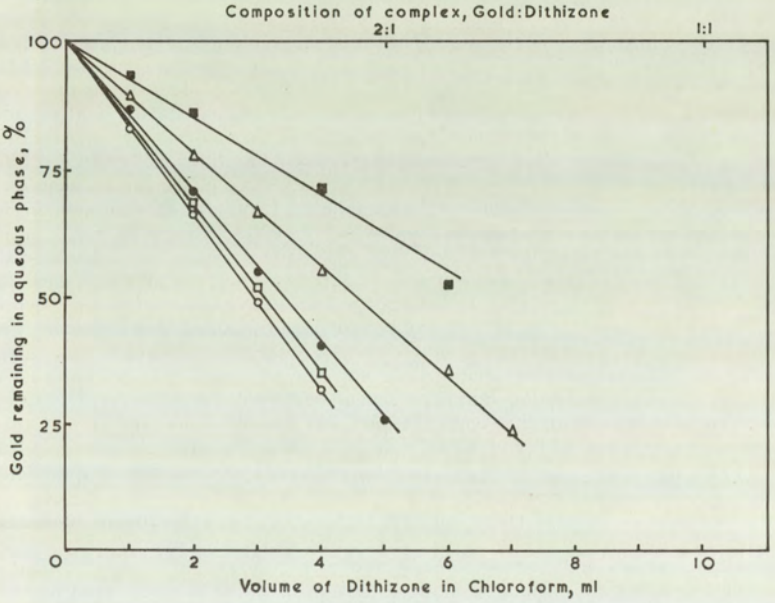

Fig. 1—Extraction of gold by dithizone from the following media:
○ 0·03*N* H_2SO_4
□ 0·1*N* H_2SO_4
● 0·01*N* HCl
△ 0·18*N* HCl
■ 1·2*N* HCl
(2 ml of $2{\cdot}54 \times 10^{-3}M$ gold solution extracted for 3 min with increasing volumes of $5{\cdot}08 \times 10^{-4}M$ dithizone in chloroform; gold remaining in aqueous phase determined spectrophotometrically as bromaurate.[8] Prolonged shaking increased the tendency to form the 2:1 complex. Mole ratios for gold:dithizone of 2:1 and 1:1 stated on figure were calculated from the above concentrations of gold and dithizone solutions.)

$[Pd(HDz)_2]_{org}$ is reported as green-brown and PdDz as grey-violet but insoluble in organic solvents.[3] Our experiments, carried out both spectrophotometrically and radiometrically (using ^{109}Pd as a tracer), are in good agreement with the above, except that PdDz was found to be soluble in carbon tetrachloride and in chloroform. The violet organic extract, prepared by shaking $1 \times 10^{-4}M$ dithizone in carbon tetrachloride with an aqueous solution of palladium chloride in $0{\cdot}1N$ sulphuric acid (one-fold molar excess of palladium to dithizone), has broad maximum absorbances at 340 and 550 mμ. Under these conditions, this chelate is extracted over the range $1N$ sulphuric acid to pH 5 (acetate buffer) and good reproducibility of substoichiometric separation can be reached. The time necessary for reaching extraction equilibrium is 2·5 min for 50% stoichiometry and 7 min for 90% stoichiometry. During the extraction, green-brown $Pd(HDz)_2$ is first formed, which by prolonged shaking is converted to violet PdDz. However, with an excess of dithizone, as is normally employed in analytical chemistry, $Pd(HDz)_2$ is mostly formed [equation (1)]; any PdDz formed by equation (2) is converted to $Pd(HDz)_2$ according to equation (3).

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Summary—Contrary to some previous reports, it has been found that gold reacts with dithizone in the ratio 1:1 forming a red-brown complex, and in the ratio 2:1 forming a yellow complex, both extractable into chloroform. The proportion of these two complexes in the organic extract depends critically on several factors. Therefore, the use of dithizone as a spectrophotometric reagent and especially as an extractive titrant for gold cannot be recommended. Previous reports on the composition and colour of the dithizonates of palladium are confirmed, except that PdDz is soluble in carbon tetrachloride and in chloroform.

Zusammenfassung—Im Gegensatz zu früheren Berichten wurde gefunden, daß Gold mit Dithizon im Verhältnis 1:1 zu einem rotbraunen und im Verhältnis 2:1 zu einem gelben Komplex reagiert, die beide in Chloroform extrahierbar sind. Das Verhältnis dieser beiden Komplexe im organischen Extrakt hängt kritisch von mehreren Faktoren ab. Daher kann die Verwendung von Dithizon als spektralphotometrisches Reagens und speziell als Reagens zur extraktiven Titration von Gold nicht empfohlen werden. Frühere Berichte über Zusammensetzung und Farbe der Palladium-Dithizonate werden bestätigt, mit der Ausnahme, daß PdDz sich in Tetrachlorkohlenstoff und Chloroform löst.

Résumé—Contrairement à quelques indications antérieures, on a trouvé que l'or réagit avec la dithizone dans le rapport 1:1 en formant un complexe rouge-brun, et dans le rapport 2:1 en formant un complexe jaune, tous deux extractibles en chloroforme. La proportion de ces deux complexes dans l'extrait organique dépend essentiellement de différents facteurs. Par conséquent, on ne peut recommander l'emploi de la dithizone comme réactif spectrophotométrique et spécialement comme agent de dosage par extraction de l'or. Les indications antérieures sur la composition et la couleur des dithizonates de palladium sont confirmées, à l'exception du fait que PdDz est soluble en tétrachlorure de carbone et chloroforme.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF GOLD BY NEUTRON-ACTIVATION ANALYSIS

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Summary—A highly selective, rapid, one-step radiochemical separation procedure for gold has been developed. It is based on the solvent extraction of gold diethyldithiocarbamate from a 0·01–10*N* sulphuric or hydrochloric acid medium using a substoichiometric amount of copper diethyldithiocarbamate in chloroform. The separation has been applied to the determination of traces of gold by neutron-activation analysis in high-purity lead, the rock W-1, gold-doped semiconductor-grade silicon and a biological material (kale). Amounts of gold down to 2×10^{-10} g have been determined.

NEUTRON-ACTIVATION analysis is well suited to the determination of traces of gold in various materials, especially for the high sensitivity which can be reached by this method. Gold is a mono-isotopic element and by its activation with thermal neutrons the following nuclear reaction occurs:[1]

$$^{197}\mathrm{Au}(n, \gamma)^{198}\mathrm{Au}$$

($t_{\frac{1}{2}} = 2{\cdot}7$ days; $\sigma = 98$ barns; $\beta^- = 0{\cdot}96$ MeV; $\gamma = 0{\cdot}41$ MeV). From the above data it follows that under suitable conditions (irradiation in a flux of 10^{12} neutrons. $cm^{-2}.sec^{-1}$ to saturation activity, followed by radiochemical separation) it is theoretically possible to determine down to 10^{-11} g of gold. The following possible nuclear interference reactions

$$^{198}\mathrm{Hg}(n, p)^{198}\mathrm{Au}$$

$$^{198}\mathrm{Pt}(n, \gamma)^{199}\mathrm{Pt} \rightarrow {}^{199}\mathrm{Au}$$

must be considered in the case of a mercury or platinum matrix. Also, the reaction[32]

$$^{198}\mathrm{Au}(n, \gamma)^{199}\mathrm{Au}$$

($t_{\frac{1}{2}} = 3{\cdot}1$ days; $\sigma = 26{,}000$ barns; $\beta^- = 0{\cdot}30,\ 0{\cdot}25,\ 0{\cdot}46$ MeV; $\gamma = 0{\cdot}16,\ 0{\cdot}21,\ 0{\cdot}05$ MeV) must be taken into account, especially in the case of prolonged irradiation.

Neutron-activation analysis has been used for the determination of traces of gold in such industrially important materials as semiconductors,[2] high-purity metals,[3,4] lithium compounds,[5,25] petrochemicals,[6] as well as in sea water,[7] meteorites,[8,9] rocks,[10] minerals,[9,11,13] biological materials,[14–16] *etc.* These methods necessitate the use of radiochemical separation procedures by means of which the radio-gold is separated in a radiochemically pure form suitable for chemical yield determination. The monograph by Emery and Leddicotte[17] contains several separation procedures for gold which well illustrate the complicated and time-consuming nature of these standard methods.

