COPRECIPITATION WITH NICKEL CYCLOHEPTANEDIONEDIOXIMATE

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
March 1975

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TO MY PARENTS

DOCTOR OF PHILOSOPHY (1975)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Coprecipitation with nickel cycloheptanedionedioximate

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NUMBER OF PAGES: xiv, 225

SCOPE AND CONTENTS:

The development of a new PFHS (precipitation from homogeneous solution) method for the determination of nickel is reported. Cycloheptanedionedioxime was generated from 1,2-cycloheptanedione and hydroxylamine in solution in the presence of nickel ions to produce nickel cycloheptanedionedioximate crystals. The reported method of synthesis of 1,2-cycloheptanedione was modified in order to obtain a pure product.

We report the results from kinetic studies on the nickel cycloheptanedionedioximate precipitation reaction both in the absence and in the presence of two foreign ions, cobalt(II) and copper(II).

The developed PFHS method was useful in studies on the coprecipitation of cobalt and copper with nickel cycloheptanedionedioximate. Distribution diagrams were prepared using the two classical distribution laws for both systems studied. None of the limiting laws provided a satisfactory explanation of the observed data. Deviations observed in the behaviour of homogenous distribution coefficient and logarithmic distribution coefficient, D and λ, are interpreted in terms of kinetic parameters. The functional relationship between D and λ and the rate of nickel cycloheptanedionedioximate

precipitation is reported.

A kinetic model, which relates the rate of precipitation per particle and the distribution coefficients was also tested in both co-precipitation systems. The model was found to be useful only to a limited extent.

ACKNOWLEDGEMENTS

The author sincerely thanks Dr. O.E. Hileman, Jr. for his advice, assistance and understanding during the course of this study.

She also expresses her appreciation to Dr. J.H. Crocket and Dr. K. Fritze for their advice.

She would like to thank the other members of the research group for their useful discussions and especially for the lasting friendships which she gained by offering them doughnuts and cookies.

Study leave granted by the Rangoon Arts and Science University, Burma, and the financial assistance provided by the Canadian International Development Agency are gratefully acknowledged.

The author is also grateful to Stephen Lee for his encouragement and assistance during the final stages of this project.

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I.A.(1) Conventional precipitation method

The phenomenon of precipitation, so familar from our experience in qualitative analysis, is in reality one of the most complicated processes we deal with. As Professor Diehl's remark suggests —

> "The reaction between nickel salts and the organic compound dimethylglyoxime, yielding the brilliant red insoluble nickel compound familiar to all who have studied qualitative analysis was discovered by the Russian chemist Tschugaeff in 1905. The striking beauty of the compound and its remarkable insolubility are frequent cause of comment. No less striking, however, is the very anomalous chemical character of the compound and the remarkable change its advent made on the analytical chemistry of the metals, particularly that of nickel.----"*

there are many aspects of precipitation processes that scientists have been trying to understand. Even though the reaction seems apparently simple in a precipitation procedure, scientists have encountered numerous problems in understanding, during the normal stages of nucleation and crystal growth. And yet, gravimetric analysis has been the most fundamental and the most applied method known to chemists. Gravimetry, in fact, is one of the oldest methods known for the separation and

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*Quoted from the introduction of the monograph by H. Diehl "The Application of Dioximes to Analytical Chemistry", The G. Frederick Smith Chemical Co., Columbus, Ohio, 1940.

determination of chemical compounds. Though new and rapid instrumental techniques are being developed in the present day of modern technology, there are still occasions where a gravimetric determination is the most useful method of analysis. Despite the occasional lengthy and tedious procedure, it is well recognized as the most accurate and reliable means of chemical analysis.

Since the development of organic chelating agents (in the Forties) which are sensitive to some metals, the application of gravimetric procedures has been extended significantly. The ability of a reagent to precipitate certain metal ions is generally recognized although the complete story of precipitation process is seldom explained.

A gravimetric method, however, can be used only if it fulfills the following general requirements: (1) the precipitation must be complete; (2) the precipitate finally weighed must be a pure substance of known chemical composition. The purity of a precipitate may be affected by coprecipitation and post-precipitation processes as well as other factors such as particle size, solubility, foreign ions, specificity etc. The direct addition of a precipitant to a solution, which is the usual procedure in a conventional procedure, results in a heterogeneity of conditions. In the vicinity where the precipitant has been introduced, the formation of the solid phase takes place under conditions such that the solution concentrations vary between very wide limits. Precipitates nearly always carry down certain amounts of soluble impurities and thus the problem of the contamination of precipitates has always been a major aspect of investigation in gravimetric separation.

A new gravimetric technique was undoubtedly desirable not only for the production of pure precipitates, but also to gain the ability of controlling the rate of the reaction so that the complicated phenomena involved in precipitation processes could be studied.

I.A.(2) Precipitation from homogeneous solution

In 1937, a new precipitation technique capable of producing dense, readily filterable, well-formed crystals with minimum coprecipitation was proposed by Willard and Tang (1,2). The investigators used the hydrolysis of urea in solution at 90 to 100°C to produce ammonia thus increasing the pH level of a reaction mixture gradually. The rate of hydrolysis is dependent on the temperature and can be quickly terminated at a desired pH level by cooling the reaction mixture. Thus, it offered an ideal technique for controlling the mode and rate of addition of a precipitant. The technique became known as precipitation from homogeneous solution, "PFHS". Its basic principle is that the required chemical species are generated slowly by a homogeneous chemical reaction within the solution rather than by addition of the precipitating agent in the customary manner. The precipitate is thus formed by a process which eliminates the undesirable concentration effects that are the unavoidable consequences of direct addition of the precipitant.

PFHS appeared as one successful method capable of controlling the precipitation rate in order to obtain a better product among other projects aiming for the same goal. Stock in 1900 used a mixture of solutions of potassium iodide and potassium iodate to remove the acid formed by the hydrolysis of aluminium chloride in the precipitation of hydrated aluminium oxide (3). Similar attempts to reduce the acidity of a reaction mixture in order to promote precipitation were tried by Smith (4), Chancel (5), and Dorrington and Ward (6) independently.

Since the introduction of PFHS by Willard and Tang, many workers have utilised and expanded the basic concepts. The hydrolysis of urea especially continued to form the basis of several new PFHS methods. Several reports describing a wide variety of precipitations by urea hydrolysis were contributed by Gordon and Willard (7). Such analytically important precipitates as metal oxalates (8), formates (9), 8-hydroxyquinolates (10,11), phosphates (12), and sulphates (13), have proved the successful application of the urea method in gravimetry.

In addition to the urea hydrolysis technique, other interesting PFHS methods such as the release of precipitating ions within the solution, the replacement method, direct synthesis of reagent <u>in situ</u> and precipitation from a mixed solvent appeared later in the literature. The advantages of PFHS were recognised by chemists and the principle was applied in many different ways.

Either an anion or a cation serving as a precipitant can be generated homogeneously within a solution. For the synthesis of an anion, <u>in situ</u>, a suitable hydrolytic compound capable of producing the desired ion was introduced into the metal ion solution. Solubility in water and a satisfactory rate of hydrolysis are requirements met by some amides, esters, amines and acids and a variety of them have been used as precursors.

Hexamethylenetetramine (14) and acetamide (15,16) have been used to release hydroxyl ion. Oxalate ion was produced by hydrolysis of dimethyl (17,18,19) or diethyl oxalate (20,21,22) whereas thioacetamide was used for generation of sulphide (23). Other precursors are capable of producing the sulphate ion (24-29), carbonate ion (30), iodate ion (31), chromate (32) and phosphate (33) and 8-hydroxyquinolate ions (34).

In the cation release technique, the desired cation is usually held in solution initially as a relatively stable complex. Destruction of the complex by changing the pH of the solution or by a chemical attack (35) slowly releases the cation into the solution. EDTA complexes have been thus utilized (36,37). The pH of the solution can be altered by the hydrolysis of a suitable ester to produce an acid or by the volatilisation of ammonia from the system (38,39). Alternatively cations can be released by a replacement method making use of the different stabilities of cation complexes. The metal to be precipitated is first complexed and then a solution of another metal that forms a more stable complex is added releasing the metal forming the less stable complex. Firsching reported the precipitation of barium sulphate by adding a nickel solution to a mixture of barium EDTA complex and sulphate ion (40). A similar method was developed by the same author in which barium ion from the barium EDTA complex was displaced when a dilute solution of magnesium chromate was added (41). Nickel dimethylglyoximate has been precipitated by a similar PFHS method (42). Cerium (III) was converted to the desired cerium (IV) in the presence of iodate in the method of changing oxidation states of metal ions reported by Willard and Yu (43).

Another technique for PFHS involves the direct synthesis of precipitating agent in solution. It has greatly improved and extended the use of chelating agents as precipitants for several metals. The first direct synthesis method was reported in 1955 by Tarasevich (44). Nitrous acid and 1,2-phenylenediamine were reacted in the presence of either copper or silver to produce 1H-benzotriazole in aqueous solution. A similar type of procedure had been developed in 1935 by Barnicoat although not classified as PFHS (45). In the determination of biacetyl in butter, nickel ion and hydroxylamine were added to precipitate nickel dimethylglyoximate. This method was not realised until 1952 when Bickerdike and Willard proposed a PFHS procedure for the precipitation of nickel dimethylglyoximate by urea hydrolysis (46). The direct synthesis of dimethylglyoxime, <u>in situ</u>, was proposed later by Gordon and Salesin (47-50) by reacting biacetyl and hydroxylamine in solution in the presence of nickel. Remarkably improved properties of the crystals were obtained by PFHS as compared with conventional precipitation.

Numerous works on the application of metal chelates in PFHS continued to appear in the literature. Furfuraldioxime (51), 8-hydroxyquinoline (52-57), cupferron (58), α-nitroso β-napthol, salicylaldioxime (59-60) (61-62), 8-hydroxyquinaldine (63) and N-benzophenyl hydroxylamine (64) were synthesised <u>in situ</u> for precipitations of several metal ions. Precipitation processes with metal organic chelates were reviewed by Gordon et al. (65) and Firsching (66,67).

A related method termed the mixed solvent method involving insoluble metal chelates was proposed by Howick and coworkers (68). The investigators prepared a water miscible organic solvent system containing all the reacting species and induced the precipitation of metal chelate by volatilization of the solvent. Similar methods were applied for some metal 8-hydroxyquinolates (69-73) and dimethylglyoximates (74).

An interesting but rarely applied method is PFHS by photochemical action. Only limited usage of the method has been reported (75,76) to date.

Since it possesses many obvious advantages over conventional methods, PFHS has been used to develop improved gravimetric methods of analysis. Several applications of PFHS in chemical technology have been developed (7). The method has been used in the removal of iron from minor constituents (77) and in the separation by fractional precipitation of chemically similar elements such as zirconium and hafnium (19) and the rare earths (17).

Use of PFHS techniques in nucleation processes and some kinetic and mechanism studies have been reported. The slow processes involved in PFHS are well suited to systematic studies of chemical reactions. It provides remarkable use in coprecipitation studies since experimental processes with near equilibrium conditions between the surface of the solid and the solution can be obtained. One can learn more about the nature of coprecipitation because the technique facilitates the measurement of distribution coefficients. In practice, however, PFHS demands fairly detailed studies of the experimental conditions necessary to develop a successful method.

I.A.(3) The chemistry of vic-dioximes and their application in PFHS methods

As stated in the previous section, precipitation processes with metal organic chelates have been widely applied in PFHS and in most applications have produced precipitates of superior quality to those conventionally precipitated. (There are a few cases reported where physically improved precipitates could not be produced by PFHS). In developing methods for the *in situ* synthesis of the organic reagents, however, some limitations have to be considered. The precipitate must be synthesised in an aqueous medium, in the presence of metallic ions and often at a fixed pH so as to insure quantitative precipitation. Several dioximes have proved to be compatible with these requirements.

There is no doubt that dioximes are recorded as superior precipitating reagents in conventional methods. Banks discussed the chemistry and uses of dioximes in a review article (78). For conventional precipitation methods, solubility of the reagent and sensitivity towards metal ions are of major concern. Structural effects are responsible for sensitivity of the dioxime. Compounds of high molecular weights and with a long hydrocarbon chain are usually desired since an increase in the chain length helps make the oxime sensitive as well as improves the gravimetric factor. Structural studies showed that the presence of benzene rings and cyclic groups in the molecule allowed formation of metal oximates in both acidic and alkaline media (79). From a structural point of view, methyl benzyl dioxime, benzyl dioxime, and α-furildioxime were reported as suitable analytical reagents (80).

The solubility of the reagent is very important for a precipitating agent. The use of an organic solvent to solubilise the reagent is inconvenient and can induce reagent coprecipitation and solubility of the precipitate. Many attempts have been made to completely solubilise dimethylglyoxime but none could provide satisfactory results (81-87). The great demand for water soluble dioximes has promoted the development of improved precipitation methods as well as synthesis of new dioximes including cyclic dioximes. Banks and coworkers reported on a collection of water soluble 1,2-dioximes as analytical reagents, but only two of them are sufficiently soluble in water for use in aqueous solution, 1,2-cyclohexanedione dioxime and 1,2-cycloheptanedione dioxime (88). From the structural point of view, these two oximes have favourable characteristics. Both reagents have been utilised with satisfactory results in some gravimetric and spectrophotometric methods (89-95).

It seems, therefore, that cycloheptanedionedioxime and cyclohexanedionedioxime could be synthesised, <u>in situ</u>, and used in a similar manner as in the precipitation of nickel dimethylglyoximate by reaction of biacetyl and hydroxylamine. Cycloheptanedionedioxime, particularly, is suitable for the purpose because of the following advantages: it is soluble in water (4.8 g/l at 19.5°C - nine times higher than the corresponding solubility of dimethylglyoxime); it has a higher molecular weight than dimethylglyoxime and has a wide range of pH values for quantitative precipitations. It possesses almost all the good characteristics of both dimethylglyoxime and cyclohexanedionedioxime without their disadvantages. Conventional precipitation with nickel ions has indicated that quantitative determination can be achieved in the presence of some anions and several cations, including aluminum, chromic, ferric, cobalt and manganese (88). Thus, an investigation of its use in a direct synthesis PFHS procedure might be worthwhile.

I.A(4) <u>Kinetic aspects of dioximate formation reactions</u>

> "As early as in 1882, the striking difference in the case of reaction of carbonyl compounds with hydroxylamine were observed and discussed. In the succeeding years, the considerable practical and theoretical significance of oxime formation stimulated numerous investigators to study the rate of oximation of a variety of compounds...."*

As noted in the above paragraph, the kinetics of oximation has been intensely studied by chemists for several years. Classical studies by Barrett and Lapworth (96), Olander (97), and others (98, 99) on reactions of carbonyl compounds with nitrogen bases have led to the conclusion that these reactions follow a second order rate law, being first order in the carbonyl compound and first order in the nitrogen base. The experiments have also revealed the striking maxima in the rate -pH profiles. The apparent similarity of semicarbazone formation and oxime formation was clearly recognized and both were usually studied together.

The work of Stemple and Schaffel concerning the kinetics and mechanisms of reactions between phenylhydrazine, semicarbazine and hydroxylamine and the optically active ketone, d-carvone established the absence of a primary salt effect, the presence of general acid catalysis

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*Francis W. Fitzpatrick and Joseph D. Gettler, J. Am. Chem. Soc. <u>78</u>, 530 (1956).

and the second order nature of the reaction (100). In 1955, Fitzpatrick and Gettler studied the kinetics of oxime formation of several ketones including acetone, furfural, cyclopentanone and cyclohexanone (101). Their results indicated a second order reaction and the absence of detectable variations in the specific rate with variation in the initial concentration of the reactants.

More detailed study on the mechanism of oximation reaction was performed by Hine (102) who proposed the reaction sequence

$$>C=O + HA \underset{}{\overset{\text{fast}}{\rightleftharpoons}} >C=O{-}{-}{-}HA \qquad \text{(a)}$$

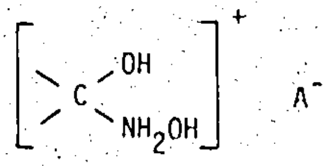
$$>C=O{-}{-}{-}HA + H_2NOH \xrightarrow{\text{slow}} >C<\begin{matrix} OH \\ NHOH \end{matrix} + HA \qquad \text{(b)}$$

$$>C<\begin{matrix} OH \\ NHOH \end{matrix} \xrightarrow{\text{fast}} >C=NOH + H_2O. \qquad \text{(c)}$$

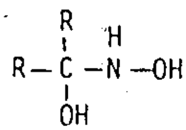
According to his suggestion the reaction rate increases with the acidity of the reaction solution up to a point due to the increased concentration of the carbonyl compound present in the form of a more reactive complex and subsequently decreases with increased acidity when the amine is transformed to its unreactive salt.

$$\text{i.e.} \quad H_3O^+ + H_2NOH \rightleftharpoons H_3NOH^+ + H_2O \qquad \text{(d)}$$

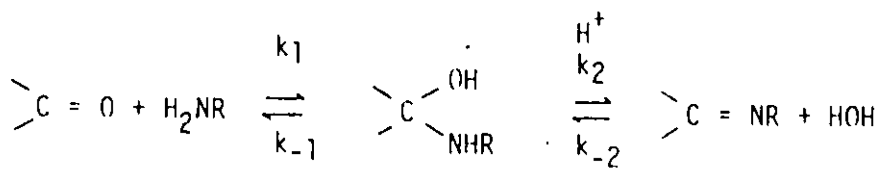
Hammett (103) shows that the structure of the intermediate could be



In 1959 when Jencks (104) published the results of his studies on the mechanism of oxime and semicarbazone formation (pyruvate anion, benzaldehyde, furfural, acetone, cyclohexanone), a carbinolamine structure was proposed as the intermediate species.



The author further proposed the following sequence for the reaction of nitrogen bases and carbonyl compounds in neutral aqueous solutions



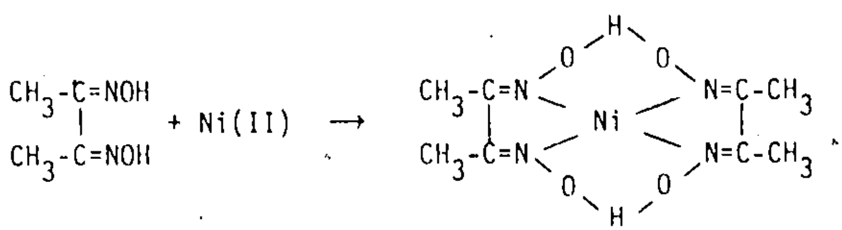
This suggested that the rate determining step at neutral pH is not the attack of the nitrogen base on the carbonyl but is the acid catalysed dehydration of the carbinolamine.

A particular oximation reaction, the reaction between biacetyl and hydroxylamine was studied by Gordon and coworkers in the precipitation of nickel dimethylglyoximate from homogeneous solution (47). The reactions were indicated as follows:

$$\begin{array}{l} CH_3-C=O \\ \quad | \\ CH_3-C=O \end{array} + H_2NOH \longrightarrow \begin{array}{l} CH_3-C-NOH \\ \quad | \\ CH_3-C=O \end{array} + H_2O \qquad (1.1)$$

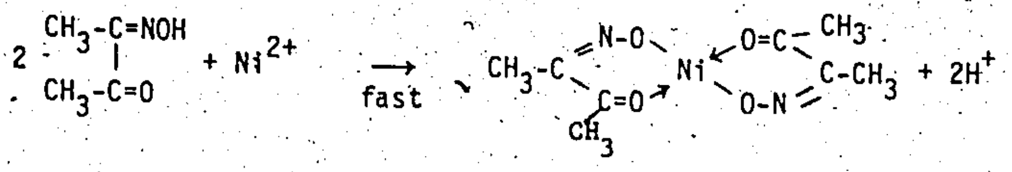
$$\begin{array}{l} CH_3-C=NOH \\ \quad | \\ CH_3-C=O \end{array} + H_2NOH \longrightarrow \begin{array}{l} CH_3-C=NOH \\ \quad | \\ CH_3-C=NOH \end{array} + H_2O \qquad (1.2)$$

The investigators reported that reactions (1.1) and (1.2) are highly pH dependent, with the rates being faster at lower pH values. In addition, the reactions between biacetyl and hydroxylamine were found to follow simple kinetics in the absence of nickel. When nickel (II) was present, reactions (1.1) and (1.2) occurred and dimethylglyoxime thus formed reacted with nickel to produce nickel dimethylglyoximate:

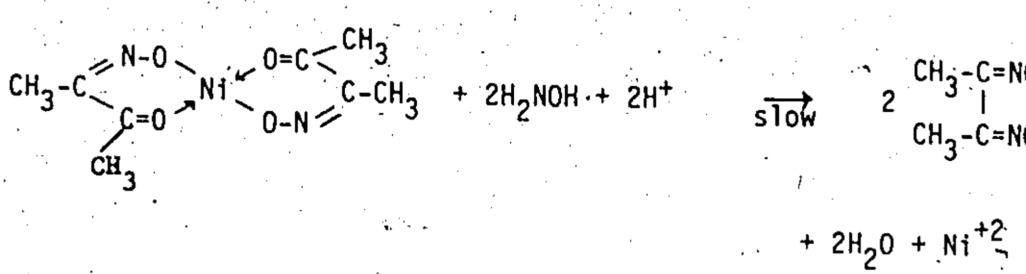


(1.3)

The kinetic studies, however, showed that the reaction was no longer simple and there was definite evidence for complex formation between biacetyl monoxime and nickel. The complex and others formed with nickel in the reaction mixture determined the overall rate of formation of nickel dimethylglyoximate. The authors proposed the following reaction sequence:



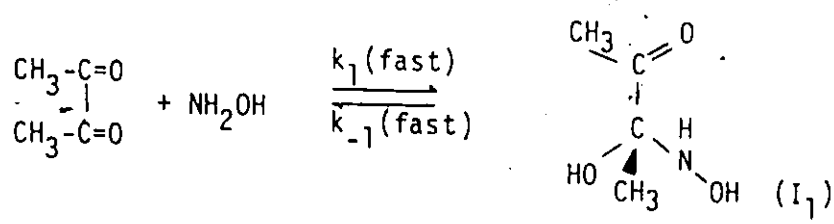
(1.4)



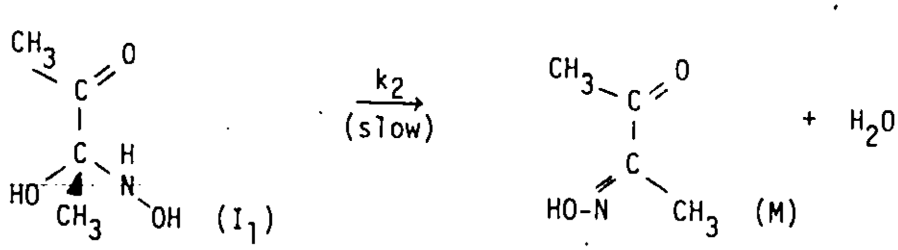
(1.5)

The same oximation reaction was further investigated by Hileman and Gordon (105). From spectrophotometric studies the authors found the evidence of the presence of two carbinolamine intermediates similar to those proposed by Jencks for simple carbonyl-hydroxylamine reactions.

The rate limiting step of the reaction is the slow dehydration of the initially formed intermediate, i.e.

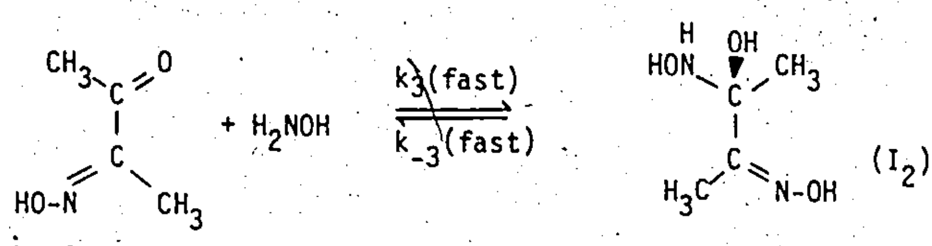


(1.6)

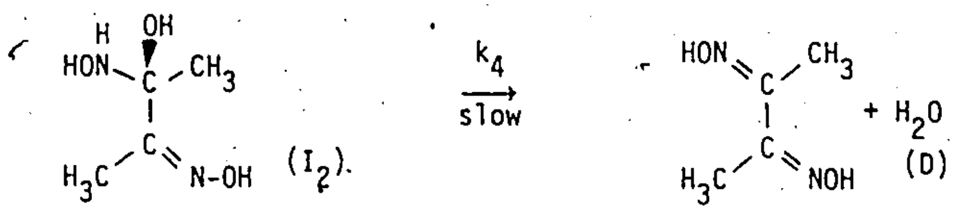


(1.7)

The second of the intermediates is encountered in the reaction of biacetyl monoxime with hydroxylamine



(1.8)



(1.9)

The authors concluded that two independent mechanisms are possible for the formation of nickel dimethylglyoximate - the direct reaction between nickel and dimethylglyoxime

$$Ni(II) + 2D \xrightarrow[fast]{} Ni\ D_2 \downarrow + 2H^+ \qquad (1.10)$$

and the formation of the complexes between the intermediate I_1 and nickel

$$Ni^{+2} + I_1 \rightleftharpoons Ni\ I_1^{\ +} + H^+ \qquad (1.11)$$

$$Ni\ I_1^+ + I_1 \rightleftharpoons Ni(I_1)_2 + H^+ \qquad (1.12)$$

where some of the $NiI_1^{\ +}$ may be converted, by dehydration of the intermediate and further reaction with hydroxylamine to NiD^+.

I.B. Coprecipitation Phenomenon

In nature, coprecipitation is a phenomenon commonly observed in geological and physiological deposits. Every mineral contains traces of elements which are not considered in the "ideal" formula of the mineral. Geologists have given attention to these trace elements, foreign to the "pure" chemical compounds and trace element geology has become an important field of research. There has been confusion, however, in the literature regarding the principles governing the distribution of trace elements in minerals as well as in chemical precipitates.

All precipitates, as discussed earlier, tend to carry down substances normally soluble under the conditions of the precipitation. Such a coprecipitation process, in gravimetric analysis, is detrimental to the preparation of pure materials. In some systems, however, such a process is of considerable advantage in that trace amounts of specific elements may be concentrated or enriched. Radioactive trace substances are often separated by addition of carrier precipitates. Coprecipitation is thus important as a means of concentrating trace materials or separating impurities in radiochemistry and gravimetric analysis. Coprecipitation is also useful in trace element geochemistry, where it can be utilised as a conceptual model in understanding the mechanism of precipitation and the properties of solid solutions.

I.B.(1) Definition and classification

The most general definition for coprecipitation is the contamination of a precipitate by substances that are normally soluble under the conditions of the precipitation. Gordon, Salutsky and Willard (7) define it in a broader sense as the precipitation of a compound in conjunction with one or more other compounds. An alternative, proposed by Hermann, is the carrying process of a tracer by a precipitate formed in the presence of the tracer (106). It is considered basically as a process where a substance, soluble by itself, is carried with an insoluble crystalline precipitate.

Classification, as in the definition, covers a number of statements of similar content. In 1936 Hahn (107) categorised coprecipitation phenomenon into two main groups: (i) isomorphous coprecipitation and (ii) adsorption. Alternate means of isomorphous coprecipitation were listed as anomalous mixed crystal formation and internal adsorption.

A more accurate classification of the several carrying processes was proposed by Kolthoff (108). According to Kolthoff, the contamination of precipitates by foreign substances is attributed to:

1. Occlusion by incorporation of foreign ions during the formation of the precipitate. Coprecipitation by mixed crystal formation is considered to be a special case of occlusion.

2. Adsorption at the surface of particles exposed to the solution and inclusion of mother liquor.

3. Chemical compound formation. Coprecipitation by this means is rare.

Gordon and coworkers characterised carrying processes as isomorphous mixed-crystal formation, anomalous mixed-crystal formation, adsorption and occlusion (7).

Although the distinction between the various types of coprecipitation is not sharp, a systematic classification can be best distinguished by three basic processes; namely, solid solution formation, occlusion and surface adsorption.

Solid solution formation

Depending upon a number of factors including solubility and the ability of the host precipitate to incorporate the impurities contaminants can be incorporated into the crystal lattice as a solid solution. Components of similar chemical and crystallographical properties (as barium and radium sulphate) may exhibit isomorphous mixed crystal formation leading to solid solution formation. Some mixed crystal formation which cannot be explained on chemical or crystallographic grounds (as lead and potassium chlorate) have been defined as anomalous mixed crystal formation.

Occlusion

Occlusion results from trapping of tracer impurities at the surface of a crystal by subsequently deposited crystal layers. Incorporation of the impurity into the lattice occurs under nonequilibrium conditions in this case. The extent of occlusion depends on the rate of precipitation and the degree of supersaturation of the macrocomponent. Coprecipitation by means of occlusion is the most common cause of contamination of analytical precipitates.

Surface adsorption

Coprecipitation due to surface adsorption is important for precipitates where a large surface area is encountered. In adsorption, the microcomponent is adsorbed in a movable or diffuse layer at the surface of the precipitate. The extent of coprecipitation by adsorption depends on the rate of precipitation, presence of other ions, crystal size and many other factors.

I.B.(2) Distribution laws

The actual mechanisms of the coprecipitation process are not fully understood at present. For the solid solution formation type, however, the observed distribution of tracer between precipitate and solution can be rationalized using one or the other of two limiting laws; namely, the homogeneous distribution law or the logarithmic (or heterogeneous) distribution law.

For a system capable of establishing true thermodynamic equilibrium the distribution of the microcomponent is considered to be homogeneous. When a substance A is precipitated in the presence of a foreign ion B in solution, the reaction is considered to be

$$A(\text{solid}) + B(\text{solution}) = A(\text{solution}) + B(\text{solid}) \qquad (1.13)$$

for which the equilibrium constant "D" may be expressed as

$$D = \frac{[A]_{\text{solution}} \times [B]_{\text{solid}}}{[A]_{\text{solid}} \times [B]_{\text{solution}}} \quad . \qquad (1.14)$$

Equation (1.14) can be rearranged to give the form of the homogeneous distribution law

$$\left[\frac{[B]}{[A]}\right]_{\text{entire crystal}} = D \left[\frac{[B]}{[A]}\right]_{\text{solution}} \quad . \qquad (1.15)$$

"D" is known as the homogeneous distribution coefficient.

Equation (1.15) describes the distribution behaviour exhibited by systems in which the entire crystal is brought into equilibrium with the solution. It is the case of true thermodynamic equilibrium in which the solid phase has been digested sufficiently long for several stages of dissolution and recrystallisation to have taken place. Homogeneous distribution of tracer in mixed crystals was extensively studied by Chlopin (109), Henderson and Kracek (110) and others (111).

Not all observed distribution patterns, however, can be fitted with the homogeneous law. To rationalize these Doerner and Hoskins (112) proposed a logarithmic distribution law. It is based on the assumption that only the crystal surface is in equilibrium with the solution as the process proceeds. Accordingly, each new layer of carrier precipitate, as it forms, is considered to be in equilibrium with the particular concentration of solution existing at that time. Hahn (107) preferred to illustrate the logarithmic distribution as an onion-like arrangement with each infinitesimal crystal layer equivalent to an onion shell. As each layer is deposited there is insufficient time for resolution before the succeeding layer is deposited. The resulting distribution of trace component is thus specially heterogeneous with the crystal.

According to the Doerner and Hoskins' approach,equation (1.15) at any specific time during the experiment is

$$\left[\frac{[B]}{[A]}\right]_{\text{surface of crystal}} = D\left[\frac{[B]}{[A]}\right]_{\text{solution}} \qquad (1.16)$$

From equation (1.16), the ratio in which carrier and tracer are deposited in an elementary layer is proportional to the concentration ratio of both components in the solution at that time of precipitation. Thus, if "b" and "a" are initial quantities of tracer [B] and carrier [A] respectively and "x" and "y" are the corresponding amounts of tracer and carrier left in solution at any time after beginning of precipitation, the following differential equation is obtained,

$$\frac{d(b-x)}{d(a-y)} = \frac{dx}{dy} = \lambda \frac{x}{y} \tag{1.17}$$

where λ is an arbitrary constant.

Integration of the above equation, from initial concentrations of "b" and "a" to final concentrations of "x" and "y" leads to

$$\ln\left[\frac{b}{x}\right] = \lambda \ln\left[\frac{a}{y}\right] \tag{1.18}$$

or expressed in the more conventional way

$$\ln\left[\frac{\text{total tracer}}{\text{tracer in solution}}\right] = \lambda \ln\left[\frac{\text{total carrier}}{\text{carrier in solution}}\right] \tag{1.19}$$

Equation (1.18) is known as the logarithmic distribution law and λ is the logarithmic distribution coefficient.

It has been observed that depending upon the conditions of the precipitation, the value of one or the other of the distribution coefficients (D or λ) remains constant as the percentage of carrier precipitated increases during a coprecipitation experiment.

When the value of D or λ is greater than unity, the precipitate is enriched in tracer with respect to the solution and the coprecipitation results in an "enrichment system". In "derichment systems", those having distribution coefficient values less than unity, the tracer is deriched in the precipitate and remains mostly in solution. When D or λ is equal to unity the tracer is not fractionated between precipitate and solution. Enrichment systems are useful for carrying the microcomponent while derichment separation can be achieved in systems whose tracer is deriched with respect to the precipitate. At equal values of D and λ, a logarithmic coprecipitation type exhibits better carrying or separation efficiency than a homogeneous coprecipitation. An illustration of the distribution behaviour and the carrying efficiency of both distribution types is shown in Figure (1).

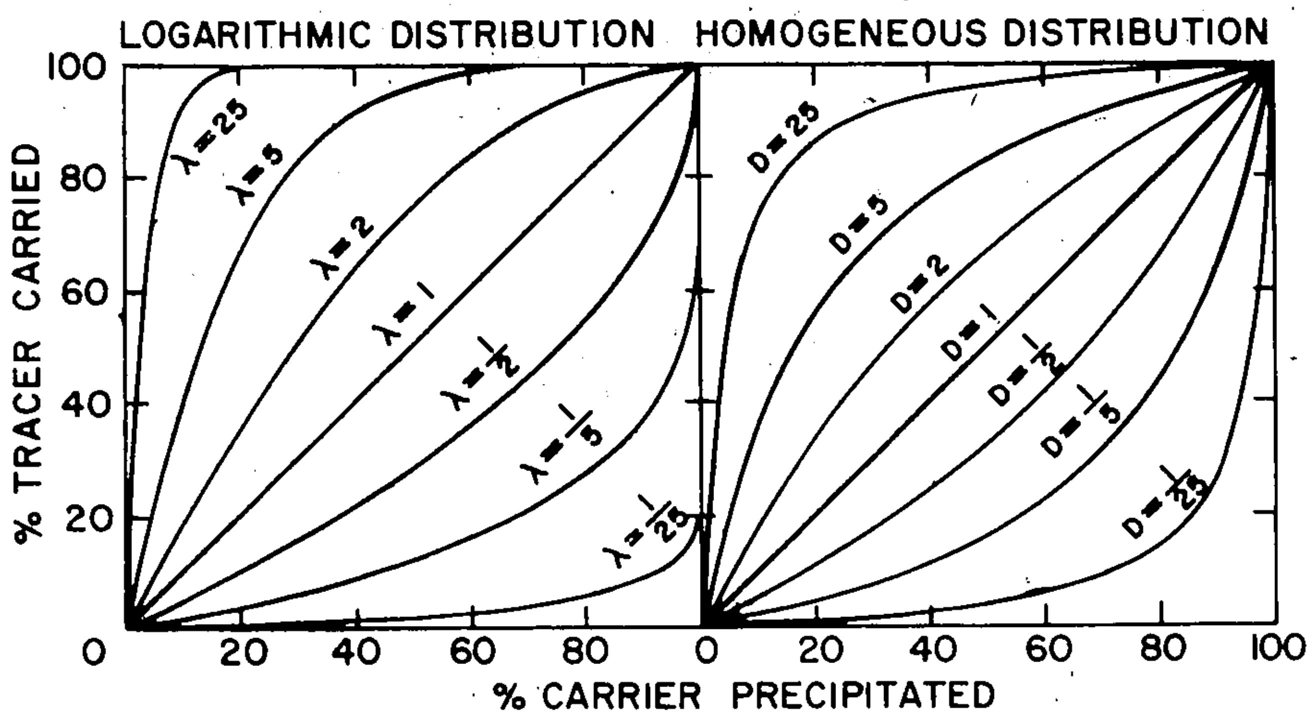
I.B.(3) <u>Precipitation conditions and resulting coprecipitation patterns</u>

It was reported that slow precipitation from a moderately supersaturated solution leads to homogeneous distribution of the tracer in the carrier precipitate (113). If a supersaturated solution is allowed to stand undisturbed and in contact with the solid phase until the supersaturation is completely eliminated, D is found to be constant. The slow precipitation rate under such conditions results in well-formed crystals and the tracer is homogeneously distributed throughout the entire crystal. R. Mumbrauer observed such behaviour in his studies of the coprecipitation of radium with barium chloride.

Rapid precipitation and prolonged digestion also leads to homogeneous distribution of the microcomponent. When a moderately

Figure (1) Comparison of carrying efficiency for the two distribution laws.

(reproduced from the thesis (106), permission requested from the University Microfilms, Ann Arbor, Michigan)


LOGARITHMIC DISTRIBUTION
HOMOGENEOUS DISTRIBUTION
% TRACER CARRIED
% CARRIER PRECIPITATED
λ = 25
λ = 5
λ = 2
λ = 1
λ = 1/2
λ = 1/5
λ = 1/25
D = 25
D = 5
D = 2
D = 1
D = 1/2
D = 1/5
D = 1/25
0
20
40
60
80
100

supersaturated solution is stirred vigorously for several hours at constant temperature, the trace element is usually found to be uniformly distributed throughout the crystal. Finely divided crystals resulting from such rapid precipitation and long digestion can undergo frequent recrystallisation which promotes equilibrium microcomponent distribution.

In the case of immediate filtration after a rapid precipitation from a moderately supersaturated solution, the microcomponent is usually found to be distributed in accordance with the logarithmic distribution equation. This is due in part to the shortage of time for recrystallisation. The best way of obtaining a logarithmic distribution is to carry out a precipitation very slowly from a saturated solution. Precipitation by isothermal evaporation of a saturated solution was demonstrated by Riehl and Kading (114) to give a logarithmic distribution of tracer in the precipitate. Under this condition, the assumption of equilibrium between the solution and each newly formed crystal layer is likely to be followed. An alternate way of performing a very slow crystallisation is by controlled in situ synthesis of the precipitant (PFHS). The observed behaviour of most of the systems studied employing a PFHS method have been successfully rationalized using the logarithmic distribution law.

Depending on the precipitation conditions used, the nature of precipitating ions and other factors, either of the two distribution patterns could result. Nevertheless, there have been cases where conflicting results were obtained from the same system. Also, there are systems in which neither of the limiting laws is successful in analysis of data.

I.B.(4) Coprecipitation models

(a) Equilibrium model

Many have speculated about the existence of a quantitative relationship between observed distribution coefficients and the solubilities of components in systems where coprecipitation involves solid solution formation. The equilibrium model represents an expression in which the distribution coefficient of an ideal system is equal to the ratio of the solubility products of the macro and micro components respectively. Based on thermodynamic arguments, Ratner (111) derived such a relationship which is applicable only to symmetrical electrolytes. Feibush, Rowley and Gordon (115) later tested the equilibrium model in coprecipitation studies of rare earth oxalate binary systems. The equation derived from the equilibrium model for precipitates of the A_2P_3 type was

$$D = \sqrt{\frac{K_{sp(A_2P_3)}}{K_{sp(B_2P_3)}}} \qquad (1.20)$$

where A is the carrier element and B is the trace component. Their observations, however, did not justify the equilibrium model. Recently, Munakata and Toyanasu (116) reported that the coprecipitation of some rare earth elements with calcium oxalate deviates from the equilibrium model (equation (1.20)) but, in the coprecipitation of alkaline earth oxalates (strontium and calcium) the model rationalises the observed data. The applicability of the model to most coprecipitation studies is very much in doubt and it generally has been considered that there is no simple relationship between solubility and observed distribution coefficients.

(b) Kinetic model

Early evidence by Gordon, Reimer and Burtt (117) and Hermann (106) has demonstrated the importance of kinetics in coprecipitation phenomena. It is believed that, for systems which obey the Doerner-Hoskins distribution law, a relationship can exist between λ and the rate of precipitation. Besides, the thermodynamic approach of the equilibrium model is strictly limited to systems where diffusion and repeated recrystallisation are possible. Apparently, the kinetic approach seems favourable for many systems. Feibush, Rowley and Gordon (115) proposed a new expression which related λ and the rate constants of the precipitation reactions involved. In their kinetic model, λ, the logarithmic distribution coefficient is equal to the ratio of the rate constants of precipitation of carrier and tracer components. The assumption was made that the rate of precipitation of each species is proportional to its respective solution concentration. By substitution, equation (1.17) becomes

$$\frac{\frac{d(b)_{aq}}{dt}}{\frac{d(a)_{aq}}{dt}} = \frac{k_{p-b}}{k_{p-a}} \cdot \frac{B_{(aq)}}{A_{(aq)}} \tag{1.21}$$

where (B) is the concentration of tracer, (A) is the concentration of carrier and k_{p-b} and k_{p-a} are respective rate constants.

Block and Gordon (118) later modified equation (1.21) for systems of different ionic charges of tracer and carrier to the following form

$$\log \frac{B_i}{B_f} = \frac{4}{2.303} \left(\frac{1}{V^{1/4}}\right) \left(A_i^{1/4} - A_f^{1/4}\right) \tag{1.22}$$

where:

A_i and A_f are initial and final concentrations of carrier

B_i and B_f are initial and final concentrations of tracer

and V is the volume of the solution.

Equation (1.22) holds for the coprecipitation of a tracer of (+3) charge with a carrier of (+4) charge.

Supporting the kinetic approach, Hermann (106) related the distribution coefficient to supersaturation. The rate of precipitation is considered to be a function of supersaturation in his approach. He showed that

$$\lambda_{obs} = \frac{\lambda}{(1+(\lambda-1)S)} \tag{1.23}$$

where: λ_{obs} is the experimentally determined distribution coefficient

λ is the true limiting distribution coefficient

S is the fractional supersaturation defined as $\frac{y-d}{y}$

y is the concentration of carrier in the supersaturated solution

d is the concentration of carrier in the saturated solution.

(c) Combination model

From their study on coprecipitation of lead with barium sulphate from homogeneous solution, Klein and Fontal (119) derived a new equation describing the logarithmic distribution coefficient as a function of the rate of precipitation, the number of growing crystals and two rate constants. The proposed equation is

$$\frac{I}{N}(\lambda-1) = k_2\lambda - k_1 \tag{1.24}$$

where k_1 and k_2 are the rate constants in the reaction of

$$B_{(aq)} + A \text{ (crystal)} \underset{k_2}{\overset{k_1}{\rightleftarrows}} A\text{ (aq)} + B \text{ (crystal)} \tag{1.25}$$

I = the total precipitation rate of carrier and tracer and

N = the total number of crystals.

For the coprecipitation of tracer ion (B) with the precipitate of carrier ion (A), the following assumptions were made.

(1) (B) and (A) diffuse from the bulk solution to the active sites and reach there in proportion to their concentration ratio.

(2) Every ion which approaches an active site is incorporated into the crystal.

(3) Once incorporated at an active site, the reactions leading to an equilibrium distribution of tracer in the crystal begin.

(4) The number of active sites (M) is proportional to the total number of crystals (N) with the proportionality constant incorporated into the rate constants k_1 and k_2.

The first three assumptions rationalise the relationship between λ and precipitation rate. The authors defined the total precipitation rate as the sum of individual precipitation rate of ions

$$\text{i.e.} \quad I = \frac{d[A]}{dt} + \frac{d[B]}{dt} \tag{1.26}$$

The final equation derived is

$$\frac{d[B]}{d[A]} = \frac{[B]}{[A]} \cdot \left[\frac{I-k_1M}{I-k_2M}\right] \tag{1.27}$$

which has the same form as

$$\left[\frac{d[B^{+n}]}{d[A^{+n}]}\right]_{\text{crystal surface}} = \lambda \cdot \left[\frac{[B^{+n}]}{[A^{+n}]}\right]_{\text{aqueous}} \tag{1.28}$$

Equation (1.28) was derived from the assumption that only the surface of the crystals takes part in the distribution reaction and that the distribution within the crystal is fixed. By analogy, the logarithmic distribution coefficient was defined by

$$\lambda = \left[\frac{\frac{I}{M} - k_1}{\frac{I}{M} - k_2}\right] \tag{1.29}$$

where M = total number of active sites.

Equation (1.29) describes the observed values of λ in terms of rate of precipitation per active site, and two rate constants, the ratio of which is the equilibrium constant for the distribution reaction.