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The purpose of the present paper was to develop a substoichiometric separation procedure for gold, which, from its generally higher selectivity and the avoidance of determining the chemical yield,[18] would permit a considerable simplification over the radiochemical procedures commonly used. During recent years such substoichiometric procedures have been successfully applied to the determination of various trace metals by neutron-activation analysis. From the theory of substoichiometry,[18] it follows that a reproducible substoichiometric separation can be developed only when the metal under consideration forms a very stable, readily extractable chelate with the reagent employed. Moreover, the chelating agent itself must not be easily decomposed by light, oxidising agents, *etc.*

The selectivity of the separation of gold is affected by the extractability of the chelate formed. Dithizone seems to be particularly suitable for the substoichiometric determination of gold because the extractability of metal dithizonates decreases in the following order:[19] Pd(II), Au(III), Hg(II), Ag(I), Cu(II), Bi(III), Pt(II), In(III), Zn(II), Cd(II), Co(II), Pb(II), Ni(II), Sn(II) and Tl(I) and dithizone solutions in organic solvents are sufficiently stable against decomposition. However, our attempts to use this reagent for the substoichiometric separation of gold were unsuccessful. The main reason is that two types of dithizonate, AuHDz and Au_2Dz (where H_2Dz represents dithizone itself), are formed, the ratio of which depends on pH, excess of dithizone used and chloride ion concentration.[20] For this reason a reproducible substoichiometric separation of gold by dithizone can only be achieved by a strict control of the conditions. It is preferable to maintain the chloride ion concentration at the lowest possible level, which, from a practical point of view, is not very convenient.

Attention was, therefore, turned to other chelating agents containing the reactive —SH group, such as dialkyldithiophosphates and dithiocarbamates. The relative order[21] of extraction of metal chelates with di-n-butyl phosphorodithioic acid [Pd(II), Au(III), Cu(I), Hg(II), Ag(I), Cu(II), Sb(III), Bi, Pb, Cd, Ni and Zn] does not differ very much from that of the dithizonates. A similar conclusion is reached in the case of the metal diethyldithiocarbamates on the basis of the systematic study of Bode and Neumann[22]—with one significant exception—the extraction of gold diethyldithiocarbamate. Using diethyldithiocarbamate as a chelating agent and carbon tetrachloride as the organic solvent, gold was found[22] to be extracted only partially (*ca.* 30%) above pH 1, while Pd, Pt, Cu, Hg, Ag, *etc.*, are extracted even from 10*N* sulphuric acid. This observation unexpectedly places gold amongst the least extractable metals with this particular chelating agent. From our experiments it follows that this is because of the low solubility of gold diethyldithiocarbamate in carbon tetrachloride; with chloroform as solvent, however, this chelate can be extracted quantitatively even from very strong mineral acid solutions. It is impossible to use sodium diethyldithiocarbamate or diethylammonium diethyldithiocarbamate for the substoichiometric separation because both reagents are rapidly decomposed. Of various metallic salts of the parent reagent which offer a greater stability, copper diethyldithiocarbamate has been found extremely suitable in the present case. Its solution ($4{\cdot}83 \times 10^{-4}M$ in chloroform) can be kept without significant change in strength for at least 2 months. Moreover, in acid solutions, gold replaces the copper in the chelate very quickly and the colour of the organic extract changes from dark brown to golden yellow. For these reasons an extractive titration can be used for

checking the concentration of gold or of the extractant. It can also be expected that the procedure will be highly selective, because the extraction of copper diethyldithiocarbamate (which is evidently a weaker complex than that of gold) is well known to be one of the most selective methods for the determination of copper.

EXPERIMENTAL

Apparatus

Scintillation counter. The detector used was a 1·75 in. diameter × 2 in. NaI(Tl) well-type crystal: well volume 5 ml. This was associated with a single channel gamma-ray spectrometer. In all experiments a setting of discriminator voltage corresponding to 0·07 MeV was used. This ensured only low selectivity, but higher sensitivity of counting the ^{198}Au activity.

Reagents

All reagents were prepared from analytical reagent grade chemicals.

Gold carrier solution (2·06 mg/ml; $1{\cdot}05 \times 10^{-2}M$). Prepared from a weighed amount of metallic gold (metal leaves *ca.* 0·0001 mm, General Chemical Co., Division of Fisons Scientific Apparatus Ltd., Loughborough, England) by dissolution in *aqua regia*. The resulting solution was evaporated almost to dryness, then diluted to a standard volume with 1*N* hydrochloric acid.

Copper diethyldithiocarbamate solution ($4{\cdot}83 \times 10^{-4}M$). Prepared by mixing 250 ml of an aqueous solution of sodium diethyldithiocarbamate (0·2253 g; B.D.H. Ltd., Poole, England) with 25 ml of copper sulphate solution (2·5 g of pentahydrate), the precipitate thus formed being extracted by two 250-ml portions of chloroform and the combined extracts diluted to 1000 ml with the same solvent. The concentration of the resulting solution was checked by absorbance measurement at 436 mμ. Assuming that the molar extinction coefficient is the same in chloroform as in carbon tetrachloride ($1{\cdot}3 \times 10^4$),[19] the concentration of the prepared solution was $4{\cdot}83 \times 10^{-4}M$, which was in good agreement with the amount of sodium diethyldithiocarbamate weighed originally. By extractive titration in a medium of 1*N* hydrochloric acid (the end-point being a change in colour from golden yellow to dark brown), 1·00 ml of gold was equivalent to 10 ml of copper diethyldithiocarbamate, which indicates that a 1:1 chelate of gold with diethyldithiocarbamate is formed.

Radiotracer solutions. Used for direct interference studies and prepared by irradiation of the corresponding elements (or their chlorides or sulphates) in a flux of 6×10^{11} neutrons.cm^{-2}.sec^{-1} for 6 hr (Universities of Manchester and Liverpool Research Reactor).

Irradiation

The test samples were weighed (see Table IV), sealed in quartz ampoules (rocks) or wrapped in spectrographically-tested analytical reagent grade aluminium foil (lead, kale and silicon) and irradiated in a reactor simultaneously with an appropriate amount of gold standard. The time of irradiation (24 hr to 5 days), reactor flux (6×10^{11} to 6×10^{12} neutrons.cm^{-2}. sec^{-1}) and time of cooling (usually *ca.* 1 day) were chosen according to the content of gold expected. For irradiation the Harwell reactors BEPO and DIDO and the Universities of Manchester and Liverpool Research Reactor were used.

Development of Method

All preliminary experiments were carried out using $1{\cdot}05 \times 10^{-2}\,M$ gold carrier solution and $4{\cdot}83 \times 10^{-4}\,M$ copper diethyldithiocarbamate solution in chloroform. With the exception of the direct interference studies, the solution of gold carrier was labelled with ^{198}Au which contained a negligible amount of isotopic carrier.

Reproducibility

The optimum acidity for the substoichiometric separation of gold was first investigated. To a series of 100-ml separatory funnels, containing 25 ml of different concentrations of sulphuric or hydrochloric acids or of water alone, 0·5 ml of labelled gold carrier solution was added; the pH of the resulting solutions was adjusted by adding dilute aqueous ammonia and/or small amounts of 0·1*M* acetate or borate buffer solutions to reach different values in the pH range 0–8·5. After adding 3·0 ml of copper diethyldithiocarbamate solution, the extraction was carried out for 3 min. The activities of equal volumes (2·0 ml) of the chloroform layer were measured in the scintillation counter and plotted against the acidity of the extracted solution. From the curve obtained (Fig. 1) it can be seen that a reproducible substoichiometric separation can be achieved over a very wide range of acidity (0·01–10*N* hydrochloric or sulphuric acid). For all further experiments a medium of $1{\cdot}5 \pm 1N$ hydrochloric acid was chosen.

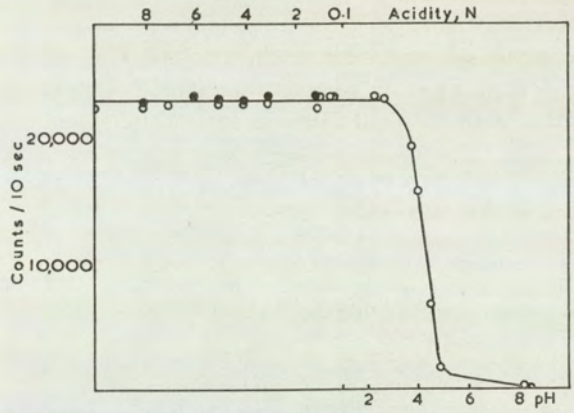

FIG. 1.—Influence of acidity on the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform (60% stoichiometry):
●—hydrochloric acid,
○—sulphuric acid.

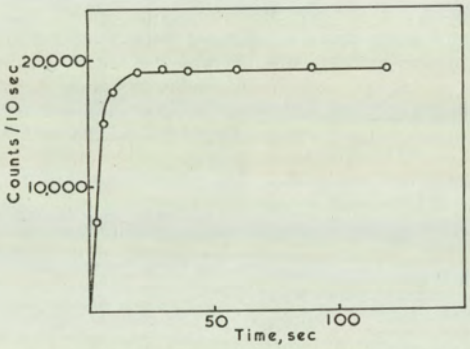

FIG. 2.—Time necessary for reaching extraction equilibrium in the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform ($1{\cdot}5 \pm 1N$ hydrochloric acid; 80% substoichiometry).

The time necessary for reaching extraction equilibrium, which also ensures the reproducibility of the substoichiometric separation, was ascertained by extraction of gold for different times from 25 ml of $1{\cdot}5 \pm 1N$ hydrochloric acid, containing 0·5 ml of labelled gold carrier solution, using 4·0 ml of copper diethyldithiocarbamate solution as the extractant. From Fig. 2, where the activities of the obtained extracts are plotted *vs.* time of shaking, it can be seen that extraction equilibrium is reached within 20 sec and that the extract is unaffected by prolonged shaking. For all further experiments an extraction time of about 1 min was chosen.

Finally, the reproducibility of the substoichiometric separation was tested in the following way. A series of solutions of $1{\cdot}5 \pm 1N$ hydrochloric acid, containing precisely known, increasing amounts of labelled gold carrier solution, were simultaneously extracted with 4·0 ml of copper diethyldithiocarbamate solution for about 1 min. The activity of the extracts was measured as before and plotted against the amount of gold originally present in the aqueous phase. From the graph obtained (Fig. 3) it can be seen that after reaching the equivalence point very good reproducibility of the substoichiometric separation was achieved.

Selectivity

The selectivity of the substoichiometric separation was studied using direct and indirect methods. In both cases only the influence of those metals the extractability of which is higher or similar[19,22] to that of copper diethyldithiocarbamate were tested. The investigation of metals which do not form extractable diethyldithiocarbamates (Na, K, Ca, Sr, rare earths, *etc.*) or form chelates of very low extractability (Zn, Ga, Tl, Mn, Fe, *etc.*) is unnecessary.

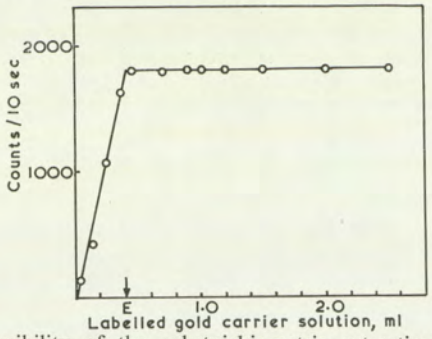

FIG. 3.—Reproducibility of the substoichiometric extraction of gold with copper diethyldithiocarbamate in chloroform (E denotes the equivalance point).

TABLE I.—INTERFERENCE WITH THE EXTRACTION* OF GOLD BY COPPER DIETHYLDITHIOCARBAMATE IN CHLOROFORM CAUSED BY THE ADDITION OF INACTIVE ELEMENTS OR OTHER SPECIES.

Element of other species added	Activity of extract,† *counts*/10 *sec*
—‡	23118
Platinum(IV) (2 mg)	23184
Tin(II) (2 mg)‡	300
Tin(IV) (1 mg)	24424
Indium(III) (2 mg)	23345
Antimony(III) (2 mg)	22475
Antimony(V) (1 mg)	24904
Arsenic(III) (2 mg)	24108
Arsenic(V) (1 mg)	24424
Molybdenum(VI) (4 mg)	24108
Palladium(II) (1 mg)	19720
Palladium(II) (2 mg)	12390
Lead(II) (3 g in 1*N* HNO_3)	23830
0·1 ml of 5 vol. H_2O_2	23178
1·0 ml of 5 vol. H_2O_2	23315
1·5*N* HNO_3 (no HCl present)	22835
1 ml of 40% HF	22950
0·5 ml of 70% $HClO_4$	22410
1 ml of 70% $HClO_4$	22740

* All extractions made from 1·5 ± 1*N* HCl unless otherwise stated.
† All activities corrected for background and decay.
‡ No H_2O_2 present

The indirect interference studies were based on the detection of any depression of the gold activity extracted as diethyldithiocarbamate, caused by the presence of various other metal ions in the original aqueous solution. In these experiments labelled gold carrier solution was mixed with the corresponding (by weight) amounts of foreign metal ions or other species (Table I) in 1·5 ± 1*N* hydrochloric acid with the addition of 1 ml of 5 vol. hydrogen peroxide solution. From the activities of the extracts obtained it can be seen that the method proposed is very selective: only palladium and tin(II) interfere. The interference of the latter is caused by reduction of the gold to the metallic state, which can easily be avoided by adding hydrogen peroxide. Comparatively large amounts of nitric acid, hydrofluoric acid, perchloric acid or hydrogen peroxide do not destroy the extractant and so can be tolerated. This is important because these species may of necessity be present in the aqueous phase obtained when dissolving test matrices.

The direct interference studies were based on using microgram or submicrogram amounts of radioisotopes of the foreign ions. These radiotracers were mixed with a non-active isotopic gold carrier solution and substoichiometric extractions carried out. The selectivity of separation, carried out from 1·5 ± 1*N* hydrochloric acid in the presence of 5 vol. hydrogen peroxide solution, is very high (Table II) and the results obtained in this way are in good agreement with indirect interference studies.

TABLE II.—INTERFERENCE WITH THE EXTRACTION OF GOLD BY COPPER DIETHYLDITHIOCARBAMATE IN CHLOROFORM CAUSED BY THE ADDITION OF RADIOACTIVE TRACERS*

Radioisotope added	^{110}Ag	^{76}As	$^{122+124}$Sb	^{64}Cu	^{197}Pt	^{99}Mo	^{203}Hg	^{109}Pd
Total activity added, *counts*/10 *sec*	41,394	159,465	228,330	312,576	1,170,162	1,441,261	226,314	225,700†
Activity of substoichiometric extract, *counts*/10 *sec*	14	29	313	32	272,720	292	127	19,027‡
Radioisotope extracted, %	0·03	0·02	0·14	0·01	23·3	0·02	0·06	8·4

* 2 mg of gold carrier present; interfering elements present in microgram amounts.
† One-twentieth of stated activity actually measured. Solution evaporated to dryness on standard aluminium planchet and counted on end-window Geiger-Müller counter.
‡ One-sixth of stated activity actually measured (see †).

Although platinum(IV) was not found to depress the extracted gold activity in the indirect interference studies (Table I), interference was obtained using labelled platinum(IV). This means that this metal must be extracted by another mechanism than that for gold; this conclusion was confirmed by an experiment in which, instead of using copper diethyldithiocarbamate in chloroform as the extractant, pure solvent (chloroform) was used alone. The same amount of radioactive platinum (*ca.* 23%) was still extracted. It will be shown later that, for nuclear reasons, the interference of platinum (and palladium) need only be considered if this metal is present in great excess compared to gold.

Dissolution procedures

To determine the losses of gold which can occur during dissolution of test samples,[23] the dissolution procedures detailed below were investigated using a non-irradiated matrix and a known amount of active gold (Table III).

Before their dissolution, any surface contamination was removed from the irradiated lead samples by careful leaching with dilute nitric acid and from the silicon samples with hydrofluoric and nitric acids.

Silicon and rocks. To the test matrix, placed in a 50-ml Teflon beaker, 1·00 ml of gold carrier solution was added and the matrix dissolved in a mixture of concentrated hydrofluoric (10 ml), hydrochloric (2 ml) and nitric (10 ml) acids. After the silicon had been fumed off, two evaporations were carried out with 5-ml portions of hydrochloric acid to a volume of about 1–2 ml in order to remove oxides of nitrogen.

Lead. To the test matrix, placed in a 500-ml conical flask, 1·00 ml of gold carrier solution was added and the matrix dissolved in a mixture of glacial acetic acid (5 ml) and 100 vol. hydrogen peroxide (*ca.* 15 ml, added in 0·5-ml portions with gentle warming between the additions). The resulting solution was evaporated almost to dryness and the evaporation repeated with 15 ml of 50% v/v hydrochloric acid plus 2 drops of concentrated nitric acid, then with 15 ml of 50% v/v hydrochloric acid alone. The residue was dissolved in the minimum volume of hot concentrated hydrochloric acid (3 g of lead requires *ca.* 150 ml of acid) to obtain a perfectly clear solution. This solution was diluted to twice its volume with water and allowed to stand in an ice-bath, whereupon

TABLE III.—INVESTIGATION OF DISSOLUTION PROCEDURES

Matrix	Weight, *g*	Activity of Au added, *counts*/10 *sec*	Activity of Au recovered, *counts*/10 *sec*	Recovery, %
Silicon	1	64373	60876	94
Lead	3	16287	15696	96*
Kale	1	30154	19232	64

* After extraction with diethyl ether.

lead chloride precipitated. The supernatant liquid was decanted into a 500-ml separatory funnel, the lead chloride being washed with two 10-ml portions of 25% v/v hydrochloric acid and the washings also added to the separatory funnel. The gold was then extracted, as the chloride, by two 50-ml portions of diethyl ether. Finally, the combined ether extracts were evaporated to dryness and the residue dissolved in 20–30 ml of $1{\cdot}5 \pm 1N$ hydrochloric acid.