The striking observation reported here was that the distribution coefficient at zero rate of precipitation is equal to the ratio of two rate constants as well as the ratio of the solubility products of carrier and tracer precipitates. Thus, the authors suggested that the observed value of the logarithmic distribution depends on both thermodynamic and kinetic factors in the forms proposed.

I.C. Scope of the Investigation

The development of a new PFHS technique for the gravimetric determination of nickel was our first goal. Based on the prediction that 1,2-cycloheptanedionedioxime should be the best reagent for replacement of the water insoluble dimethylglyoxime in the determination of nickel and palladium, our investigation was focused on this chelating agent. Analytical procedures for quantitative precipitation of nickel 1,2-cycloheptanedionedioximate from homogeneous solution were investigated. Further research on the separation of nickel as the heptoximate from selected cations (Mn(II), Co(II), Cr(III), Fe(II), Cu(II)) led to the interesting study of coprecipitation with nickel heptoximate.

The second part of the research was undertaken to study the nature of the coprecipitation of cobalt and copper with nickel cycloheptanedioximate. Furthermore, attention was focused on investigation of a model which rationalises the behaviour of coprecipitation with nickel cycloheptanedionedioximate observed during the present study.

II. EXPERIMENTAL DETAILS

II.A. Precipitation of nickel cycloheptanedionedioximate from homogeneous solution

Development of a new PFHS technique for the determination of some metals using an analytically important chelating agent is one of the aims of this project. Voter and Banks (88) have reported the good analytical qualities of 1,2-cycloheptanedionedioxime (heptoxime) observed during studies of the conventional precipitation of nickel and palladium ions. The authors suggested that heptoxime would be the best substitute for the water insoluble dimethylglyoxime in the determination of nickel. This initiated the idea of using the reagent in the PFHS method. The first approach to the problem was, thus, the generation of heptoxime in solution from its corresponding diketone and hydroxylamine. 1,2-cycloheptanedione, which is not commercially available, had to be synthesised prior to the study.

II.A. (1) Synthesis of 1,2-cycloheptanedione

The original method of synthesis proposed by Van der Haar, Voter and Banks (120) was applied. It described the simple oxidation of cycloheptanone by selenium dioxide in ethanolic medium followed by distillation.

Procedure:

A solution of 112 g (1.0 mole) of cycloheptanone in 234 ml of absolute ethyl alcohol was placed in a two liter flask. A solution of 111 g (1.0 mole) of sublimed selenium dioxide, prepared by the method of Riley and Gray (121), in a mixture of 500 ml of absolute ethyl alcohol and 1600 ml of 95% ethyl alcohol was added to the flask through a dropping funnel. Prior to this addition, the cycloheptanone alcohol solution was heated to refluxing. The period of addition was approximately one and one quarter hours. The resultant mixture was refluxed for an additional six hours, allowed to stand at room temperature for about eighteen hours and then filtered. About one litre of alcohol was distilled from the filtrate at atmospheric pressure. The residue was filtered again, and then the distillation was continued under reduced pressure. The diketone came over as a deep yellow liquid at a boiling point of 107-109°C (17 mm).

II.A.(2) <u>Modified procedure for synthesis of 1,2-cycloheptanedione</u>

Since the reported method failed to yield a pure cycloheptanedione product, a detailed study of the procedure was undertaken in order to find ways of improving it.

Procedure:

The synthesis of cycloheptanedione was initially carried out using the proposed method. A series of liquid samples was withdrawn from the reaction mixture at various times during the refluxing period and the standing period and was tested on a gas chromatograph. The fractions collected at different distillation temperatures were also tested in a similar manner. Other experimental conditions such as still pot temperature, pressure and the distillation period were also examined.

The resulting modified procedure for the synthesis of cycloheptanedione is as follows:

Procedure:

A solution of 163 g (1.5 mole) of cycloheptanone was dissolved in 350 ml of absolute ethyl alcohol in a 5 litre flask. A solution of 170 g (1.53 mole) of freshly sublimed selenium dioxide in 250 ml of absolute ethyl alcohol and 80 ml of 95% ethyl alcohol was added to the ketone solution slowly through a dropping funnel. The addition time was one and one quarter hours during which the reaction mixture was refluxed at 75°C. The resultant mixture was refluxed for an additional 7 hours, allowed to stand at room temperature for 14 hours and then filtered. Ethanol was removed (at room temperature and under reduced pressure) and the solution was filtered again. On fractional distillation under reduced pressure with the mixture being heated in an oil bath controlled so that temperature never exceeded 110°C, the cycloheptanedione came over as a yellow liquid between the temperatures of 82°C and 90°C at 3 mm Hg.

The cycloheptanedione was dissolved in anhydrous ether and crystallised from it using a dry-ice acetone freezing mixture. Purified crystals were sealed in a vial under a nitrogen atmosphere and stored in the freezing mixture.

A sample of purified cycloheptanedione was sent to a chemical laboratory for carbon and hydrogen analysis. The gas chromatogram, NMR, IR and mass spectra of the compound were also measured.

In order to determine the percentage purity and the effectiveness of the diketone, a test precipitation procedure was performed.

Procedure:

Approximately 50 mg of cycloheptanedione was accurately weighed out and dissolved in deionised water contained in a 250 ml beaker. In a second beaker, 428 mg of hydroxylamine hydrochloride (10 moles in excess of stoichiometric amount to diketone)and 120 mg of nickel(II) as the nitrate (ten fold excess of the amount required to precipitate the resulting cycloheptanedionedioxime) were mixed. The pH of the mixture was adjusted to 6.75. It was then added to the cycloheptanedione solution. The pH of the reaction mixture was readjusted to 6.75 and the final volume was made up to 200 ml. After standing at room temperature for 15 minutes the beaker and contents were heated on a hot plate for 3 to 3 1/2 hours at a temperature of 70 to 75°C. The beaker was then cooled to room temperature and the precipitated nickel heptoximate was filtered off using a preweighed sintered crucible of medium porosity. After drying at 130°C until constant weight, the crucible and contents were cooled and weighed. From the weight of nickel heptoximate obtained, the percentage purity of 1,2-cycloheptanedione was calculated.

II.A. (3) Preliminary studies on experimental conditions for the precipitation of nickel cycloheptanedionedioximate

(a) Apparatus and Reagents

Apparatus

Pyrex glassware was used and calibrated pipettes and volumetric flasks were used where applicable.

Reagents

1,2-cycloheptanedione solution

A known weight of the reagent prepared using the original method of synthesis described in section II.A.(2) was dissolved in deionized water to make a solution of approximately 3 mg per ml. The solution was filtered through a sintered glass crucible of medium porosity.

Hydroxylamine hydrochloride solution

Salt of reagent grade quality was dissolved in enough deionized water to make a solution of approximately 100 mg per millilitre in concentration. The resulting solution was filtered using a filtering crucible of medium porosity.

Nickel(II) solution

Pure nickel pellets (99.9%, British Drug House Ltd.) were dissolved in dilute nitric acid to prepare a stock solution of approximately 10 mg per millilitre in concentration. Further dilutions were made with deionized water for solutions of lower concentration. Each was standardised using the PFHS method of Gordon and Salesin (47).

Metal Ion Solutions

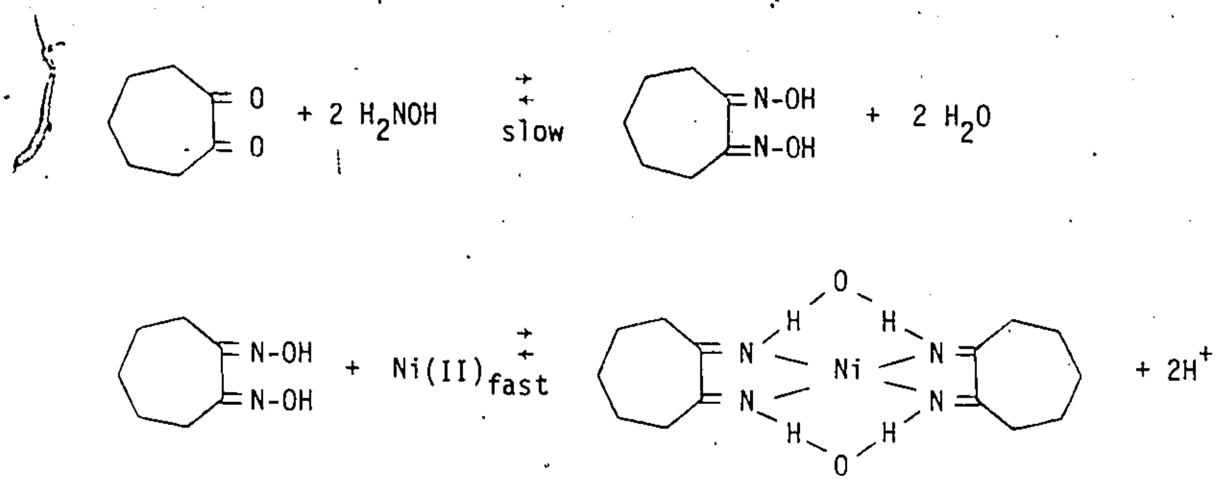
Reagent grade chloride salts of the metals other than chromium (as nitrate), were dissolved separately in deionized water and filtered. Each was diluted to a concentration of approximately 1 mg per ml.

Acid, Base and Buffer Solutions

Filtered solutions of dilute nitric acid, 3 M ammonium hydroxide and 2 M ammonium acetate were used for pH adjustments whenever necessary.

(b) Test procedure for the precipitation

The formation of nickel cycloheptanedionedioximate takes place via two overall steps.



The first step, the formation of dioxime was estimated to be the rate determining step. The very fast reaction between nickel and dioxime, as observed in conventional precipitation methods, has to be avoided. Thus, the cycloheptanedione solution was prepared separately. Addition of it to the solution mixture of nickel and hydroxylamine hydrochloride initiated the slow precipitation of yellow nickel cycloheptanedionedioxime.

Procedure:

A 10.0 mg amount of nickel in solution was pipetted into a 400 ml beaker and a volume of hydroxylamine hydrochloride solution containing 1.0 g of the reagent was added. The pH of the solution mixture was adjusted to 7.0 with solutions of ammonium hydroxide and ammonium acetate buffer (3 ml of 2 M solution). A portion of 1,2-cycloheptanedione solution which contained 86 mg of the ketone at pH 7.0, was added to it. After standing at room temperature for 15 to 20 minutes, the beaker and contents were heated on a hot plate over a two and a half hour digestion period. After cooling, the precipitate was filtered off using a sintered glass crucible of medium porosity, and was then dried at 130°C until constant weight was attained.

(c) Excess reagent studies

The stoichiometric ratio of reactants for the formation of cycloheptanedionedioximate is 2:1, hydroxylamine hydrochloride to cycloheptanedione and two moles of dioxime are required for each mole of nickel. Experiments were designed to investigate the appropriate reagent excess ratios of reactants for quantitative recovery of nickel.

Procedure:

1.0, 10.0, 20.0 and 50.0 mg of nickel were precipitated with combinations of reagent in excess of other reactants following the procedure mentioned in section (b). The pH used was 6.75 in all precipitations. The following table presents a summary of the combinations studied.

Table (1)

Study of reagent excess ratios for the precipitation of nickel cycloheptanedionedioximate from homogeneous solution

Nickel (mg)	1.00			10.0												
CHDO*/Ni(X)	2	20	100	2										4	6	10
HX†/CHDO(X)	10	100	10	2	4	6	8	10	20	50	100	500	1000	10	10	10

Nickel (mg)	20.0		50.0
CHDO*/Ni(X)	2	5	2
HX†/CHDO(X)	10	10	10

*CHDO = 1,2-cycloheptanedione

†HX = Hydroxylamine Hydrochloride

X = reagent excess

$$= \frac{\text{moles of reagent added}}{\text{molar amount of reagent required to precipitate the moles of reacting species in solution}}$$

(d) Effects of pH, temperature and digestion time

The wide range of pH reported for precipitation of nickel heptoximate by conventional methods was tested within the PFHS procedure.

Precipitation procedures were performed using the method described in section (b) but at various individual pH values (2.35, 2.37, 2.67, 3.41, 3.42, 4.15, 5.30, 5.74, 5.97, 6.02, 7.05, 7.12, 7.17, 7.21, 7.63, 9.05, and 10.05).

Any temperature effect on the precipitation was studied over the range of 60° to 90°C. The same experimental procedure was repeated at each temperature setting.

A similar study was made for digestion time variations including 2, 2 1/2, 3 and 4 hour reaction times.

II.A.(4) Development of a PFHS method for the determination of nickel "alone"

Based on the information gathered from the previous experiments, a method for the determination of nickel "alone" was proposed. It was tested in the precipitation of 1.0, 5.0, 10.0, 20.0, 25.0 and 50.0 mg of nickel using the conditions (reagent excess ratios) for precipitation with 50.0 mg.

Procedure:

Place an appropriate amount of nickel solution in a 400 ml beaker. Add a 10:1 stoichiometric excess (hydroxylamine hydrochloride: diketone) of hydroxylamine hydrochloride solution. Dilute with deionised water to 150 ml and adjust the pH to 6.75 with ammonia and ammonium acetate buffer solutions. Add a 2:1 stoichiometric excess (diketone: nickel) of cycloheptanedione solution (pH previously adjusted to 6.75). Make up the total volume to 200 ml and allow the yellow precipitate to appear. After half an hour, heat the beaker and contents for three hours at 70-75°C. Cool to room temperature and filter the mixture using a medium porosity sintered glass crucible. Wash the precipitate with deionised water and dry at 130°C to constant weight.

II.A.(5) Determination of nickel in the presence of foreign ions

(a) Effect of foreign ions

Some common cations (Fe^{+2}, Cu^{+2}, Mn^{+2}, Co^{+2} and Cr^{+3}) often interfere in a determination of nickel. Effects of their presence on the precipitation of nickel heptoximate were studied. In addition, the influence of some anions (chloride, acetate, fluoride, thiocyanate, tartarate and citrate) commonly used as buffers and as complexing agents for interfering cations during the gravimetric determination of nickel were also studied.

Procedures:

(i) Each 10 mg portion of nickel(II) solution was precipitated with 1,2-cycloheptanedione and hydroxylamine by the PFHS method described in section II.A.(4) in the presence of (a) Fe^{+2}, (b) Cu^{+2}, (c) Mn^{+2}, (d) Co^{+2}, and (e) Cr^{+3} ions. For each study, the amount of foreign ion added was varied from 1 to 5 mg and any effects of individual amounts of each particular ion on the apparent recovery of nickel(II) was noted.

(ii) Similar precipitation procedures were carried out for 10 mg of nickel when ammonium salts of (a) citrate, (b) thiocyanate, (c) oxalate, (d) fluoride and (e) tartarate were present. Any effect of each anion on the apparent recovery of nickel(II) was studied at three different levels (1.0, 2.5 and 5.0 g) for each interfering ion.

(iii) Additional experiments were performed to precipitate nickel heptoximate in the presence of both foreign cations and ammonium salts of anions. 10 mg of nickel was precipitated with appropriate amounts of reactants as reported in section II.A.(4) with various combinations of external substances studied in procedures (i) and (ii) present.

(b) Determination of nickel in a steel sample

Nickel in steel and related products is frequently analysed by gravimetric methods. Iron, copper and chromium usually interfere and a technique which can overcome these problems is desired. Based on the observations attained from preliminary investigations, a procedure for the determination of nickel in a steel sample was devised. The National Bureau of Standards steel sample (32.e) was analysed for its nickel composition.

Procedure:

Approximately 0.7 g of accurately weighed steel sample was dissolved in a hydrochloric-nitric acid mixture in a 400 ml beaker and the resulting solution was evaporated to near dryness. 7 ml of 60% perchloric acid solution (10 ml per g of sample taken) was then added and the resulting mixture was boiled to fumes. After dissolving the perchlorate salts in deionised water, 5 g of tartaric acid in solution was added and the resulting mixture was filtered. The filtrate was neutralised with ammonia and 1 g of hydroxylamine hydrochloride in solution was added. A volume of cycloheptanedione solution containing 90 mg of the reagent was finally added and the mixture was adjusted to pH 6.25. This was allowed to stand at room temperature for 8 1/2 hours. The precipitates were filtered off using a sintered glass crucible of medium porosity, washed with deionised water and dried to constant weight at 130°C.

II.B. Kinetic Studies

II.B.(1) Preliminary Studies

Some coprecipitation studies on metal oxalates have revealed a significant influence of precipitation rate on the resulting coprecipitation pattern (106,117). Preliminary experiments were performed to investigate the rate of nickel heptoximate formation.

(a) Apparatus and reagents

Apparatus

Constant temperature bath

A constant temperature bath type 2073A supplied by Forma Scientific Inc. was used to keep reactant solutions at the desired constant temperature.

Glassware

Pyrex glassware was used and calibrated pipettes and volumetric flasks were used where applicable. Filtering crucibles utilized were of pyrex glass with medium porosity.

Reagents

Nickel(II) solution, cycloheptanedione solution, hydroxylamine hydrochloride solution, acid, base and buffer solutions were prepared as mentioned in section II.A.(3).

(b) Procedure

Seven to ten 250-ml beakers containing identical amounts of nickel and hydroxylamine hydrochloride solutions, proportionately mixed according to the reagent excess ratios selected, were prepared. The pH of each mixture was adjusted to the desired value with ammonia and ammonium acetate solutions. They were then placed in a constant temperature bath set at a chosen reaction temperature. A separate vessel containing cycloheptanedione solution, pre-adjusted to the same pH, was also allowed to come to the same temperature. After 3 1/2 to 4 hours, an equal volume of cycloheptanedione solution, selected for a particular reagent excess ratio, was added to each beaker and the time of mixing was recorded. At selected reaction times, one beaker was removed from the bath and the precipitation was stopped immediately by filtering the solution through a sintered crucible of medium porosity. Each precipitate was dried at 130°C to constant weight.

This procedure was applied during preliminary experiments as summarised in the following table.

Table (2)
Preliminary studies on the experimental condition of the nickel cycloheptanedionedioximate precipitation

Nickel (mg)	CHDO/Ni (X)	HX/CHDO (X)	pH	Temp °C	Reaction time when the precipitation was stopped by filtration (hour)
5.0	2	10	6.75	75	0.25,0.50,1.0,1.5,2.0,2.5,3.0,3.5
5.0	2	10	6.75	23	0.50, 1.0,2.0,3.0,4.0,5.0,6.0,7.0,8.0,10
5.0	2	2	6.75	23	0.50,1.0,2.0,3.0,4.0,5.0,6.0,7.0
5.0	2	2	7.25	23	0.25,0.50,1.0,2.0,2.5,3.0,4.9,5.0,6.0,7.0,8.0
5.0	2	2	7.25	15	0.50,0.75,1.0,1.5,2.0,2.5,3.0,3.5,4.0
3.0	2	2	7.25	15	0.58,0.67,0.75,0.83,1.0,1.2,1.3
3.0	1 1/2	2	7.25	15	0.58,0.67,0.75,0.83,1.0,1.2,1.3

II.B.(2) Studies on the rate of precipitation of nickel cycloheptanedionedioximate when nickel "alone" is present

After selection of the best experimental conditions, a precipitation of nickel heptoximate was performed with smaller initial amounts of nickel.

(a) Apparatus and reagents

Apparatus

Constant temperature bath

The same instrument described in section II.B.(1) was used.

Reaction tubes

Test tubes of 28 mm inner diameter and 100 mm height (cellulose nitrate, supplied by "International" Co.) were utilised as reaction tubes. A volume mark for 25.0 ml capacity was made and each was calibrated with respect to class 'A' volumetric flasks.

Reaction tube holder and shaker

A mechanical shaker which holds a maximum of ten reaction tubes was designed and constructed. The apparatus is illustrated in Figure (2).

Filtering Apparatus

The centrifugal filter holder of type (no. 4305) was supplied by Gelman Co. and has three separable parts. The middle part has a piece of metal screen which holds a 20 mm diameter filter paper. The solution from the top portion passes through the filter and is collected in the bottom container. A maximum volume of 27 ml can be handled. The apparatus is shown in Figure (2). Filter papers supplied by the same company were G.A.(1) type which has an average pore size of 5.0 micron.

Figure (2) The centrifugal filter holder and the mechanical shaker

Centrifuge

A refrigerated centrifuge (model PR2, "International" Co.) which can be operated in the temperature range of -20 to +40°C was used for centrifugation.

Atomic Absorption Spectrophotometer

For analysis of nickel, a Perkin-Elmer model 303 atomic absorption spectrophotometer equipped with a multielement lamp was used. It includes a DCR2 direct concentration read-out unit.

Glassware

Pyrex glassware was used and calibrated pipettes and volumetric flasks were used where applicable.

Reagents

Nickel(II) solution, hydroxylamine hydrochloride solution, acid, base and ammonium acetate solutions were prepared as mentioned in section II.A.(3). Cycloheptanedione solution was obtained by dissolving a known amount of purified compound in deionised water. Preparation and purification of the cycloheptanedione was carried out according to the procedure described in section II.A.(2). The prepared diketone solution of approximately 3 mg per ml was filtered using a sintered glass crucible of medium porosity.

(b) Procedure:

3.0 mg amount of nickel in solution and a volume of hydroxylamine hydrochloride which contains 60 mg of the salt were mixed in a small beaker. The mixture was adjusted to pH 7.25 and transferred to a reaction tube. Five to seven reaction solutions were prepared and cooled to 15°C by standing in the reaction tube and shaker which was placed in a constant temperature bath. A cycloheptanedione solution of pH 7.25 was also adjusted to the same temperature. After 3 1/2 to 4 hours cooling time, a volume of cycloheptanedione solution which contained 19.5 mg of the diketone was added to each of the reaction tubes. Each was made up to 25.0 ml volume with deionised water of the same temperature and shaking was started. The time of mixing was recorded.

At different stages of precipitation (35, 40, 45, 50, 60, 70 and 80 minutes reaction time) a reaction tube was removed from the bath and immediately transferred to a centrifugal filter holder. Precipitates and filtrates were separated by immediate centrifugation. The temperature of the centrifuge was set at the experimental temperature as well. All the collected fractions were treated for analysis according to the detailed procedure reported in the schematic diagram shown as Figure (3).

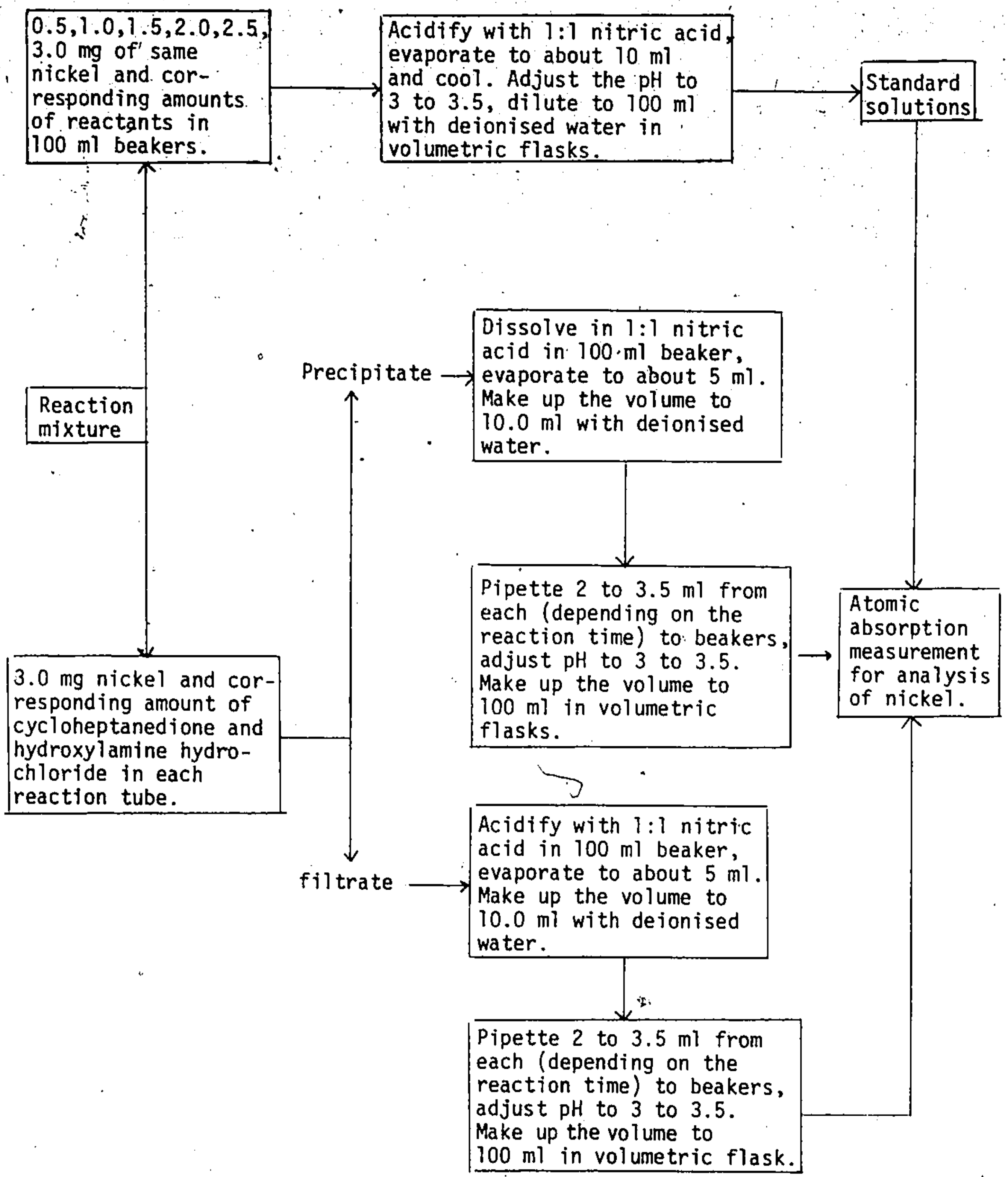
II.B.(3) Studies on the rate of precipitation of nickel cycloheptanedionedioximate in the presence of cobalt.

See section II.(C).

II.B.(4) Studies on the rate of precipitation of nickel cycloheptanedionedioximate in the presence of copper

See section II.(D).

Figure (3) Schematic diagram representing the procedure performed during a kinetic study of the nickel heptoximate precipitation reaction.


0.5,1.0,1.5,2.0,2.5, 3.0 mg of same nickel and corresponding amounts of reactants in 100 ml beakers.
Acidify with 1:1 nitric acid, evaporate to about 10 ml and cool. Adjust the pH to 3 to 3.5, dilute to 100 ml with deionised water in volumetric flasks.
Standard solutions
Reaction mixture
Precipitate
Dissolve in 1:1 nitric acid in 100 ml beaker, evaporate to about 5 ml. Make up the volume to 10.0 ml with deionised water.
Pipette 2 to 3.5 ml from each (depending on the reaction time) to beakers, adjust pH to 3 to 3.5. Make up the volume to 100 ml in volumetric flasks.
Atomic absorption measurement for analysis of nickel.
3.0 mg nickel and corresponding amount of cycloheptanedione and hydroxylamine hydrochloride in each reaction tube.
filtrate
Acidify with 1:1 nitric acid in 100 ml beaker, evaporate to about 5 ml. Make up the volume to 10.0 ml with deionised water.
Pipette 2 to 3.5 ml from each (depending on the reaction time) to beakers, adjust pH to 3 to 3.5. Make up the volume to 100 ml in volumetric flask.

II.C. Coprecipitation of cobalt with nickel cycloheptanedionedioximate

In a gravimetric determination of nickel, such cations as iron, cobalt and copper usually interfere and it is desirable to investigate their coprecipitation behaviour with some analytically important nickel chelates. The experimental procedure was similar to that used in the kinetic study when nickel "alone" was present in solution. The trace element was added together with carrier nickel.

II.C.(1) Apparatus and Reagents

Apparatus

Atomic Absorption Spectrophotometer

For analysis of nickel and cobalt the same atomic absorption spectrophotometer (Perkin-Elmer model 303 with DCR2 read-out unit) was utilised. Reaction tubes, shaker unit, filter holders, centrifuge, constant temperature bath and glassware used were the same as those mentioned in section II.B.(2).

Radioactivity measurement

Determination of ^{60}Co was made by the gamma ray counting technique with a well type, 3" x 3" NaI(Tl) detector. The detector was supplied by Harshaw Co. It was attached to a preamplifier (Hewlett-Packard Co., model 5554A) and a single channel analyser (Camberra, model 1431). The scaler-time unit used for read-out was supplied by Nuclear Chicago Co. (model 8703).

Pipettes for radioactive samples

Eppendorf micropipettes with disposable tips were used for measuring volumes of radioactive samples.

Separation of radionuclide

Radioactive cobalt was separated from nickel solution on an ion exchange column packed with strongly basic anion resin (Dowex 1-X8, 100-200 mesh). Pyrex columns of 7 mm ID x 27 cm length were used. A thistlefunnel shaped reservoir was attached to each column.

Reagents

Nickel ion solution, cycloheptanedione, hydroxylamine hydrochloride, acid, base, and buffer solutions were prepared as described in section II.A.(3).

Cobalt ion solution was prepared from reagent grade cobaltous chloride hexahydrate and standardised by precipitation with α-nitroso-β-naphthol (123).

Radioisotope ^{60}Co (5.29 year) was produced by an (n,γ) reaction on the stable isotope ^{59}Co (as $CoCl_2$). The spectrum of the irradiated sample showed close resemblance to the standard gamma-ray spectrum of cobalt-60. A stock solution of specific activity (8.5×10^5 dps/ml) was prepared and appropriate dilutions were made with .1 M hydrochloric acid whenever necessary.

II.C.(2) Procedure

7 to 9 reaction tubes containing identical amounts of nickel and hydroxylamine hydrochloride (3 mg nickel and 60 mg hydroxylamine hydrochloride) were prepared as in section II.B.(2). Equal amounts of cobalt, stable or radioactive isotope, were added to each of them. Addition of cycloheptanedione, shaking, and separation of precipitates

from the mother liquor at different reaction times were carried out as described in section II.B.(2).

Analysis of nickel in the filtrate and cobalt in both precipitate and filtrate were carried out by following the procedural sequence illustrated in Figure (4). (The scheme is for 1.0 μg of tracer cobalt but it was also used for other trace levels of radioactive cobalt. When stable cobalt isotope was used, the method was the same except that cobalt was analysed by an atomic absorption technique).

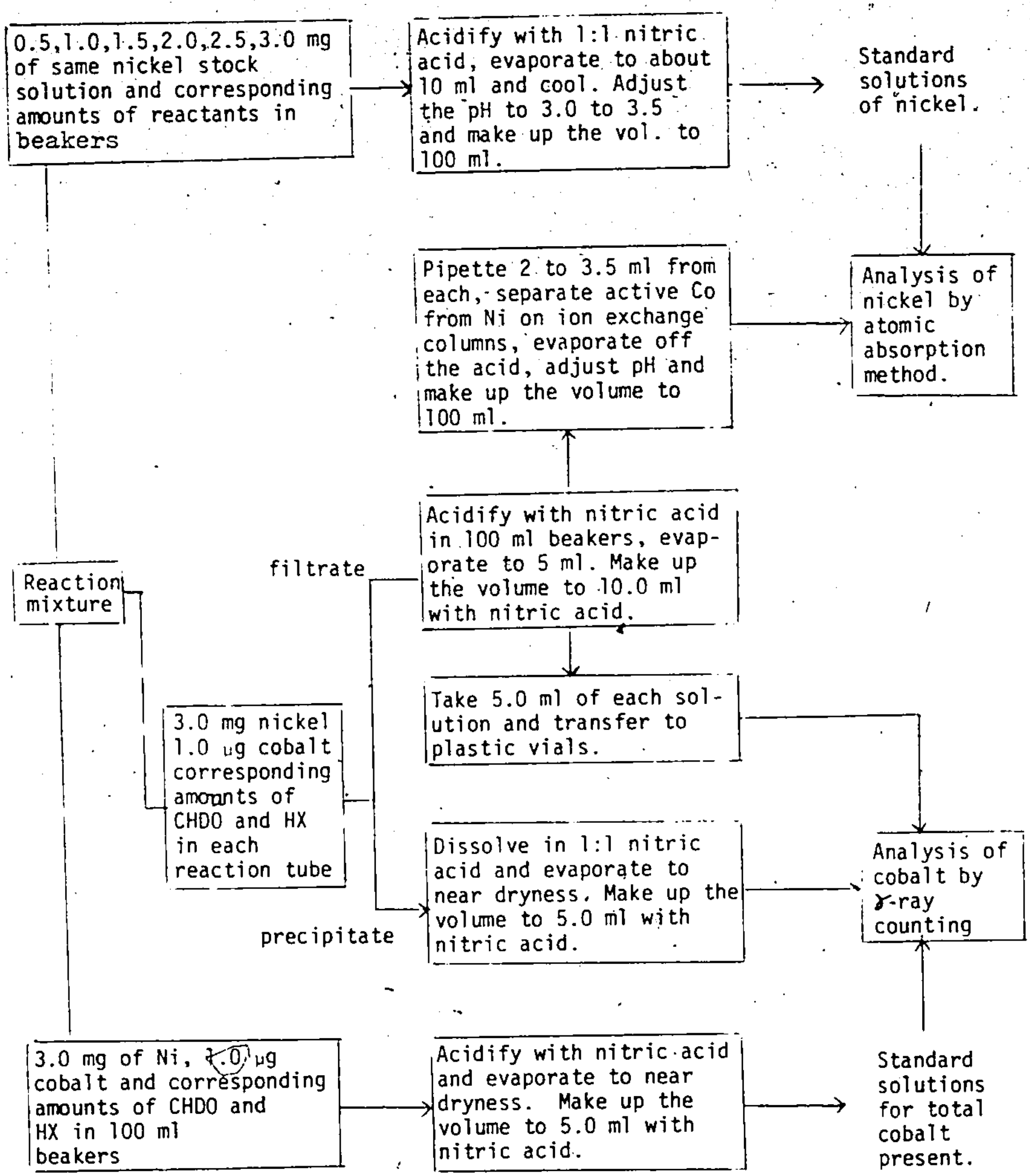
Separation of active cobalt from nickel in the filtrate

Prior to analysis of nickel in each filtrate, radioactive cobalt was separated from it by using an ion exchange technique.

Procedure:

2 to 3.5 ml of the filtrate portion (depending on the reaction time) was mixed with 7.5 ml of 10 M HCl and was allowed to pass through the prepared ion exchange column, packed with strongly basic anion resin, preconditioned with 10 M HCl. Three additional 10 ml volumes of 10 M HCl were used for elution. Effluent containing cobalt-free nickel was evaporated to remove acid and processed further as described in the schematic diagram for determination of nickel (Figure (4)). Active cobalt remaining on the resin was eluted with 1 M HCl followed by washing with deionised water.

Figure (4) Schematic diagram of the procedure for the coprecipitation of cobalt with nickel heptoximate


0.5,1.0,1.5,2.0,2.5,3.0 mg of same nickel stock solution and corresponding amounts of reactants in beakers
Acidify with 1:1 nitric acid, evaporate to about 10 ml and cool. Adjust the pH to 3.0 to 3.5 and make up the vol. to 100 ml.
Standard solutions of nickel.
Pipette 2 to 3.5 ml from each, separate active Co from Ni on ion exchange columns, evaporate off the acid, adjust pH and make up the volume to 100 ml.
Analysis of nickel by atomic absorption method.
Reaction mixture
filtrate
Acidify with nitric acid in 100 ml beakers, evaporate to 5 ml. Make up the volume to 10.0 ml with nitric acid.
Take 5.0 ml of each solution and transfer to plastic vials.
3.0 mg nickel 1.0 μg cobalt corresponding amounts of CHDO and HX in each reaction tube
Dissolve in 1:1 nitric acid and evaporate to near dryness. Make up the volume to 5.0 ml with nitric acid.
precipitate
Analysis of cobalt by γ-ray counting
3.0 mg of Ni, 1.0 μg cobalt and corresponding amounts of CHDO and HX in 100 ml beakers
Acidify with nitric acid and evaporate to near dryness. Make up the volume to 5.0 ml with nitric acid.
Standard solutions for total cobalt present.

The above procedure was applied in the following coprecipitation experiments : 3.0 mg nickel and 0.5, 1.0, 5.0, 10.0, 100.0 μg of cobalt at 15°C, 3.0 mg of nickel and 1.0 μg of cobalt at 5°C and 5.0 mg of nickel and 1 mg of cobalt at 23°C. Three repetitive runs were performed for each experiment except the one at 5°C.

II.D. Coprecipitation of copper with nickel cycloheptanedionedioximate

Copper reacts with 1,2-cycloheptanedionedioxime to form a brown insoluble complex. Its interference in the conventional precipitation of nickel cycloheptanedionedioximate has been reported (92). A coprecipitation study similar to that of cobalt with nickel heptoximate was performed.

II.D.(1) Apparatus and Reagents

Apparatus

Spectrophotometer

Spectrophotometric measurements were made using a Spectronic 600 spectrophotometer supplied by Bausch and Lomb, Inc.with cells supplied by the Scientific Cell Company Ltd.

Atomic absorption spectrophotometer, constant temperature bath, reaction tubes, shaker, centrifuge and glassware used were the same as described in section II.A.(3).

Reagents

Nickel ion solution, cycloheptanedione and hydroxylamine hydrochloride, acid, base and buffer solutions were prepared as mentioned in section II.A.(3).

Copper ion solution

Copper ion solution was prepared from reagent grade copper sulphate pentahydrate and was standardised by precipitation as cuprous thiocyanate (122).

Dibenzyldithiocarbamate solution

A 0.01% reagent solution was prepared from reagent grade zinc dibenzyldithiocarbamate salt in carbon tetrachloride.

II.D.(2) Experimental procedures

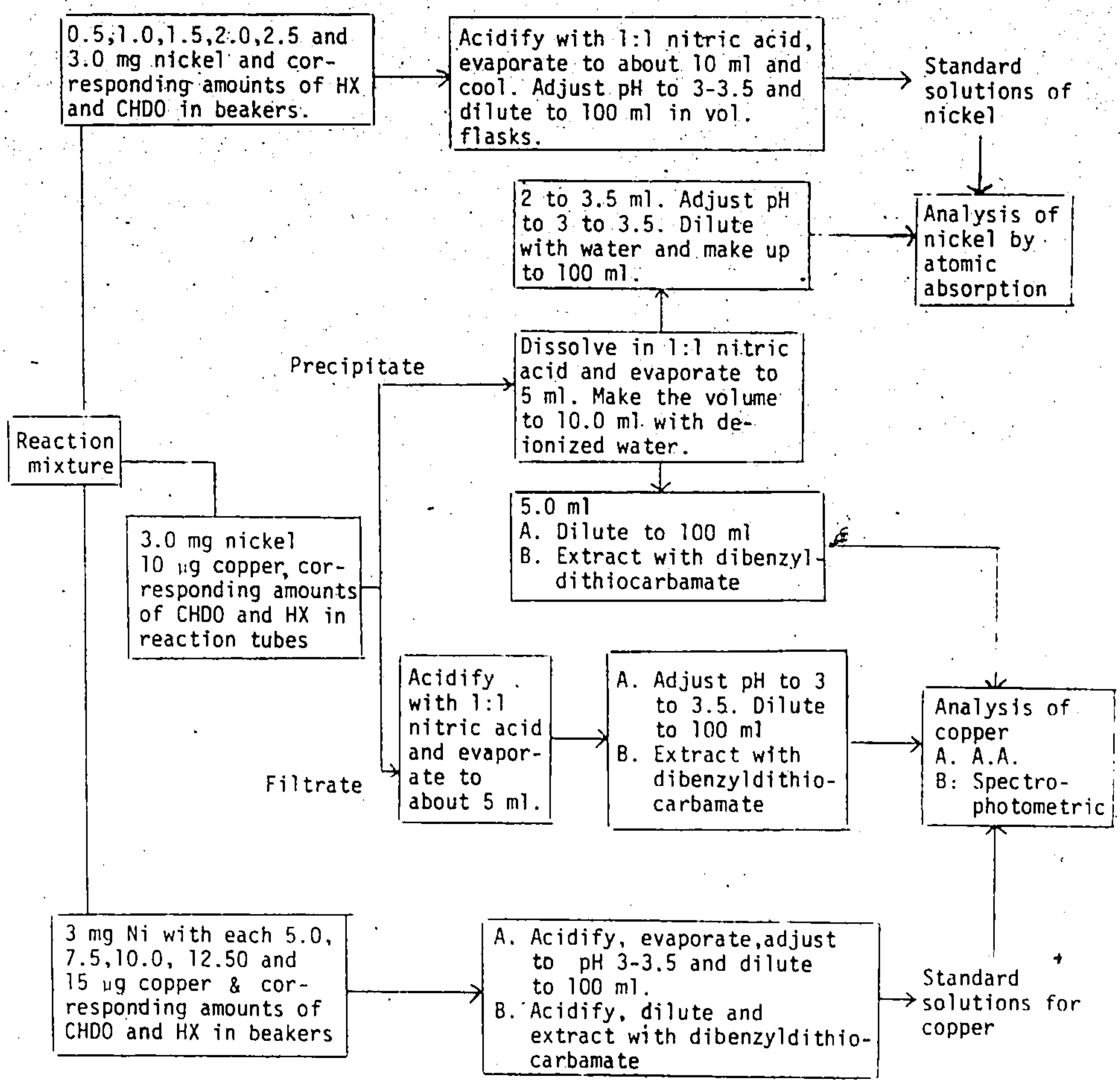
A similar procedure to that used during studies on the co-precipitation of cobalt with nickel heptoximate was applied but with cobalt (II) replaced by copper (II) (Section II.C.(2)). The schematic diagram, included as Figure (5), shows the detailed stepwise experimental procedure. Analysis of nickel was done on the precipitate fractions using the procedure reported in section II.C.(2).

Analysis of copper was carried out in one of two ways - either by atomic absorption or by a U.V.-visible spectrophotometric determination. The atomic absorption method was applied for samples with a copper content greater than 10.0 μg (procedure A). Samples of smaller copper content were analysed by the spectrophotometric method (procedure B).

Procedure B:

The sample to be analysed for copper was transferred to a 250 ml beaker and diluted to 100 ml with deionised water and dilute sulphuric acid. The acidity of the solution was approximately one normal. It was transferred and shaken with a 10 ml portion of 0.01% dibenzyldithiocarbamate

Figure (5). Schematic diagram of the procedure for the coprecipitation of copper with nickel heptoximate


0.5,1.0,1.5,2.0,2.5 and 3.0 mg nickel and corresponding amounts of HX and CHDO in beakers.
Acidify with 1:1 nitric acid, evaporate to about 10 ml and cool. Adjust pH to 3-3.5 and dilute to 100 ml in vol. flasks.
Standard solutions of nickel
2 to 3.5 ml. Adjust pH to 3 to 3.5. Dilute with water and make up to 100 ml.
Analysis of nickel by atomic absorption
Precipitate
Dissolve in 1:1 nitric acid and evaporate to 5 ml. Make the volume to 10.0 ml with deionized water.
Reaction mixture
5.0 ml
A. Dilute to 100 ml
B. Extract with dibenzyldithiocarbamate
3.0 mg nickel 10 μg copper, corresponding amounts of CHDO and HX in reaction tubes
Acidify with 1:1 nitric acid and evaporate to about 5 ml.
A. Adjust pH to 3 to 3.5. Dilute to 100 ml
B. Extract with dibenzyldithiocarbamate
Analysis of copper
A. A.A.
B: Spectrophotometric
Filtrate
3 mg Ni with each 5.0, 7.5,10.0, 12.50 and 15 μg copper & corresponding amounts of CHDO and HX in beakers
A. Acidify, evaporate,adjust to pH 3-3.5 and dilute to 100 ml.
B. Acidify, dilute and extract with dibenzyldithiocarbamate
Standard solutions for copper

solution in carbon tetrachloride in a 250 ml separatory funnel. After the separation, the organic layer was transferred to a second separatory funnel. The former funnel was carefully rinsed with fresh carbon tetrachloride 30 ml of water, 5 ml of 8N sulphuric acid and 2 ml of 0.5 N potassium permanganate solution were added and the whole mixture was shaken for four minutes. After settling for a few minutes, the mixture was shaken briefly with 3 ml of 10% hydroxylamine hydrochloride solution. When all the permanganate colour completely disappeared, the carbon tetrachloride layer was removed and discarded. The aqueous layer was extracted again with a 10 ml portion of 0.01% dibenzyldithiocarbamate reagent. The resulting transmittance of the coloured organic layer was measured at 435 mμ on a spectrophotometer. Standard solutions were processed in a similar manner.

Following the procedural scheme of Figure (5) coprecipitation experiments were carried out with 3.0 mg of nickel and 2.5, 5.0, 10.0, 25.0, 50.0, 100.0 μg of copper at 5°C and with 3.0 mg of nickel in the presence of 100.0 μg of copper at 15°C. The scheme is representative for 10.0 μg of copper but it was also used for other levels of copper present.