Biological material (kale).[14] To the test matrix, placed in a 250-ml beaker, 1·00 ml of gold carrier solution was added, followed by 2 ml of 100 vol. hydrogen peroxide. The beaker was covered with a clock glass and 5 ml of concentrated sulphuric acid carefully added *via* the beaker lip, then the beaker contents swirled gently until effervescence ceased. Next 5 ml of concentrated nitric acid were added, the beaker again swirled gently, and finally 2 ml of 70% perchloric acid added. The covered beaker was heated until white fumes appeared, then allowed to cool appreciably before adding 20 ml of *aqua regia*. Heating was resumed and evaporation continued to the appearance of white fumes of sulphuric acid. The resulting clear solution, after cooling, was diluted to about 30 ml with $1{\cdot}5 \pm 1N$ hydrochloric acid.

Extraction procedures

The dissolved samples were diluted to 20–50 ml with water or acid so as to obtain a medium of $1{\cdot}5 \pm 1N$ hydrochloric acid, then transferred to 100-ml separatory funnels. After adding 0·5 ml of 5 vol. hydrogen peroxide, extraction was carried out with 7·0 ml of copper diethyldithiocarbamate solution for about 1 min. In the case of the biological material (kale), where only 64% recovery of gold was obtained after dissolution (Table III), a volume of 5·0 ml of extractant was used so as to be below the stoichiometric requirement. To the appropriate amount of irradiated gold standard (y_s), 1·00 ml of gold carrier solution was added and the gold extracted in exactly the same way as described above for the test solutions. In the case of the samples of rock W-1 (or other very impure test materials) the organic extract obtained must be washed with $1N$ hydrochloric acid and filtered to remove the last traces of aqueous phase. The activities of exactly the same volumes of separated organic extracts from the test (a) and standard (a_s) samples were measured using the scintillation counter; the amount of gold present in the test sample (y) was then calculated from the equation

$$y = y_s \frac{a}{a_s}.$$

RESULTS

The results obtained for the various test materials are summarised in Table IV. The reproducibility in the case of the silicon, lead and kale is good. The results for the analysis of the rock W-1 differ rather more, but the difference cannot be explained by the presence of radionuclides other than that of gold in the extracts; the decay measurements of these extracts confirmed their radiochemical purity (Fig. 4). In any case, the mean value of the present experiments is in good agreement with the results of other workers on the rock W-1.

The gold concentration of the gold-doped semiconductor-grade silicon, calculated on the basis of the equilibrium segregation coefficient for gold in silicon, is *ca.* 4×10^{-2} ppm. If this estimate were to be corrected for the Burton-Slichter layer,[33] because of the rather high crystal pulling speed employed in the preparation of this particular crystal of silicon, then a figure around that found by neutron-activation analysis would be obtained. There is little doubt that the latter figure is the more precise.

As expected, the gold content of the biological material (kale) is very low; the results are in excellent agreement with those of Morris and Gupte,[12] also obtained by neutron-activation analysis. From the close agreement of our results with the figure obtained by Hoste,[24] it seems that the dissolution procedure for the high-purity lead developed by us is fully satisfactory and isotopic exchange between carrier and radio-gold formed by neutron activation has been completed.

DISCUSSION

The selectivity of the substoichiometric separation of gold using copper diethyl dithiocarbamate is very high. This fact, to be expected from theoretical considerations

Table IV

Sample	Gold-doped semiconductor-grade silicon (1153)*				
Weight, *g*	0·4472	0·5904	0·8949	1·0984	1·1429
Gold standard, *μg*	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$	$1·04 \times 10^{-1}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	14613	14613	14613	14613	14613
Activity‡‡ from gold sample (*counts*/10 *sec*)	6149	9297	10985	14016	14625
Gold found, *μg*	$4·4 \times 10^{-2}$	$6·6 \times 10^{-2}$	$7·8 \times 10^{-2}$	$9·9 \times 10^{-2}$	$10·4 \times 10^{-2}$
ppm	$9·6 \times 10^{-2}$	$11·0 \times 10^{-2}$	$8·7 \times 10^{-2}$	$9·1 \times 10^{-2}$	$9·1 \times 10^{-2}$
Mean value, *ppm*	$9·5 \times 10^{-2}$				
Results of other authors, *ppm*	—				

Sample	High-purity lead (VM_3)†				
Weight, *g*	1·6350	2·0500	2·5120	3·2270	3·6130
Gold standard, *μg*	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$	$2·08 \times 10^{-2}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	6932	6932	6932	6932	6932
Activity‡‡ from gold sample (*counts*/10 *sec*)	680	773	1315	1093	1673
Gold found, *μg*	$2·0 \times 10^{-3}$	$2·3 \times 10^{-3}$	$4·0 \times 10^{-3}$	$3·3 \times 10^{-3}$	$5·0 \times 10^{-3}$
ppm	$1·3 \times 10^{-3}$	$1·1 \times 10^{-3}$	$1·6 \times 10^{-3}$	$1·0 \times 10^{-3}$	$1·4 \times 10^{-3}$
Mean value, *ppm*			$1·3 \times 10^{-3}$		
Results of other authors, *ppm*	$1·0 \pm 0·4 \times 10^{-3}$ (ref. 24)				

Sample	Rock W-1‡			Dried leaves of kale (*Brassica oleracea*)¶‡‡‡		
Weight, *g*	1·0000	0·5000**	0·5000**	0·2000††	1·0006	1·0023
Gold standard, *μg*	$4·0 \times 10^{-2}$	$4·0 \times 10^{-2}$	$4·0 \times 10^{-2}$	$4·2 \times 10^{-2}$	$4·2 \times 10^{-2}$	$4·2 \times 10^{-2}$
Activity‡‡ from gold standard (*counts*/10 *sec*)¶¶	15237	15237	15237	15237	11609	11609
Activity‡‡ from gold sample (*counts*/10 *sec*)	1940	3269	3288	82	720	794
Gold found, *μg*	$5·1 \times 10^{-3}$	$8·6 \times 10^{-3}$	$8·6 \times 10^{-3}$	$2·1 \times 10^{-4}$	$2·5 \times 10^{-3}$	$2·7 \times 10^{-3}$
ppm	$0·5 \times 10^{-2}$	$1·7 \times 10^{-2}$	$1·7 \times 10^{-2}$	$1·1 \times 10^{-3}$	$2·5 \times 10^{-3}$	$2·7 \times 10^{-3}$
Mean value, *ppm*		$1·1 \times 10^{-2}$***			$2·1 \times 10^{-3}$	
Results of other authors, *ppm*	$1·1 \times 10^{-2}$ (ref. 26)	$8·4 \times 10^{-3}$ (ref. 9)	$4·9 \times 10^{-3}$ (ref. 28)		$2·2 \times 10^{-3}$††† (ref. 12)	

* Provided by Mullard Southampton Works, Southampton, England.
† Provided by Professor Dr. J. Hoste, University of Ghent, Ghent, Belgium.
‡ Provided by U.S. Geological Survey, Washington, D.C., U.S.A.
¶ Provided by Dr. H. J. M. Bowen, The University, Reading, England.
** Two equal aliquots from a 1-g sample after dissolution.
†† This constituted a preliminary test. The sample was irradiated in a quartz ampoule and, apart from the gold carrier solution, half quantities of the reagents detailed in the dissolution procedure (p. 7) were used. The final evaporation was taken nearly to dryness and the residue taken up in 2 ml of concentrated hydrochloric acid plus 10 ml of water. A 59% recovery of gold was obtained under these conditions (*cf.* Table III).
‡‡ All samples were counted for a period sufficient to obtain a total of at least 10,000 counts.
¶¶ The stated activities are the mean of two standards.
*** Obtained by averaging the results from the two 0·5-g "samples," then averaging this figure with the result from the 1-g sample.
††† Average of $2·1 \times 10^{-3}$, $2·0 \times 10^{-3}$, $2·4 \times 10^{-3}$, $2·4 \times 10^{-3}$ ppm (ref. 12). Samples heated at 80° for *ca.* 4 hr before being weighed for analysis.
‡‡‡ Samples weighed without drying; material reported to have water content of 3–5%.