II.E. Determination of total number of crystals formed during the precipitation of nickel heptoximate

The rate of precipitation per active site is an important experimental variable in the coprecipitation model of Klien and

Fontal (119). It is assumed here that the number of active sites is proportional to the number of crystals formed during the precipitation. The number of crystals was determined using a conventional blood cell type counting technique.

II.E.(1) Apparatus and reagents

Apparatus

Particle counting instrument

A "Coulter counter" model "B" equipped with 100 μ aperture tube was used. The instrument was supplied by Coulter Electronics, Inc.

Filtering apparatus

A four gallon pressure filtering apparatus supplied by Cornelius Co. was used for filtering the electrolyte solution. The filter paper used was of sartorious membrane PVC type which has a 0.45 micron average pore size. Pressure was applied to the system using compressed nitrogen.

Reaction tubes, shaker, constant temperature bath, centrifuge and glassware used were the same as described in section II.B.(2).

Reagents

Chemicals reported in section II.C and II.D were utilized for precipitation procedures.

Electrolyte solution

A solution of 1M potassium chloride (reagent grade) which had been pressure filtered at least twice was used as electrolyte. A few drops of 1% w/v Titron X in the electrolyte solution served as a dispersing reagent.

II.E.(2) Procedures

(a) Background counting

Procedure:

The Coulter counter probe equipped with 100 μ aperture tube was filled with electrolyte solution after flushing the glassware with the same solution. It was then immersed in the electrolyte solution contained in a 250-ml beaker. At least five readings of the background count were determined and recorded (resistance matching = 32L, amplification = 1/2, aperature current = 2, lower threshold = 1.0, upper threshold = 103.0, mode = separate).

(b) Determination of number of crystals in the precipitation of nickel heptoximate in the presence of cobalt

Procedure:

Seven to nine reaction tubes each containing 3.0 mg of nickel, 60 mg hydroxylamine hydrochloride and 0.5 μg of radioactive cobalt (60) were prepared in the same way as mentioned in section II.C.(2). They were held in the reaction tube holder-shaker at a constant temperature of 15°C. A solution of 1,2-cycloheptanedione, cooled to the same temperature was used for addition of 19.5 mg of the reagent to each reaction tube. The time of mixing the reagents was recorded for each tube.

At particular pre-determined reaction times, one reaction tube was removed from the bath and diluted to appropriate volume at once with electrolyte solution. (Dilution was made so as to obtain total counts of 10,000 to 100,000 per ml of sample solution.) A 250 ml beaker containing the diluted sample was placed on the beaker stand and the total number of particles was counted immediately. The method used was the same as that of background counting. Similar measurements were made at reaction intervals of 35, 40, 45, 50, 55, 60, 65, 70 and 75 minutes. Flushing the instrument with electrolyte and checking the background were performed between measurements of each sample.

Two identical experiments were repeated on the precipitation of nickel heptoximate in the presence of 1.0 μg of cobalt (60) at 15°C and with additional time intervals of 2.0, 5.50, 6.50, and 7.50 hours.

(c) Determination of number of crystals in the precipitation of nickel heptoximate in the presence of copper

Procedure:

Two similar experiments to that of section (b) were repeated but cobalt (II) was replaced by copper (II) and the temperature was changed to 5°C. 25 μg of copper was precipitated together with 3.0 mg of nickel. Dilutions and countings were made at reaction intervals of 80, 90, 100, 120, 130, 140, 160, 180 and 210 minutes.

III. DATA PROCESSING AND ERROR ANALYSIS

III.A. Data Analysis in Kinetic Studies

The observables used in the kinetic plots were amounts of nickel in the precipitate, initial concentration of cycloheptanedione, initial concentration of hydroxylamine hydrochloride and reaction time.

For kinetic plots, values of

$$\left[\frac{[CHDO]^{o} - 2(\text{nickel in ppt})}{[HX]^{o} - 4(\text{nickel in ppt})}\right] \quad \text{and reaction time (t)}$$

were used as variables in the least square program (program (1), Appendix III). The calculated values of slope and the intercept provided the apparent rate constant (k') and integration constant (c'). Corresponding standard deviation values from the computer output were used for calculation of the errors associated with each (k') and (c')at the 95% confidence level.

To report the error associated with the average rate constant ($\bar{k}'$), all values of k' with the associated error of each were processed as follows.

$$\text{Variance of } \bar{k}' = \left[\frac{\partial \bar{k}'}{\partial k_1'}\right]^2 \text{Var. of } k_1' + \left[\frac{\partial \bar{k}'}{\partial k_2'}\right]^2 \text{Var. of } k_2' + \ldots$$

$$\ldots. + \left[\frac{\partial \bar{k}'}{\partial k_n'}\right]^2 \text{Var. of } k_n'.$$

$$\text{or Variance of } \bar{k}' = \left[\frac{1}{N}\right]^2 [\text{Var. of } k_1' + \text{Var. of } k_2' + \ldots + \text{Var. of } k_n']$$

$$\text{Error in } \bar{k}' = \sqrt{\frac{\text{Var. of } \bar{k}_1}{N}} \cdot t_{(n-1)_{0.975}}$$

N = number of observations

Similarly, errors associated with the average integration constant were calculated as

$$\text{Error in } \bar{c}' = \sqrt{\frac{\text{Var. of } \bar{c}'}{N}} \cdot t_{(n-1)_{0.975}}$$

$t_{(n-1)0.975}$ = random variable for N at 95% confidence level.

The error calculated as above for the average apparent rate constant ($\bar{k}'$) was directly transferred and reported as the error associated with the true rate constant value (k).

III.B. Calculation of Distribution Coefficients

III.B.(1) Primary observables

The primary observables required for data analysis are total (initial) nickel, nickel in the solution and nickel in the precipitate at various stages of the precipitation reaction, total (initial) tracer, tracer in solution and tracer in the precipitate at various stages of the precipitation reaction.

In the determination of nickel by the atomic absorption technique, the standard solutions for calibration purposes were prepared from the nickel stock solution used for the preparation of the reaction mixture. The observed amounts of nickel present in the filtrate and the precipitate samples, therefore, were relative to the total nickel added to the initial reaction mixture. For convenience, relative concentrations were used in calculations rather than absolute values of the concentrations.

During the preliminary investigations, both the filtrate samples and precipitate samples were analysed for their nickel content. (These were prepared from the filtrate and precipitate portions resulting from filtration of the reaction mixture during the precipitation using the procedure noted in section (II.B.)). Within the accuracy of the experiments, the observed mass balance showed good agreement with the initial nickel added (see table (1), Appendix III). When cobalt was used as the tracer, nickel was analysed in the filtrate samples only and precipitate samples only were used for the analysis of nickel when copper tracer was present in the system. The additional data were obtained by use of the mass balance relationship.

A linear least square program which prepares a calibration plot and provides the concentrations of nickel for each sample analysed (program (1), Appendix III) was used for data analysis. The program computes the slope of the straight line and the intercept with their associated errors. A plot of the input data is also printed in the computer output.

Between four and seven measurements usually were taken for each sample solution analysed by atomic absorption. The observed concentrations were then computed by a standard deviation program (program (2), Appendix III). The program provides the mean value of the "n" number of measurements, the variance and the standard deviation of the mean for each observable. The variance value was used for calculating the error associated with the observable at the 95% confidence level, i.e.

$$\text{error} = \sqrt{\frac{\text{Variance}}{n}} \times t_{(n-1)0.975}$$

A similar procedural sequence was applied to the analysis of copper in the filtrate and precipitate samples. The error associated with each observable was similarly reported at the 95% confidence level. A typical mass balance is reported in table (2), Appendix III. When Cobalt-60 was used as the tracer, a gamma ray counting technique was applied. The standard deviation recorded for each sample was the square root of the total number of counts observed. Total tracer (initial) was used as the standard for counting and the tracer in solution and tracer in precipitate was calculated relative to the total amount. A good mass balance was usually observed. An example of the mass balance is reported in table (4), Appendix III.

III.B.(2) <u>Calculation of errors associated with the distribution coefficients</u>

The equations used for calculation of the distribution coefficients are

$$\lambda = \frac{\ln\left[\frac{[\text{Total tracer}]}{[\text{Tracer in solution}]}\right]}{\ln\left[\frac{[\text{Total carrier}]}{[\text{Carrier in solution}]}\right]} \quad \text{and} \quad D = \frac{\left[\frac{[\text{Tracer in precipitate}]}{[\text{Carrier in precipitate}]}\right]}{\left[\frac{[\text{Tracer in solution}]}{[\text{Carrier in solution}]}\right]}$$

(a) Error associated with λ

$$\text{Let } \lambda = \frac{\ln\left[\frac{[TT]}{[TS]}\right]}{\ln\left[\frac{[CT]}{[CS]}\right]}$$

where, [TT] = total tracer

[TS] = tracer in solution

[CT] = carrier total

[CS] = carrier in solution

Thus, the variance of λ = $\left[\frac{\partial\lambda}{\partial(TT)}\right]^2 . \text{Var. }(TT) + \left[\frac{\partial\lambda}{\partial(TS)}\right]^2 . \text{Var. }(TS)$

$$+ \left[\frac{\partial\lambda}{\partial(CT)}\right]^2 . \text{Var. }(CT) + \left[\frac{\partial\lambda}{\partial(CS)}\right]^2 . \text{Var. }(CS)$$

Since the variance of TT (total tracer) and variance of CT (total carrier) are relatively small compared to those of TS (tracer in solution) and CS (carrier in solution), the expression becomes

$$\text{Var. of } \lambda = \left[\frac{\partial\left\{\dfrac{\ln\left[\dfrac{(TT)}{(TS)}\right]}{\ln\left[\dfrac{(CT)}{(CS)}\right]}\right\}}{\partial(TS)}\right]^2 . \text{Var. }(TS) + \left[\frac{\partial\left\{\dfrac{\ln\left[\dfrac{(TT)}{(TS)}\right]}{\ln\left[\dfrac{(CT)}{(CS)}\right]}\right\}}{\partial(CS)}\right]^2 . \text{Var. }(CS).$$

$$= \left[-\frac{1}{(TS).\ln\left[\dfrac{(CT)}{(CS)}\right]}\right]^2 . \text{Var. }(TS) + \left[-\frac{\ln\left[\dfrac{(TT)}{(TS)}\right]}{(CT).\left[\ln\dfrac{(CT)}{(CS)}\right]^2}\right]^2 . \text{Var. }(CS).$$

A computer program (program (3), Appendix III) was utilised for calculation of variance in λ. Errors associated with λ at the 95% confidence level were then calculated.

(b) Error associated with D.

$$\text{Let } D = \frac{\left[\frac{(TP)}{(CP)}\right]}{\left[\frac{(TS)}{(CS)}\right]}$$

$$\text{Then, variance of } D = \left[\frac{\partial D}{\partial(TP)}\right]^2 . \text{Var. } (TP) + \left[\frac{\partial D}{\partial(CP)}\right]^2 . \text{Var. } (CP)$$

$$+ \left[\frac{\partial D}{\partial(TS)}\right]^2 . \text{Var. } (TS) + \left[\frac{\partial D}{\partial(CS)}\right]^2 . \text{Var. } (CS)$$

$$= \left[\frac{(CS)}{(CP)(TS)}\right]^2 . \text{Var. } (TP) + \left[\frac{(TP)(CS)}{(CP)^2.(TS)}\right]^2 . \text{Var. } (CP) +$$

$$\left[\frac{(TP)(CS)}{(CP).(TS)^2}\right]^2 . \text{Var. } (TS) + \left[\frac{(TP)}{(CP)(TS)}\right]^2 . \text{Var. } (CS)$$

Variance of D values were calculated using a computer program (program (4), Appendix III) and error associated with each D at the 95% confidence level was then calculated.

III.C. Data Analysis in the Application of Klein's Equations

The observables required for use in Klein's equation $\frac{I}{N}(\lambda-1) = k_2\lambda-k_1$ have been discussed in previous sections, except the total number of particles (N) which were formed during the precipitation of nickel heptoximate. As discussed in section II.E., the total number of particles were measured at least five times for each sample. The average value of counts for each sample was calculated using the standard deviation program (program (2), Appendix III) and the error associated with each was reported at the 95% confidence level.

Values of $\frac{I}{N}(\lambda-1)$ and λ were used as variables in the least square program (program (1), Appendix III) and the resulting values of slope and intercept were recorded as values of (k_2) and (k_1) respectively. Program (1) also provided their associated standard deviation values. In calculating the error associated with the rate constant ratio $(\frac{k_1}{k_2})$, the corresponding standard variation values of k_1 and k_2 were used. The equation used was

$$\text{Variance of } \left[\frac{k_1}{k_2}\right] = \left[\frac{1}{k_2}\right]^2 \cdot \text{Var. } (k_1) + \left[\frac{k_1}{(k_2)^2}\right] \cdot \text{Var. } (k_2)$$

The associated error was then calculated at the 95% confidence level.

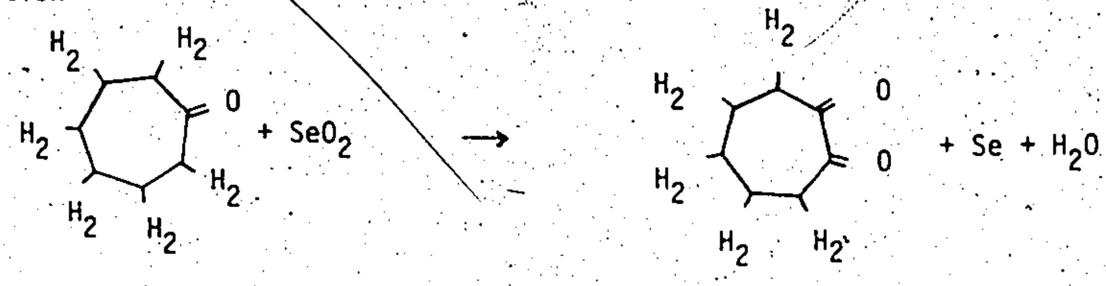
IV. RESULTS AND DISCUSSION

IV.A. Precipitation of nickel 1,2-cycloheptanedionedioximate from Homogeneous Solution

As discussed in section I.C., one of the aims of the project was the development of a PFHS method for the determination of nickel. Attention was focused on the direct synthesis of cycloheptanedione in solution and subsequently on the precipitation of nickel as nickel cycloheptanedionedioximate. Among other vic-dioximes, cycloheptanedionedioxime has been especially recommended for analytical use as a reagent for the gravimetric determination of nickel in conventional methods (88). Using PFHS procedures, the most successful method reported for the determination of nickel is the method of direct synthesis of dimethylglyoximate from biacetyl and hydroxylamine hydrochloride in the presence of nickel ions. By analogy, a PFHS technique was developed in the present research by generating, in situ, cycloheptanedionedioxime from cycloheptanedione and hydroxylamine for the determination of nickel. Since the required 1,2-cycloheptanedione was not available commercially, it had to be synthesised prior to our studies.

IV.A.(1) Preparation of 1,2-cycloheptanedione

The cycloheptanedione was synthesised by reacting cycloheptanone with freshly sublimed selenium dioxide in alcoholic medium. The reaction produced cycloheptanedione and selenium metal according to the following equation



When this reaction was carried out following the procedure proposed by Van der Harr, Voter and Banks (120), the observed yield of the product was very low - usually less than 20%, based on the monoketone. The percentage purity of the resulting diketone was also low, i.e. multiple peaks were observed during a gas chromatographic analysis. The presence of compounds with molecular weight higher than the diketone was indicated in the spectrum in addition to a small amount of unreacted cycloheptanone. The product, when dissolved in water, left small amounts of undissolved residue. The resultant crystals of nickel cycloheptanedionedioximate prepared from it by reaction with hydroxylamine in the presence of Ni(II) showed slight positive deviation in the weight of nickel recovered.

The purity of the product was not discussed by Van der Harr et al. since the diketone was immediately transformed to cycloheptanedionedioxime. The authors, however, were aware that the compound, on standing over a period of a few weeks, decomposed as indicated by a darkened appearance. All other procedures proposed for the preparation of cycloheptanedione cited in the literature (124,125) involved the immediate conversion to some other compounds after its preparation; thus the purity of resulting cycloheptanedione was not commented upon in detail.

It has been reported in the preparation of cyclohexanedione, however, that the diketone is usually contaminated by higher boiling derivatives when cyclohexanone and its monomethyl derivatives were reacted with selenium dioxide in alcoholic medium (126). The possibility of more advanced oxidation accompanied by dehydration was predicted in reaction of selenium dioxide and cyclic diketones of large rings. The by-products observed in our preparation of cycloheptanedione could have been formed by this reaction pathway.

Purification of the compound by solvent extraction and by fractional distillation on a spinning band column failed to isolate the diketone from the by-products. Ways of improving the method of preparation were thus considered.

A detailed study of the method of preparation was undertaken as reported in section II.A.(2). A series of liquid samples were withdrawn from the reaction mixture at various times during the refluxing period and were tested on a gas chromatograph. The series of spectra recorded at different reaction times provided identification of the compounds formed during the course of the reaction. The data obtained between six to seven hours refluxing showed near completion of the diketone formation and some traces of side products beginning to appear. The detection of a small amount of the starting monoketone suggested that a little excess of selenium dioxide should be present in the reaction mixture. A fourteen hour standing time was found to be the minimum period required for the highest yield of cycloheptanedione. It was also observed that the distillation of the crude product at very high still pot temperatures enhanced the formation of higher molecular weight components. From these observations the new set of experimental conditions for the method of preparation of cycloheptanedione, reported in section II.A.(2), were established.

The resulting compound was purified by crystallisation from anhydrous ether at the temperature of dry ice-acetone freezing mixture. The purified compound, when checked on a gas chromatograph, gave a single peak. Elemental analysis data, reported by a commercial laboratory, are compared with the theoretical values in Table (3).

Table (3)

Elemental analysis of 1,2-cycloheptanedione

	Observed value	Theoretical value
% Hydrogen	8.11	7.99
% Carbon	66.3	66.6
% Oxygen (by difference)	25.6	25.4

Partial characterization of the compound was carried out by spectroscopic methods. The data are reported in appendix I. The mass spectrum of the compound (Fig. (1) of appendix I) showed a molecular peak at 126 mass units. The calculated molecular weight of 1,2-cyclo-heptanedione is 126.16. In Fig. (2) of appendix I, the nuclear magnetic resonance spectrum of the compound is recorded. It shows two types of hydrogen resonance peaks having an area ratio of 2:3. This is due to the presence of four hydrogens which are α to the keto groups and six others which are at equivalent β and γ positions. The strong absorption of a carbonyl group from an α diketone is observed in the infrared spectrum (Fig. (3) of Appendix I) at 1710 cm^{-1}. The hydroxyl absorption at 3400 cm^{-1} indicates the presence of the enolised form of cycloheptanedione.

The percentage purity of the purified product was determined by using the procedure reported in section II.A.(2). The observed weight of cycloheptanedione was calculated from the final weight of nickel cycloheptanedionedioximate crystals. The percentage yield of the compound, calculated on the theoretical value, varied from 100 to 103 percent.

IV.A.(2) Studies on the precipitation of nickel cycloheptanedionedioximate from homogeneous solution

Data from preliminary experiments showed that the precipitation of nickel cycloheptanedionedioximate using reagent excess ratios of 2:1 for (CHDO/Ni) and 10:1 for (HX/CHDO) gave satisfactory results of nickel recovered. During the precipitation period, the yellow colour of nickel heptoximate appeared within 7 to 10 minutes after mixing the reagents. Standing times of 15 to 20 minutes at room temperature before digestion of the precipitates at higher temperatures provided a slow generation of dioxime in solution and hence a slow rate of precipitate formation. Foaming and creeping of the precipitates on the wall of the beaker were noted at digestion temperatures over 85°C.

Precipitates, prepared by controlled-room temperature standing periods and subsequent digestion temperatures, were made up of large, easy to handle and dense crystals suitable for gravimetric procedures. Thus, a thorough study of the conditions of precipitation was initiated.

(a) Excess reagent studies

Table (4) shows the effects of various reagent levels (cycloheptanedione and hydroxylamine hydrochloride) when used in precipitation procedures with various initial concentrations of nickel. Values of Δmg indicate the difference between the weight of nickel calculated from the observed precipitate weight and the known weight of nickel added to the reaction solution initially. Analytically acceptable Δ mg values resulted from reactions with CHDO/Ni ratios of 2 to a maximum of 10 and HX/CHDO ratios in the range of 8 to 10. Negative Δ mg values, however, were observed in the precipitations in which the reagent excess ratio of CHDO/Ni was 2 and values of HX/CHDO ratio were less than 10.

When the HX/CHDO ratio exceeds 100 and the CHDO/Ni ratio is 2, only slight deviations in Δ mg are noted but the reagent consumption is very high. The maximum amounts of reagents used for precipitation of nickel heptoximate were a CHDO/Ni ratio of 20 and a HX/CHDO ratio of 100. Analytically acceptable results were obtained. For every nickel level, the combination of reagent ratios of CHDO/Ni equal to 2 and HX/CHDO equal to 10 provided satisfactory results of nickel recovered. Thus this combination was recommended for quantitative precipitation of nickel heptoximate.

Table (4)

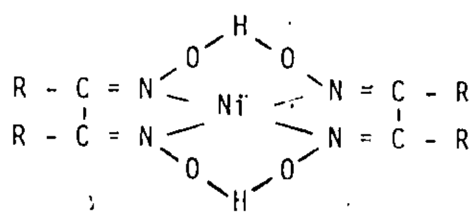
Effect of reagent excesses on the precipitation of nickel heptoximate

Ni (mg)	CHDO/Ni (X)	HX/CHDO (X)	Δ mg
1.00	2	10	-0.02
	20	100	+0.03
			+0.04
	100	10	-0.02
10.00	2	2	-2.37
	2	4	-0.91
	2	6	-0.63
	2	8	±0.00
	2	10	+0.01
	2	20	-0.01
	2	50	+0.01
	2	100	±0.00
	2	500	-0.04
	2	1000	-0.62
	4	10	-0.01
	6	10	±0.00
	10	10	±0.03
			±0.00
20.00	2	10	-0.12
	5	10	-0.01
50.00	2	10	+0.04

CHDO = cycloheptanedione
HX = hydroxylamine hydrochloride
X = reagent excess ratio

(b) Effect of pH, temperature and digestion time

Banks and Voter reported that the precipitation of nickel heptoximate by a conventional method was quantitative at pH 2.7 or greater (presumably ammoniacal solutions) (88). Precipitation in slightly acidic medium, however, was recommended since nickel could be separated from certain cations without the use of complexing agents. When a similar reagent, cyclohexanedionedioxime, was used to precipitate nickel in the conventional way, the precipitation was reported to be quantitative at pH 3.0 and greater. Heptoxime (cycloheptanedionedioxime) and nioxime (cyclohexanedionedioxime) have a distinct advantage in this respect over dimethylglyoxime which can only be used in neutral or alkaline media. The ability of both oximes to precipitate nickel in both acidic and alkaline media must be due in part to a structural effect. A systematic investigation of the compounds formed between nickel and various dioximes of structure type

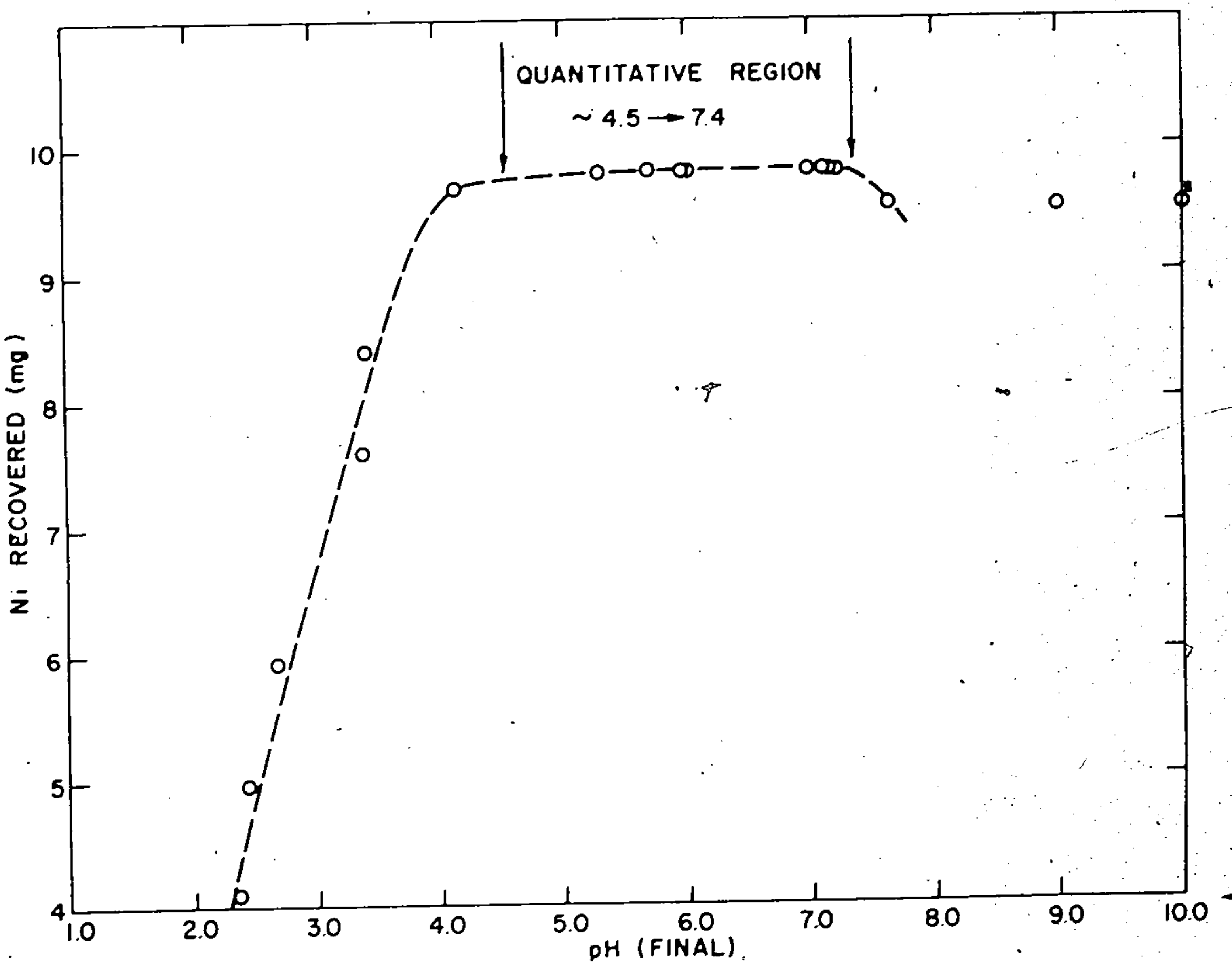


has revealed that, with increasing chain length in R, the nickel compound starts to form at lower pH values (79).

In our studies, the quantitative region for the precipitation of nickel heptoximate was found to be between pH 4.25 and 7.35. The effect of pH on the precipitation reaction is illustrated in Fig. (6). Precipitation reactions carried out at pH values outside this region resulted in low weights of nickel precipitate.

Figure (6) The effect of pH on the precipitation of nickel cycloheptanedionedioximate.

*Hanna, J.D., unpublished results.


QUANTITATIVE REGION
~ 4.5 → 7.4
Ni RECOVERED (mg)
10
9
8
7
6
5
4
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
pH (FINAL)

(c) Development of a PFHS procedure for the determination of nickel "alone"

Preliminary investigations conducted to determine the appropriate concentrations of reagents, pH, and a digestion sequence resulted in a set of experimental conditions for a new PFHS method for the determination of nickel alone. The method as detailed in section II.A.(4) was applied to the precipitation of 1.00 to 50.0 mg of nickel using the suggested conditions for 50.00 mg of nickel. Table (5) shows that the results obtained were precise and accurate.

In addition, the method is simple and easy. Crystals produced by relatively slow precipitation are large, dense and easy to filter.

(d) Determination of nickel in the presence of foreign ions

Nickel has been precipitated as nickel cycloheptanedionedioximate conventionally in the presence of aluminium, chromic, manganese, vanadate, plumbous, magnesium, zinc, cadmium, antimonite, arsenite, beryllium, ferric, titanous, cuprous, cobaltous, molybdate, and bismuth ions (88, 95). Voter and Banks discovered that aluminium, chromic, antimonite, arsenate, ferric, titanic and bismuth ions when present must be complexed with either tartrate or citrate to prevent their coprecipitation as hydroxides (88). It was further reported that cobaltous ion, which forms a brown complex compound with heptoxime, remains in solution if the cobaltous ion concentration is not too high. If appreciable amounts of cobaltous ion are present, however, a re-precipitation was recommended. The interference of cobalt in the conventional precipitation of nickel dimethylglyoxime was similarly eliminated by using excess dimethylglyoxime (127,128).

Table (5)

Precipitation of nickel alone with 1,2 cycloheptanedione.[a]

Ni taken (mg)	1.00[b]	5.00[b]	10.00	20.00	25.00	50.00
	+0.05	+0.04	+0.01	±0.00	+0.02	+0.05
Δ mg	+0.03	-0.02	±0.00	±0.00	±0.00	+0.03
found	±0.00	-0.03	-0.02	-0.01	-0.03	-0.05

(a) Standard procedure for 50 mgs. of Ni used in all cases.

(b) J.D. Hanna - unpublished results.

Voter and Banks, also investigated the effects of various anions on the determination of nickel as nickel heptoximate. Their results showed that acetate, tartrate, chloride, citrate, perchlorate, sulphate, sulphosalicylate, nitrate and thiocyanate when added as their ammonium salts or as their respective acids caused little interference in the precipitation. Besides the authors added, that the presence of ammonium acetate helped prevent the adsorption of excess reagent by the nickel heptoximate. After their investigation, the authors proposed a method for the determination of nickel as nickel heptoximate in iron and steel samples containing cobalt and copper.

A successful adaptation of their method was reported in 1969 in the determination of nickel radionuclides in bone and environmental samples (94). The method was particularly suited for the purpose because nickel could be precipitated from acidic medium (perchloric and nitric acid solution)required for the digestion of the biological materials and nickel could be precipitated in the presence of citrate, acetate and thiocyanate which complexed many of the radioisotopes known to be present in the environmental samples.

As in the conventional method for determination of nickel by cycloheptanedionedioxime one would expect to find useful applications of the PFHS technique if possible interferences from certain cations and anions could be eliminated. The study of some selected ions were thus initiated to investigate their effects on the proposed PFHS procedure.

Five cations (cobaltous, manganous, copper, ferrous and chromic) and some anions which are commonly used as complexing agents (chloride, tartrate, citrate, thiocyanate, fluoride, and oxalate) were studied to investigate their influence on the precipitation of nickel heptoximate from homogeneous solution. A summary of observations from these studies is reported in Table (6).

Table (6) shows that the anions studied have no or little effect on the precipitation of nickel heptoximate. These observations are in accord with those of Voter and Banks. Anyone, or combinations of these anions may be used as complexing agents or buffers in the system.

Among the cations studied, Co(II), Fe(II) and Cu(II) caused the most serious interferences in precipitation. The final weights of nickel in the heptoximate precipitates showed high calculated recoveries of nickel. Possibly these ions form stable complexes with heptoxime and have structures similar to that of nickel heptoximate. If this is the case, solid solution formation, one type of coprecipitation process could result. Coprecipitation of cobalt, iron and copper with nickel heptoximate was noted in the conventional precipitation procedure though no definite classification was mentioned (88).

In the PFHS method, amounts of cobalt up to a 1:2 cobalt to nickel ratio caused no serious interference when a large excess of cycloheptanedione was present. For larger ratios a double precipitation was found to be necessary to successfully separate the nickel from cobalt. This observation is in agreement with that of Voter and Banks. The data gathered are recorded in Table (7) and (7a).

The interference of iron was eliminated by oxidation to Fe(III) followed by masking with tartrate ion. Tartrate, however, can reduce

Table (6)

Study of complexing agents[a]

Ni (mg)	Heating time(hrs) and Temp. (C°)	NH_4Cl[b] (g)	Tartaric acid (g)	NH_4 citrate (g)	NH_4SCN (g)	NH_4F (g)	Δmg
20.00	3,80-90	1.0g					+0.05, ±0.00
20.00	3,80-90	2.5g					+0.05, +0:04
20.00	3,80-90	5.4g					+0.01, ±0.00
20.00	3,80-90		1.0				-0.05, -0.06
20.00	3,80-90		4.0				±0.00, -0.04
20.00	3,80-90		6.0				+0.02, +0.01
20.00	4,80-90		1.0				-0.06, -0.05
20.00	4,80-90		2.0				-0.04, +0.04
20.00	4,80-90		4.0				-0.04, ±0.00
20.00	4,80-90		6.0				+0.02, +0.01
10.00	3,70-75		0.25				-0.05, -0.04
10.00	3,70-75		1.00				+0.02, +0.03
10.00	3,70-75		2.50				-0.04, -0.02
10.00	3,70-75		5.00				-0.02, +0.03
25.00	4,80-90		2.50				-0.03, -0.06
10.00	3,70-75			0.25			-0.01, ±0.00
10.00	3,70-75			1.00			-0.02, ±0.00
10.00	3,70-75			2.50			+0.02, -0.05
10.00	3,70-75			5.00			-0.01, ±0.00
10.00	3,70-75				0.25		-0.02, -0.06
10.00	3,70-75				1.00		+0.03, +0.02
10.00	3,70-75				2.50		+0.04, -0.04
10.00	3,70-75				5.00		+0.05, +0.01
10.00	3,70-75					0.25	-0.02, -0.02
10.00	3,70-75					1.00	+0.02, +0.02
10.00	3,70-75					2.50	+0.04, ±0.00
10.00	3,70-75					5.00	+0.09, +0.04

[a] pH of the reaction mixture was 6.75 in all cases

[b] J.D. Hanna and P. Jones, unpublished results

Table (7)

Precipitation of nickel heptoximate in the presence of diverse ions

Ni (mg)	CHDO/Ni (X)	Mn^{+2} (mg)	Co^{+2} (mg)	Cr^{+3} (mg)	Tartrate (g)	Δmg
10.00	10	1				±0.00, ±0.01, +0.04
10.00	10.25	1				+0.04, +0.01
10.00	10.50	1				+0.04
10.00	10	2				+0.06, +0.06
10.00	10	5				-0.03, +0.01, ±0.00
10.00	10	10				+0.04, +0.05
10.00	2		1			+0.06
10.00	2.25		1			+0.04, +0.02, +0.03
10.00	2.75		2			±0.00, -0.03
10.00	2.9		5			+0.09, +0.15
10.00	2.9		10			+0.14
10.00	2.75		*5			-0.73, -0.02
10.00	2.75		*10			+0.02, ±0.00
10.00	2.75		*50			-2.81, -2.31
10.00	10			1	0.25	+0.01, -0.03
10.00	10			1	0.50	+0.02, -0.05
10.00	10			1	1.00	+0.02, +0.03
10.00	10			1	2.50	+0.05
10.00	10			5	1.25	+0.01, +0.04, +0.05
10.00	10			10	2.50	+0.02, ±0.00, +0.05

Initial conditions

HX/CHDO = 2X in all cases

pH = 6.75

Digestion time = 3 hours at 70-75°C

*Double precipitation was carried out.

Table (7a)

Precipitation of nickel heptoximate in the presence of diverse ions

Ni (mg)	CHDO/Ni (x)	Cu^{+2} (mg)	Fe^{+2} (mg)	$Na_2S_2O_3$ (g)	Tartrate (g)	Δ mg
10.00	10	5		0.1		+0.15
10.00	10	5		0.1		+0.01
10.00	10	10		0.2		+0.05, ±0.00
10.00	10	20		0.4		+0.05, ±0.00
10.00	10	20		0.4		+0.05
10.00	10	20		0.4		-0.03
10.00	10	50		0.8		+0.03
10.00	10	50		0.8		±0.00
10.00	10	50		0.8		+0.03
10.00	10		5		1.25	+0.01
10.00	10		5		1.25	-0.02
10.00	10		10		2.50	+0.12, -0.03
10.00	10		10		2.50	+0.04
10.00	10		20		5.00	+0.01
10.00	10		20		5.00	+0.08
10.00	10		50		10.00	+0.01, +0.04
10.00	10		70		15.00	+0.06

Initial conditions

HX/CHDO = 2X in all cases

pH = 6.75

Digestion time = 3 hours at 70-75°C

Fe(III) in solutions of high pH values and thus the precipitation was carried out at pH 6.25 when iron was present. The modified method gave satisfactory results of nickel recovered in the presence of iron up to a maximum nickel to iron ratio of 1:5.

Copper II was most successfully masked with thiosulphate at a pH of 6.25 or lower. The copper contamination was pH dependent in ammonical solutions containing thiosulphate (129). Since the copper contamination is a minimum at pH values 6.5 and lower, the precipitation of nickel heptoximate was carried out at a pH of 6.25. The copper thiosulphate complex decomposes at temperatures higher than 45°C and thus it was necessary to perform the reaction at lower temperatures. When copper was present, the reaction mixture containing copper, nickel and hydroxylaminehydrochloride was initially adjusted to pH 3 to 5 and heated to 35 to 40°C. A proper amount of thiosulphate was then added. After standing for several minutes, the pH was adjusted finally to 6.25 and cycloheptanedione solution was added. The nickel heptoximate crystals were digested for a period of 5 hours or more at room temperature. This modified procedure provided satisfactory results for the determination of nickel up to a 1:5 nickel to copper ratio. The results are shown in Table (7a).

Chromic ion also interferes with the precipitation of nickel heptoximate from homogeneous solution since the hydroxide forms easily in the reaction mixture. When complexed with tartrate ion, however, this interference was eliminated. Tartrate was found to be an effective complexing agent for chromic ion in both precipitation methods,PFHS and conventional.

Manganous ion interferes less than the other cations studied. No masking agent was necessary for manganese contents not exceeding the nickel concentration.

After a series of investigations on diverse ions, the precipitation procedure with modifications was used to precipitate the nickel contained in a National Bureau of Standards steel sample, No. 32(e) in order to test the effectiveness of the method.

(e) Determination of nickel in a steel sample as nickel cycloheptanedionedioximate

The procedure reported in section II.A.(5) was used to precipitate nickel in a National Bureau of Standards sample,[No. 32(e)]. The modified procedure gave satisfactory recovery of nickel when the experimental conditions were properly controlled. Results are shown in Table (8). A minimum reaction time of 7 hours at room temperature was required for complete precipitation of nickel. Very long digestion times (over 15 hours) resulted in low recoveries of nickel. This is in contrast with Salesin and Gordon's method for determination of nickel in a steel sample as the dimethylglyoximate. A digestion time of 24 hours at room temperature was suggested.

The present method was developed mainly for determination of nickel in the presence of large amounts of iron and traces of other ions, (Cr, Co, Mn, V, Pb, etc.). If a sample of high copper content is to be analysed, the procedure can be adapted by referring

Table (8)

Determination of nickel in a steel sample

Ni present %	Ni found %	Average Ni found %
1.19	1.19	1.20±0.01[a]
	1.20	
	1.21	
	1.20	
	1.23	
	1.19	
	1.19	
	1.18	
	1.20	

[a] The associated error at 95% confidence level.

to the modification of procedure to eliminate the copper. Similar modifications can be made if the sample contains high percentage of cobalt.

IV.B. Kinetic Studies

Previous reports have indicated that the rate of the precipitation has a profound effect on the distribution pattern of trace components within the precipitate(106,115). Most of the classical studies, however, have not utilised the reaction rate as an useful tool for interpretation of results. In some of these studies, it was noted that neither of the two limiting distribution models successfully rationalised the data obtained. Structural properties of the tracer and carrier precipitates were considered to be important factors in understanding the coprecipitation behaviour of the tracer in some particular metal chelate systems (130,131). Only a few recent studies have utilised the reaction rate as an additional guideline for data analysis and interpretation of results(116,118). It is our belief that knowledge of the kinetic aspects of the precipitation reaction will be useful in explaining the observations resulting from coprecipitation.

Kinetic aspects of the reaction between carbonyl compounds and nitrogen bases were discussed in section I.A.(4). As stated in that section, Jencks reported the presence of carbinolamine type intermediates in these reactions. The rate limiting step of the proposed reaction sequence in neutral solutions is the acid catalysed dehydration of this addition product (104).

In the precipitation of nickel dimethylglyoximate generated from biacetyl and hydroxylamine in solution in the presence of nickel, Gordon and coworkers utilised Janck's model as a guideline in evaluating their observations (104). The authors reported the presence of carbinolamine type intermediates and presence of complexes formed between nickel ion and these intermediates. The proposed reaction sequence was successfully applied in data analysis in the kinetic and mechanism studies of nickel dimethylglyoximate formation reaction in solution. The reaction sequence and possible pathways leading to the formation of nickel dimethylglyoximate were discussed.

IV.B.(1) Effects of temperature, pH, and excess reagent ratios on the nickel heptoximate formation reaction

The influence of solution temperature on the rate of nickel heptoximate formation is demonstrated in Fig. (7). In the diagram the precipitation performed at the highest temperature (75°C) reaches near completion in less than one half an hour. The reaction curve which corresponds to 23°C shows a slower reaction rate. A relatively slow reaction is necessary in a coprecipitation study to perform the required experimental steps (stopping the precipitation by filtration at different times and washing the precipitates, etc.). Thus, the temperature was lowered to 15°C and a significant reduction of the reaction rate was observed. A maximum of a six hour reaction period is available for experimental procedures before 100 percent precipitation occurs.

During the preliminary experiments, the effects of pH and the amounts of precipitating reagents used on reaction rate were also noted.

Figure (7). The effect of solution temperature on the rate of nickel cycloheptanedionedioximate formation.