(see p. 830), has been confirmed not only by the preliminary studies (Tables I and II) but also by checking the radiochemical purity of the organic extracts obtained from the various test samples (Fig. 4). Furthermore, the high-purity lead is known to contain Ag, As, Cu, Hg, Sb and Tl in trace amounts (determined by neutron-activation analysis)[24] and the rock W-1 to contain Ag, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, F, Ga, Ge, In, La, Li, Mo, Nb, Nd, Ni, Pb, Pd (0·02 ppm), Rb, Re, Sb, Sc, Sm, Sn,

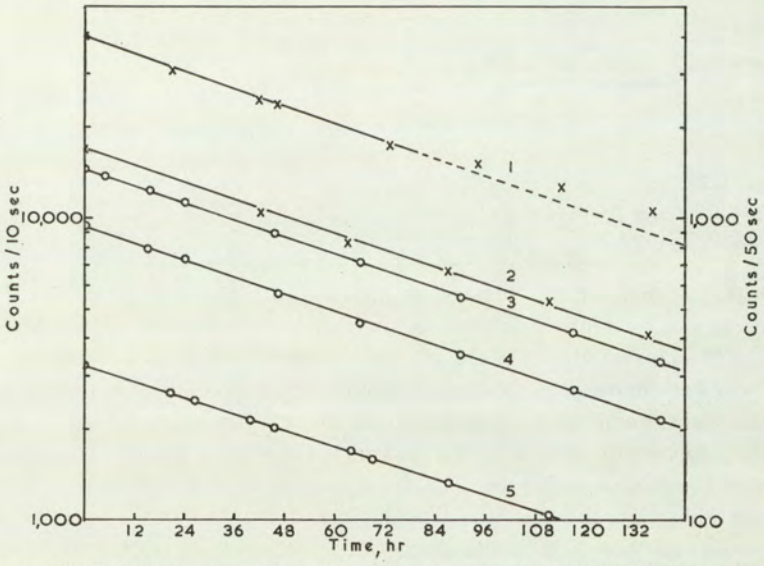

FIG. 4.—Typical decay curves of the chloroform extracts of gold diethyldithiocarbamate obtained from various irradiated materials (samples 1 and 2 refer to the right-hand vertical scale; samples 3–5 refer to the left-hand vertical scale; all extracts were measured for a period sufficient to obtain a total of at least 5,000 counts):

1—biological material (kale),
2—high-purity lead,
3—gold-doped semiconductor-grade silicon,
4—gold standard,
5—rock W-1.

It would appear from curve 1 that there is a long-lived component associated with the separated ^{198}Au activity. The nature of this component is (at this time) unknown, but we believe it will make very little difference to the results calculated for gold in kale.

Sr, Ta, Th, Tl, U, V, W, Y, Yb, Zn and Zr at trace levels (0·001 to 300 ppm) and large amounts of Fe, Mg, Ca, Na, K, Ti, P and Mn, the main constituents being SiO_2 and Al_2O_3.[29]

As was mentioned above, platinum and palladium are extracted simultaneously with gold, but these elements are activated by thermal neutrons to a much lesser extent than is gold[7] and the half-lives of their radioisotopes formed by (n, γ) reactions are shorter than that of ^{198}Au (Table V). Moreover, by setting the discriminator level of the scintillation counter to the value corresponding to 0·25 MeV, allowing the activity to decay sufficiently for the ^{199}Pt to have disappeared, and still counting all the radiation above this level, the sensitivity of determination of gold is only slightly reduced and interference from platinum is almost completely avoided. (There will be a very small contribution from the 0·28 MeV γ-ray of 20 hr ^{197}Pt.) This precaution is only necessary in the case of a platinum matrix. Also, a method proposed by Morris

and Killick[27] or its combination with the present method can be recommended with this matrix.

TABLE V[32]

Stable isotope	Product of (n, γ) reaction	Half-life	Principal γ-energies, *MeV*
^{196}Pt	^{197m}Pt	80 min	0·337
^{196}Pt	^{197}Pt	20 hr	0·077 (19%)
			0·19 (2·5%)
			0·28 (0·6%)
^{198}Pt	^{199}Pt	30 min	0·074
			0·197
			0·318
			0·540
^{108}Pd	^{109}Pd	13·5 hr	—
^{110}Pd	^{111m}Pd	5·5 hr	0·17
^{110}Pd	^{111}Pd	22 min	—

Recently, a very simple substoichiometric radiochemical procedure for determination of gold by neutron-activation analysis has been published by Alimarin and Perezhogin.[30] This method, based on the extraction of gold chloride using tetraphenylarsonium chloride in chloroform solution, is especially interesting because it is the first substoichiometric separation to employ an extractable ion-association compound. Disadvantages of Alimarin and Perezhogin's method compared to that proposed in the present paper are that the separation is more affected by the presence of chloride ions (more than 0·5*N* hydrochloric acid cannot be used) and the volume of aqueous solution from which the extractions are made is relatively small (10 ml). Various high-purity metals (copper, zinc, lead, bismuth) were analysed by Alimarin and Perezhogin, but no interference studies were carried out.

CONCLUSION

Metallic salts of diethyldithiocarbamic acid in chloroform solution are very suitable for substoichiometric separations. Using these reagents it has been possible to develop substoichiometric methods for arsenic[31] and now gold; these separations are far simpler than previously published radiochemical procedures for the two elements. Unfortunately, quantitative extraction data (extraction constants) of metal diethyldithiocarbamates are still not available and for this reason it is not possible to calculate the theoretical optimum conditions for the separation and selectivity of the method now proposed for gold and to compare them with those conditions found experimentally. For the same reason, conditions for the substoichiometric determination of platinum, silver, mercury, thallium and tin by neutron-activation analysis cannot be predicted, although the extraction of these metals in the form of their diethyldithiocarbamates seems to be suitable for this purpose.

Our future work will be directed towards applying the solvent extraction of gold, using a substoichiometric amount of a metallic salt of diethyldithiocarbamate in an organic solvent, to the determination of trace amounts of gold by isotope dilution. This type of separation would also seem to have potentialities as a basis for the radiometric titration or spectrophotometric determination of gold.

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the Birmingham College of Advanced Technology for the provision of a visiting lectureship (J.R.) and a research assistantship (D.A.B.) which enabled the work reported to be carried out.

Zusammenfassung—Eine hochselektive, schnelle, einstufige radiochemische Abtrennmethode für Gold wurde entwickelt. Sie beruht auf flüssig–flüssig–Extraktion von Gold-diäthyldithiocarbamat aus 0,01 bis 10 N Schwefel- oder Salzsäure mit einer unterstöchiometrischen Menge Kupfer-diäthyldithiocarbamat in Chloroform. Die Abtrennung wurde auf die Bestimmung von Goldspuren durch Neutronenaktivierungsanalyse in hochreinem Blei, im Gestein W-1, in Gold-dotiertem Halbleitersilicium und in einer Probe von biologischem Material (Grünkohl) angewandt. Goldmengen bis herunter zu $2 \cdot 10^{-10}$ g wurden bestimmt.

Résumé—On a élaboré une technique de séparation radiochimique de l'or en un seul stade, hautement sélective et rapide. Elle est basée sur l'extraction par solvant du diéthyldithiocarbamate d'or à partir d'un milieu 0,01–10*N* en acide sulfurique ou chlorhydrique, en utilisant une quantité substoechiométrique de diéthyldithiocarbamate de cuivre en chloroforme. On a appliqué la séparation au dosage de traces d'or par analyse par activation de neutrons dans le plomb hautement pur, la roche W-1, le silicium qualité semi-conducteur dopé â l'or, et un produit biologique (chou vert). On a dosé des quantités d'or ne dépassant pas 2×10^{-10} g.

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SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF GOLD BY RADIOACTIVE ISOTOPE-DILUTION ANALYSIS

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Summary—A radioactive isotope-dilution method for the determination of traces of gold has been developed. It is based on the solvent extraction of gold diethyldithiocarbamate from 0·5*N* sulphuric acid containing ascorbic acid, by means of a substoichiometric amount of zinc diethyldithiocarbamate in chloroform. The separation has been applied to the analysis of gold-doped semiconductor-grade silicon and of gold-bearing ores. Amounts of gold down to 5×10^{-7} g/20 ml of test solution can be determined.

THE success of a neutron-activation method for the substoichiometric determination of traces of gold[1] suggested that an isotope-dilution method involving the same separation procedure could be developed. Isotope-dilution analysis has been applied to the determination of a number of elements,[2] but no reference could be found to its application to gold.

EXPERIMENTAL

Apparatus

Scintillation counter. The detector used was a 1·75-in. diameter × 2 in. NaI(Tl) well-type crystal (well-volume 5 ml), associated with a single channel gamma-ray spectrometer. A discriminator voltage setting corresponding to 0·07 MeV ensured a high sensitivity of counting the ^{198}Au activity.