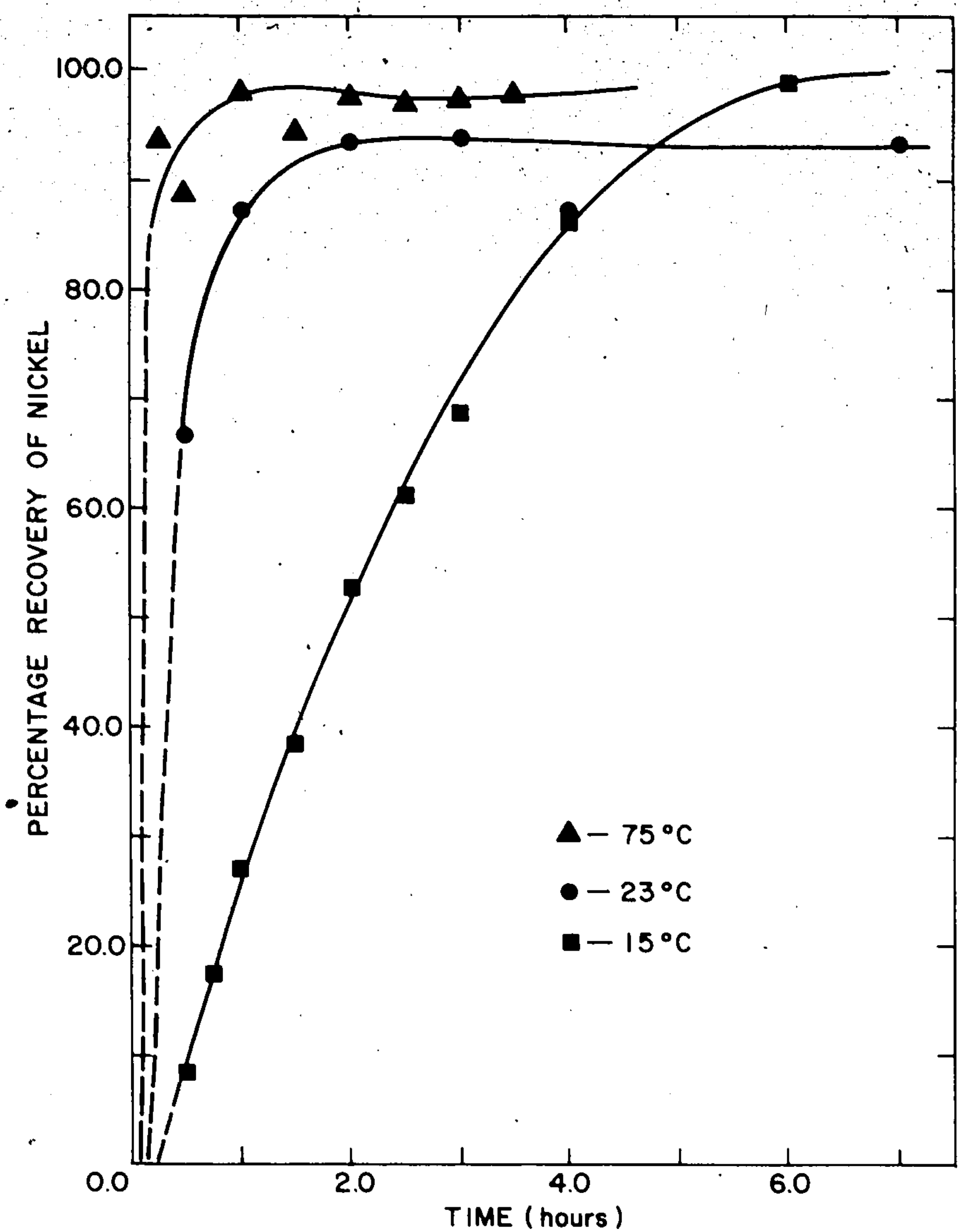
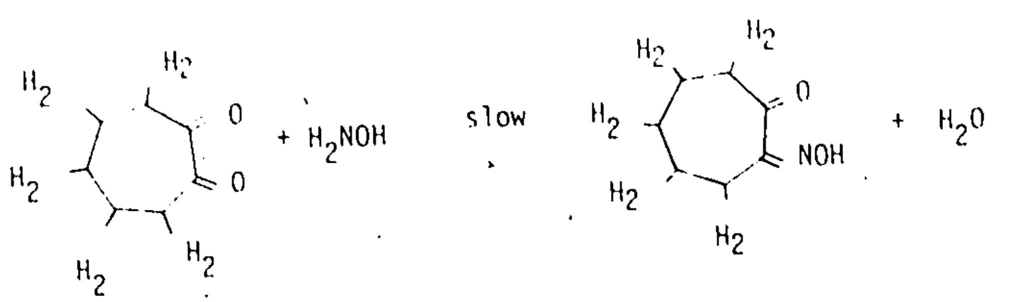

100.0
80.0
60.0
40.0
20.0
0.0
2.0
4.0
6.0
PERCENTAGE RECOVERY OF NICKEL
TIME (hours)
— 75 °C
— 23 °C
— 15 °C

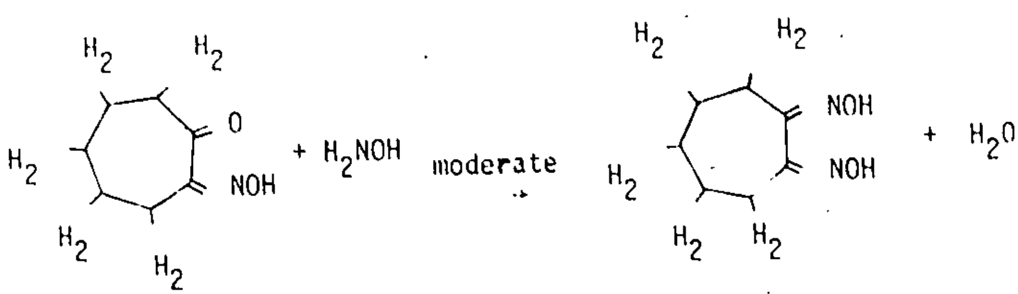
Figure (8) illustrates the reaction profiles of precipitations performed under different initial experimental conditions (Table 1, section II.A.) Curve (1) resulted from a precipitation reaction at 23°C, pH of 6.75, with a CHDO/Ni reagent excess ratio(2)and a HX/CHDO ratio(10). Curve (2) was obtained from a reaction with the initial HX/CHDO ratio reduced to 2. A further reduction of rate was observed curve (3), when the pH level of the reaction was increased to 7.25. A rate of precipitate formation suitable for the subsequent coprecipitation study, shown by curve 4, was obtained by decreasing both the CHDO/Ni initial concentration ratio and then decreasing the temperature of reaction to 15°C. Further studies were conducted using the latter initial conditions.

IV.B.(2) Kinetic model for nickel cycloheptanedionedioximate formation reaction

By analogy with arguments regarding the kinetics of nickel dimethylglyoximate precipitation reported by Gordon and Hileman, the rate of formation of nickel cycloheptanedionedioximate can be rationalized by the reaction sequence shown below.



(4.1)



(4.2)

Figure (8) Precipitation of nickel cycloheptanedionedioximate under various experimental conditions.

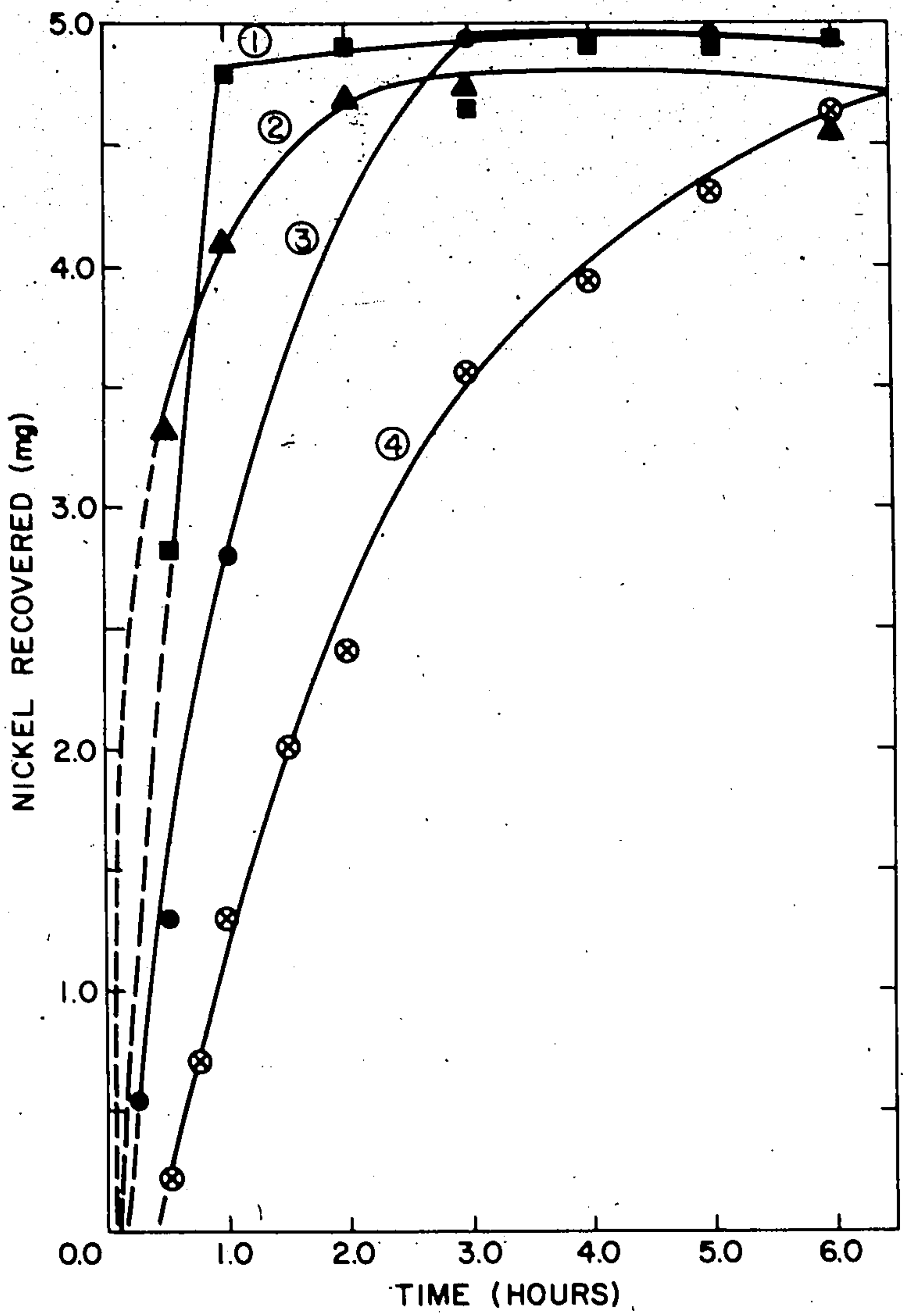
(1) CHDO/Ni = 2X, HX/CHDO = 10X, pH = 6.75, 23°C

(2) CHDO/Ni = 2X, HX/CHDO = 2X, pH = 6.75, 23°C

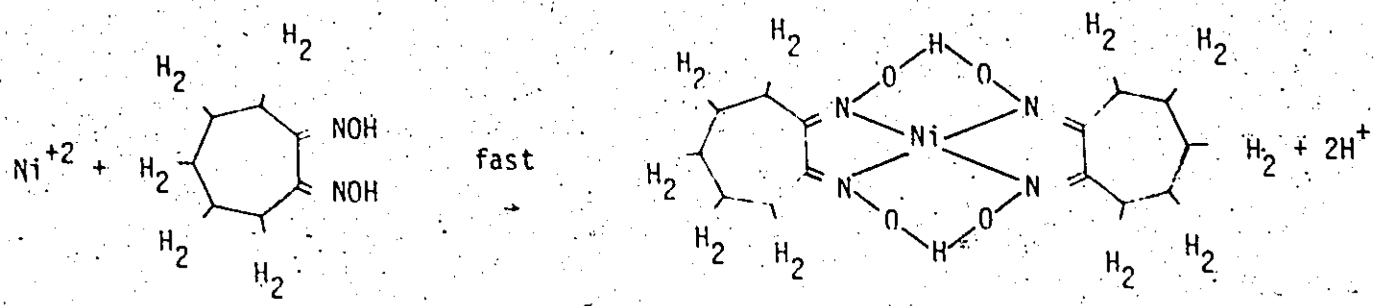
(3) CHDO/Ni = 2X, HX/CHDO = 2X, pH = 7.25, 23°C

(4) CHDO/Ni = 2X, HX/CHDO = 2X, pH = 7.25, 15°C

Initial nickel = 5.018 mg



NICKEL RECOVERED (mg)
TIME (HOURS)
5.0
4.0
3.0
2.0
1.0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
①
②
③
④



(4.3)

The rate limiting equation for nickel heptoximate formation is assumed to be reaction (4.1) which is first order in both cycloheptanedione and hydroxylamine hydrochloride. The rate equation, then, follows from

$$CHDO + HX \xrightarrow{slow} CHDOM \qquad (4.1a)$$

where: CHDO = cycloheptanedione

HX = hydroxylamine hydrochloride and

CHDOM = cycloheptanedionemonoxime

$$\frac{d[CHDO]}{dt} = -K\,[CHDO]\,[HX] \qquad (4.4)$$

In terms of the variable x, representing the increase in the amount of nickel in the precipitate in a given time t, equation (4.4) becomes

$$\frac{dx}{dt} = \frac{d[Ni]}{dt}\,ppt = K\,\{[CHDO]^{o}-2(x)\}\,\{[HX]^{o}-4(x)\} \qquad (4.5)$$

where: (x) = amount of nickel in the precipitate at time t,

$[CHDO]^{o}$ = initial concentration of cycloheptanedione,

$[HX]^o$ = initial concentration of hydroxylamine hydrochloride and

$[CHDO] = [CHDO]^o - 2[x]$; $[HX] = [HX]^o - 4[x]$

Upon integration between the limits $t = 0$ to $t = t$ and $[Ni]^o$ to $[Ni]^t$ respectively, equation (4.5) becomes

$$\frac{1}{2[HX]^o-4[CHDO]^o} \ln \left[\frac{\{[HX]^o-4(x)\}}{\{[CHDO]^o-2(x)\}}\right] = kt + \frac{1}{2[HX]^o-4[CHDO]^o} \ln \left[\frac{[HX]^o}{[CHDO]^o}\right] \quad (4.6)$$

Equation (4.6) is in the form

$$\ln \left[\frac{\{[HX]^o-4(x)\}}{\{[CHDO]^o-2(x)\}}\right] = k't + c' \quad (4.7)$$

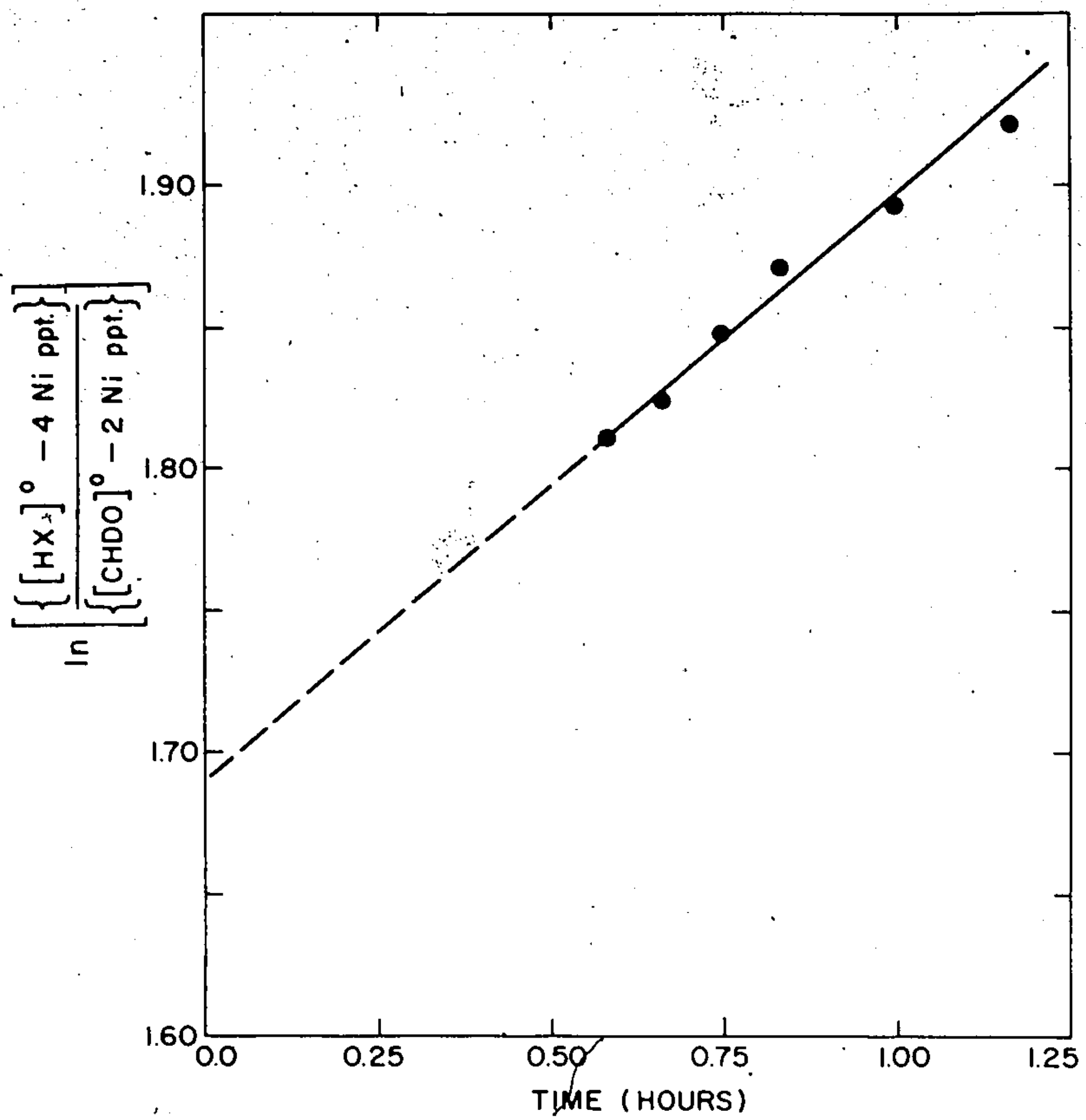
where $k' = k\,\{2[HX]^o-4[CHDO]^o\}$ and (4.8)

$$c' = \ln \left[\frac{[HX]^o}{[CHDO]^o}\right] \quad (4.9)$$

If the proposed model is correct, a plot of $\ln \left[\frac{\{[HX]^o-4(x)\}}{\{[CHDO]^o-2(x)\}}\right]$ vs time should yield a straight line with a slope of k' and an intercept of c'.

Figure (9) shows such a plot using data collected during a precipitation reaction with initial reaction conditions reported in section II.B. Calculated values of k' and c' from the slope and intercept are 0.207 ± 0.04 hr^{-1} and 1.69 ± 0.04. The theoretical value of c' is 1.72. These two values of c' agree within the accuracy of the experiments. Thus the proposed kinetic model rationalises the observed data.

Figure (9) The kinetic plot of nickel cycloheptanedionedioximate formation reaction when nickel "alone" is present.


1.90
1.80
1.70
1.60
0.0
0.25
0.50
0.75
1.00
1.25
TIME (HOURS)
ln [{[HX₄]° − 4 Ni ppt.} / {[CHDO]° − 2 Ni ppt.}]

Values of the apparent rate constant k' and the reaction constant c' were determined in the replicates of precipitation reactions. Average values were calculated and are recorded in Table (9). The true rate constant k for the reaction was then calculated using average value of $\bar{k}'$ according to equation(4.8). Substitution of derived data in equation(4.5)gives the rate of precipitation of nickel cycloheptanedione-dioximate at 15°C.

Similar data analyses were carried out for precipitation reactions at temperatures of 23°C and 5°C and were compared with that of 15°C. Table(10) shows a summary of the values of rate constant and integration constant resulting from precipitation reactions performed at different temperatures. The observed c' values agree well with the theoretical value of c and thus indicates that the proposed model is successful in data analysis. An Arrhenius plot for the nickel heptoximate formation system was prepared and reported in Figure (10). The activation energy of the reaction was observed to be 11.9 kcal mole^{-1}.

To study the effects of trace level amounts of Co(II) and Cu(II) on the rate of nickel cycloheptanedionedioximate precipitation, the experiments reported in section II.(C) and II(D) were carried out. The resulting data were processed using the proposed kinetic model as a guide. Figure(11) is a kinetic plot resulting from data collected during a nickel heptoximate formation reaction in the presence of 0.5 μg of cobalt. Similar plots were prepared for each trace level.

Table(11) represents a summary of observed kinetic data resulting from the precipitation reactions of nickel heptoximate in the presence of different quantities of cobalt (0.50, 1.0, 5.0, 10.0, and 100.0 micrograms).

Table (9)

Observed apparent rate constant and integration constant values for the nickel cycloheptanedione dioximate reaction

Run No.	k'	k'(average)	c'	$\bar{c}$'(average)
1	0.207±0.036		1.691±0.005	
2	0.219±0.040		1.650±0.009	
3	0.136±0.033		1.697±0.009	
4	0.151±0.026		1.696±0.006	
5	0.139±0.017		1.705±0.004	
6	0.258±0.029		1.599±0.008	
7	0.162 ±0.0081	0.187±0.011	1.688±0.002	1.676±0.002
8	0.213±0.056		1.722±0.005	
9	0.132±0.037		1.680±0.003	
10	0.253±0.11		1.627±0.02	

Initial conditions

[Ni] = 0.00203 mole l^{-1}

[CHDO] = 0.00613 mole l^{-1}

[HX] = 0.0345 mole l^{-1}

[NH_4Ac] = 0.0240 mole l^{-1}

pH = 7.25

Temperature = 15°C

Theoretical integration constant(c) = 1.727

Table (10)

Observed rate constant and reaction integration constant values for the nickel cycloheptanedionedioximate precipitation reaction

Temperature	Average apparent rate constant $\bar{k}'$ (hr^{-1})	True Rate constant k(hr^{-1})	Observed Reaction constant c'	Theoretical reaction constant c
5°C	0.067 ±0.02	1.50 ±0.02	1.654±0.006	1.727[a]
15°C	0.19 ±0.01	4.20 ±0.01	1.676±0.002	1.727[a]
23°C	0.37 ±0.1	6.11 ±0.1	1.366±0.005	1.440[b]

[a]The reagent excess ratios used for precipitation reaction were CHDO/Ni = 2X and HX/CHDO = 1.5 X

[b]The reagent excess ratios used for the precipitation reaction were CHDO/Ni = 2X and HX/CHDO = 2X.

Figure (10) ln K versus $\frac{1}{T}$ (T = absolute temperature) for the nickel heptoximate formation system.

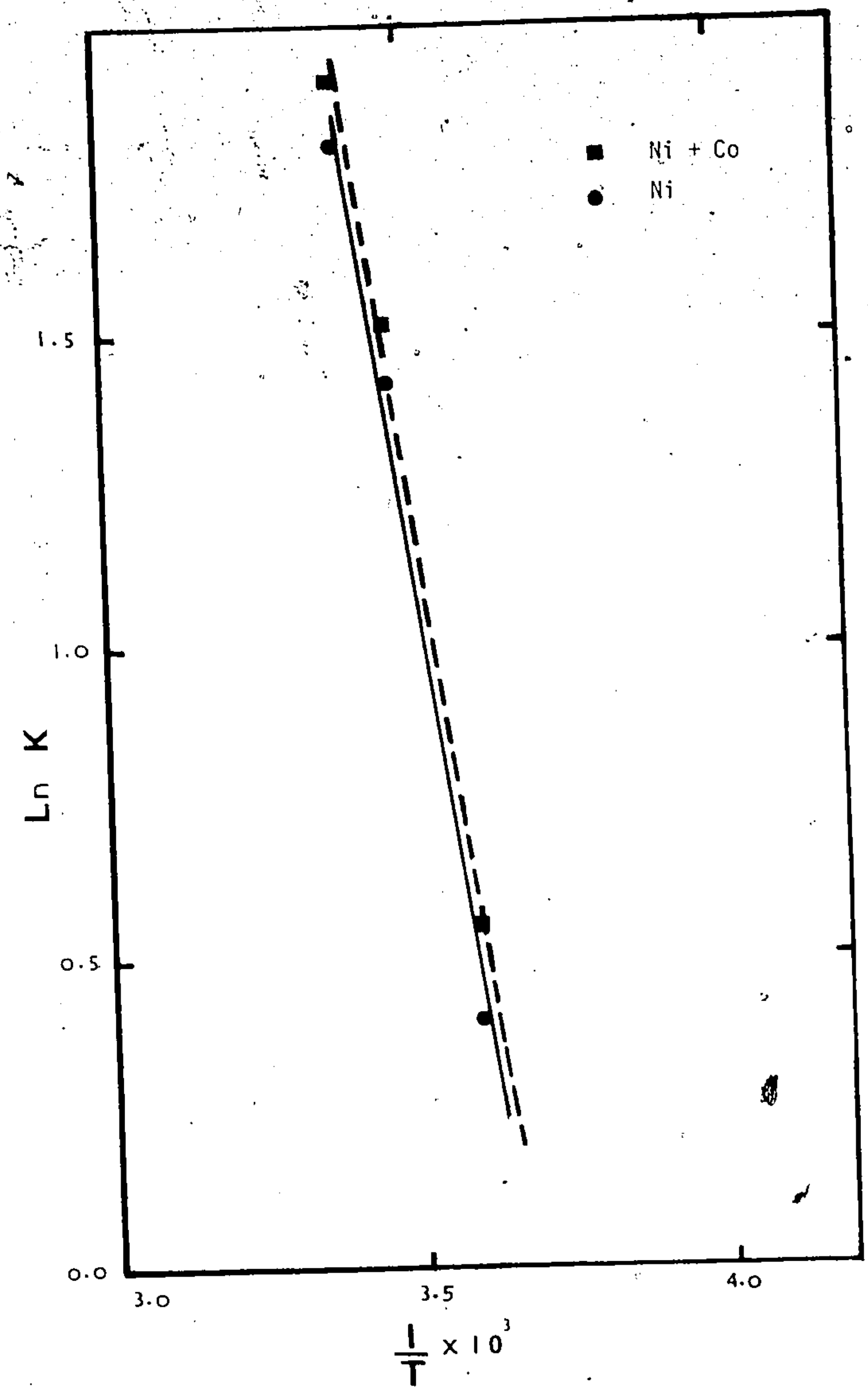

Ni + Co
Ni
Ln K
1.5
1.0
0.5
0.0
3.0
3.5
4.0
$\frac{1}{T} \times 10^3$

Fig. (11) The kinetic plot of nickel cycloheptanedionedioximate formation in the presence of cobalt.

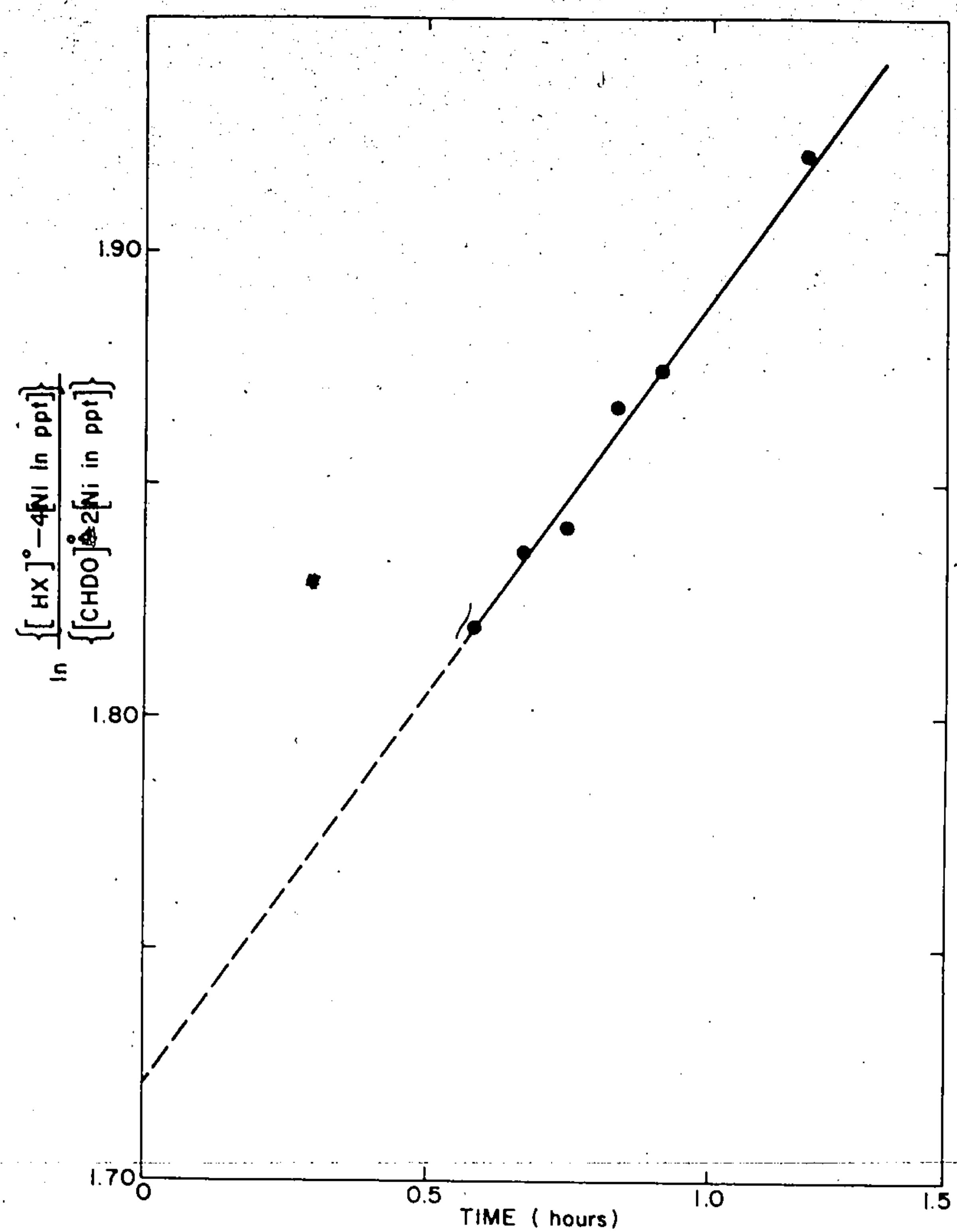

1.90
1.80
1.70
0
0.5
1.0
1.5
TIME (hours)

Table (11)

Observed rate constant and integration constant values for nickel heptoximate formation reaction in the presence of different quantities of cobalt

Cobalt present (μg)	k'	$\bar{k}$ (average)	c'	$\bar{c}$ (average)
0.50	0.262±0.019		1.662±0.004	
1.0	0.214±0.019		1.659±0.004	
5.0	0.261±0.058	0.239±0.03	1.630±0.02	1.661±0.004
10.0	0.282±0.034		1.680±0.008	
100.0	0.204±0.095		1.675±0.01	

Initial conditions

[Ni] = 0.00203 mole l^{-1}

[CHDO] = 0.00613 mole l^{-1}

[HX] = 0.0345 mole l^{-1}

[NH_4Ac] = 0.0240 mole l^{-1}

pH = 7.25

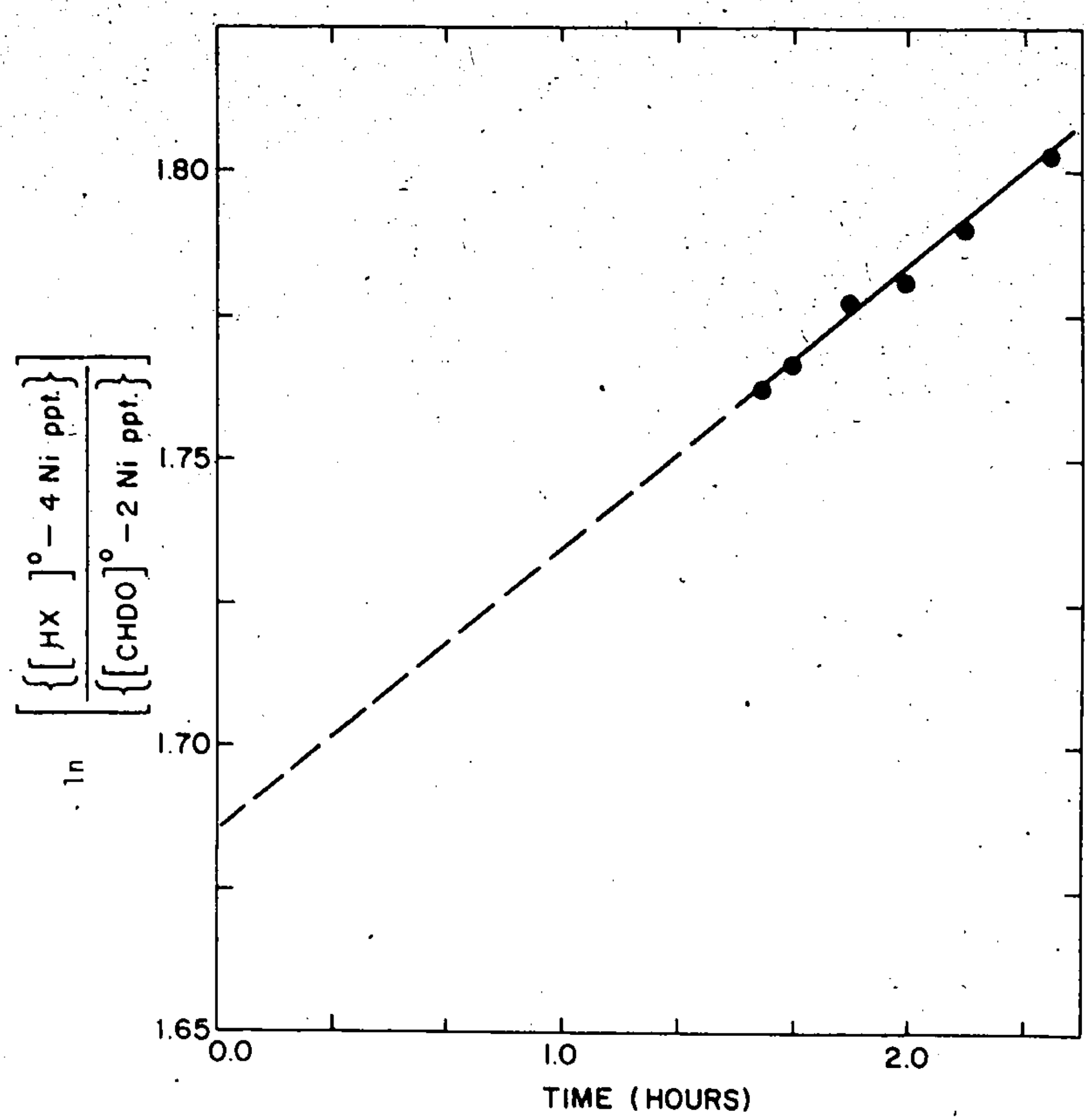
Temperature = 15°C

1 μg of Co = 6.93×10^{-7} mole l^{-1}

Theoretical integration constant (c) = 1.728

Recorded data indicate that the observed rate constant of the reaction in the presence of cobalt is independent of the amount of cobalt present. When compared with the rate constant value of the reaction in the absence of cobalt at 15°C, however, a slight enhancement in the apparent rate constant $\bar{k}'$ (0.19±0.01 to 0.24±0.03) was noted. The presence of cobalt seems to have an effect on the rate of nickel heptoximate reaction. The average apparent rate constant value $\bar{k}'$ was calculated from all rate constant values observed during precipitation reactions in the presence of different trace levels. Similar data analysis was carried out for precipitation reactions in the presence of cobalt performed at different reaction temperatures. Table (12) shows the rate constant data from reactions at 5°C, 15°C and 23°C. An Arrhenius plot was prepared and it is recorded in Figure (10). Approximately the same value of activation energy was observed in both nickel heptoximate formation reactions in the absence and in the presence of cobalt.

The effect of trace amounts of copper on the nickel heptoximate precipitation reaction was similarly studied. A kinetic plot (Figure (12)) was prepared from data observed during a precipitation reaction when 25.0 μg was present as tracer. Calculated values of k' and c' from the slope and intercept of such kinetic plots were gathered for all reactions in the presence of various trace levels of copper. And data are recorded in Table (13). For all copper levels studied (2.5, 5.0, 10.0, 25.0, 50.0 and 100.0 μg) at 5°C, no significant change in reaction rate between each level was observed. The calculated average value of $\bar{k}'$, the rate constant for nickel heptoximate precipitation in the presence of copper, however, Figure (12). The kinetic plot of nickel cycloheptanedionedioximate formation in the presence of copper .



1.80
1.75
1.70
1.65
0.0
1.0
2.0
TIME (HOURS)
ln [{[HX]° − 4 Ni ppt.} / {[CHDO]° − 2 Ni ppt.}]

Table (12)

Observed rate constant and integration constant values for the nickel cycloheptanedionedioximate precipitation reaction in the presence of cobalt

Temperature	Average apparent rate constant $\bar{k}'$ (hr^{-1})	True Rate constant k(hr^{-1})	Observed reaction constant c'	Theoretical reaction constant c
5°C	0.073 ± 0.003	1.658 ± 0.003	1.658±0.01	1.727[b]
15°C	0.24±0.03	4.60 ± 0.03	1.661±0.004	1.727[b]
23°C	0.41±0.4	6.76 ± 0.4	1.38 ±0.06	1.440[a]

[a]The reagent excess ratio for precipitation reaction was CHDO/Ni = 2X and HX/CHDO = 2X.

[b]The reagent excess ratio for precipitation reaction was CHDO/Ni = 2X and HX/CHDO = 1.5X

Table (13)

Apparent rate constant (k') of nickel heptoximate formation reaction in the presence of different quantities of copper

Copper present (µg)	k'	$\bar{k}$ (average)	c'	$\bar{c}$ (average)
2.50	0.035±0.034		1.7165±0.013	
5.00	0.040±0.010		1.7085±0.0031	
10.0	0.054±0.015	0.046±0.013	1.6904±0.0031	1.6956±0.0036
25.0	0.050±0.042		1.6854±0.010	
50.0	0.041±0.033		1.6935±0.010	
100.0	0.054±0.025		1.6756±0.0062	

Initial conditions

[Ni] = 0.00203 mole l^{-1}

[CHDO] = 0.00613 mole l^{-1}

[HX] = 0.0845 mole l^{-1}

[NH_4Ac] = 0.0240 mole l^{-1}

pH = 7.25

Temperature = 5°C

1 µg of copper = 6.63 x 10^{-7} mole l^{-1}

Theoretical integration constant (c) = 1.7283 shows a slight decrease from the previously recorded rate constant value in the absence of copper. The $\bar{k}'$ changes from 0.067±0.02 to 0.46±0.01. This indicates, therefore, that the presence of copper seems to retard the rate of nickel heptoximate precipitation reaction. The present observation parallels the previous statements of Schweitzer and McDowell (132) and Classen and Bastings (129).

Observed rate constant data from the set of precipitation reactions of nickel heptoximate in the presence of copper performed at different temperatures are recorded in Table (14).

The information thus obtained, regarding the kinetics of the nickel cycloheptanedionedioxime precipitation reaction will be useful in interpretation of the data observed in coprecipitation studies.

IV.C Coprecipitation with Nickel 1,2-Cycloheptanedionedioximate

Coprecipitation of cobalt with nickel dimethylglyoximate has been known since the introduction of dimethylglyoximate into analytical use. Brunck, who first proposed the use of the reagent for the gravimetric determination of nickel observed the interference of cobalt in precipitation procedures (133). The author recommended the use of about five times the stoichiometric amount of dimethylglyoxime required to precipitate nickel present with no mention of any relation to the quantity of cobalt present (128). Since early investigations on the coprecipitation of cobalt and other cations with nickel dimethylglyoximate, most authors have agreed that interference of cobalt can be eliminated under proper conditions (134). It was generally accepted that when cobalt is present, an excess of

Table (14)

Observed rate constants and integration constant values for the nickel cycloheptanedionedioximate precipitation reaction in the presence of copper

Temperature	Average apparent rate constant $\bar{k}'(hr^{-1})$	True rate constant $k(hr^{-1})$	Observed integration constant[(a)] c'
5°C	0.046±0.01	1.03 ±0.01	1.696±0.004
15°C	0.21±0.2	4.60±0.2	1.688±0.05

[(a)] Theoretical value for integration constant c' for both temperatures is 1.727.

dimethylglyoxime sufficient to complex all the cobalt must be added (135). These classical studies have also indicated that large amounts of cobalt and copper seem to retard the precipitation of nickel dimethylglyoximate, but the difficulty may be overcome by using excess reagent and by allowing extra time for precipitation (83).

The coprecipitation behaviour of cobalt with nickel dimethylglyoximate precipitated by conventional methods was studied by Schweitzer and McDowell using microgram amounts of the radioisotope cobalt-60 (132). The investigators observed high levels of coprecipitation of cobalt at the beginning of the precipitation. The entrainment of tracer decreased with digestion time, however. According to the authors, the coprecipitation of cobalt could result from a trapping process and an adsorption process on the large surface area of the precipitate during the initial stages of precipitation. On digestion, the precipitates dissolved and reformed probably through Ostwald ripening, thus releasing the trapped cobalt. The authors also predicted that the small amount of cobalt remaining in the solid phase after long digestion was in the form of a solid solution. The formation of a solid solution may be facilitated by similar structures of nickel and the cobalt dimethylglyoximate complex (136,137). No discussion in connection with distribution laws was reported.

A similar study on the coprecipitation of cobalt with nickel dimethylglyoximate was reported by Lyle and Maghzian in 1967 (138). The PFHS method of Salesin and Gordon (47) was applied in which the dimethylglyoxime was generated *in situ* from biacetyl and hydroxylamine hydrochloride. The nature of the coprecipitation of cobalt with nickel dimethylglyoximate was investigated using microgram through milligram amounts of tracer. Results from their study showed that the fractional amount of cobalt carried down was quite low. The reported data indicate that the tracer is "deriched" with respect to the precipitate although this was not discussed. For microgram through one milligram amounts of cobalt, the fraction entrained was higher than those when more than one milligram of cobalt was present in solution. In contrast, at trace levels greater than one milligram the entrainment of tracer increased with an increase in the initial cobalt present. The extent of coprecipitation within each experimental run increased linearly with an increase in the fraction of carrier precipitated for all trace levels. The authors added that the amount of cobalt entrainment observed when using the PFHS method was smaller than that observed during studies employing the conventional method (132) and (138).

A coprecipitation study of palladium and nickel dimethylglyoximate systems was reported by the same investigators. The metal dimethylglyoximates were precipitated from homogeneous solution containing biacetyl and hydroxylamine hydrochloride as well as biacetylmonoxime and hydroxylamine hydrochloride. Trace component enrichment in the solid phase was observed irrespective of whether the carrier was nickel or palladium when precipitated from biacetyl systems at 23°C and 50°C. Observations from the biacetylmonoxime system were opposite to those noted above. In addition, the authors reported an interesting observation from the coprecipitation study of palladium with nickel dimethylglyoximate from the biacetyl-hydroxylamine system. A significant reduction of entrainment of tracer was noted on changing the reaction temperature from 50°C to 23°C. A more striking observation was that the carrier precipitate was enriched in tracer when microgram amounts of palladium tracer were used but the solution was enriched in tracer when milligram amounts of tracer (identical to that of nickel) were present in solution. It seems, therefore, that a reduction in the fractional amount of tracer entrainment can be brought about by reducing the reaction temperature or by using higher initial quantities. These results parallel the previous observations in cobalt-nickel dimethylglyoximate system where the fraction of coprecipitation decreased with an increase in the tracer amount.

The authors discussed that observations from metal chelate systems were in contrast to those of purely inorganic systems in which a change in the molar ratio of the metal ions over a wide range does not affect the distribution coefficients. Also, in most of the systems studied, neither of the two limiting laws describing the coprecipitation as a function of fractional precipitation of carrier rationalised the observed data.

In 1964, Southern and Lyle reported on their coprecipitation studies of some metal tervalent ions (scandium, yttrium, cerium and indium) with aluminium tris-(8-hydroxyquinolate) (130). The precipitation was carried out by slow isothermal evaporation of aqueous acetone solutions. Very low fractional amounts of tracer (less than 0.5%) were found in the aluminium 8-hydroxyquinolate precipitate when scandium(III), yttrium(III) and cerium(III) ions were used as tracers in the presence of acetate ion in the solution. The fraction of tracer entrainment was independent of the fraction of the aluminium precipitated. Besides, values of the distribution coefficient, D and λ, were reported to vary considerably as the extent of precipitation increased.

Contrary to those observations, the coprecipitation of trace amounts of indium with aluminium 8-hydroxyquinolate in the presence of acetate ion showed a high fractional amount of tracer (10% to 90%) in the carrier precipitate. Values of D and λ were approximately equal and constant over the whole range of precipitation.

The authors considered that the observed difference in behaviour of those ions could be due to structural differences between the complexes produced in solution. Aluminium and indium yield tris-(8-hydroxyquinolate) complexes from solutions containing acetate ion. Other ions (Sc, Y, Ce), when precipitated in a similar manner could produce complexes in the form of $M[C_9H_6NO]_2 \cdot X$ where X is a monovalent anion. Yttrium 8-hydroxyquinolate for example was shown to be $Y[C_9H_6NO]_2 \cdot O \cdot CO \cdot CH_3$ from an elemental analysis of the precipitate. The investigators concluded that the fractional coprecipitation of tracer remained small unless the tracer took the form of $M(C_9H_6ON)_3$.

This statement was further examined by Bailey and Lyle (131) in their coprecipitation studies of iron and zinc with aluminium 8-hydroxyquinolate. Iron(III), which forms the "aluminium type" 1:3 complex, showed similar behaviour to that of indium. Considerably high fractional entrainment of tracer in the carrier precipitate was observed. And the distribution of iron tracer was shown to follow the logarithmic law of

Doerner and Hoskins. The doubly charged zinc ion exhibited a much different distribution pattern. Values of D and λ are approximately equal and both progressively decreased with increasing fractional precipitation of the carrier. The initial values of D of approximately 2 (enrichment system) were reduced to a minimum of 0.4 (derichment system) within one experimental run. The reduction in λ values was less significant. The elemental analysis of the zinc 8-hydroxyquinolate complex suggested that the complex was in the form of $Zn[C_9H_6ON]_2 \cdot 2H_2O$. The authors believed that the influence of structural properties on coprecipitation systems studied was significant although the explanation of the observed distribution coefficients was not clear.

The authors further suggested that dynamic factors should also be considered in discussing the observed data in addition to the structural properties. The effects of the rate of evaporation of the solvent during the precipitation process and the rate of deposition of carrier on growing crystallites on distribution coefficient (λ) were discussed.

Interference of copper with nickel dimethylglyoximate has been known since the introduction of the reagent to the method of gravimetric determination of nickel (139). Nevertheless, very little information regarding the extent of interference is available in the literature. Classen and Bastings reported from their preliminary investigation that copper interferes by consuming part of the available reagent, by partially inhibiting precipitation and by direct contamination of nickel dimethylglyoximate precipitate with small amounts of copper (129). The authors also reported the temperature dependence of the copper contamination in ammoniacal citrate solution. The fractional amount of copper entrainment in the nickel dimethylglyoximate was small at higher temperatures and was found to be a minimum at 90°C.

Interference of copper with the precipitation of nickel cycloheptanedionedioximate by conventional methods was also known (88,140), but no report of a systematic coprecipitation study of the system could be found.

Additional coprecipitation studies of some interferring ions with analytically important metal chelates are undoubtedly required. Interference of certain ions is always an important problem in gravimetric procedures. Possible contributing factors such as structural properties, supersaturation of the system, reaction rate and others in coprecipitation processes also need to be examined. Systematic studies on coprecipitation of cobalt and copper with nickel cycloheptanedionedioximate were thus initiated.

IV.C.(1) <u>Coprecipitation of cobalt with nickel cycloheptanedionedioximate</u>

As discussed in section IV.B, the interference of cobalt with the precipitation of nickel cycloheptanedionedioximate from homogeneous solution was observed when appreciable quantities of cobalt were present. The usual way of eliminating this interference-addition of excess reagent to the system - was not very successful when large amounts of cobalt were present in the solution. Therefore, a systematic coprecipitation study was performed using microgram (Co-60) through milligram amounts of Co(II) with milligram amounts of Ni(II) carrier. The experimental procedures reported in section II.C.(1) were used.

One of the characteristics of PFHS is the possibility of control of the rate of reaction. Thus, the method is well suited for coprecipitation studies. The PFHS procedure with the experimental conditions selected for a slow reaction (section II.C.(1)) offered a useful technique for the present study.

The two classical limiting laws were used initially as guidelines for data analysis. Distribution coefficients (D and λ) were calculated according to equations (1.15) and (1.19) of section I.B.(2). Observed and derived data are recorded in Appendix (II). For each trace level, the distribution coefficients were found to be a function of percentage of carrier precipitated. The nature of the dependence is shown in Figure (13) (23°C) and Figures (14), (15), (16), (17) and (18) (15°C).

Figure (13) represents the data from a preliminary experiment at 23°C. 5.0 mg of nickel were precipitated in the presence of 1.0 mg of cobalt with reagent excess ratios of CHDO/Ni (2) and HX/CHDO (2). A very fast decrease of λ and D with the extent of carrier precipitated can be noted. As well, a rapid approach to constant-low numerical D and λ values near 100% precipitation was observed. This trial experiment suggested that future experiments should be performed with a slower rate of precipitation so that a reasonably large number of precise values of the distribution coefficients during the precipitation could be obtained.

Decreasing the reaction temperature to 15°C and using less initial concentrations of reagents (CHDO/Ni = 1.5 and HX/CHDO = 2 for 3.0 mg of nickel) resulted in a lower rate of precipitation (see section IV.B.). Figures (14), (15), (16), (17) and (18) represent the data resulting from

Figure(13). Distribution diagram of the coprecipitation of cobalt with nickel cycloheptanedionedioximate.*.

(1.0 mg of cobalt and 5.0 mg of nickel)

*Data from run no. 1.

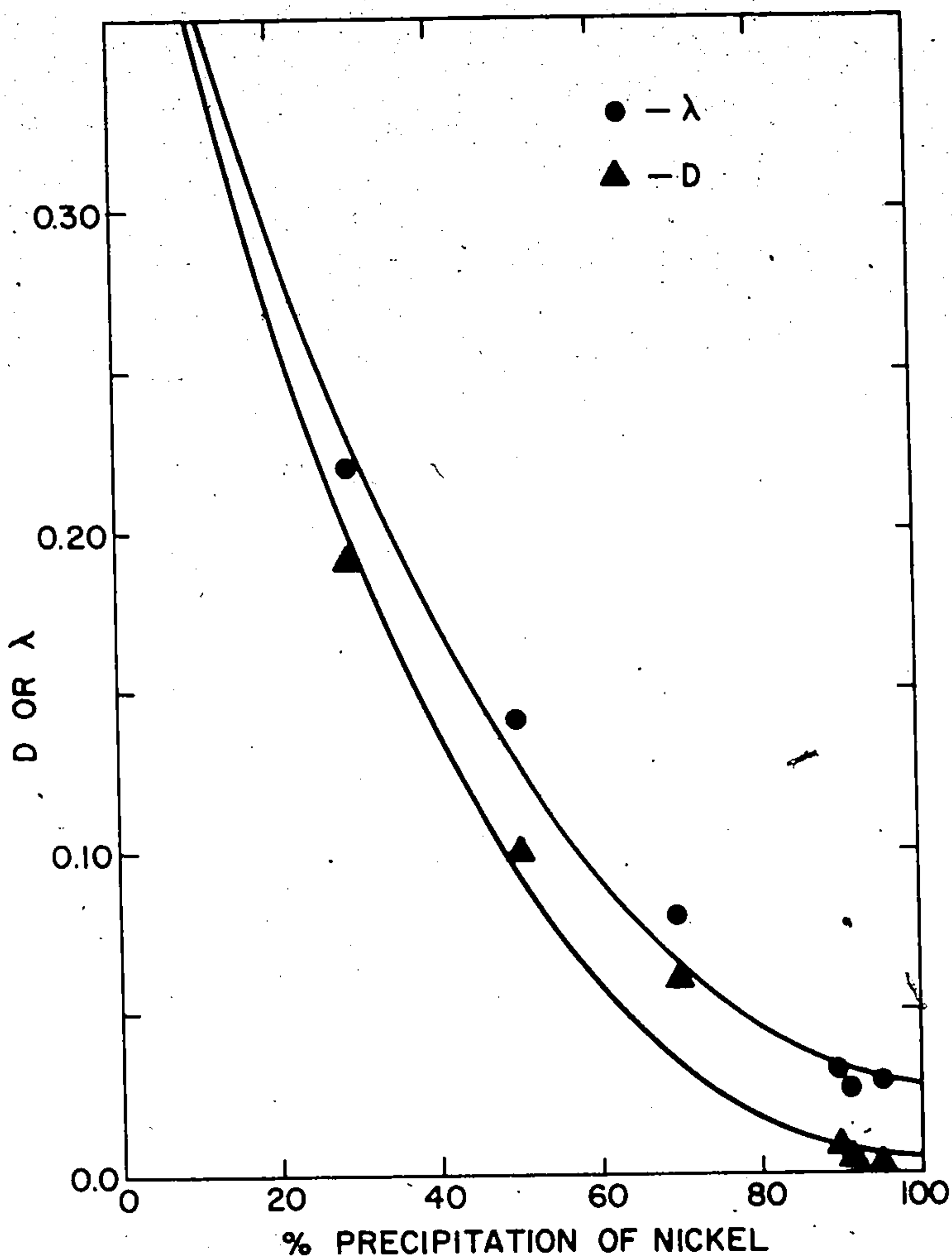

● — λ
▲ — D
D OR λ
0.0
0.10
0.20
0.30
0
20
40
60
80
100
% PRECIPITATION OF NICKEL

Figure (14). Distribution diagram of the coprecipitation of cobalt with nickel cycloheptanedionedioximate.*

(0.5 μg of cobalt and 3.0 mg of nickel)

*Data from run no. 1.

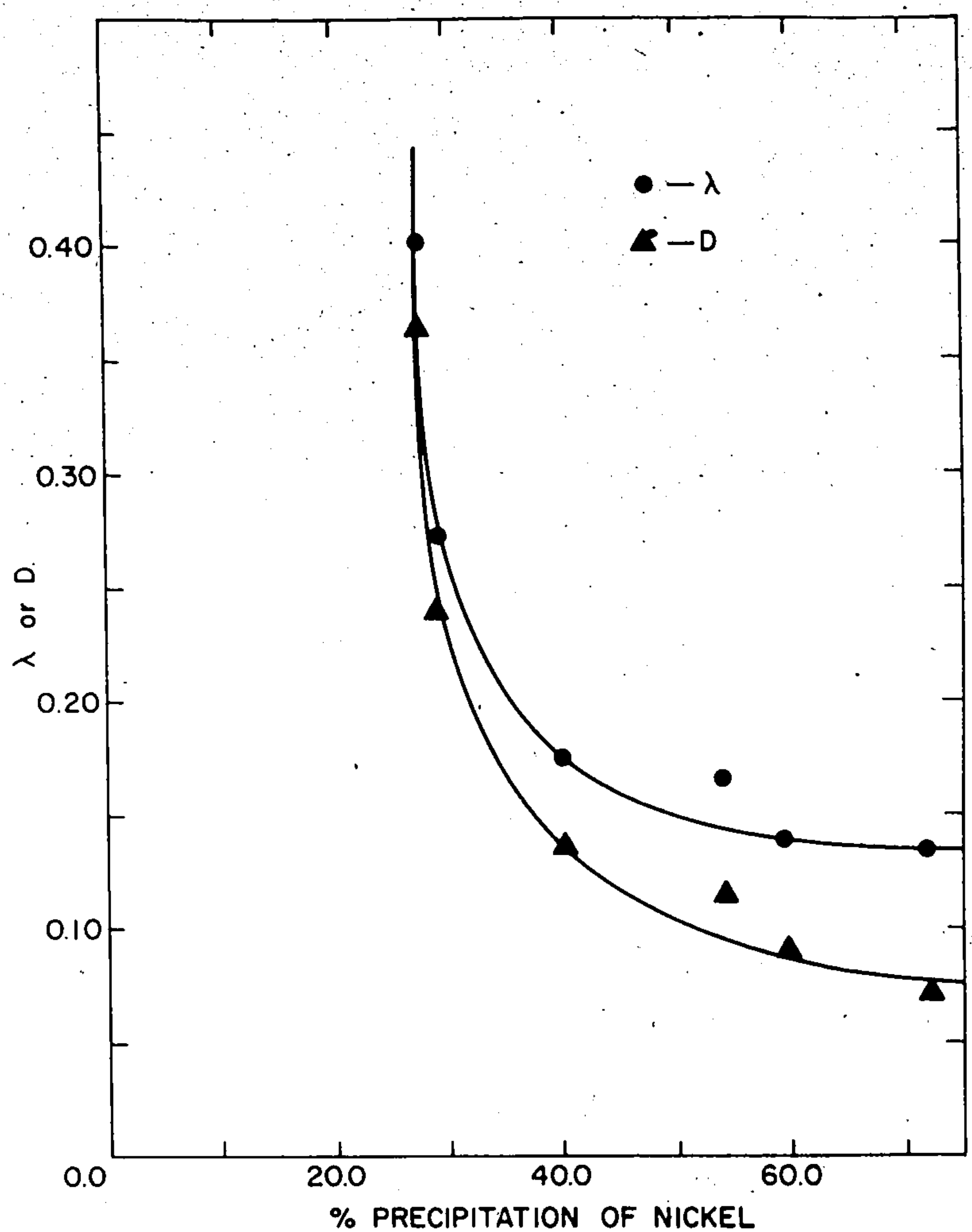

● — λ
▲ — D
0.40
0.30
0.20
0.10
λ or D
0.0
20.0
40.0
60.0
% PRECIPITATION OF NICKEL

Figure (15). Distribution diagram of the coprecipitation of cobalt with nickel cycloheptanedionedioximate*.

(1.0 μg of cobalt and 3.0 mg of nickel)

*Data from run no. 3.

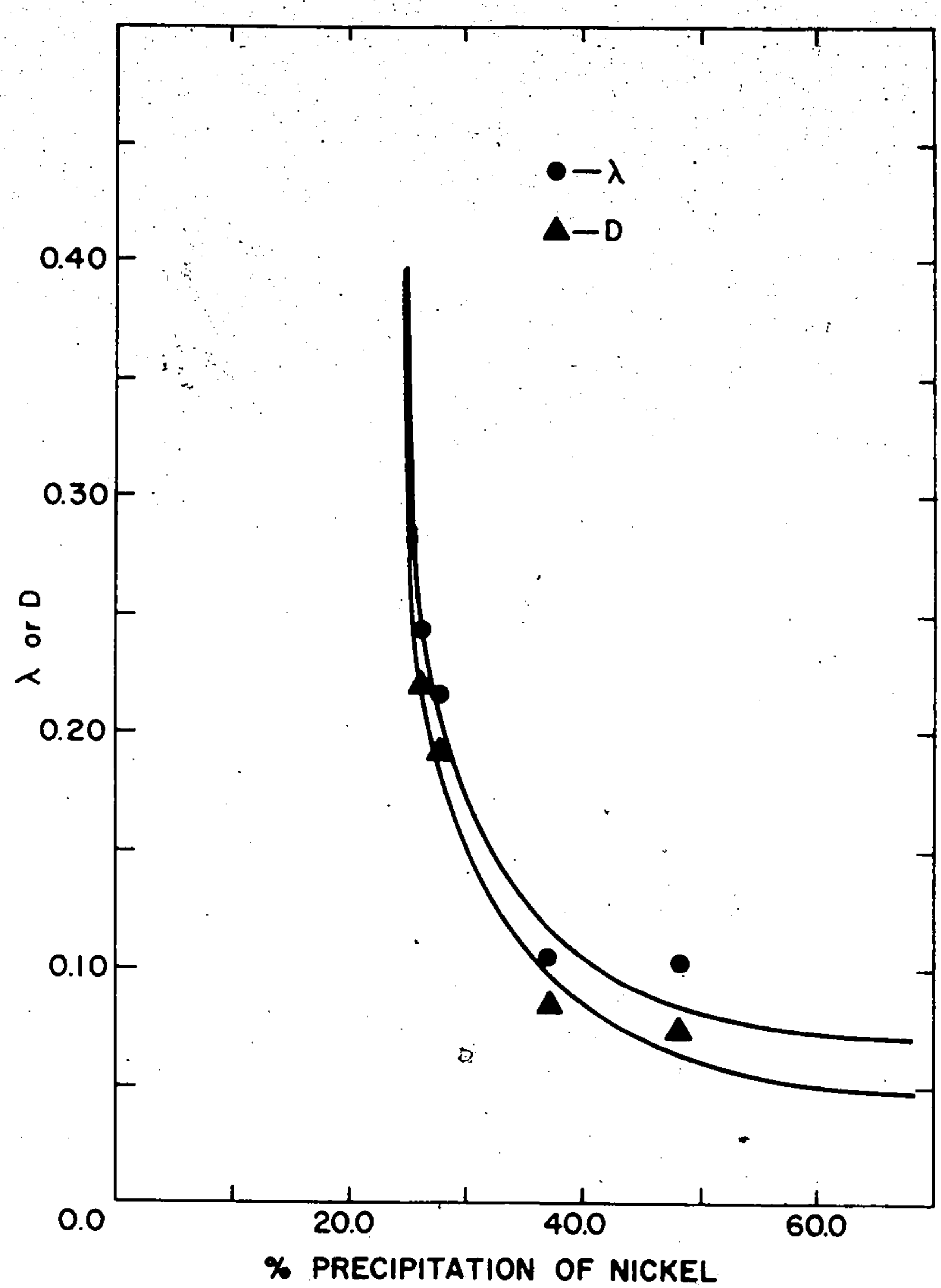

●—λ
▲—D
0.40
0.30
0.20
0.10
0.0
λ or D
20.0
40.0
60.0
% PRECIPITATION OF NICKEL

Figure (16). Distribution diagram of the coprecipitation of cobalt with nickel cycloheptanedionedioximate.*

(5.0 μg of cobalt and 3.0 mg of nickel)

*Data from run no. 1.

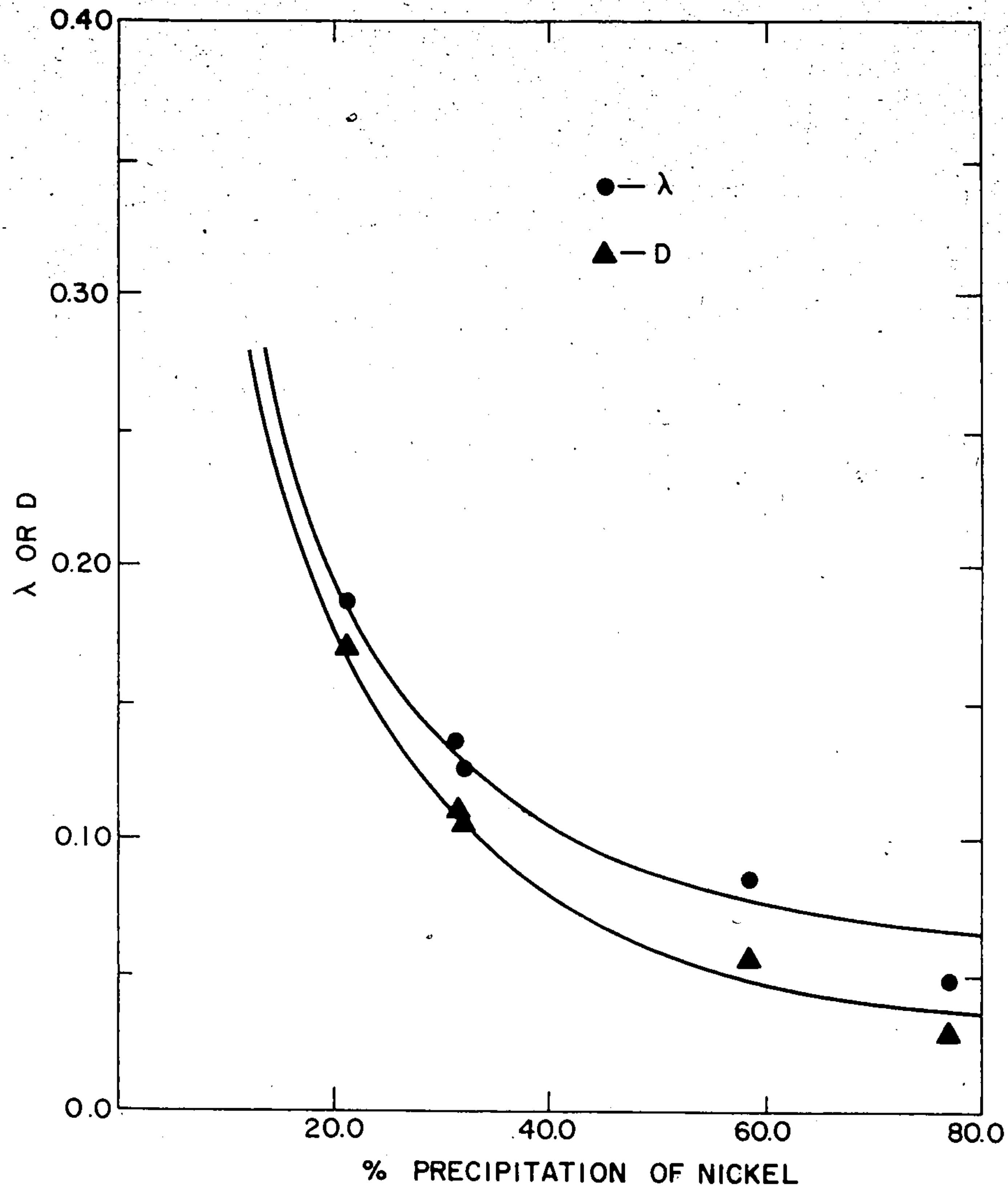

0.40
0.30
0.20
0.10
0.0
λ OR D
● — λ
▲ — D
20.0
40.0
60.0
80.0
% PRECIPITATION OF NICKEL

Figure (17). Distribution diagram of the coprecipitation of cobalt with nickel cycloheptanedionedioximate.*

(10.0 μg of cobalt and 3.0 mg of nickel)

*Data from run no. 3.

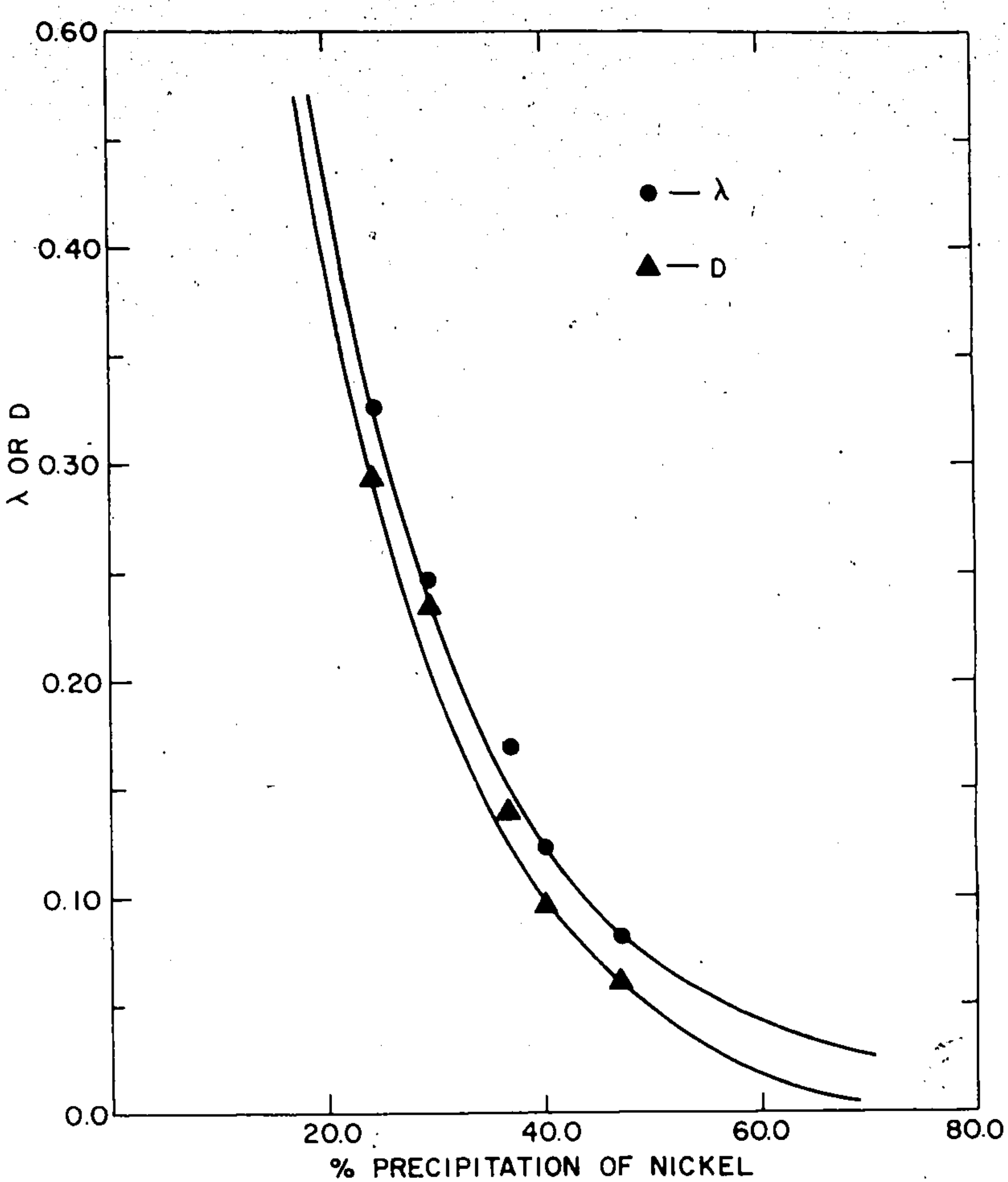
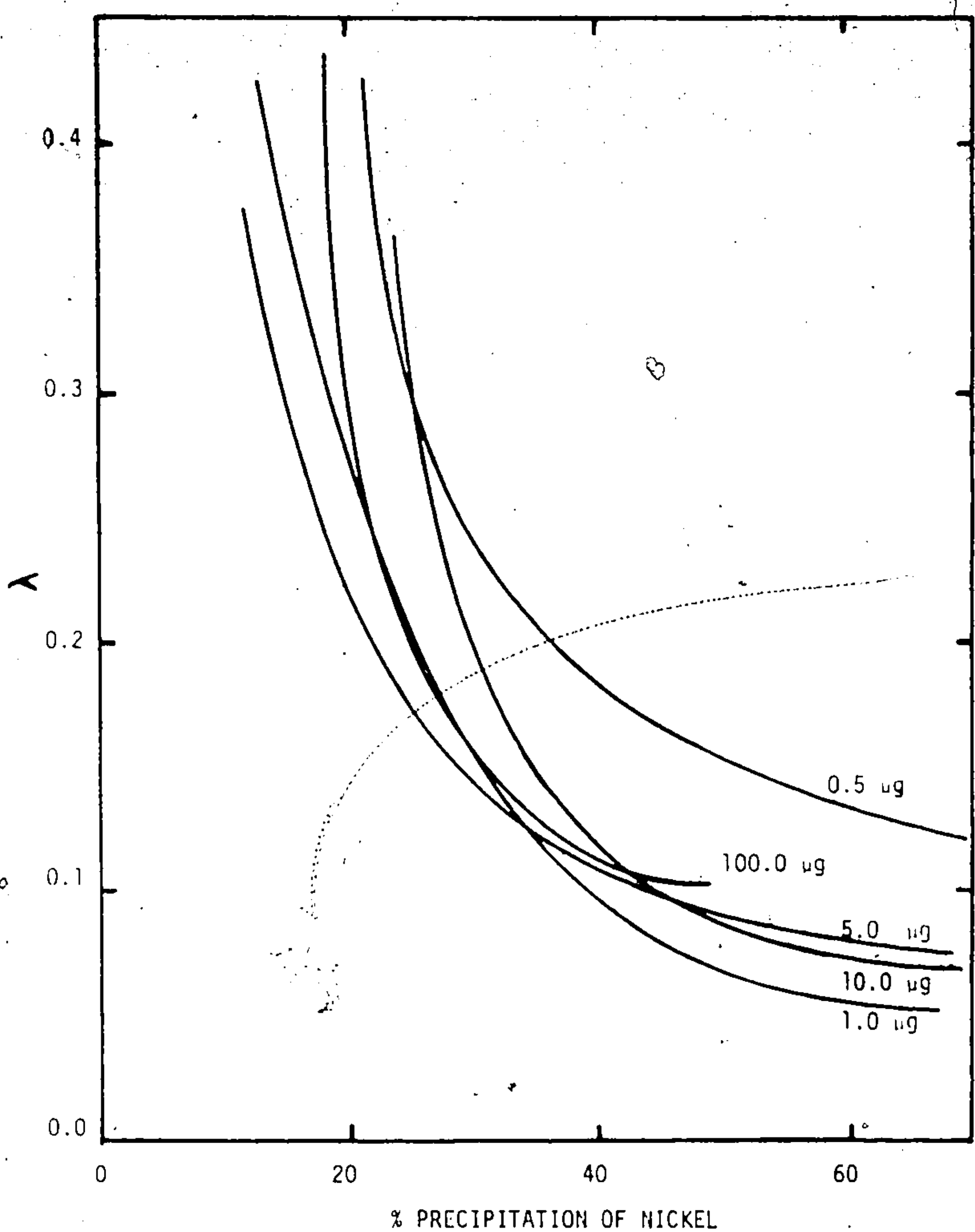

0.60
0.40
0.30
0.20
0.10
0.0
λ OR D
● — λ
▲ — D
20.0
40.0
60.0
80.0
% PRECIPITATION OF NICKEL

Figure (18). Averaged logarithmic distribution coefficients vs % precipitation of nickel.



λ
0.4
0.3
0.2
0.1
0.0
0
20
40
60
% PRECIPITATION OF NICKEL
0.5 μg
100.0 μg
5.0 μg
10.0 μg
1.0 μg

coprecipitation experiments carried out under such reaction conditions and in the presence of different quantities of cobalt. The distribution diagrams show characteristics similar to those observed during the preliminary experiment. The distribution coefficients decrease more slowly with the extent of carrier precipitation at the lower rate of reaction and a reasonable quantity of data points were observed before the numerical values of D and λ approached a minimum.

At both temperatures, calculated values of D and λ were less than unity indicating that the precipitate is deriched in tracer, i.e. a derichment system. The distribution coefficients show significant variation with the fraction of carrier precipitated as noted from the diagrams. Coprecipitation was high at the beginning of the precipitation reaction (λ = 0.35, D = 0.33) and decreased toward the end of it. Numerical values at the end were very small (λ and D = 0.03) and approximately constant. Values of D were slightly lower than those of λ at each point during the precipitation reaction.

The high initial coprecipitation of tracer observed in the present system parallels the reported observation of Schweitzer and McDowell on the cobalt-nickel dimethylglyoximate system. Similar observations were also reported by Block et al. (118) in the coprecipitation of scandium with uranium oxalate. The latter authors explained that a high initial coprecipitation level was due to the high supersaturation of carrier at the beginning of the reaction.

Figures (14), (15), (16) and (17) respectively represent the data from single runs where 0.5 μg, 1.0 μg, 5.0 μg and 10.0 μg of cobalt were used as tracer. In figure (18), averaged distribution curves resulting from all experimental runs with 0.5 μg through 100 μg of trace levels are recorded. All of them show the same trend in variation of λ with the extent of carrier precipitation independent of initial amount of tracer present. Similar curves were obtained when D values were used. At one point of percentage precipitation no significant trend in the numerical values of D or λ with changes in the initial amount of tracer present was observed.

The fractional amounts of tracer precipitated were also calculated and are summarized in Table (15). The data indicate no significant difference between fractional precipitation for 1.0 μg, 5.0 μg and 10.0 μg of cobalt. There seems to be a trend, however, toward higher fractional incorporation as the initial amount of tracer increases to 100.0 μg. This may be explained by an adsorption process where ions from systems of large tracer content have higher in probability to get adsorbed on the carrier precipitate. Significant variation may be observed only between systems of considerable difference in tracer content. The data obtained in the 0.5 μg study seem to present an anomaly.

The high initial amounts of incorporation of tracer resulting in large numerical values of D and λ and the subsequent decrease within each run, however, could not be interpreted in terms of an adsorption process. A kinetic explanation for this observed variation in the calculated values of the distribution coefficients during any one precipitation experiment was then considered.

Predictions made in previous studies regarding the relation of the rate of precipitation reaction and the logarithmic distribution coefficient

Table (15)

Coprecipitation of cobalt with nickel cycloheptanedionedioximate*

% Ni precipitated	% Co precipitated	%Ni precipitated	% Co precipitated	% Ni precipitated	% Co precipitated
(0.5 μg Co)					
27.5	12.3	25.8	7.17	47.9	6.21
29.3	9.03	27.5	6.80	50.3	5.87
40.2	8.62	37.3	4.85	52.4	5.39
54.3	12.1	48.0	6.60	62.9	6.53
59.8	15.9	13.0	4.89	24.8	8.79
72.4	16.2	29.7	3.27	29.6	8.41
16.6	5.70	46.9	4.68	40.1	6.08
34.2	8.38	71.1	7.64	36.8	7.63
45.6	9.50	60.6	7.70	46.9	5.15
46.3	8.30	15.5	6.17		
49.2	10.9	26.5	5.32	(100 μg Co)	
32.0	8.44	32.0	4.36	12.5	4.87
40.2	8.29	35.4	1.37	15.2	4.89
47.6	10.0			21.5	5.04
55.3	10.2	(5.0 μg Co)		22.7	4.07
65.1	10.5	21.3	4.32	23.3	3.43
74.4	13.3	32.2	4.76	24.9	3.68
22.3	8.35	44.5	7.23	8.01	2.30
23.3	8.91	58.5	7.21	9.83	2.70
28.2	7.73	76.7	8.1	13.5	7.49
29.2	8.50	11.5	2.97	19.5	8.30
37.3	8.18	29.4	6.64	22.2	8.90
22.7	8.15	32.9	4.94	23.7	9.60
29.4	9.50	37.6	4.76	26.4	13.2
32.6	8.59	18.3	5.62	27.1	10.3
		27.3	5.41	29.1	7.17
(1.0 μg Co)		35.6	5.21	29.6	10.7
33.3	4.80	47.2	6.20		
33.7	5.12	(10 μg Co)			
47.8	6.51	25.8	7.09		
16.1	5.92	53.9	6.99		
16.3	11.0	64.7	8.33		
29.1	5.26	75.1	9.48		
59.2	3.36	28.2	5.46		

*Percentage values are arranged in order of the increasing reaction time within each run.

include (106):

(a) λ is constant when the rate of precipitation is constant.

(b) If the rate is not constant, λ increases linearly with an increase in rate of precipitation in derichment systems.

(c) If the rate is not constant, λ increases with a decrease in the rate of precipitation in enrichment systems.

The above statements indicate the qualitative relationship between reaction rate and observed logarithmic distribution coefficients. Hermann reported such an observation in the coprecipitation study of americium with lathanum oxalate - an enrichment system. From figure (19) the decrease of λ values with an increase of fractional rate of precipitation of carrier can be noted. And λ approaches a maximum limiting value at zero rate of precipitation.

Similar plots were prepared using data available from our coprecipitation study on the cobalt-nickel cycloheptanedionedioximate system. Data collected in the kinetic study of the nickel heptoximate precipitation reaction (section IV.B) provided the rate of the precipitation reaction as a function of reaction time or percentage of carrier precipitated. Figure (20) is a plot resulting from kinetic studies of nickel heptoximate precipitation reaction in the presence of cobalt tracer at 15°C. Average values of rate constant ($\bar{k}'$) and integration constant ($\bar{c}'$) reported in Table (11) were utilised in preparation of this plot.

Figures (21) through (28) represent the data resulting from coprecipitation experiments in which 0.5, 1.0, 5.0 and 10.0 μg of cobalt respectively were used as tracer. The diagrams show the dependence of

Figure.(19). λ vs rate of precipitation of Lanthanum oxalate. (Reproduced from the thesis (106), permission requested from the University Microfilms,Ann Arbor, Michigan.)

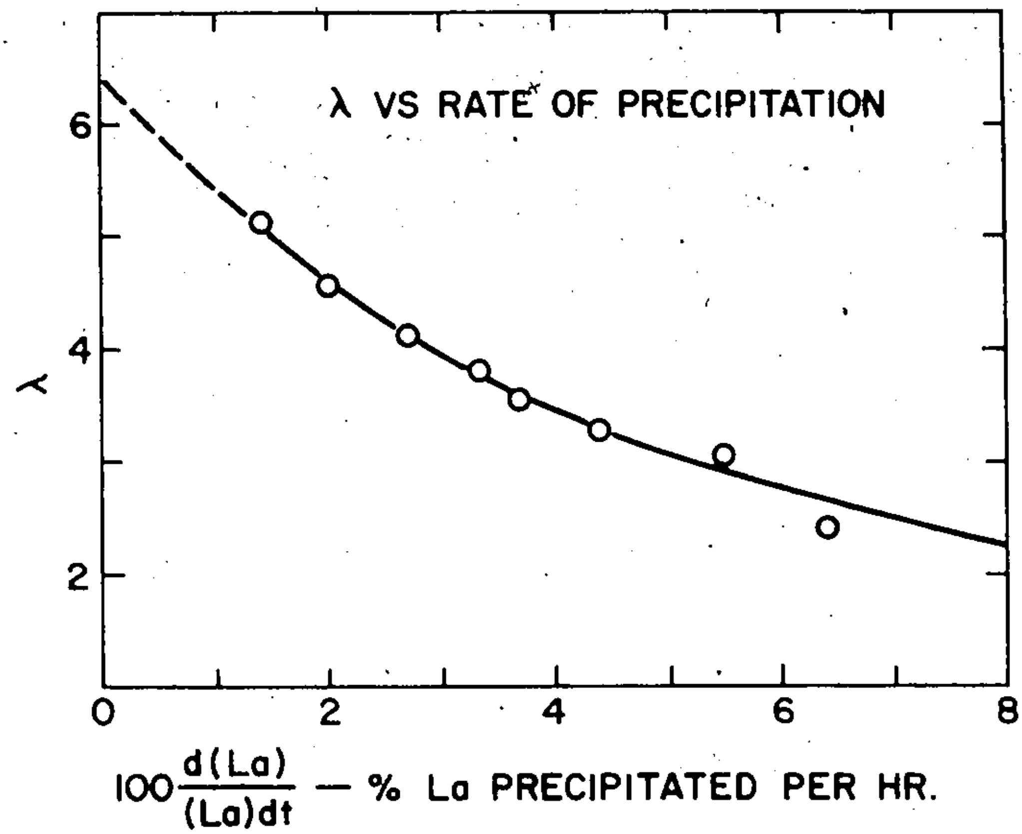
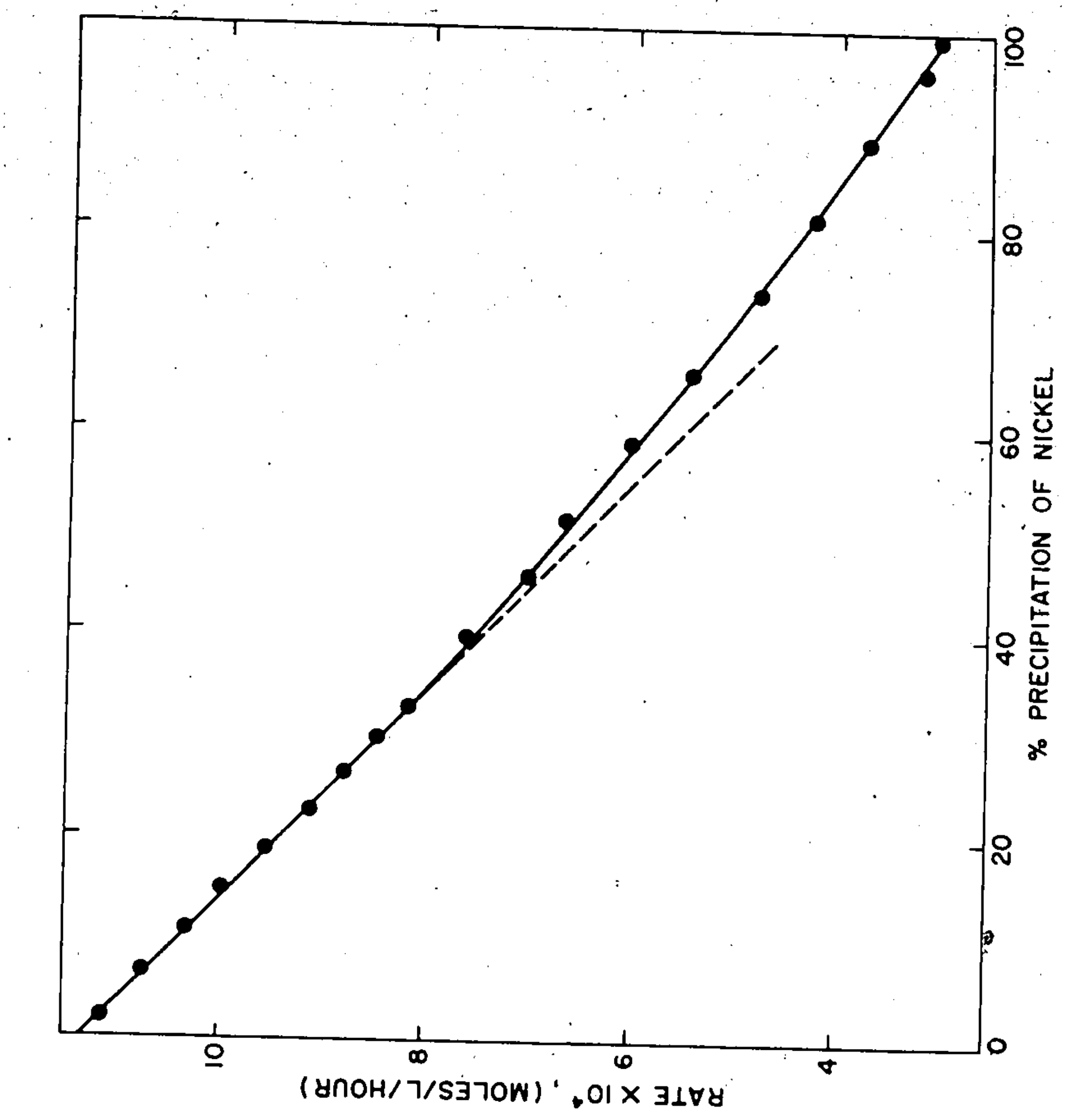

λ VS RATE* OF PRECIPITATION
λ
6
4
2
0
2
4
6
8
100 d(La)/(La)dt — % La PRECIPITATED PER HR.

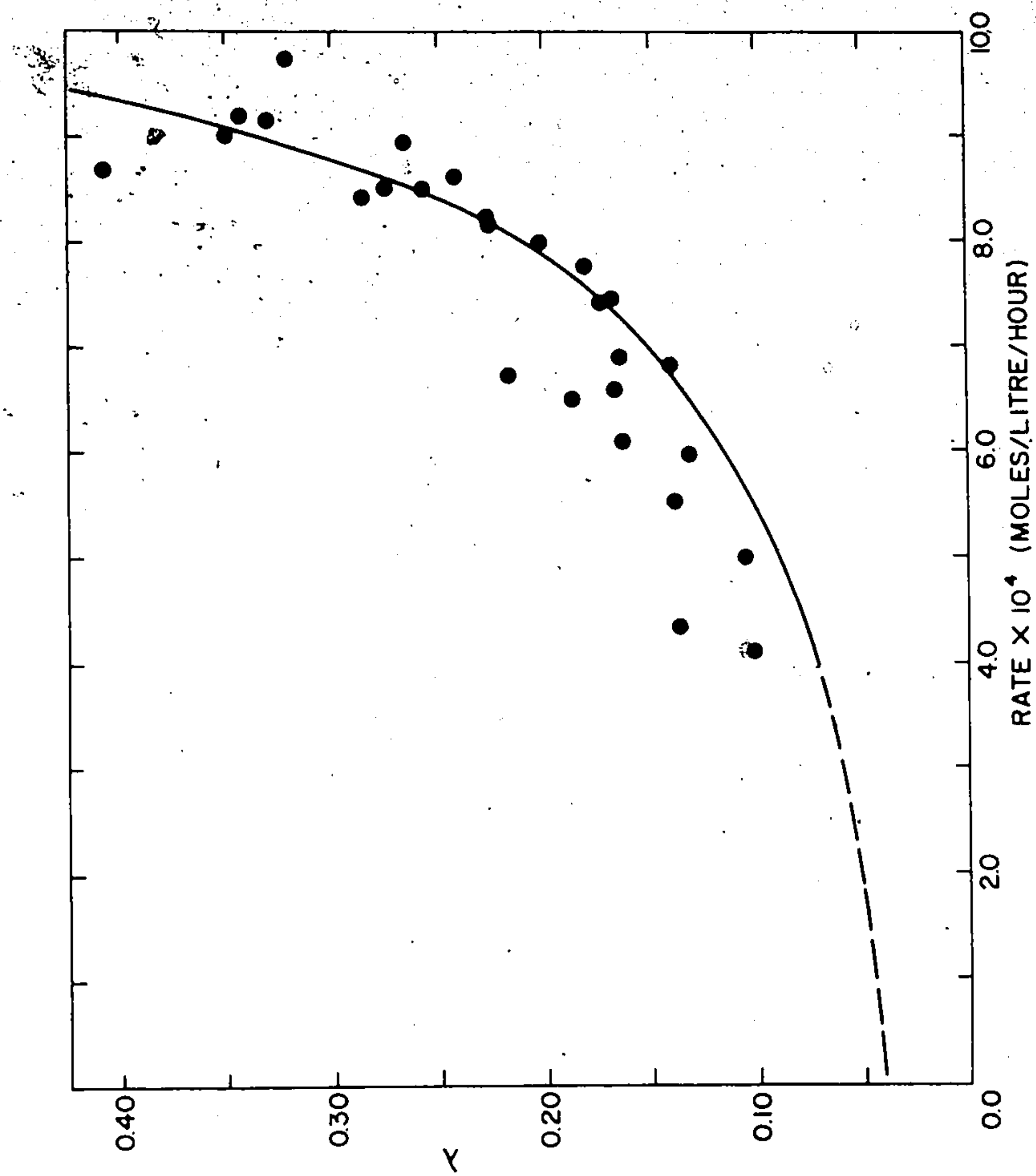
Figure (20). Rate of precipitation of nickel cycloheptanedione-dioximate as a function of percentage nickel precipitated.



RATE × 10⁴, (MOLES/L/HOUR)
10
8
6
4
0
20
40
60
80
100
% PRECIPITATION OF NICKEL

Figure.(21). λ vs rate of precipitation of nickel cycloheptanedionedioximate.