Reagents

All reagents were prepared from analytical reagent grade chemicals unless otherwise stated. Electronic grade nitric and hydrochloric acids and micro analytical reagent grade sulphuric acid were used.

Labelled gold stock solution (1·0 *μg/ml in* 2·5*M hydrochloric acid*). About 10 mg of metallic gold (metal leaves *ca.* 0·1-*μ* thick, General Chemical Co., Division of Fisons Scientific Apparatus Ltd., Loughborough, England) were irradiated in a flux of 6×10^{11} neutrons cm^{-2} sec^{-1} for 6 hr (Universities of Manchester and Liverpool Research Reactor). The amount of ^{198}Au produced by ^{197}Au(n, γ)^{198}Au($t_{1/2}$ = 2·7 days; σ = 98 barns; β^- = 0·96 MeV; γ = 0·41 MeV)[3] was sufficient for experiments over about 17 days. After irradiation the gold was dissolved in *aqua regia*, and the solution was twice evaporated almost to dryness with hydrochloric acid to remove oxides of nitrogen. The solution was then diluted appropriately with 2·5*M* hydrochloric acid.

Non-labelled gold stock solution (1·0 *μg/ml in* 2·5*M hydrochloric acid*). Prepared from a weighed amount of non-irradiated gold as described above.

Gold solutions of lower concentrations were prepared by dilution of the stock solutions.

Zinc diethyldithiocarbamate solution (1×10^{-4}*M*). Prepared by mixing 25 ml of zinc sulphate solution (0·0285 g of the heptahydrate) with 125 ml of an aqueous solution of sodium diethyldithiocarbamate [0·0225 g, preferably freshly purified (see p. 880)] containing 5 ml of 0·2*M* sodium acetate/acetic acid buffer (pH 4·7). The precipitate formed was extracted with two 200-ml portions of chloroform, and the combined extracts diluted to 500 ml with the same solvent. The reagent was standardised by a spectrophotometric extractive titration with 10^{-4}*M* copper solution (prepared by

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dilution of $10^{-2}M$ copper sulphate standardised iodometrically). The absorbance of the copper diethyldithiocarbamate was measured at 440 mμ (zinc diethyldithiocarbamate shows no absorbance at this wavelength).

Distilled water. The water used must be as pure as possible, and we have found that double distilled as obtained from a Scorah Type 4 glass distillation unit (L.V.D. Scorah, 44 Northfield Road, Birmingham 30, England) satisfactory. To check the purity a sample was extracted with dithizone ($5 \times 10^{-6}M$ in chloroform). No change in the green colour of the reagent was taken as the criterion of purity.

DEVELOPMENT OF METHOD

Preliminary experiments

Our neutron-activation studies[1] showed that 0·01–10N sulphuric or hydrochloric acid was a suitable medium from which to extract gold reproducibly with copper diethyldithiocarbamate in chloroform. Preliminary experiments showed that the following factors were of importance in the

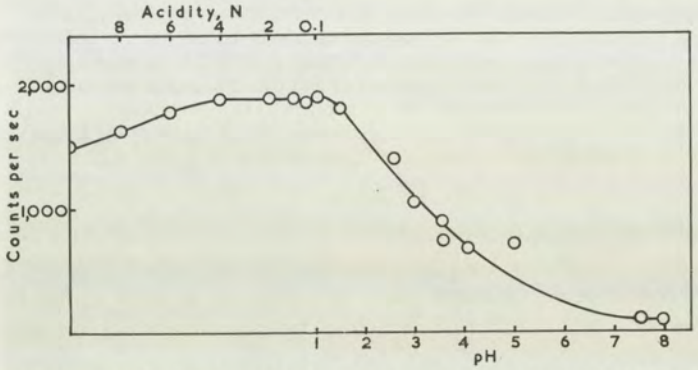

FIG. 1.—Influence of acidity on the substoichiometric extraction of gold from sulphuric acid with zinc diethyldithiocarbamate in chloroform.

extraction of gold under the conditions required for isotope-dilution analysis.

1. Sulphuric acid is a better solvent medium than hydrochloric acid—chloride competes more strongly with chelating agent for the gold in the absence of a gold-carrier.

2. Zinc diethyldithiocarbamate gives better extraction of gold than does copper diethyldithiocarbamate—the difference in extraction constants is greater for zinc and gold than for copper and gold.

3. The presence of a mild reducing agent, ascorbic acid, is particularly advantageous—reduction of gold to gold(I) seems necessary for complete complex formation.

Reproducibility

The optimum conditions for a reproducible substoichiometric extraction of gold diethyldithiocarbamate in the presence of ascorbic acid were next established.

Any sulphuric acid concentration from 0·1 to 4N was found to be suitable (Fig. 1). For all further experiments 0·5N sulphuric acid (containing 1 ml of 1% ascorbic acid solution) was used. Extraction equilibrium was reached in 1·5 min with 1·25 μg of gold and in 2 min with 0·1 μg (Fig. 2). An extraction time of 5 min was therefore used in all further experiments.

Stability of solutions. The reproducibility of the substoichiometric separation using a labelled gold solution of 1·0 μg/ml was good (Fig. 3, upper curve), but when the gold concentration was 0·1 μg/ml the reproducibility became poor. This was traced to two causes: the labelled gold solution in 1M hydrochloric acid was slowly hydrolysing, and the zinc diethyldithiocarbamate solution in chloroform ($5 \times 10^{-8}M$) was not very stable.

The maximum period during which different solutions of gold and zinc diethyldithiocarbamate were found to be stable (not more than 10% change from the initial concentration) is given in Table I. If the sodium diethyldithiocarbamate was purified to remove oxidation products,[4] the zinc diethyldithiocarbamate solution prepared from it was more stable ($2{\cdot}5 \times 10^{-7}M$ solution stable for at least 3 hr).

With a freshly labelled gold solution (0·1 μg/ml) and fresh reagent solution ($5 \times 10^{-8}M$) good reproducibility of separation was now achieved (Fig. 3, lower curve), but below this concentration reproducibility was poor.

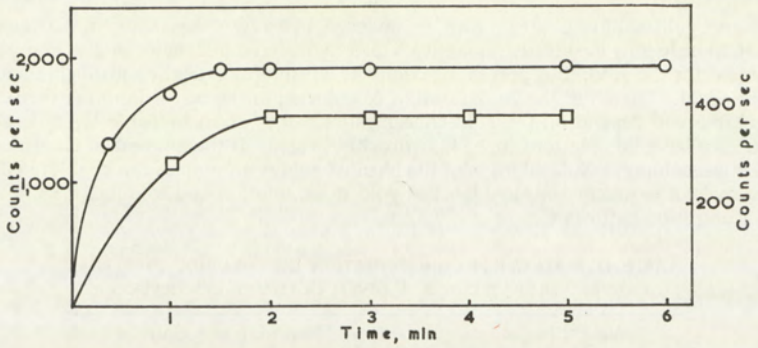

FIG. 2.—Time necessary to reach extraction equilibrium in the substoichiometric extraction of gold with zinc diethyldithiocarbamate in chloroform (20 ml of 0·5*N* sulphuric acid).
○—Left-hand axis, 1·25 μg of gold;
□—Right-hand axis, 0·10 μg of gold.

TABLE I.—STABILITY OF GOLD AND ZINC DIETHYLDITHIOCARBAMATE SOLUTIONS

Solution	Concentration		Maximum period of stability, *hr*
	μg/ml	*M*	
Gold in 2·5*M* hydrochloric acid	5·40		504 (21 days)
	1·06		53
	0·12		24
Zinc diethyldithiocarbamate in chloroform		1×10^{-6}	4
		1×10^{-7}	1·5
		5×10^{-8}	0·5
		1×10^{-8}	0·25

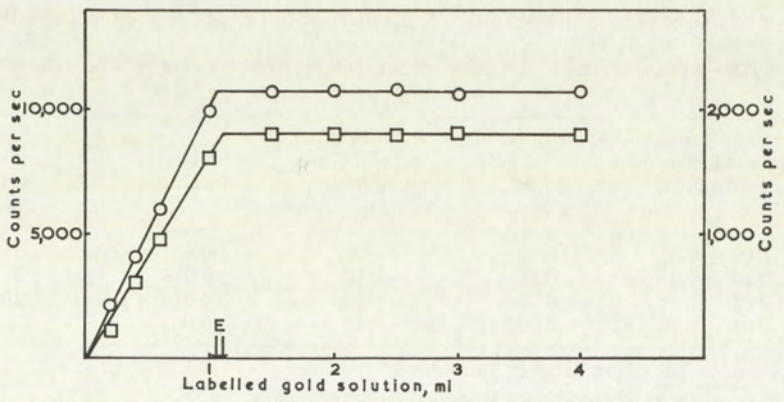

FIG. 3.—Reproducibility of the substoichiometric extraction of gold with zinc diethyldithiocarbamate in chloroform (20 ml of 0·5*N* sulphuric acid; 3 ml of organic phase separated for counting; *E* denotes the equivalence point).
○—Left-hand axis, extraction of labelled gold solution (1·0 μg/ml) with 5 ml of $5 \times 10^{-7}M$ zinc diethyldithiocarbamate;
□—Right-hand axis, extraction of labelled gold solution (0·1 μg/ml) with 5 ml of $5 \times 10^{-8}M$ zinc diethyldithiocarbamate.