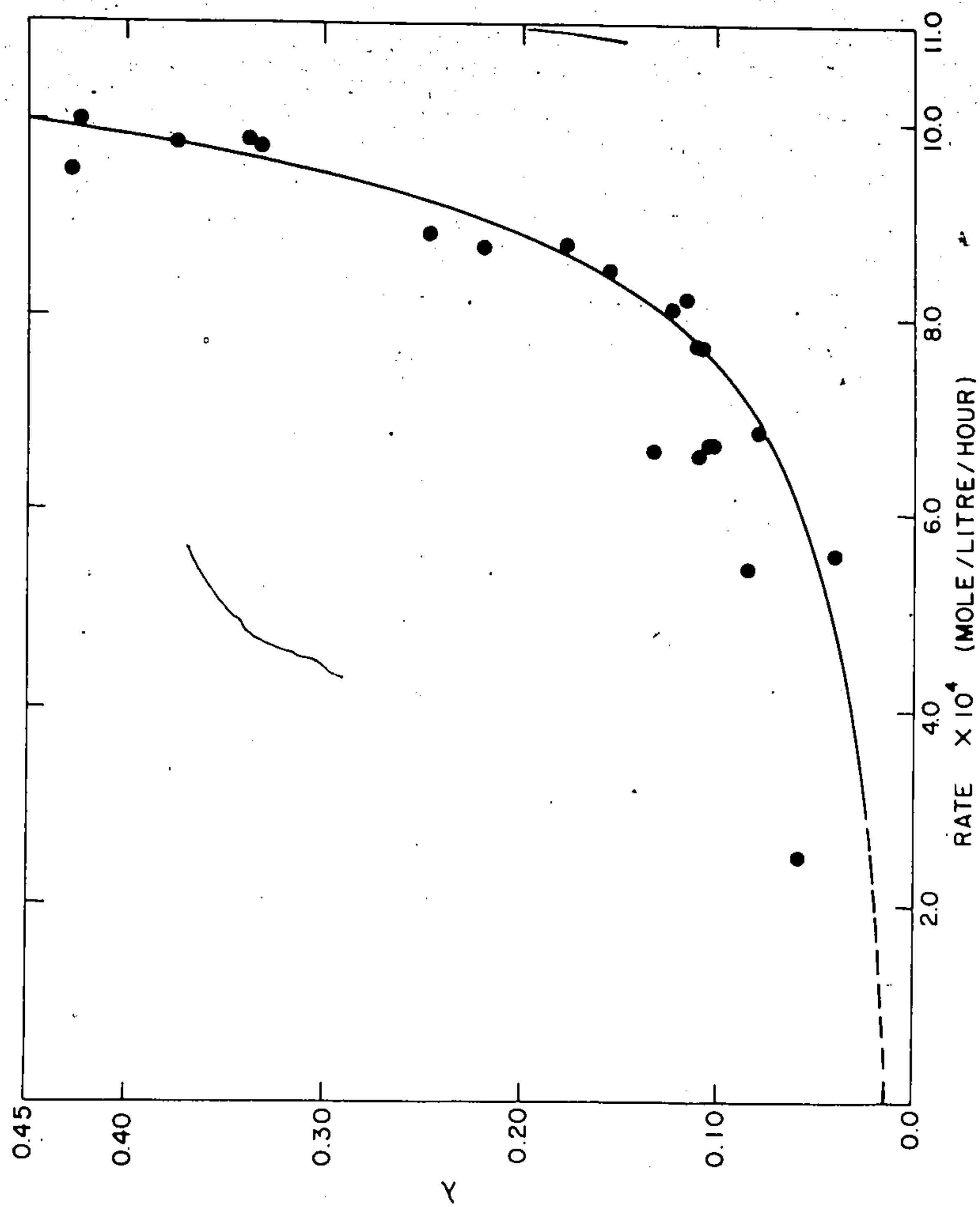
(0.5 μg cobalt present, averaged from all runs)



RATE X 10⁴ (MOLES/LITRE/HOUR)
0.0
2.0
4.0
6.0
8.0
10.0
Y
0.10
0.20
0.30
0.40

Figure. (22). λ vs rate of precipitation of nickel cycloheptanedione-dioximate.

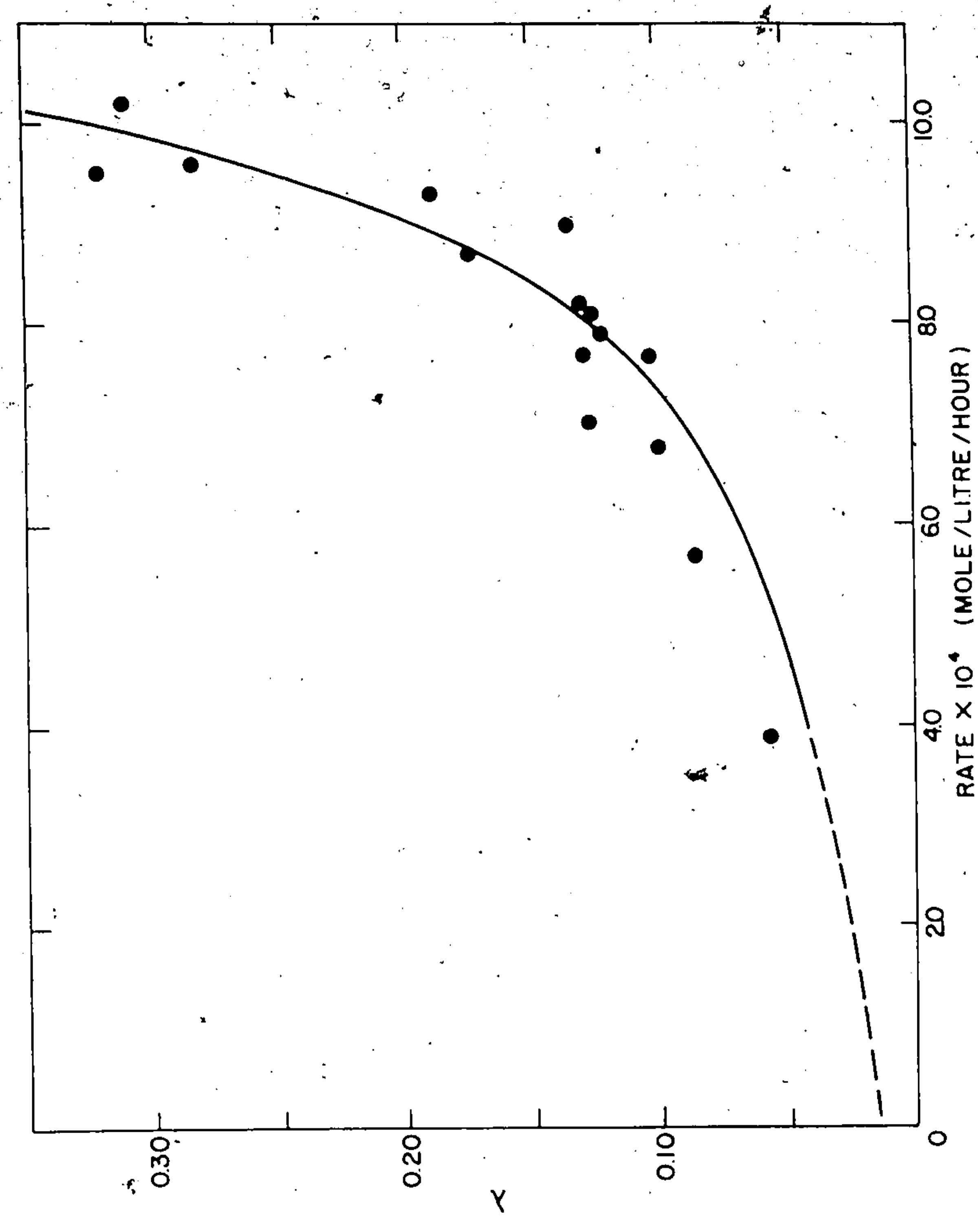
(1.0 μg cobalt present, averaged from all runs)



0.45
0.40
0.30
0.20
0.10
0.0
γ
2.0
4.0
6.0
8.0
10.0
11.0
RATE × 10⁴ (MOLE/LITRE/HOUR)

Figure.(23). λ vs rate of precipitation of nickel cycloheptanedionedioximate.

(5.0 μg cobalt present, averaged from all runs)



RATE X 10⁴ (MOLE/LITRE/HOUR)
γ
0
2.0
4.0
6.0
8.0
10.0
0.10
0.20
0.30

Figure. (24). λ vs rate of precipitation of nickel cycloheptanedionedioximate.

(10.0 μg cobalt present , averaged from all runs)

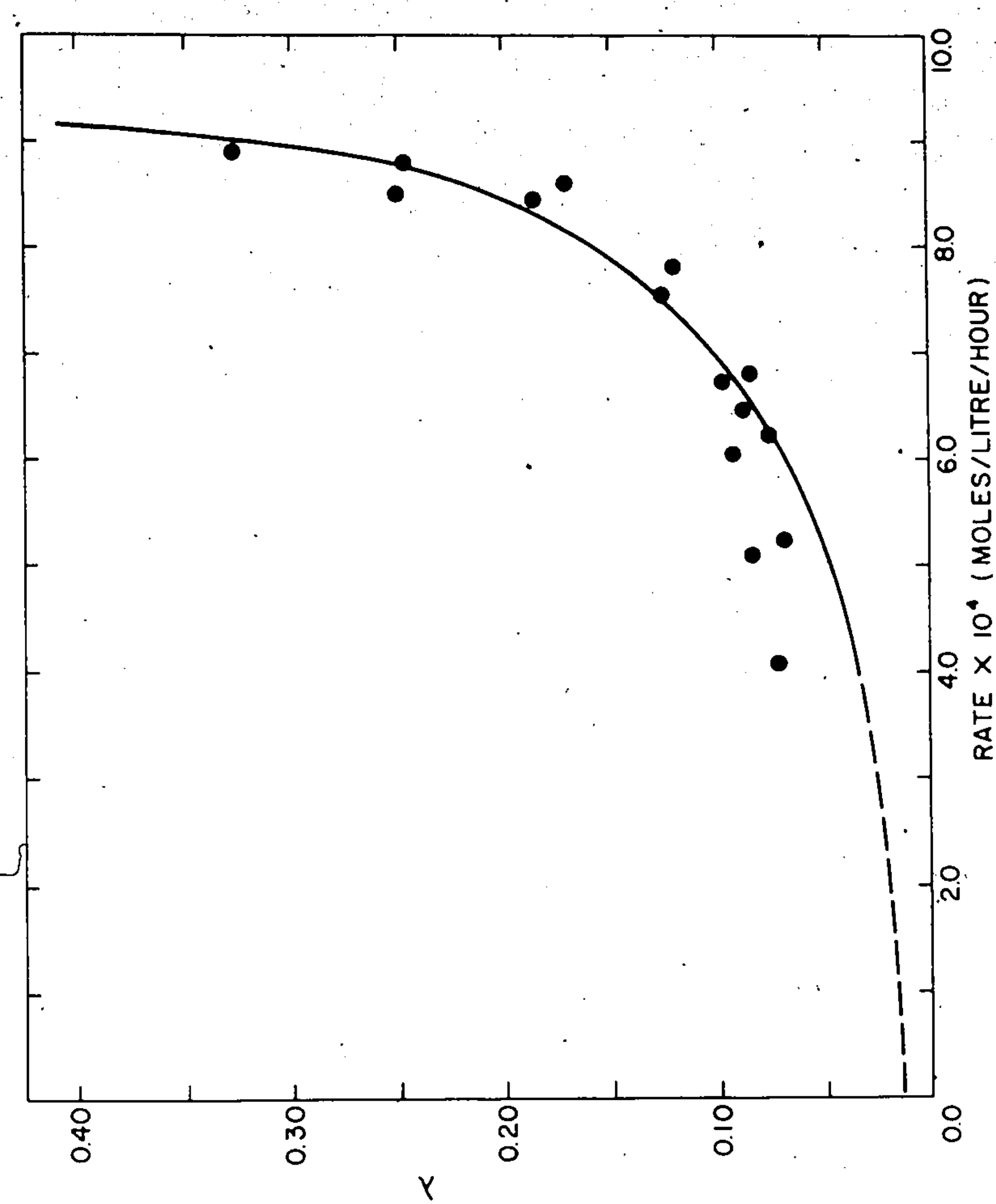

RATE X 10^4 (MOLES/LITRE/HOUR)
0.0
2.0
4.0
6.0
8.0
10.0
γ
0.0
0.10
0.20
0.30
0.40

Figure.(25). D vs rate of precipitation of nickel cycloheptanedionedioximate.

(0.5 μg cobalt present, averaged from all runs)

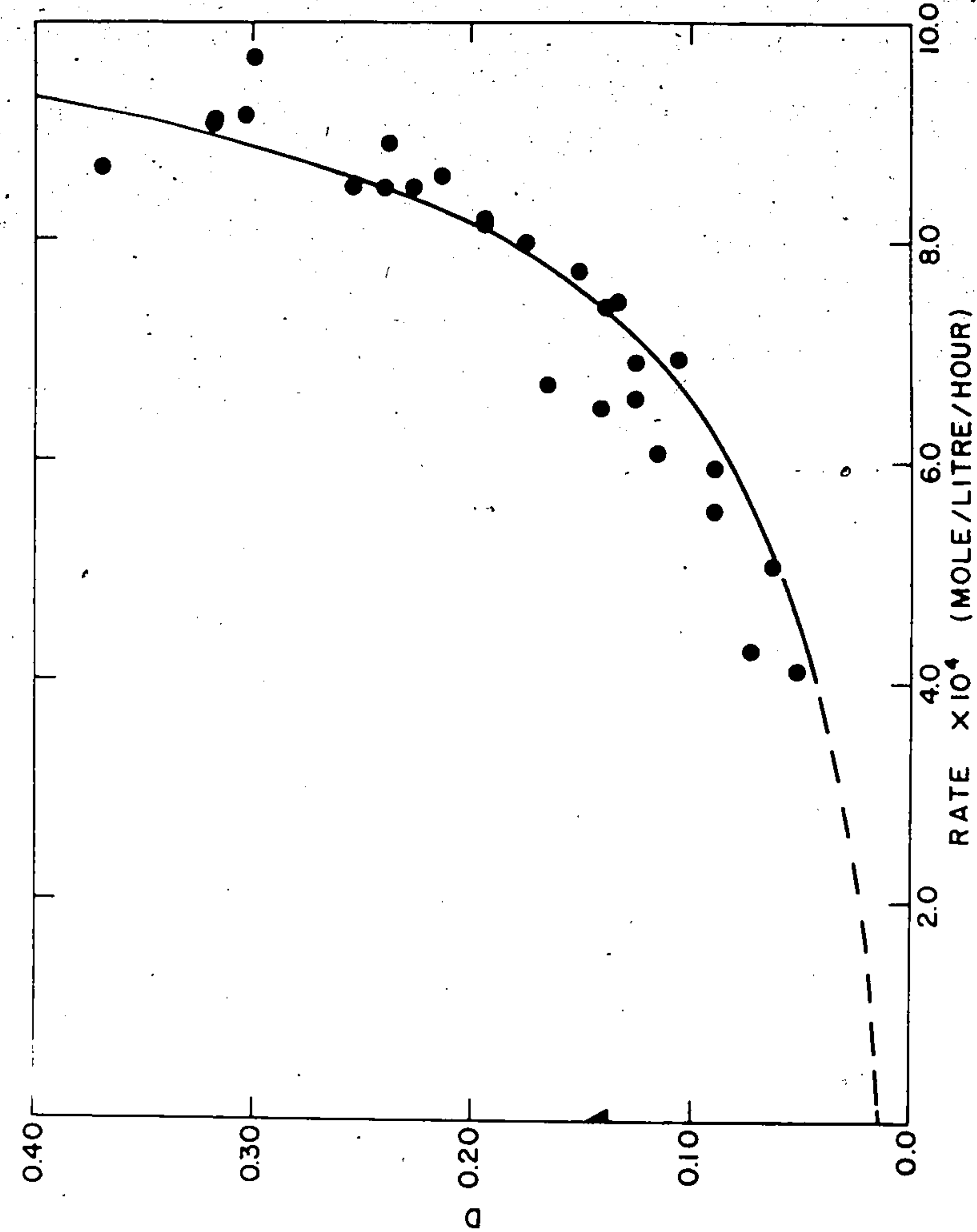
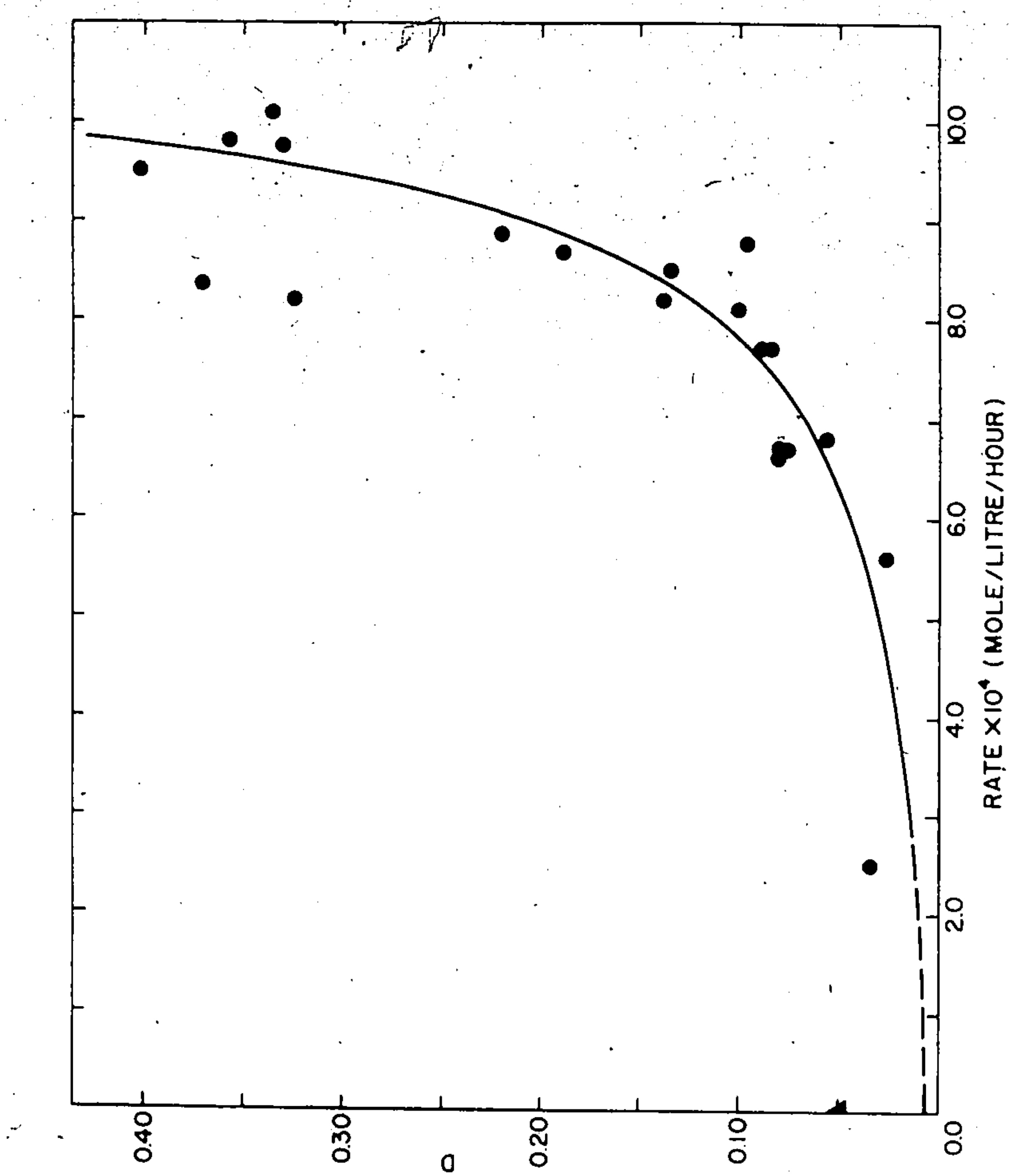

0.40
0.30
0.20
0.10
0.0
a
2.0
4.0
6.0
8.0
10.0
RATE ×10⁴ (MOLE/LITRE/HOUR)

Figure.(26). D vs rate of precipitation of nickel cycloheptanedionedi-
oximate.
(1.0 μg cobalt present , averaged from all runs)



D
0.0
0.10
0.20
0.30
0.40
RATE X10⁴ (MOLE/LITRE/HOUR)
2.0
4.0
6.0
8.0
10.0

Figure.(27). D vs rate of precipitation of nickel cycloheptanedionedi-oximate.

(5.0 μg cobalt present, averaged from all runs)

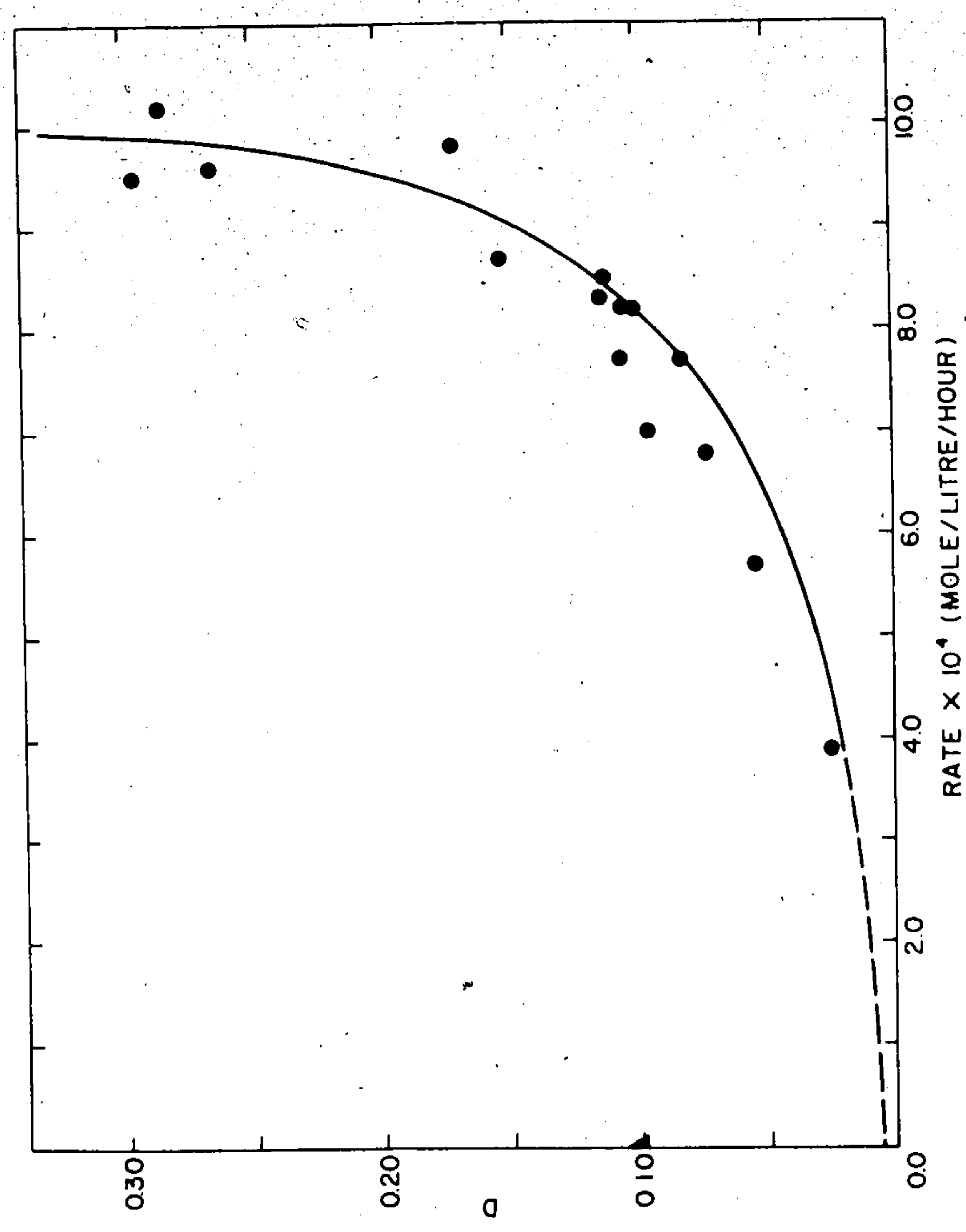
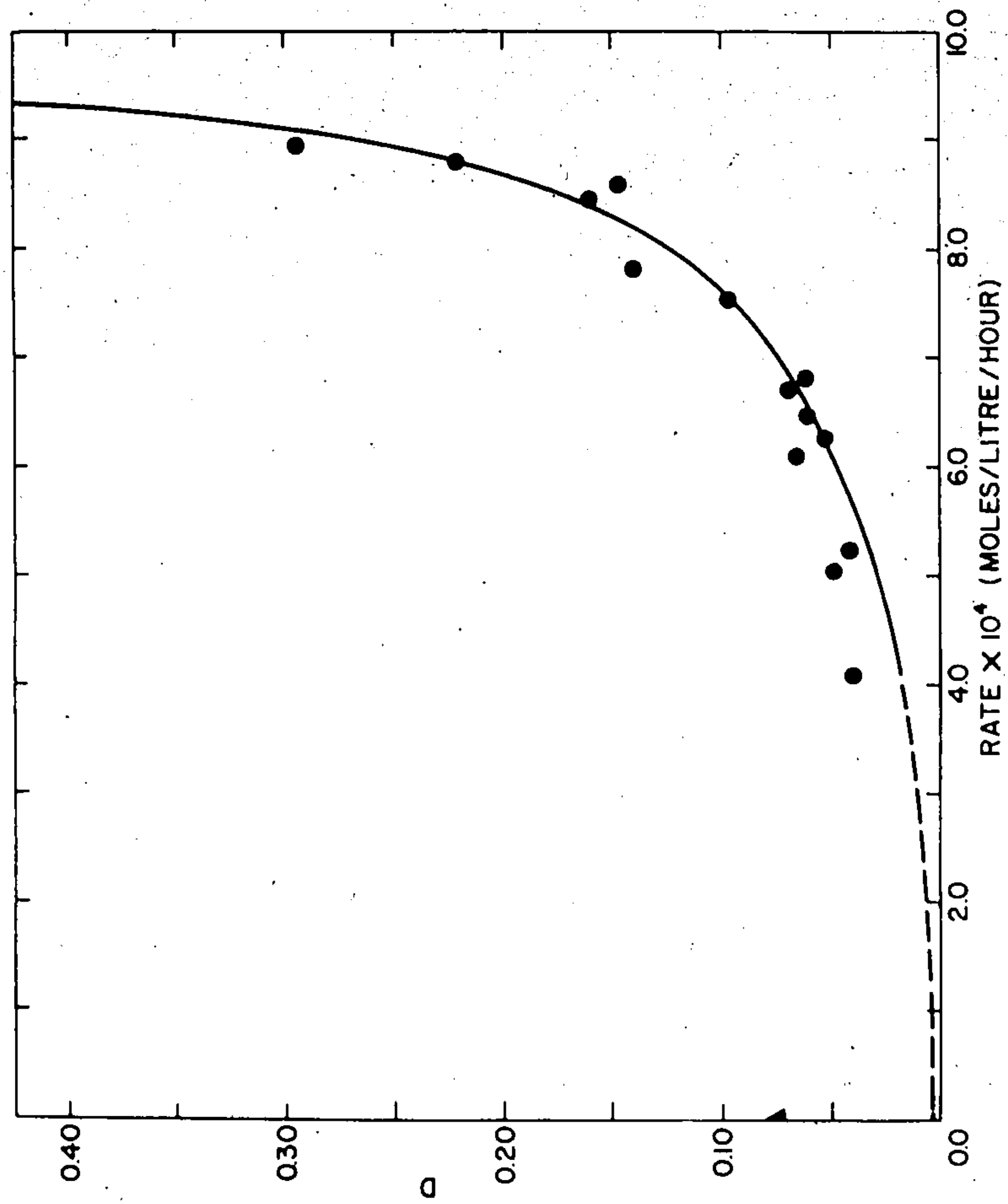

RATE × 10⁴ (MOLE/LITRE/HOUR)
D
0.0
2.0
4.0
6.0
8.0
10.0
0.10
0.20
0.30

Figure. (28). D vs rate of precipitation of nickel cycloheptanedionedioximate.

(10.0 μg cobalt present, averaged from all runs)



D
0.0
0.10
0.20
0.30
0.40
RATE X 10⁴ (MOLES/LITRE/HOUR)
2.0
4.0
6.0
8.0
10.0

distribution coefficients on the reaction rate. As expected for a derichment system, values of D and λ decrease with a decrease of reaction rate within any one experimental run. A linear model was searched for the extrapolation of the curve to the zero rate of precipitation. An ln λ vs rate was found to yield a straight line plot. The solid and the dotted lines of the figures were drawn to the point calculated from the intercept of the linear model.

In addition, an explanation of the shape of the distribution diagrams reported in which observed distribution coefficients decrease with the extent of carrier precipitation (Figures 13 - 18) can now be found. High initial values of λ and D are due to the high rate of reaction at the beginning of the precipitation and low values of λ and D are observed at the final stages of precipitation where the reaction rate is relatively low.

Dependence of distribution coefficients on the rate of reaction is therefore significant as predicted by kinetic models (see section I.B.(4)). The kinetic model of Gordon and group (115) could not be applied to the present system since the observed logarithmic distribution coefficients are not constant with the extent of carrier precipitation. Klein's model, however, provides such a relationship between the rate of precipitation per particle and the distribution coefficient (λ) so that it can be applied to systems where distribution coefficients are not constant with the extent of carrier precipitation. The mathematical expression proposed by Klein (1.24) was used as a guideline for data analysis. The assumption was made that the number of active sites (M) is proportional to the total number of crystals (N) in the precipitation of nickel heptoximate.

The number of particles formed during the precipitation of nickel heptoximate was determined by using a Coulter counter. The experimental procedures reported in section II.E. were followed. The number of particles formed at different reaction times were recorded. Figure (29) is a representative plot using data collected from a particle counting experiment with initial conditions mentioned in section II.E.(1). This provides the total number of particles formed at any time during the precipitation.

The calculated rate of the precipitation reaction, the number of crystals formed and the observed distribution coefficient values were related using Klein's model - shown as equation (1.24).

Observed and calculated data from coprecipitation experiments performed with different trace levels of cobalt were used in data processing and plots of $\frac{I}{N}(\lambda-1)$ against λ were prepared. Figures (30), (31), (32) and (33) are such plots resulting from coprecipitation systems containing initial amounts of 0.5, 1.0, 5.0 and 10.0 micrograms of tracer cobalt, respectively. Each plot gives a straight line with a slope of k_2 and an intercept whose numerical value is equal to k_1.

k_1 and k_2 are the apparent rate constants for the reaction

$$Co(II)_{solution} + Ni(C_7H_{11}O_2N_2)_{2\,solid} \underset{k_2^o}{\overset{k_1^o}{\rightleftarrows}} Ni(II)_{soln} + Co(C_7H_{11}O_2N_2)_{2\,solid}$$

The rate constant ratio, $\frac{k_1^o}{k_2^o}$, is equal to the ratio of the solubility products of carrier and tracer precipitates. From a thermodynamic point of view, $\frac{k_1^o}{k_2^o}$ is equal to the distribution coefficient, D_0, at zero rate of precipitation. If the model is valid for the present system, the value of $\frac{k_1^o}{k_2^o}$ will be equal to the homogeneous distribution coefficient (D) at zero rate of precipitation as well as the ratio of solubility products of carrier and tracer precipitates respectively.

Figure (29). Number of particles observed during the precipitation of nickel cycloheptanedionedioxímate vs reaction time. (cobalt tracer present)

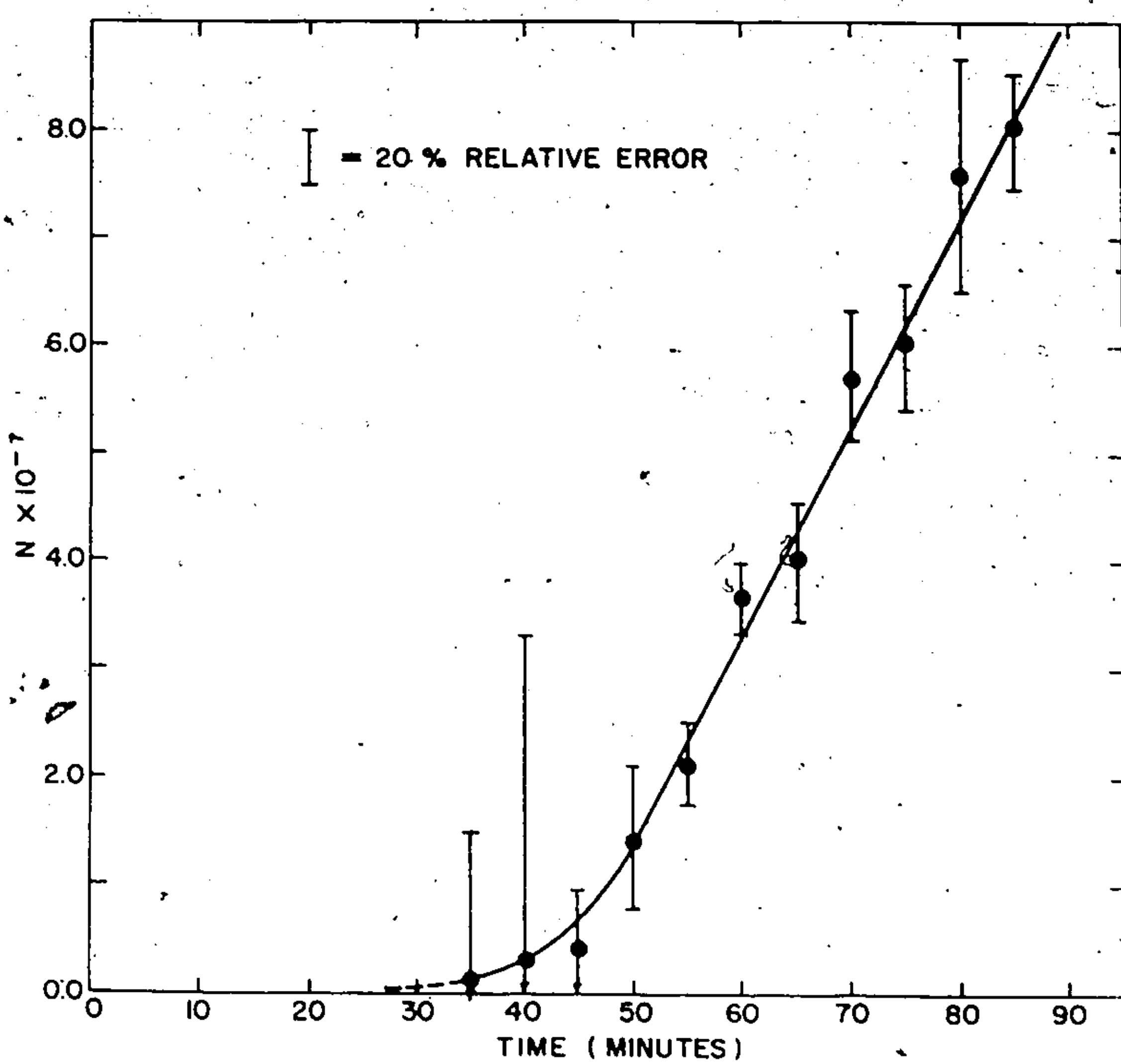

= 20 % RELATIVE ERROR
8.0
6.0
4.0
2.0
0.0
N X 10⁻⁷
0
10
20
30
40
50
60
70
80
90
TIME (MINUTES)

Figure.(30). Variation of λ with rate of precipitation I and number of crystals N .

(0.5 μg cobalt present)

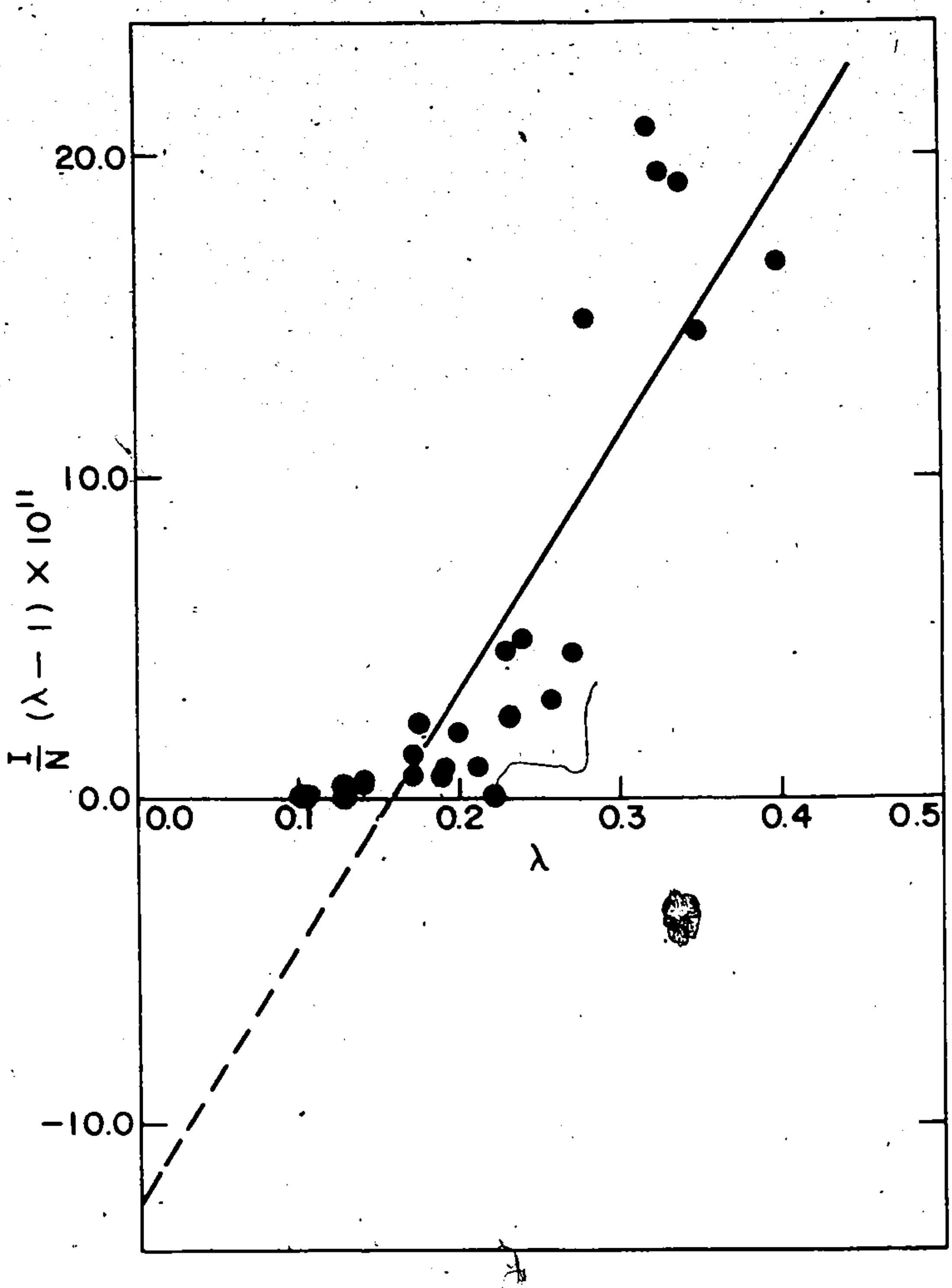

20.0
10.0
0.0
-10.0
0.0
0.1
0.2
0.3
0.4
0.5
λ
I/N (λ − 1) × 10^11

Figure.(31). Variation of λ with rate of precipitation I and number of crystals N.

(1.0 μg cobalt present)

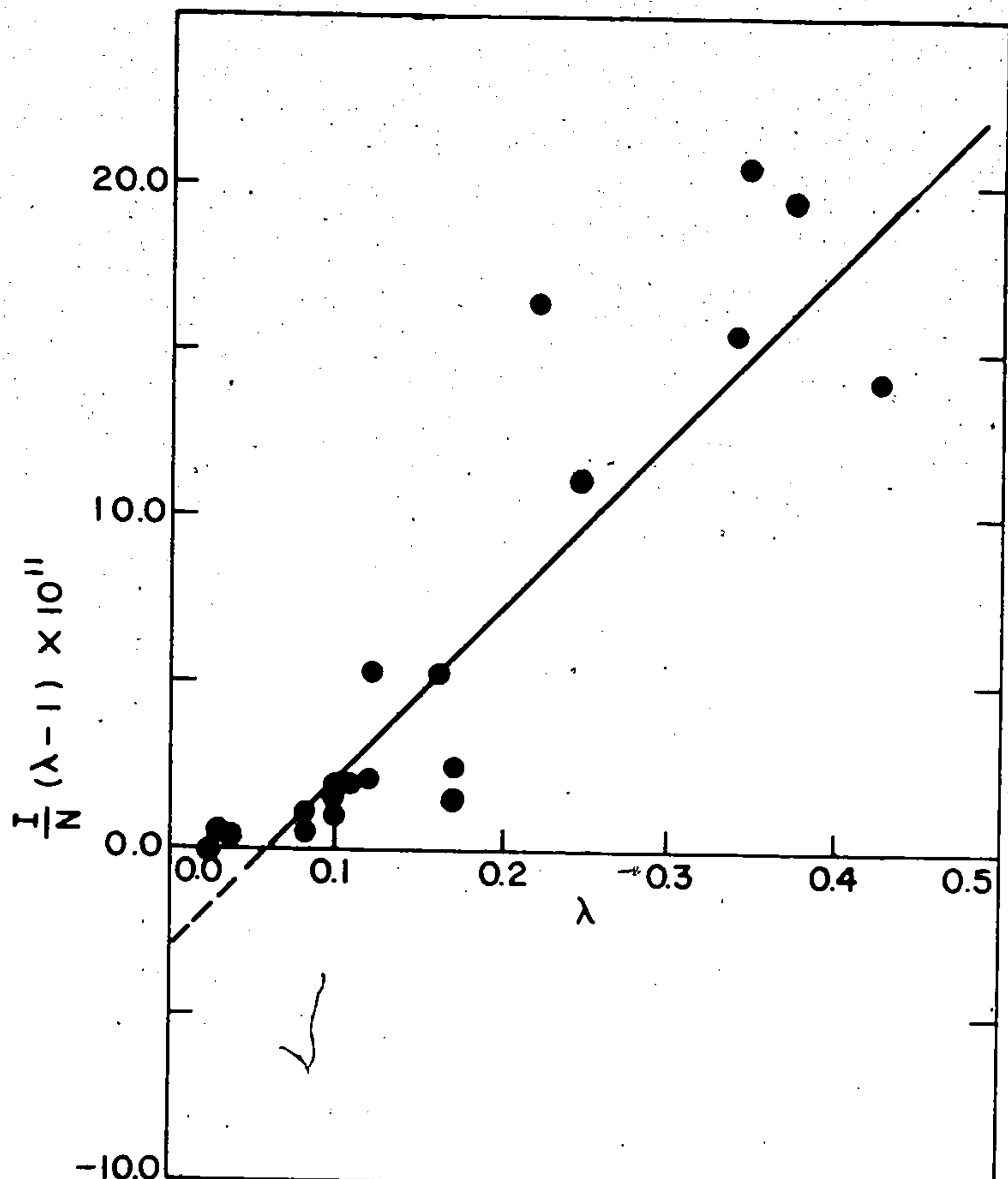

20.0
10.0
0.0
-10.0
0.0
0.1
0.2
0.3
0.4
0.5
λ
$\frac{I}{N}(\lambda-1) \times 10^{11}$

Figure.(32). Variation of λ with rate of precipitation I and number of crystals N.

(5.0 μg cobalt present)

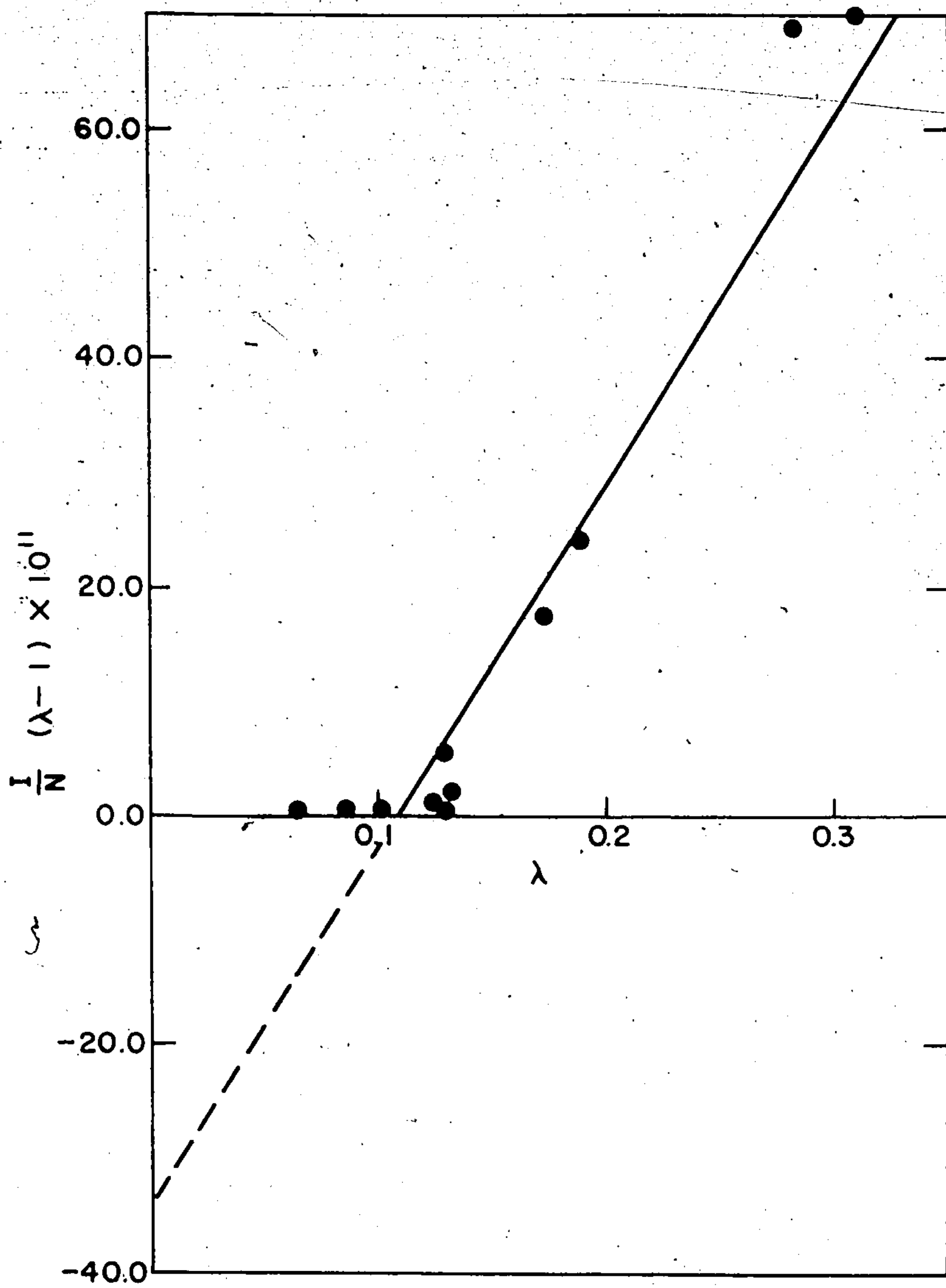
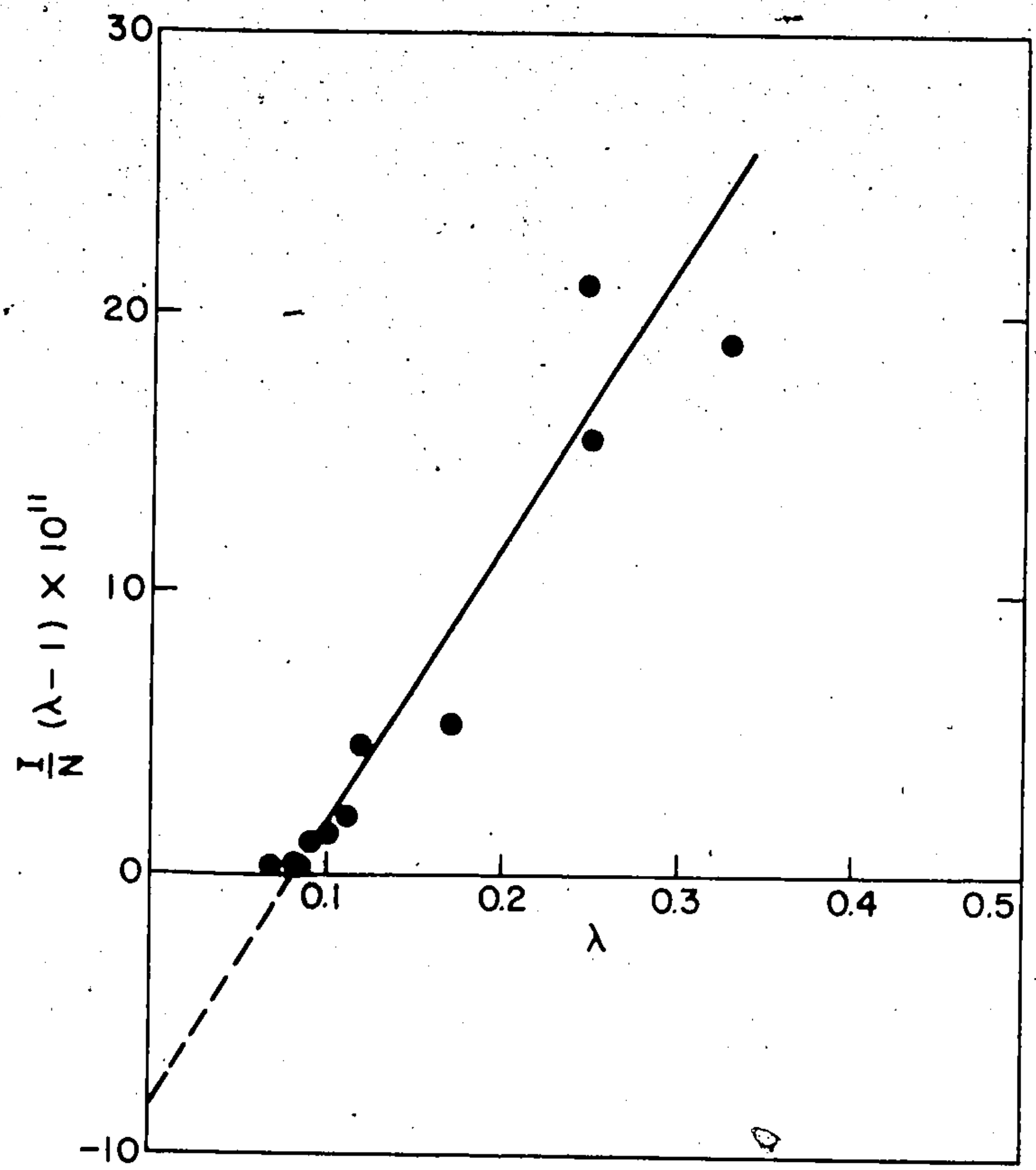

60.0
40.0
20.0
0.0
-20.0
-40.0
0.1
0.2
0.3
λ
$\frac{1}{N}(\lambda - 1) \times 10^{11}$

Figure.(33). Variation of λ with rate of precipitation I and number of crystals N.

(10.0 μg cobalt present)


30
20
10
0
-10
0.1
0.2
0.3
0.4
0.5
λ
$\frac{I}{N}(\lambda - 1) \times 10^{11}$

The solubility product value for cobalt cycloheptanedionedioximate is not available in the literature. The solubility product ratio could not be used for model testing. Values of distribution coefficients, D, however, were recorded previously as a function of the rate of precipitation. Values at zero rate of precipitation were thus evaluated quantitatively in the following way. In preliminary data processing, it was discovered that distribution coefficients are related to the rate of reaction in the form of equation

$$y = a\, e^{bx}$$

where y = observed distribution coefficient

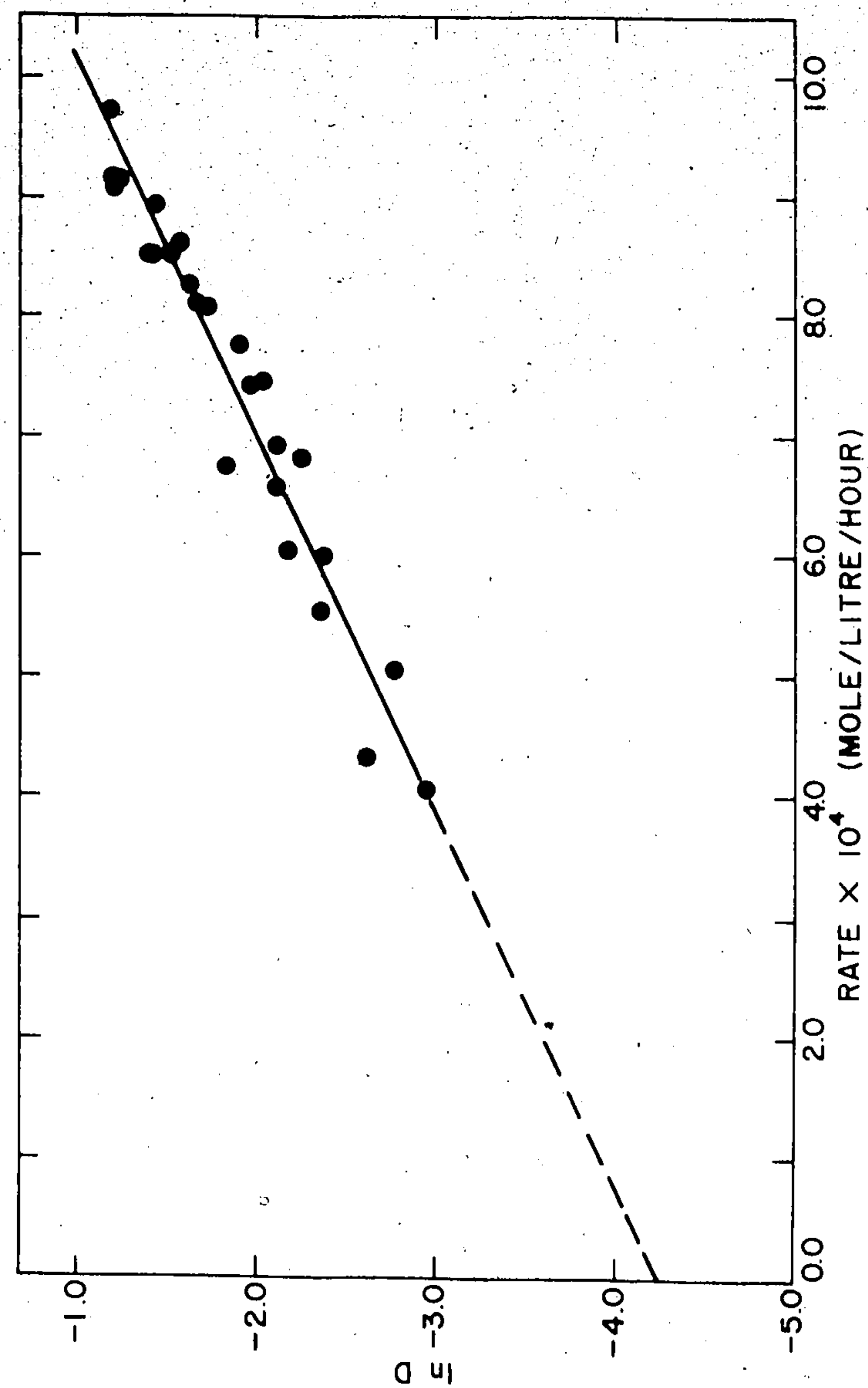
x = the rate of precipitation reaction

and a and b are some arbitrary constants.

A plot of ln D against rate of reaction gave a straight line with a slope of (b) and an intercept of (ln a). A test procedure, using data collected from an experiment where 0.5 μg of tracer cobalt was used, gave the plot shown in Figure (34). The model thus rationalises the observed data and the value of intercept provides the numerical value of D at zero rate of precipitation.

Similar plots were prepared for all systems containing different trace levels and corresponding values of D at zero rate of precipitation. These values of D were compared with the corresponding values of $\frac{k_1}{k_2}$. The data are reported in Table (16). Data from Table (16) indicate that values of D and k_1/k_2 are not in good agreement. Such deviation could arise from various factors. A major source of error is the determination

Figure (34). ln D vs rate of precipitation of nickel cycloheptanedionedioximate.



ln D
-1.0
-2.0
-3.0
-4.0
-5.0
0.0
2.0
4.0
6.0
8.0
10.0
RATE × 10^4 (MOLE/LITRE/HOUR)

Table (16)

Observed values of rate constant ratio and D_o in coprecipitation of cobalt with nickel cycloheptanedionedioximate

Cobalt present (μg)	"D_o" at zero rate of precipitation	k_1/k_2 (observed)
0.5	0.015	0.15 ± 0.01
1.0	0.010	0.048 ± 0.01
5.0	0.010	0.10 ± 0.04
10.0	0.0044	0.075 ± 0.01
	Average 0.010 ± 0.007	Average 0.093 ± 0.02

of the total number of crystals. At the beginning of the reaction, the number of particles formed is relatively small and the counting errors are fairly large. Relative errors for each count at different reaction times are illustrated in Figure (29). These data points correspond to the large λ values observed at the beginning of the reaction and cause a large uncertainty in the straight line plots.

IV.C.(2) <u>Coprecipitation of copper with nickel cycloheptanedionedioximate</u>

As stated earlier, the interference of copper with the precipitation of nickel cycloheptanedionedioximate was observed in both precipitation processes, PFHS and conventional, when appreciable quantities of copper were present in solution. Results from classical studies have led workers to predict that copper interferes with the precipitation of nickel dimethylglyoximate by partially retarding the precipitation and by direct contamination of the precipitate (83,129). During the kinetic studies, a slight reduction in the rate of nickel heptoximate precipitation was observed in the presence of copper (see section IV.B.(2)). In preliminary studies the high apparent weight of nickel observed in the precipitation of nickel heptoximate in the presence of copper was also reported (see Table 7(a)). The extent of contamination as well as the nature of coprecipitation of copper with nickel dioximate crystals are important since contamination of copper is often observed in the gravimetric determination of nickel. A coprecipitation study on copper-nickel cycloheptanedionedioximate system was therefore initiated.

The experimental procedures reported in section II.D.(2) were applied. The PFHS procedure with the experimental conditions selected for a slow precipitation raaction (section II.C.(1)) provided a useful technique for the present coprecipitation study.

Microgram amounts of copper were used with milligram amounts of nickel as carrier in the precipitation reaction. Analysis of copper in the presence of nickel by atomic absorption technique provided satisfactory results when copper levels used were 25 ug or larger. For the 10 μg trace level, the precipitate samples contained very small amounts of tracer and the analysis of copper by atomic absorption method could not be performed. Only the filtrate samples were analysed for the tracer content. Concentration of samples containing a small amount of copper by a chelation-extraction method using APDC/MIBK (Ammonium pyrrolidine dithiocarbamate and methyl isobutyl ketone) and some other systems did not improve the sensitivity since both copper and nickel react with these chelating agents. A double extraction-spectrophotometric procedure for the determination of microgram levels of copper in dyes and rubber chemicals was adapted for the analysis of samples when the tracer level used was 5 ug or smaller (141). The experimental procedure, as detailed in section II.D.(2), was followed. The method included the extraction of both nickel and copper as their dibenzyldithiocarbamate complexes. Destruction of coloured complexes with potassium permanganate and re-extraction removed most of the nickel. The proposed procedure, when applied in the present study, gave results with satisfactory precision provided the experimental conditions were carefully controlled. The intensity of the colour developed depends both on the extraction time and the length of standing time before measurement.

The observed data were processed using the two classical limiting laws initially as guidelines. Distribution coefficients, D and λ, were calculated according to equations (1.15) and (1.19) reported in section I.B.(2). Observed and derived data collected are recorded in Appendix (II).

A preliminary experiment performed at 15°C resulted in distribution coefficient values which are approximately unity. The poor selectivity thus observed could be due to the relatively fast rate of reaction for that system. Precipitation at 5°C provided a slower rate of reaction. Figures (35) through (37) represent the distribution diagrams resulting from coprecipitation experiments carried out under experimental conditions reported (section II.D.(2)) and in the presence of 2.5, 5.0, 10.0, 25.0 and 50.0 μg of copper respectively.

At all trace levels studied, calculated values of the distribution coefficients, D and λ, were larger than unity. This indicated that the precipitate was enriched in tracer, i.e. an enrichment system. The distribution coefficients were relatively constant with the extent of carrier precipitated. Besides, values of D and λ were similar although D values were slightly higher than those of λ at each point during the precipitation reaction. Numerical values of both D and λ lie between approximately 1.0 and 2.5. This observation parallels the data from the zinc-aluminium 8-hydroxyquinolate coprecipitation system reported by Lyle, et al. (131). The authors suggested that the observation could be the result of a difference in chemical composition (structure) between the two metal chelates.

Figures (35 through 39) also indicate the independence of distribution coefficients from the initial amounts of tracer present in solution, i.e. approximately equal and constant values of D and λ are noted. Average values

Figure (35). Distribution diagram of the coprecipitation of copper with nickel cycloheptanedionedioximate.
(2.5 μg copper and 3.0 mg nickel, all runs)

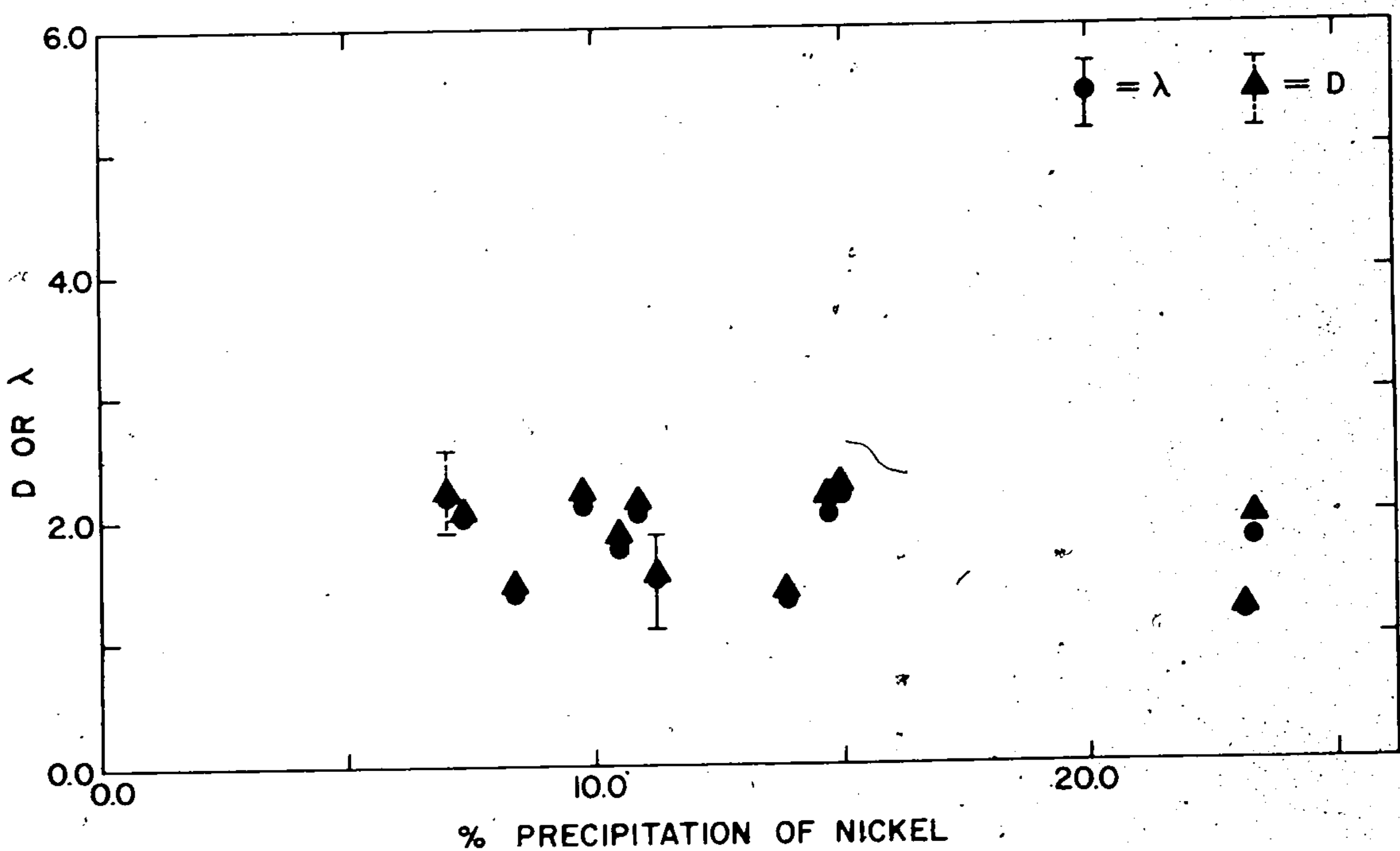
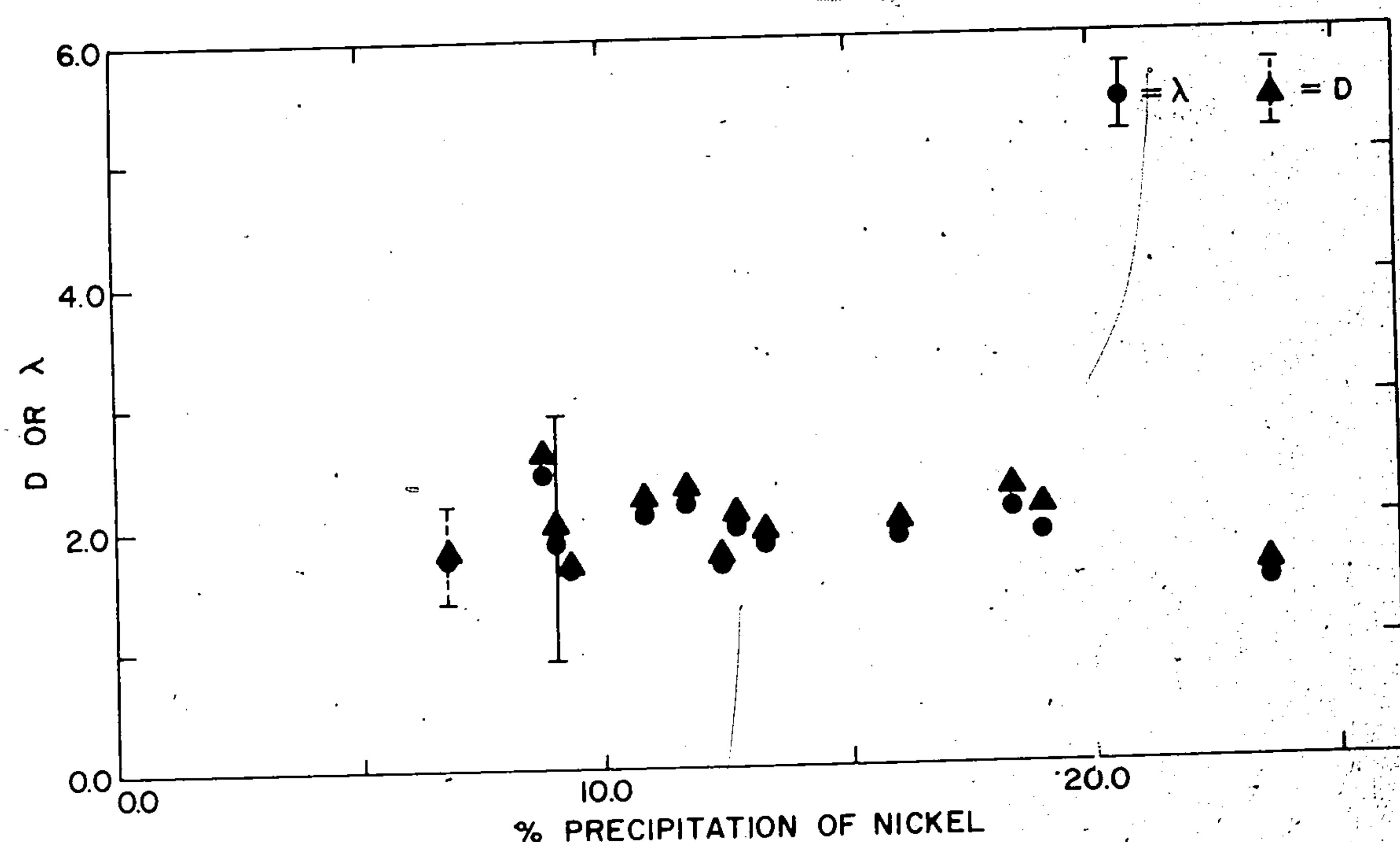

6.0
4.0
2.0
0.0
D OR λ
0.0
10.0
20.0
% PRECIPITATION OF NICKEL
= λ
= D

Figure (36). Distribution diagram of the coprecipitation of copper with nickelcycloheptanedionedioximate.
(5.0 μg copper and 3.0 mg nickel, all runs)



6.0
4.0
2.0
0.0
D OR λ
0.0
10.0
20.0
% PRECIPITATION OF NICKEL
= λ
= D

Figure (37). Distribution diagram of the coprecipitation of copper with nickel cycloheptanedionedioximate.
(10.0 μg copper and 3.0 mg nickel, all runs)

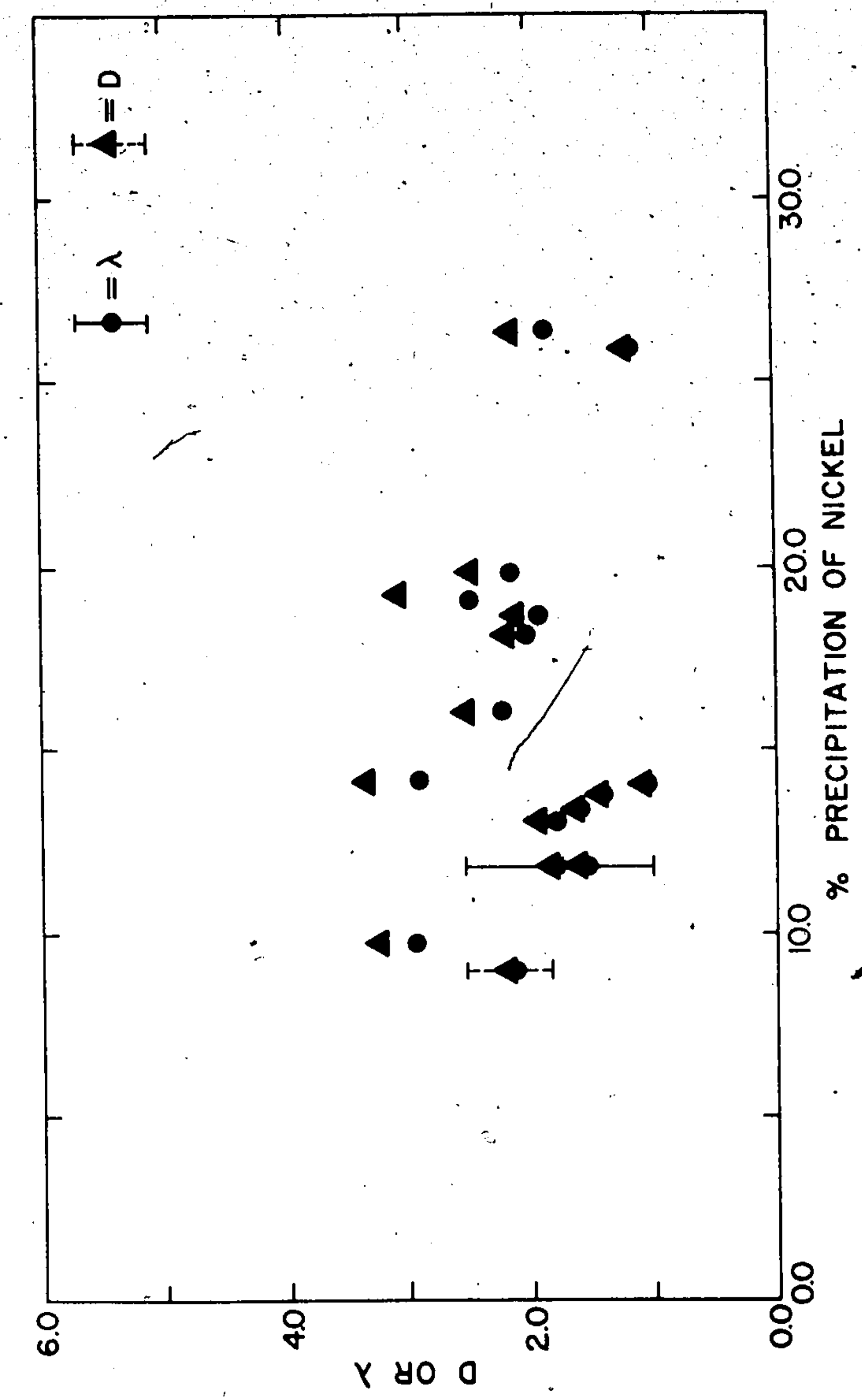
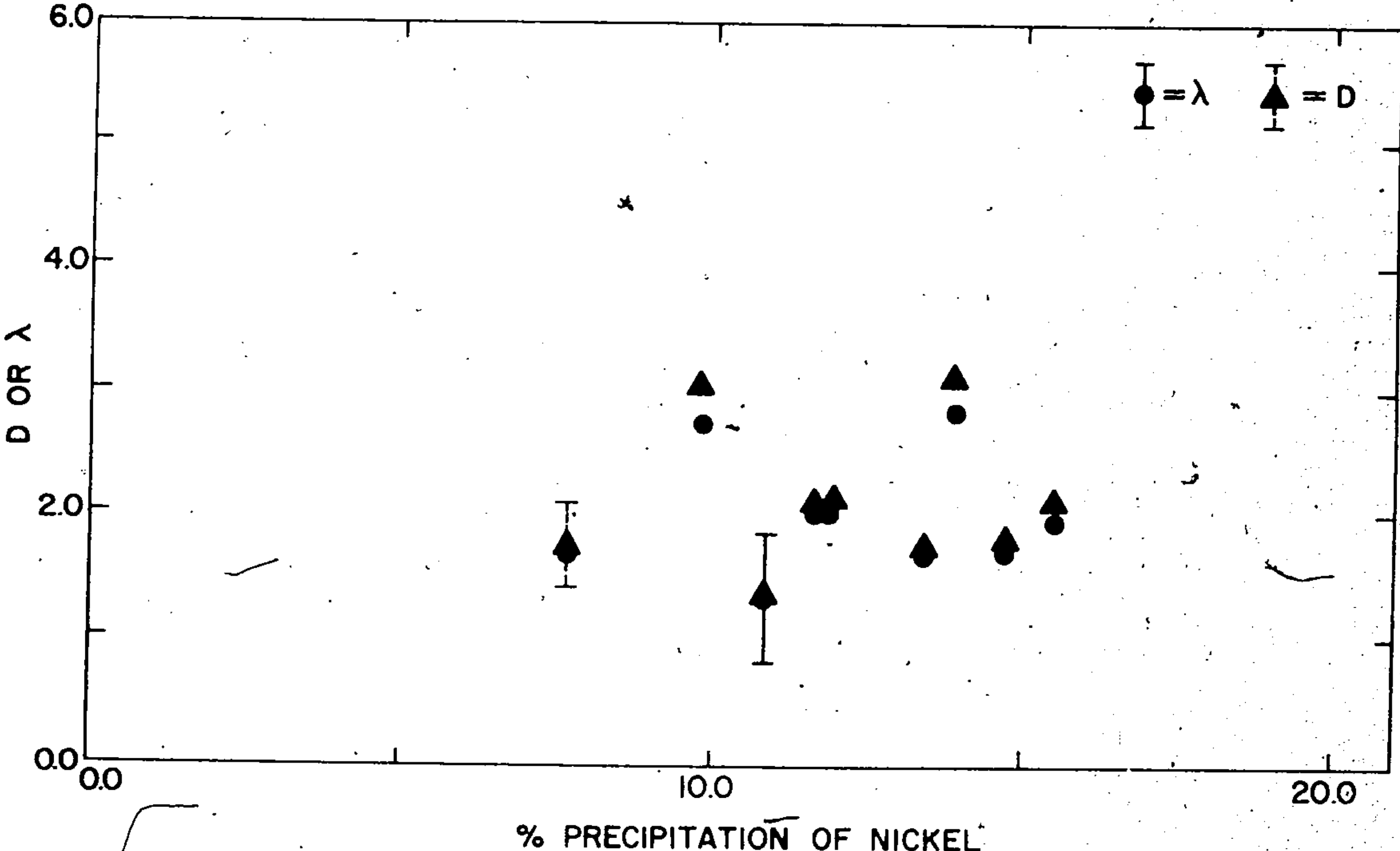

= λ
= D
0.0
10.0
20.0
30.0
% PRECIPITATION OF NICKEL
0.0
2.0
4.0
6.0
D OR λ

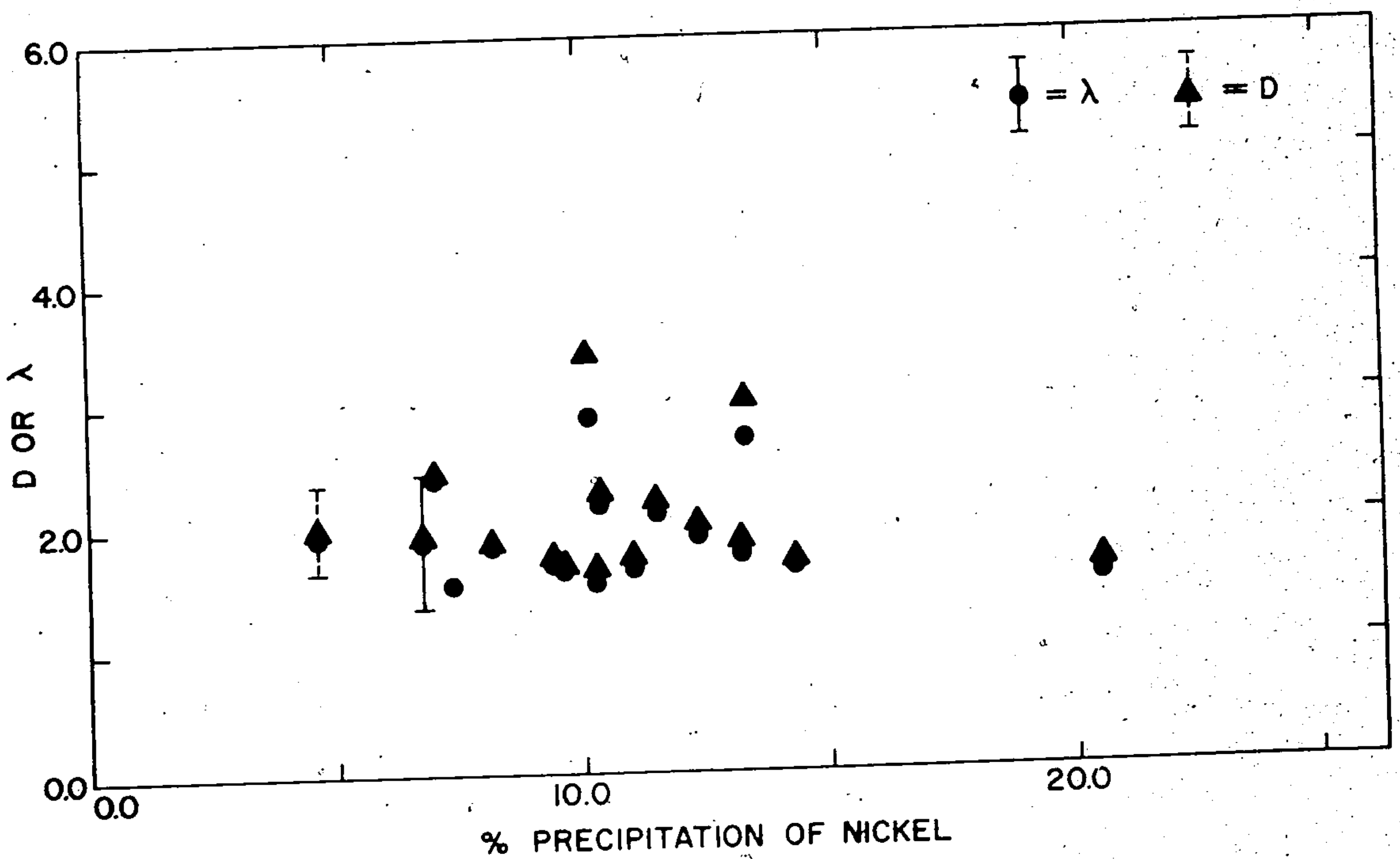
Figure (38). Distribution diagram of the coprecipitation of copper with nickel cycloheptanedionedioximate.
(25.0 μg copper and 3.0 mg nickel, all runs)



= λ
= D
6.0
4.0
2.0
0.0
D OR λ
0.0
10.0
20.0
% PRECIPITATION OF NICKEL

Figure (39). Distribution diagram of the coprecipitation of copper with nickel cycloheptanedionedioxime.

(50.0 μg copper and 3.0 mg nickel, all runs)



= λ
= D
6.0
4.0
2.0
0.0
D OR λ
0.0
10.0
20.0
% PRECIPITATION OF NICKEL

of D and λ for all the trace levels are gathered and reported in Table (17). The data observed are very much different from those observed when studying the coprecipitation of cobalt with nickel cycloheptanedione-dioximate.

Fractional amounts of tracer incorporated were also calculated for all trace levels and compared. No significant effect of the amount of tracer present on the fractional entrainment of tracer was observed. The fractional amounts of tracer incorporated are significantly higher than those of cobalt nickel heptoximate system (derichment system).See Table (18).

An additional experiment was carried out for longer reaction time so that experimental data could be collected at higher percentages of carrier precipitated. Approximately 55% of carrier precipitation was obtained within a 7 1/2 hour reaction time. Observed data showed that the fractional tracer entrainment decreased with an increase in the fractional amounts of carrier precipitated (see Figure (40)). The entrainment of tracer was greatly reduced at higher percentage of carrier precipitation or on longer digestion time. And the reduction was significant. Observed numerical values of D and λ (originally an enrichment system) were also reduced to less than unity (derichment system). The data gathered are reported in Appendix (II). A similar observation was reported by Lyle et al. in the coprecipitation of palladium with nickel dimethylglyoximate from homogeneous solution.

The coprecipitation of copper with nickel heptoximate can be rationalised in the following way. Copper may be entrained in the nickel

Table (17)

Observed distribution coefficient values in coprecipitation of copper with nickel cycloheptanedionedioximate

Copper present (μg)		Observed λ (average)	Observed D (average)
2.5		1.84±0.14	1.96 ±0.16
5.0		1.96±0.08	2.14 ±0.07
10.0		1.96±0.09	2.17 ±0.08
25.0		2.00±0.15	2.17 ±0.13
50.0		1.97±0.08	2.10 ±0.08
	Average	1.95±0.10	2.11 ±0.10

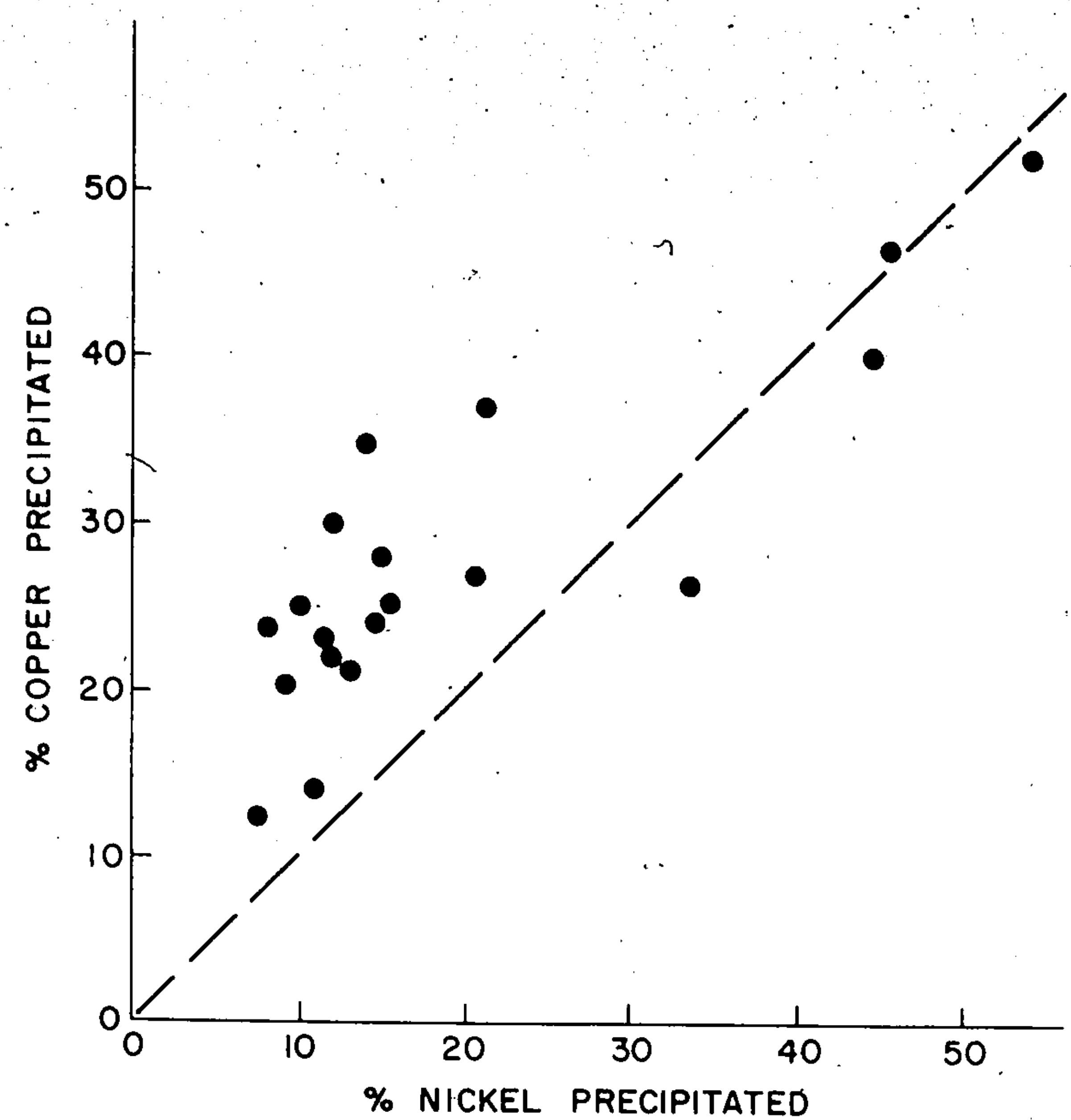
Table (18)

Coprecipitation of copper with nickel cycloheptanedionedioximate*

% Ni precipitated	% Cu precipitated
(2.5 μg Cu)	
7.72	12.3
9.89	16.7
13.7	29.5
14.0	29.0
23.1	27.6
23.2	37.4
7.42	16.3
8.30	12.7
10.9	17.2
10.4	16.1
11.2	16.8
15.1	27.9
(5.0 μg Cu)	
9.28	20.4
13.2	21.1
12.4	20.4
12.6	21.9
16.0	22.2
23.7	32.1
6.86	18.2
9.10	19.2
10.2	28.7
13.5	14.5
17.2	30.4
21.9	40.1
2.79	20.0
11.7	21.2
10.8	21.9
18.9	27.4
18.1	40.0
(10.0 μg Cu)	
13.9	14.3
13.4	20.5
19.8	38.4
18.5	33.0
25.9	31.0
11.6	19.2
13.7	18.7
13.3	23.0
14.2	36.3
18.0	33.5
26.7	44.4
13.2	26.0
9.55	25.7
12.1	18.4
16.3	34.0
19.2	42.5
(25.0 μg Cu)	
9.81	23.1
11.8	23.1
13.9	31.9
14.7	24.0
15.5	28.2
7.70	12.5
10.9	14.3
11.8	23.9
13.5	25.9
(100.0 μg Cu)	
5.99	11.6
6.91	13.2
10.4	13.6
11.5	20.2
13.1	24.8
14.5	25.5
4.8	11.1
7.42	17.5
9.41	13.3
11.0	21.6
10.4	22.8
13.2	35.3
6.8	15.1
8.2	14.6
9.6	14.6
10.1	26.0
12.3	23.7
20.6	27.2

*Percentage values are arranged in order of the increasing reaction time for each run.

Figure (40). Coprecipitation of copper with nickel cycloheptanedionedioximate.


% COPPER PRECIPITATED
0
10
20
30
40
50
0
10
20
30
40
50
% NICKEL PRECIPITATED

heptoximate crystal by an adsorption process and possibly by a co-deposition process as well. As discussed earlier, copper exhibits the characteristics of an enrichment system and the fractional amount of tracer coprecipitation is independent of initial concentration of tracer. Since copper forms an insoluble complex with heptoxime, copper heptoximate crystals may co-deposit on the carrier precipitate during the initial stages of the pre-cipitation process. On longer digestion the carrier precipitate releases the entrained tracer probably through an Ostwald ripening process. Con-sequently a reduction in the level of tracer entrainment could occur near the end of the reaction resulting in low values of the distribution coefficients

Klein's model was similarly tested in the coprecipitation of copper with nickel cycloheptanedionedioximate. The number of particles formed during the nickel heptoximate formation reaction at 5°C is recorded as a function of reaction time in Figure (41). Figure (42) shows the rate of precipitation I in the presence of copper at different stages of precipitation reaction. The variation of λ with rate of precipitation I and number of crystals N was calculated according to Klein's expression (equation 1.24) and data are recorded in Figure (43) through (48). Trace levels used in those experiments were 2.5, 5.0, 10.0, 25.0 and 50.0 μg respectively. Rate constant ratios ($\frac{k_1}{k_2}$) were similarly calculated from these plots.