Role of chloride ions

Very dilute gold solutions are known to undergo hydrolysis especially if the temperature is increased. Chloride ions in sufficient quantity retard hydrolysis, but they can also compete with the chelating agent for the gold, thus preventing complete consumption of the substoichiometric amount of chelating agent. Therefore the concentration of chloride in the test solution is very critical, and that permissible will depend on the gold concentration; it is given in Table II. It is advisable to prepare the labelled gold solutions in 2·5*M* hydrochloric acid. If the amount of chloride ions introduced into a test solution by the addition of the labelled gold is more than can be tolerated (Table II), it is best to make a more concentrated labelled gold stock solution and to dilute it with water to the desired concentration before use.

TABLE II.—MAXIMUM CONCENTRATION OF CHLORIDE IONS THAT CAN BE TOLERATED FOR A GIVEN GOLD CONCENTRATION

Weight of gold in 20 ml of test solution, μg	Maximum concentration of chloride ions, M
1·0	0·36
0·5	0·18
0·2	0·06
0·1	0·05

Accuracy and precision

To a series of 50-ml separatory-funnels 20 ml of 0·5*N* sulphuric acid were added followed by 1·0 ml of labelled gold solution (1·06 μg/ml) and 1·0 ml of non-labelled gold solution (1·00 μg/ml). Then 1 ml of 1 % ascorbic acid solution was added followed by 5 ml of $5 \times 10^{-7}M$ zinc diethyldithiocarbamate in chloroform (substoichiometric amount). The funnels were shaken for 5 min, and 3·0 ml of the organic phase were separated for counting (activity A_2). An extraction was next made under the same conditions but with 2·0 ml of labelled gold solution and no non-labelled gold. The activity (A_1) of an equal volume of the organic phase was measured; this was sometimes referred to as the standard. The same procedure was used with labelled gold solutions of 0·1, 0·05, and 0·02 μg/ml concentration, the concentration of the chelating reagent being reduced accordingly.

The weight of non-labelled gold determined (x) can be calculated from the substoichiometric formula applied to isotope dilution[14]

$$x = y\left(\frac{A_1}{A_2} - 1\right)$$

where $y =$ the weight of labelled gold used. A summary of our results is given in Table III.

TABLE III.—ACCURACY AND PRECISION OF SUBSTOICHIOMETRIC DETERMINATION OF GOLD BY ISOTOPE-DILUTION ANALYSIS

Weight (x) of non-labelled gold added, μg	Weight (y) of labelled gold added, μg	Weight ($\bar{x}$)* of non-labelled gold found, μg	Standard deviation, s†	Number of tests, n
1·00	1·06	1·03	0·057	15
0·10	0·11	0·10	0·016	15
0·05	0·05	0·06	0·013	10
0·01	0·02	0·01	0·003	6

* $\bar{x}$ = mean weight of non-labelled gold found.

† $s = \sqrt{\Sigma\Delta^2/n - 1}$, where Δ is the deviation from the mean.

Selectivity

The selectivity of the substoichiometric separation was investigated in the presence of a number of ions which either have extraction constants similar to that for the gold-diethyldithiocarbamate system,[5] or cause interference by some other mechanism, *e.g.*, reduction of the gold or oxidation of the diethyldithiocarbamate. The effect of reagents likely to be present after the dissolution of various test samples was also studied.

The procedure was that described under *Accuracy and precision* except that 1 ml of labelled gold solution (1·00 μg/ml in 2·5*M* hydrochloric acid) was used together with 100 or 1000 μg of the foreign ion to be examined. No non-labelled gold was added and the extraction was carried out with 4 ml of $2{\cdot}5 \times 10^{-7}M$ chelating agent, the activity of 2·5 ml of the organic phase being measured. Ideally, a result of $x = 0$ should be obtained because no non-labelled gold was present. In practice, if $-0{\cdot}1 > x > +0{\cdot}1$ μg the foreign ion was considered to interfere. The results of the selectivity studies are summarised in Table IV.

TABLE IV.—INFLUENCE OF FOREIGN IONS ON THE SUBSTOICHIOMETRIC EXTRACTION OF GOLD WITH ZINC DIETHYLDITHIOCARBAMATE

Foreign ion present		Foreign ion interfering	
1000 μg	100 μg	1000 μg	100 μg
Ag(I) As(III) As(V) Bi(III) Cd(II) Co(II) Cr(VI) Cu(II) Fe(II) Fe(III) Hg(II) In(III) Mo(VI) Ni(II) Pb(II) Pd(II) Pt(IV) Se(IV) Sb(III) Sb(V) Sn(II) Sn(IV) Te(IV) Tl(I) Zn(II)	Ag(I) Bi(III) Cr(VI) Cu(II) Hg(II) Pb(II) Pt(IV) Se(IV) Sb(III) Sn(II) Te(IV)	Ag(I)† Bi(III)† Cr(VI)† Cu(II)† Hg(II) Pd(II)§ Pt(IV) Se(IV) Sb(III) Sn(II)† Te(IV)	Ag(I)† Cu(II)‡ Hg(II)‡ Pd(II)§ Se(IV) Sb(III) Sn(II)† Te(IV)
6, 8 and 10*M* HNO_3 2*M* HBr 1 ml of 0·1*M* EDTA 1 ml of 1% DMG* 1 ml of 40% HF		2 ml of 10*M* HNO_3 1 ml of 2*M* HBr Cl^- (see Table II)	

* DMG = Dimethylglyoxime.
† Interference removed by preliminary extraction of gold with diethyl ether.
‡ Interference prevented by addition of EDTA.
§ Interference removed by extraction with dimethylglyoxime in chloroform.

Elimination of interferences

Three methods were investigated for eliminating interferences.

Preliminary extraction of gold. Extraction of gold into diethyl ether from chloride or bromide solutions is well known.[6–8] Some authors prefer the use of isopropyl ether[7] or ethyl acetate.[8] According to Morrison and Freiser[6] gold can be quantitatively extracted as $HAuCl_4$ into diethyl ether from 1·5–3*M* hydrochloric acid.

We found that when 1·0 μg of gold in 10 ml of 2*M* hydrochloric acid was shaken with 20 ml of diethyl ether for 3 min, about 80% of it was extracted. The interferences were studied by repeating this extraction in the presence of 100 or 1000 μg of the foreign ions concerned. The ether phase was separated and washed with 5 ml of 2*M* hydrochloric acid, added to 0·5 ml of 3*M* hydrochloric acid and heated at 50° on a water-bath to remove the ether. The resulting solution was diluted to 20 ml with 0·5*N* sulphuric acid and the gold separated and determined as under *Accuracy and precision*. Our results are summarised in Table IV.

If the hydrochloric acid concentration during evaporation of the diethyl ether was less than 3*M* hydrolysis occurred and not all the gold was in a form extractable by the chelating agent. Hydrolysis also occurred if sulphuric or nitric acid was used, even if they were more concentrated than 3*N*. During evaporation of the ether, gold was lost if chloride was absent. Therefore, chloride must be present to prevent hydrolysis and the loss during evaporation. The lowest amount of gold for which 0·5 ml of 3*M* hydrochloric acid would not interfere in the final separation was 0·5 μg (Table II).

The possibility of stripping the gold from diethyl ether solutions was studied; from an ether solution (20 ml) containing 0·7–0·8 μg of gold, half the gold could be transferred with two 20-ml portions of water, each shaken for 3 min with the ether phase. Before the substoichiometric separation it was then necessary to scrub with chloroform to remove traces of diethyl ether and to make the solution 0·5*N* with respect to sulphuric acid; if the ether was not removed it diluted the chelating agent, leading to erroneous results.

This stripping method was successful for solutions initially containing 1 μg of gold in 10 ml of 2*M* hydrochloric acid, the final concentration of gold being 0·4 μg/20 ml of solution which is near the lower limit for the method (0·1 μg/20 ml). The evaporation procedure gave about 0·8 μg of gold in 20 ml of test solution and therefore was preferred.

The extraction of gold from bromide solutions was then examined. Gold was more efficiently extracted by diethyl ether (*ca.* 80%) than by isopropyl ether (*ca.* 70%) with the same volumes and extraction times. The degree of stripping by water was higher from isopropyl ether solutions (*ca.* 85%) than diethyl ether solutions (*ca.* 70%). Even so, neither the evaporation nor the stripping method was successful, because traces of bromide seriously interfered in the final substoichiometric separation.

EDTA. Prevention of the interference of copper(II), bismuth(III), and mercury(II) by addition of 1 ml of 0·1*M* EDTA to the test solution before the substoichiometric separation (20 ml of 0·5*N* sulphuric acid; no ascorbic acid present) was studied. In 0·5*N* sulphuric acid there was no effect but in 0·1*N* sulphuric acid these interferences were overcome (Table IV), which can be explained from the conditional formation constants of their EDTA complexes.[10] The sulphuric acid must not be less than 0·1*N*, the lowest value suitable for the substoichiometric separation (Fig. 1).

Dimethylglyoxime. Many authors[11–13] have separated palladium from aqueous solutions of gold by extracting its dimethylglyoximate into chloroform. When 3 ml of 1% aqueous sodium dimethylglyoximate solution were added to the test solution before the substoichiometric separation (20 ml of 0·5*N* sulphuric acid; no ascorbic acid present) and the solution was let stand for 30 min, interference from palladium was eliminated by extracting the palladium complex with three 10-ml portions of chloroform, shaking the mixture for 3 min each time (Table IV).

ANALYSIS OF TEST SAMPLES

Because the concentration of chloride ions must be kept to a minimum, attempts were made to dissolve a gold-doped semiconductor-grade silicon sample in a mixture of nitric and hydrofluoric acids. Complete dissolution was achieved but a considerable loss of gold was incurred (*ca.* 50%). It was therefore necessary to include chloride ions, and after dissolution to reduce their concentration to a tolerable level by a diethyl ether extraction as used for the elimination of interfering species.

Procedure

To the test sample in a 50-ml Teflon beaker was added a weight (y) of labelled gold approximately equal to the weight of gold expected in the sample. The test sample was then dissolved, initially at room temperature and finally with gentle heating, in a mixture of nitric acid (10 ml) and hydrochloric acid (2 ml) with gradual addition of hydrofluoric acid (10 ml). The solution was then evaporated to about 0·5 ml and the evaporation repeated twice, each time after addition of 5 ml of hydrochloric acid. The resulting solution was diluted with water and 2*M* hydrochloric acid to give finally 10 ml of 2*M* hydrochloric acid solution. The activity of this solution was measured before extraction so that the recovery after the dissolution could be checked: it was at least 95% for each sample analysed.

The test solution, prepared as described above, was transferred to a 100-ml separatory funnel and shaken with 20 ml of diethyl ether for 3 min. The ether phase was scrubbed with 5 ml of 2*M* hydrochloric acid and transferred to a 50-ml beaker; then 0·5 ml of 3*M* hydrochloric acid was added and the solution heated at 50° on a water-bath to remove the ether. The resulting solution was transferred to a 100-ml separatory funnel and diluted to 20 ml with 0·5*N* sulphuric acid. If necessary, EDTA was added and palladium removed with dimethylglyoxime at this stage. Finally, 1 ml of 1% ascorbic acid solution was added and the gold extracted by a substoichiometric amount of zinc diethyldithiocarbamate solution in chloroform (4 ml of $2{\cdot}5 \times 10^{-7}M$ for gold-bearing ores; 4 ml of $5 \times 10^{-8}M$ for gold-doped semiconductor-grade silicon). The extractions were carried out for 5 min, then an aliquot of the organic phase (3·0 ml in each case) was removed for counting (A_2).

For the standard (run simultaneously) the same weight (y) of labelled gold was taken as that added to the sample, and it was extracted under the same conditions as for the test sample, and the same volume of organic phase was separated for counting (A_1). The weight of gold in the test sample (x) was then calculated, using the substoichiometric equation given above. The results of our analyses are given in Table V.

CONCLUSION

The method is capable of determining gold down to 0·1 μg/20 ml of test solution, but the need to have chloride ions present during dissolution of samples and also to prevent hydrolysis raises the lower limit to 0·5 μg/20 ml of test solution. The smallest amount of gold we have actually determined in a test sample by isotope dilution is $1{\cdot}45 \times 10^{-7}$ g, compared with 2×10^{-10} g by our neutron-activation method.[1] The limit of detection for gold is about three orders of magnitude lower by neutron activation, which is to be expected.

TABLE V—RESULTS OF ANALYSIS OF TEST SAMPLES

Sample*	Gold-bearing ore RSM 25†				
Weight, *g*	1·0061	0·9857	0·9830	0·9941	0·9872
Gold standard, *μg*	1·07	1·07	1·07	1·07	1·07
Activity from gold standard, *counts/sec*	255	255	255	637	637
Activity from sample, *counts/sec*	71	68	63	147	184
Gold found, *ppm*	2·78	3·00	3·32	3·58	2·66
Mean value, *ppm*			$3·0_7$		
Result of other authors, *ppm*			3·7‡		
Sample*	Gold-bearing ore RSM 349†				
Weight, *g*	1·0073	1·0133	0·9798	0·9760	0·9908
Gold standard, *μg*	1·07	1·07	1·07	1·07	1·07
Activity from gold standard, *counts/sec*	1098	1098	1098	637	637
Activity from sample, *counts/sec*	204	193	231	125	107
Gold found, *ppm*	4·70	4·98	4·10	4·48	5·36
Mean value, *ppm*			$4·7_2$		
Result of other authors, *ppm*			3·7‡		
Sample*	Gold-doped semiconductor-grade silicon 1153§				
Weight, *g*	1·2787		1·2196		1·8894
Gold standard, *μg*	0·49		0·49		0·49
Activity from gold standard, *counts/sec*	206		206		206
Activity from sample, *counts/sec*	159		158		154
Gold found, *ppm*	0·11		0·12		0·09
Mean value, *ppm*			0·11		
Result of other authors, *ppm*			$0·09_5$¶		

* All samples were counted for a period sufficient to yield a total of at least 10,000 counts; activity from gold standard is the mean of at least 3 results.

† Provided by Royal School of Mines, Imperial College, London, England.

‡ By fire assay at Royal School of Mines, using a factor-weight sample of 32·67 g.

§ Provided by Mullard Southampton Works, Southampton, England.

¶ See reference 1.

Antimony(III), selenium(IV), and tellurium(IV) interfered if present in amounts 100 times that of the gold (w/w), and mercury(II) and platinum(IV) if present in amounts 1000 times that of the gold (Table IV).

The results obtained from the analysis of the gold-doped semiconductor-grade silicon sample (Table V) were in good agreement with those previously found by neutron activation.[1] Those for the gold-bearing ores compared reasonably well with the values from fire assay, considering the large difference in the weights of sample taken for the two methods. Sample RSM 25 contains *ca.* 12 ppm of silver and RSM 349 *ca.* 11 ppm of silver, interference from which is eliminated during the extraction with diethyl ether. No interfering elements were known to be present in the semiconductor silicon sample.

If amounts of gold greater than about 10^{-6} g are to be determined, the use of radioisotopes generally offers no advantages over spectrophotometric methods. Our investigations[9] into a spectrophotometric titration procedure for gold, based on solvent extraction of its diethyldithiocarbamate into chloroform, indicated it had no advantage over existing spectrophotometric methods for this element.

Work is now in progress to establish the composition of the gold complexes extracted with diethyldithiocarbamic acid and dithizone under the various conditions that have been used in development of our neutron-activation and isotope-dilution methods for gold.

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Zusammenfassung—Eine Methode der Verdünnung mit einem radioaktiven Isotop zur Bestimmung von Goldspuren wurde entwickelt. Es beruht auf der Extraktion von Golddiäthyldithiocarbamat aus Ascorbinsäure enthaltender 0,5 M Schwefelsäure mit einer unterstöchiometrischen Menge Zinkdiäthyldithiocarbamat in Chloroform. Die Abtrennung wurde auf die Analyse von Gold-dopiertem Halbleitersilicium und von goldführenden Erzen angewandt. Goldmengen bis herunter zu $5 \cdot 10^{-7}$ g/20 ml Probelösung können bestimmt werden.

Résumé—On a élaboré une méthode radioactive par dilution isotopique pour le dosage de traces d'or. Elle est basée sur l'extraction par solvent du diéthyldithiocarbamate d'or à partir d'acide sulfurique 0,5 *N* contenant de l'acide ascorbique, au moyen d'une quantité substoechiométrique de diéthyldithiocarbamate de zinc en chloroforme. On a appliqué la séparation à l'analyse du silicium qualité semiconducteur dopé à l'or et à celle de minerias aurifères. On peut doser des quantités d'or aussi faibles que 5×10^{-7} g/20 ml de solution essai.

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