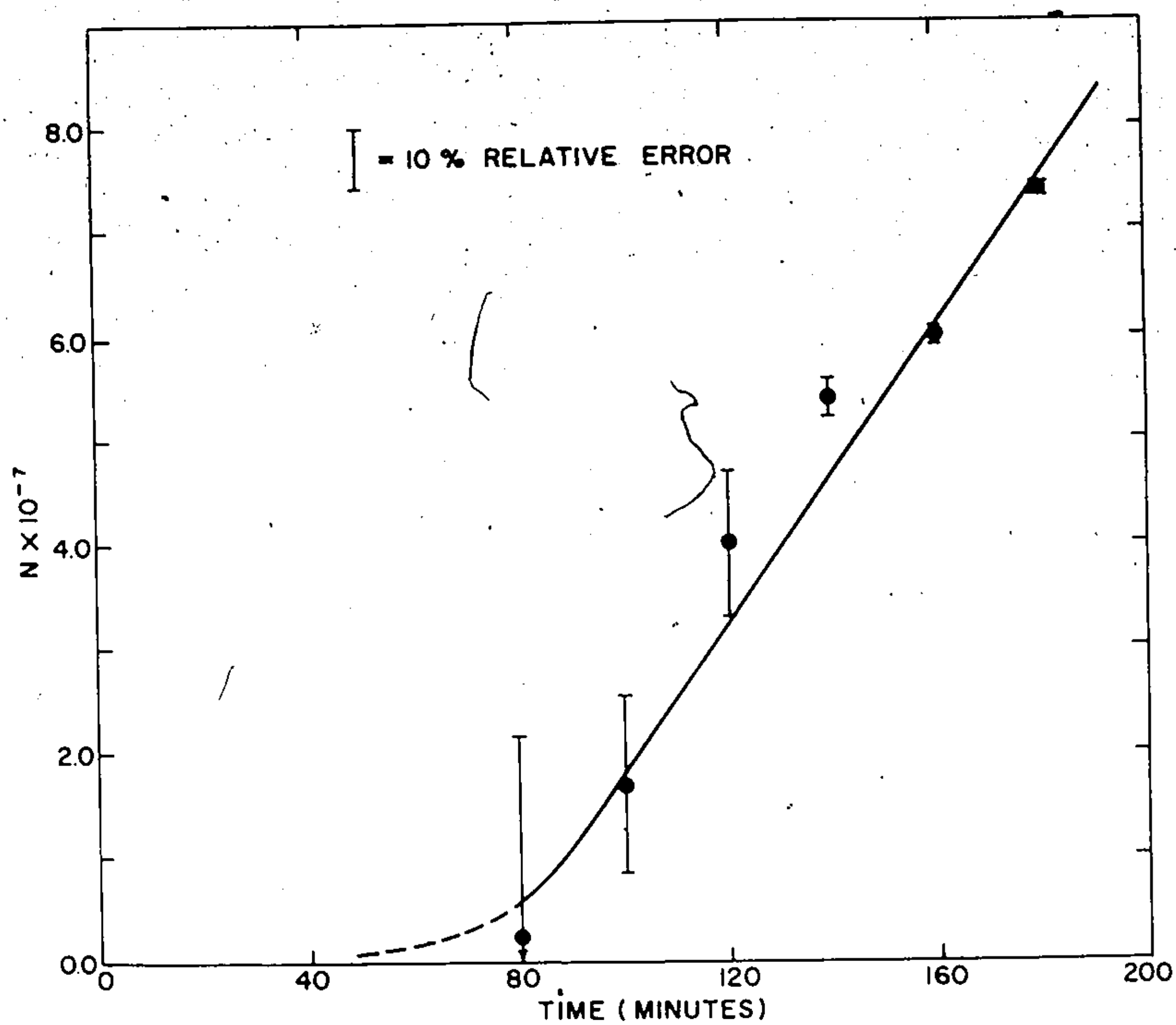
The distribution coefficient value (D_0) at zero rate of precipitation in this experiment is simply the average value of observed D's. Since observed values of D are relatively constant with the decrease in rate of reaction, D_0 is the same as the average value of all D's.

A comparison of values of D_0 and $\frac{k_1}{k_2}$ is reported in Table (19).

Observed values of D_0 as well as $\frac{k_1}{k_2}$ are precise and independent of tracer present. Agreement between D_0 and $\frac{k_1}{k_2}$, however, is relatively poor. Sources of error for the observed deviation may arise from the causes previously discussed in the coprecipitation study of cobalt with nickel heptoximate.

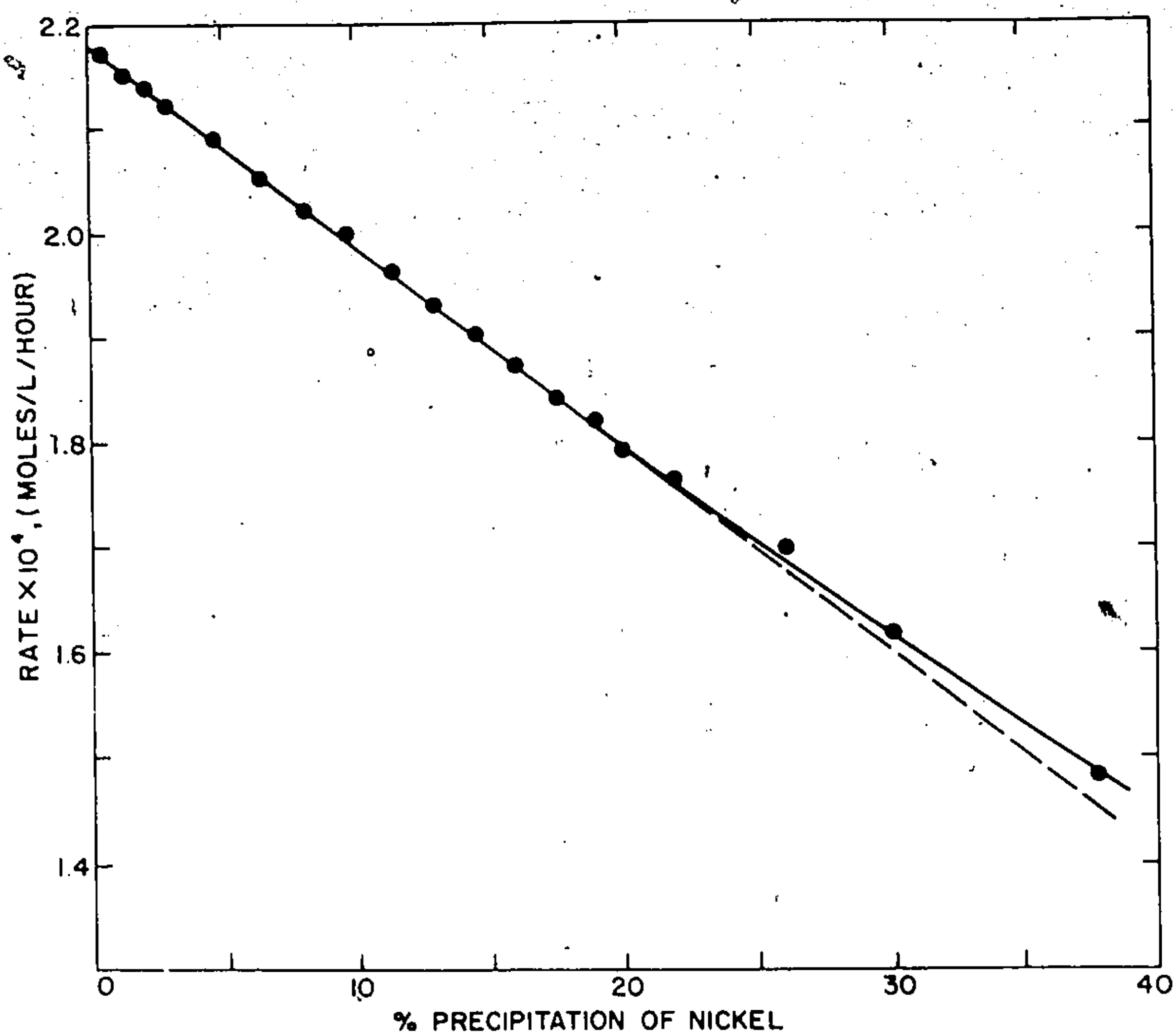
Klein's model, however, rationalises the data from coprecipitation of copper with nickel heptoximate better than those from cobalt-nickel heptoximate system.

Figure (41). Number of particles formed during the precipitation of nickelcycloheptanedionedioximate vs reaction time. (copper tracer present)



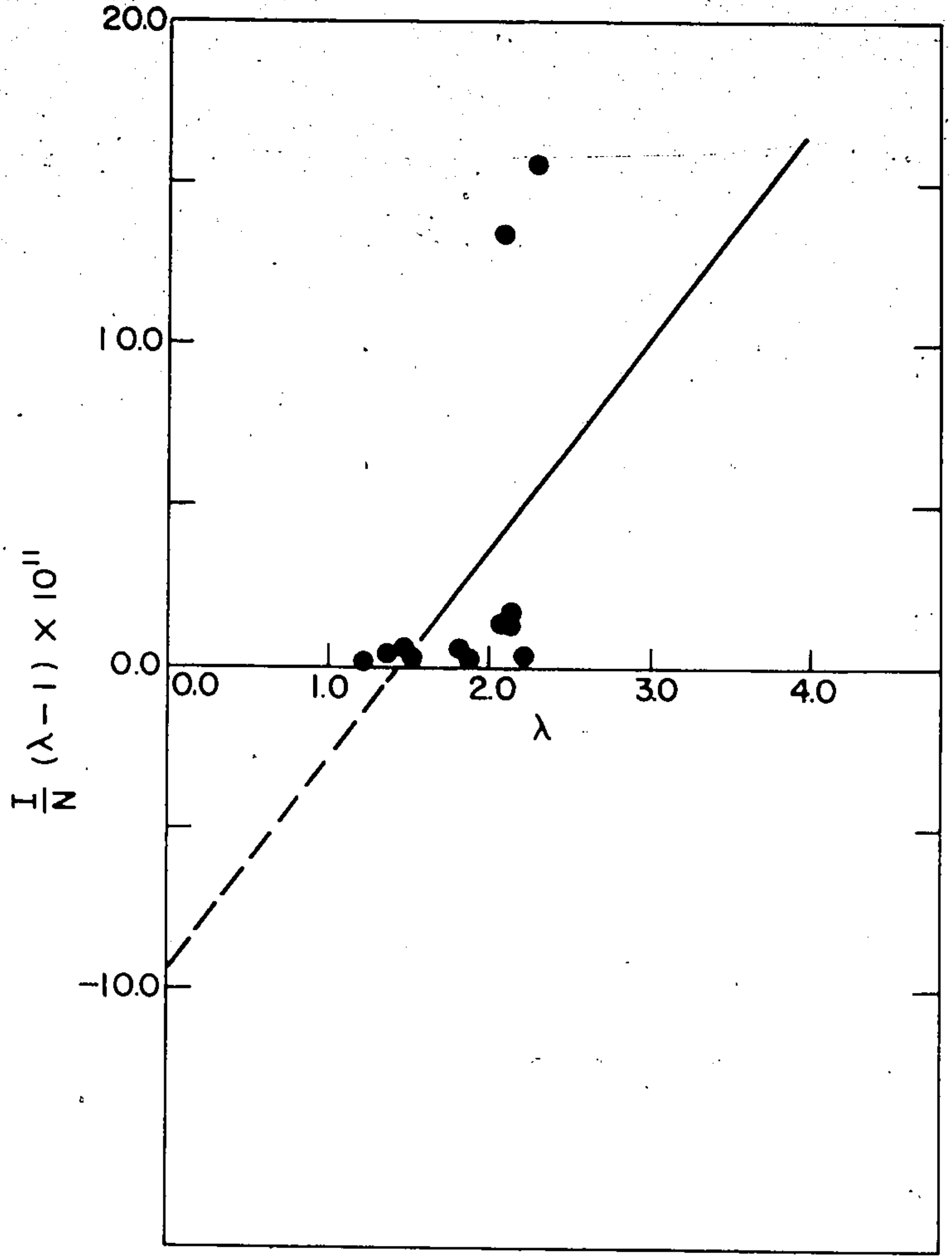
= 10 % RELATIVE ERROR
8.0
6.0
4.0
2.0
0.0
N × 10⁻⁷
0
40
80
120
160
200
TIME (MINUTES)

Figure (42). Rate of precipitation of nickel heptoximate (in the presence of copper) vs percentage precipitation of nickel.



2.2
2.0
1.8
1.6
1.4
RATE × 10⁴, (MOLES/L/HOUR)
0
10
20
30
40
% PRECIPITATION OF NICKEL

Figure (43). Variation of λ with rate of precipitation I and number of crystals N. (2.5 μg copper present)



20.0
10.0
0.0
-10.0
0.0
1.0
2.0
3.0
4.0
λ
$\frac{I}{N}(\lambda - 1) \times 10^{11}$

Figure (44). Variation of λ with rate of precipitation I and number of crystals N. (5.0 μg copper present)

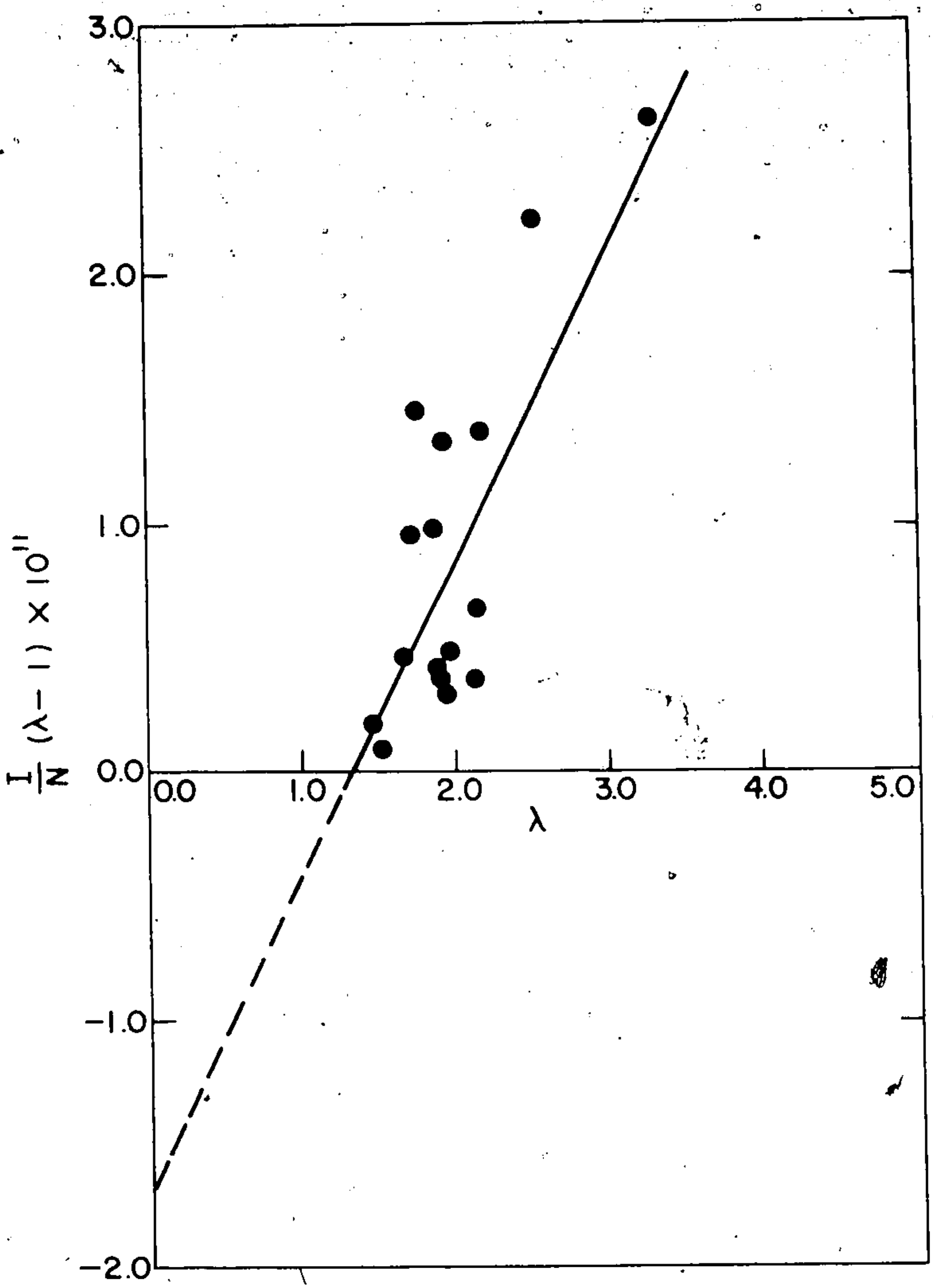

3.0
2.0
1.0
0.0
-1.0
-2.0
$\frac{I}{N}(\lambda - 1) \times 10^{11}$
0.0
1.0
2.0
3.0
4.0
5.0
λ

Figure (4.5). Variation of λ with rate of precipitation I and number of crystals N. (10.0 μg copper present)

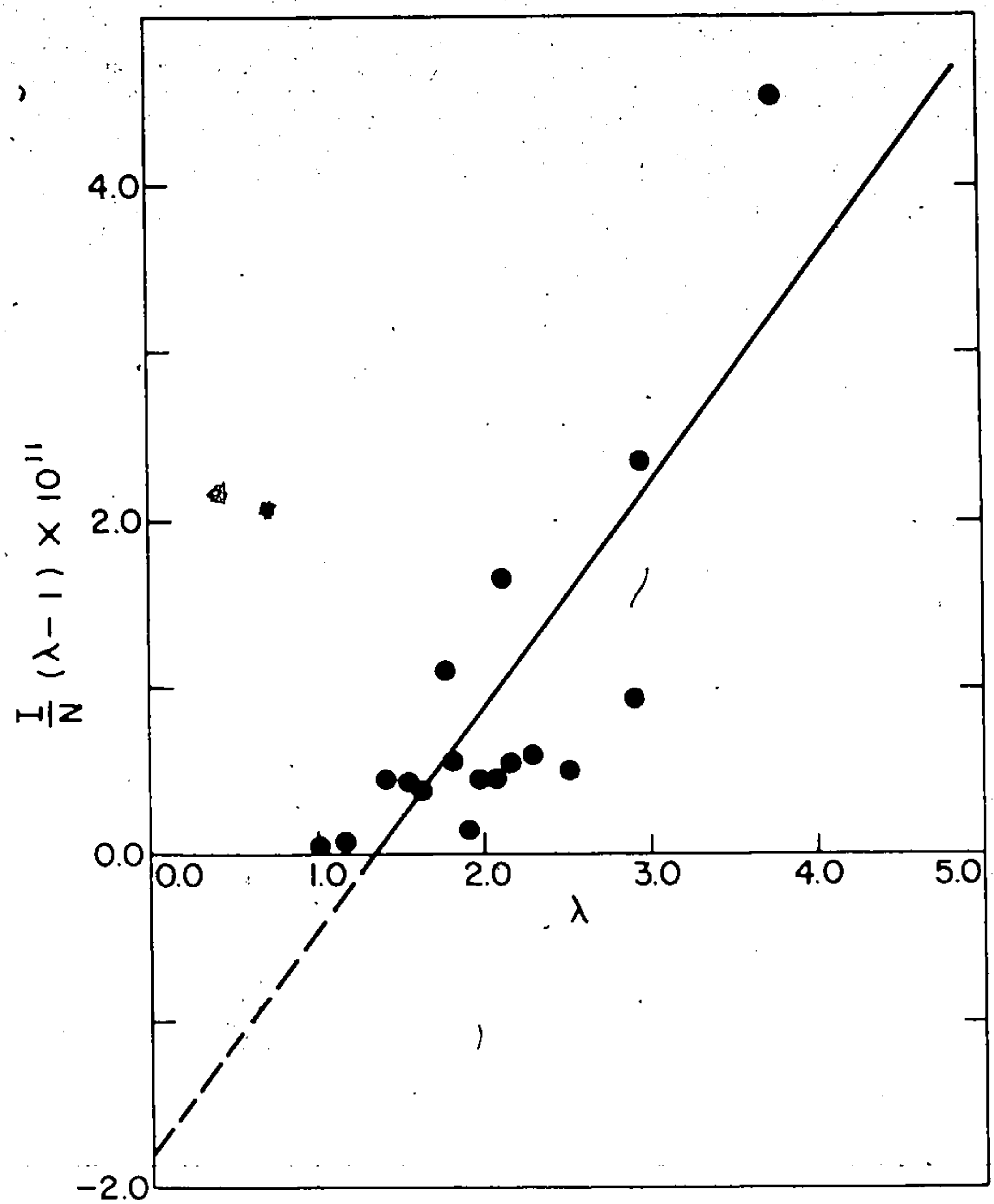

4.0
2.0
0.0
−2.0
$\frac{I}{N}(\lambda-1)\times 10^{11}$
0.0
1.0
2.0
3.0
4.0
5.0
λ

Figure (46). Variation of λ with rate of precipitation I and number of crystals N. (25.0 μg copper present)

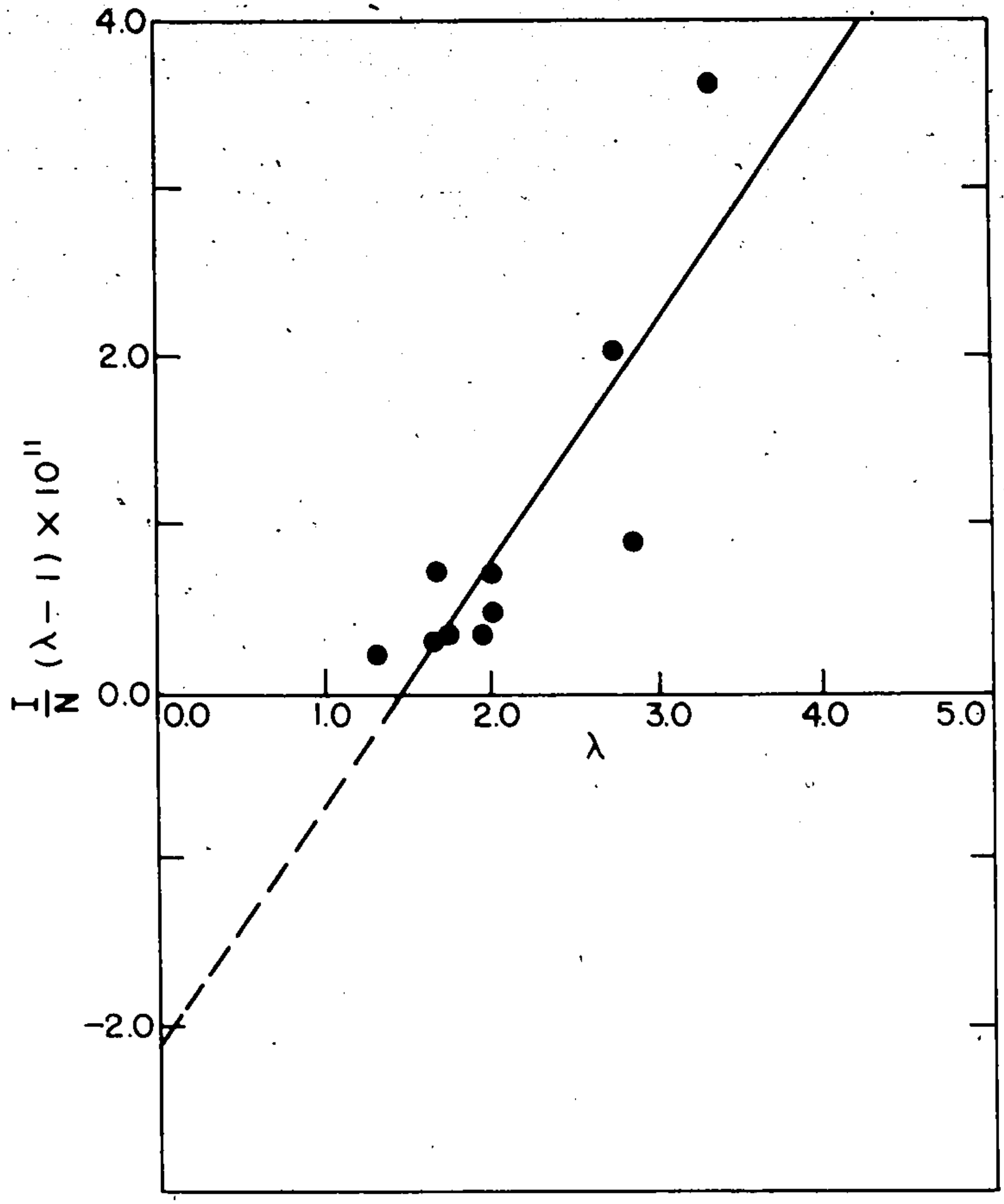

4.0
2.0
0.0
-2.0
$\frac{I}{N}(\lambda - 1) \times 10^{11}$
0.0
1.0
2.0
3.0
4.0
5.0
λ

Figure (4.7). Variation of λ with rate of precipitation I and number of crystals N. (50.0 μg copper present)

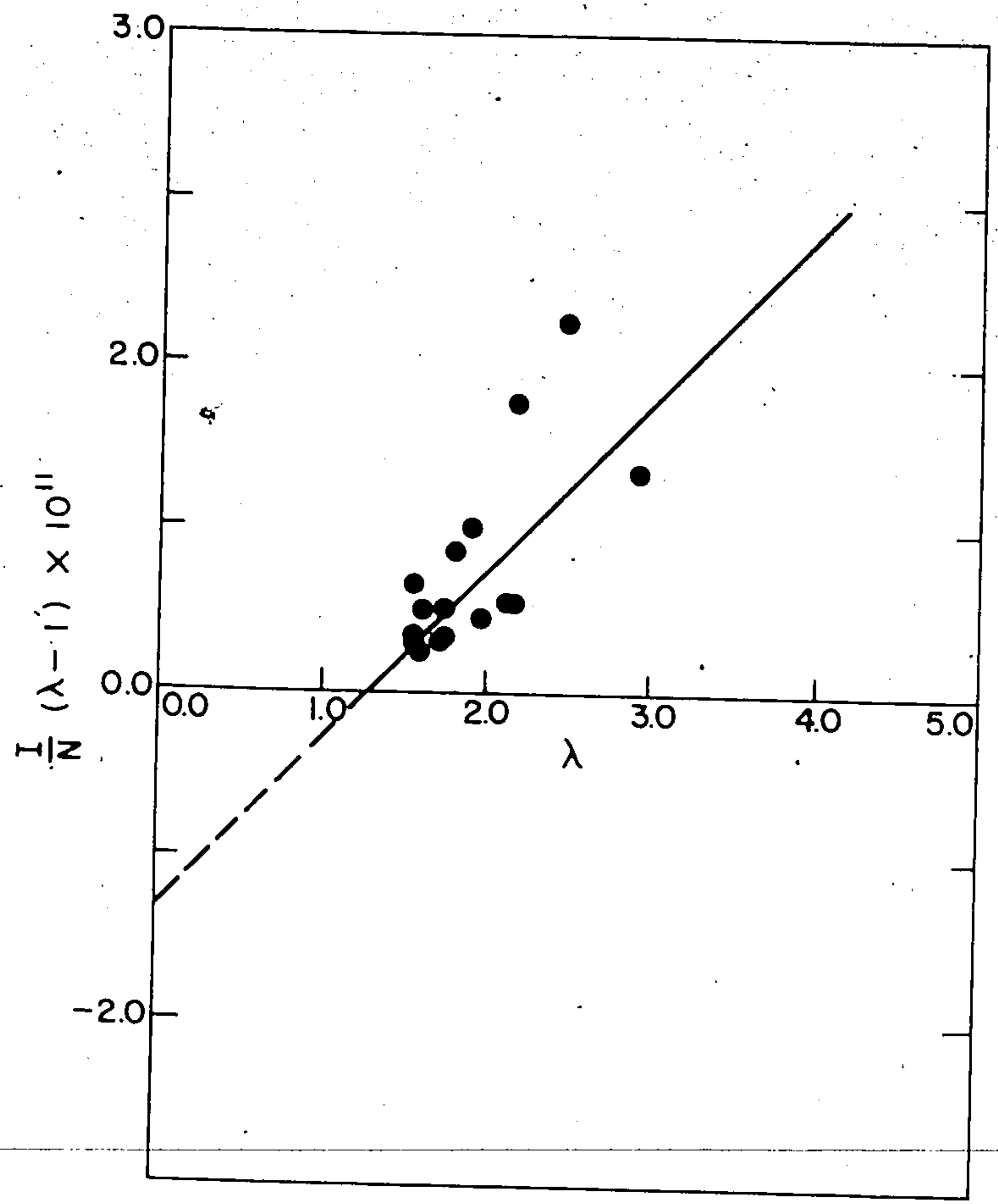

3.0
2.0
0.0
-2.0
0.0
1.0
2.0
3.0
4.0
5.0
λ
$\frac{I}{N}(\lambda-1) \times 10^{11}$

Table (19)

Observed values of rate constant ratio and D_o in coprecipitation of copper with nickel cycloheptanedionedioximate

Copper present (µg)	Average $D = D_o$	k_1/k_2 (observed)
2.5	1.96 ± 0.16	1.40 ±0.6
5.0	2.14 ± 0.07	1.30 ± 0.2
10.0	2.17 ± 0.08	1.37 ± 0.2
25.0	2.17 ± 0.13	1.46 ± 0.1
50.0	2.10 ± 0.08	1.21 ± 0.2
	Average 2.08±0.2	Average 1.35 ±0.3

V. SUMMARY AND CONCLUSIONS

During the course of this work, a new PFHS gravimetric technique for the determination of nickel was developed. Cycloheptanedionedioxime was synthesised, in situ, from cycloheptanedione and hydroxylamine in the presence of nickel ions. The proposed procedure provides a useful technique for the determination of nickel and it exhibits some advantages over the use of dimethylglyoxime. One limiting factor is that the preparation of cycloheptanedione is tedious and often results in an impure product. Use of the impure compound in the precipitation procedure leads to high final weights of the nickel heptoximate crystals. A revised procedure, however, for the synthesis of cycloheptanedione was proposed and the resulting compound was partially characterised.

The effects of some common ions on the precipitation of nickel heptoximate were also studied and modified procedures for application of the method in their presence were proposed. The procedure, when applied to the analysis of a steel sample gave quantitative results in the determination of nickel.

Previous reports regarding the dependence of distribution coefficients on the precipitation rate in some coprecipitation studies have led to the kinetic studies on the precipitation reaction. The observations from the kinetic experiments were interpreted in terms of Jenck's model. Assuming that the rate limiting step in the formation of cycloheptanedionedioxime involves the dehydration of the first addition product, a reaction sequence was proposed which is first order in both cycloheptanedione and hydroxylamine hydrochloride. Observations from kinetic measurements indicated that the proposed model rationalised the data. The energy of activation for the formation of cycloheptanedioxime was found to be 11.92 kcals mole^{-1}.

Values of rate constant and the integration constant were also calculated for the nickel heptoximate reaction in the presence of small amounts of cobalt and copper. Observed data suggested that the presence of cobalt slightly enhanced the rate of the nickel heptoximate formation reaction. In the presence of copper partial retardation of the reaction rate was observed.

The developed PFHS method provided a slow and controllable rate of precipitation. Advantage was taken of this in coprecipitation studies with nickel heptoximate. Cobalt and copper, common interferring ions with nickel precipitates were chosen as tracers in the coprecipitation studies. Observed data were initially processed using the two limiting laws as guidelines. For both systems studied, neither of these laws was successful in interpretation of the data. In the cobalt-nickel cycloheptanedionedioximate system, the observed distribution coefficients, λ and D, varied considerably with the fractional precipitation of carrier. High values of D and λ observed at the beginning of the reaction and each progressively decreased toward the end of the reaction. The copper-nickel cycloheptanedionedioximate system, however, showed approximately equal and constant values of D and λ with the extent of percentage of carrier precipitated at the initial stages of precipitation and then a gradual decrease to smaller values near the end of the reaction. Cobalt tracer exhibited the characteristics of a derichment system (values of λ and D less than unity) in the coprecipitation with nickel heptoximate. Distribution coefficients observed from coprecipitation of copper with nickel heptoximate showed values both larger and smaller than unity. The above observations are parallel to those of some coprecipitation studies with metal chelates reported in the literature. In contrast with the "purely inorganic" systems they cannot be rationalised using the classical laws.

The rate of carrier precipitation reaction, investigated during kinetic studies, was found to have significant effect on the distribution coefficients. In the cobalt-nickel heptoximate system D and λ decreased with a decrease of reaction rate within a precipitation reaction. The rate of reaction at the early stages of the precipitation was high and thus was responsible for the initially high values of D and λ observed. Similarly, low D and λ values were observed near the end of the reaction as a consequence of a very low reaction rate.

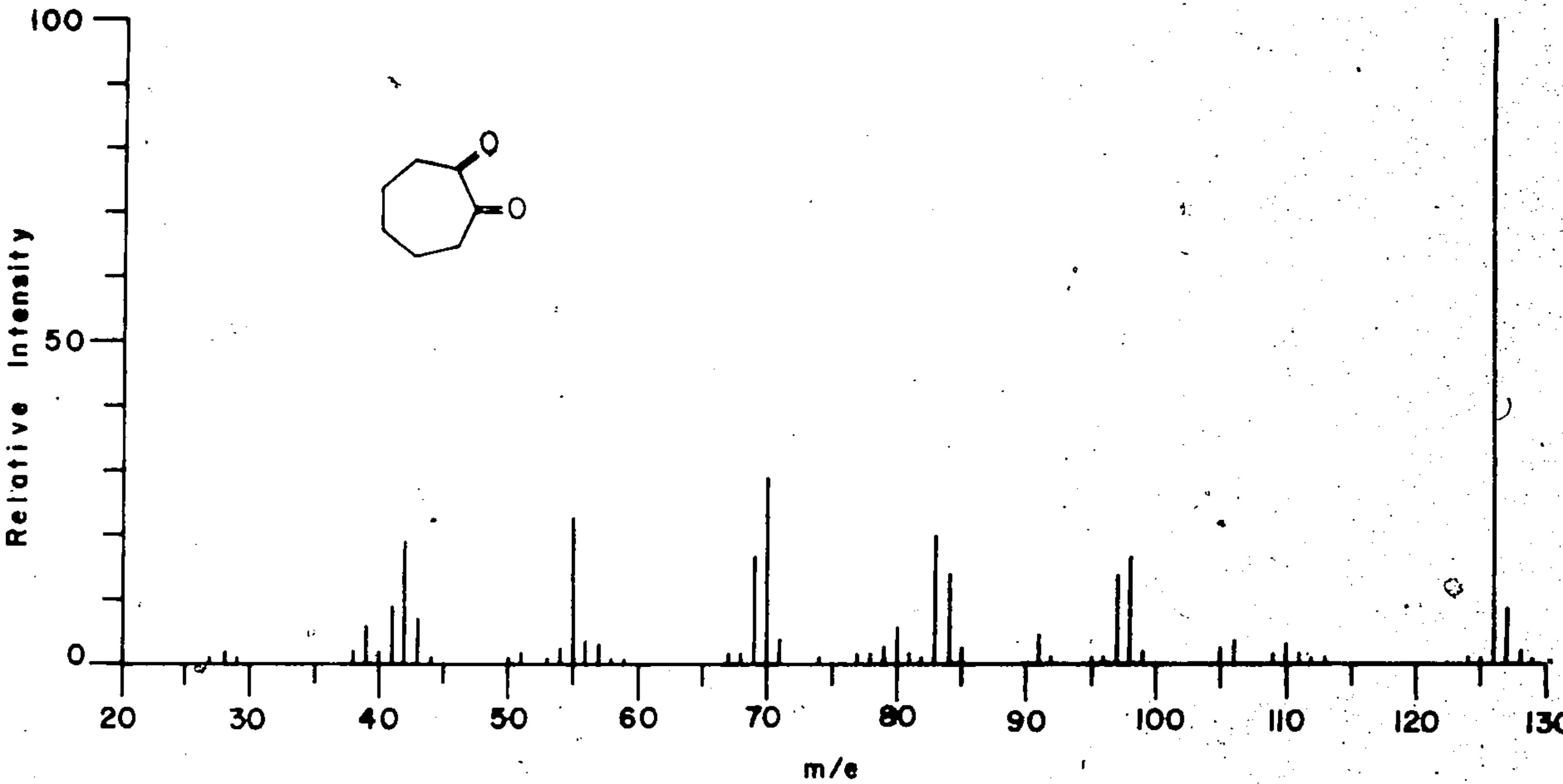
For the copper-nickel heptoximate system, the change of reaction rate with the extent of fractional precipitation of carrier was small during the precipitation performed under the conditions selected. This provides an explanation for the nearly constant values of D and λ observed during the initial stages of precipitation reaction. Significant reduction of D and λ near the end of the reaction, however, may be explained by an Ostwald ripening process. Resolution and recrystallization of precipitates release the tracer on long digestion periods.

Klein's model, which expresses the distribution coefficients as a function of the rate of precipitation per particle, was utilised to bring the rate of precipitation into the model used to rationalize the data. The model was useful only to a certain extent. Large experimental errors associated with the observations in the present systems made the interpretation difficult. The model agreed better with the data from the coprecipitation of copper with nickel cycloheptanedione-dioximate.

APPENDIX I

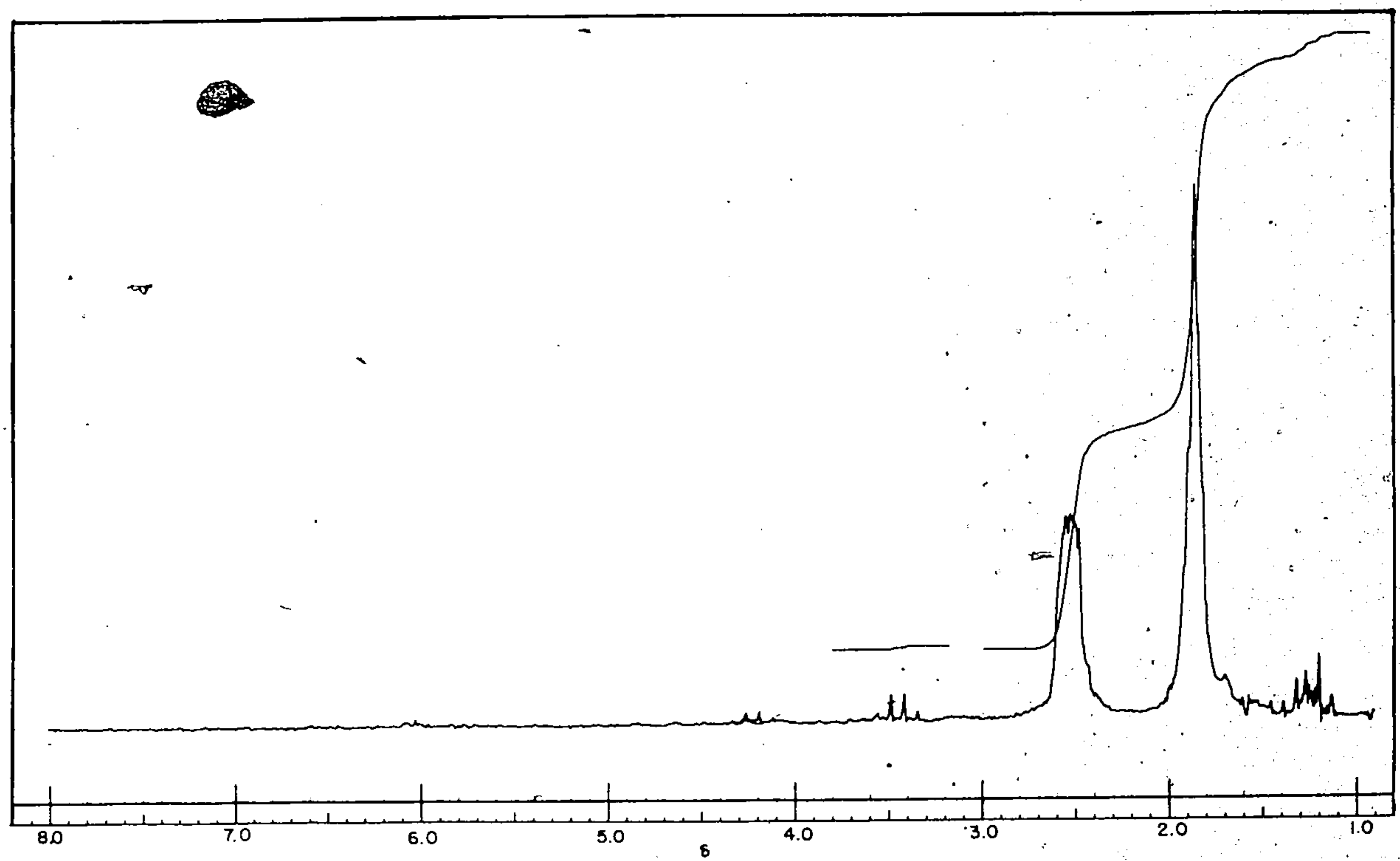
Characterizing spectra of 1,2-cycloheptanedione

Figure.(A1). Mass spectrum of 1,2-cycloheptanedione.



Mass spectrum of 1,2- cycloheptanedione

Figure.(A2). N.M.R. spectrum of 1,2-cycloheptanedione



N.M.R. spectrum of 1,2-cycloheptanedione

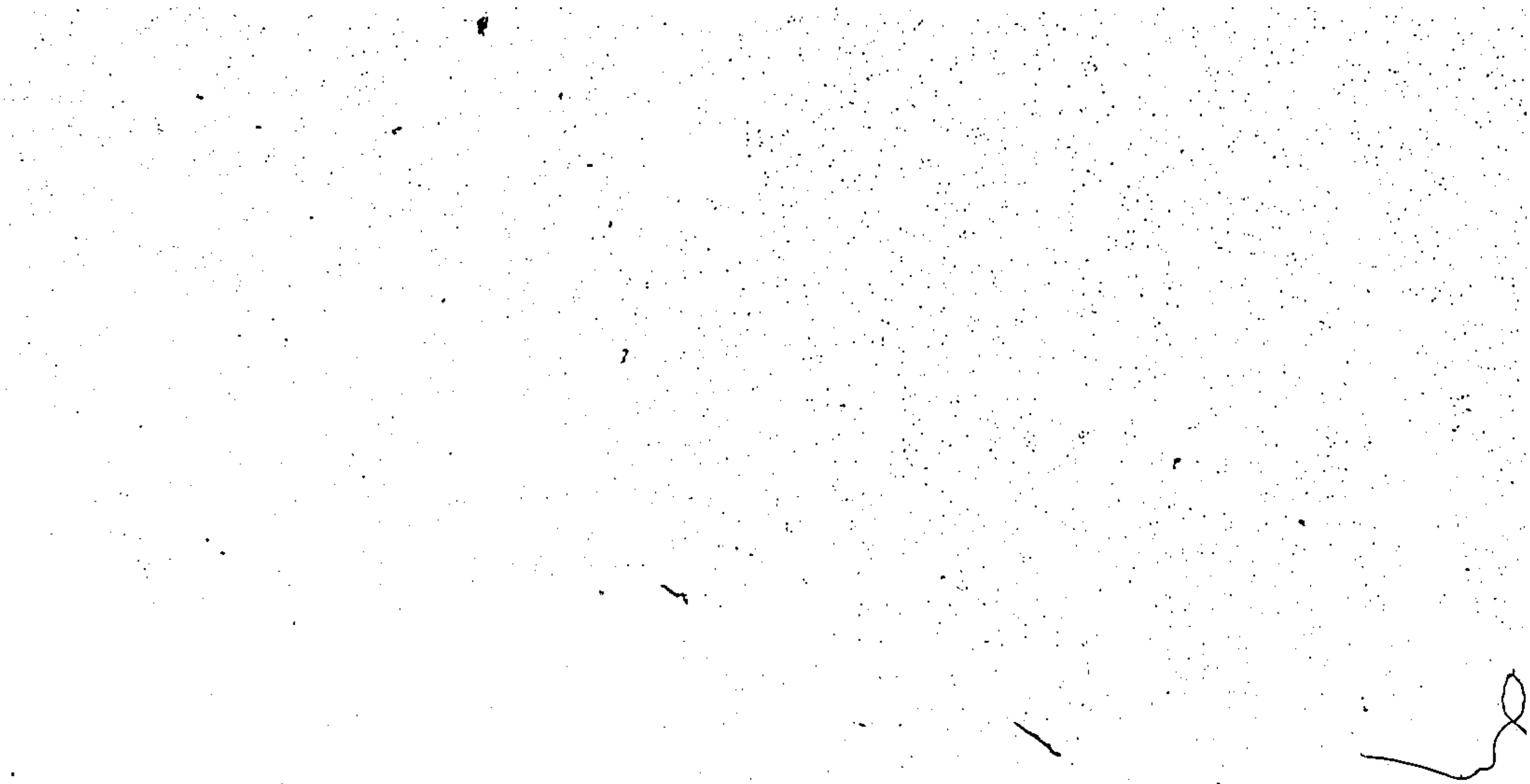
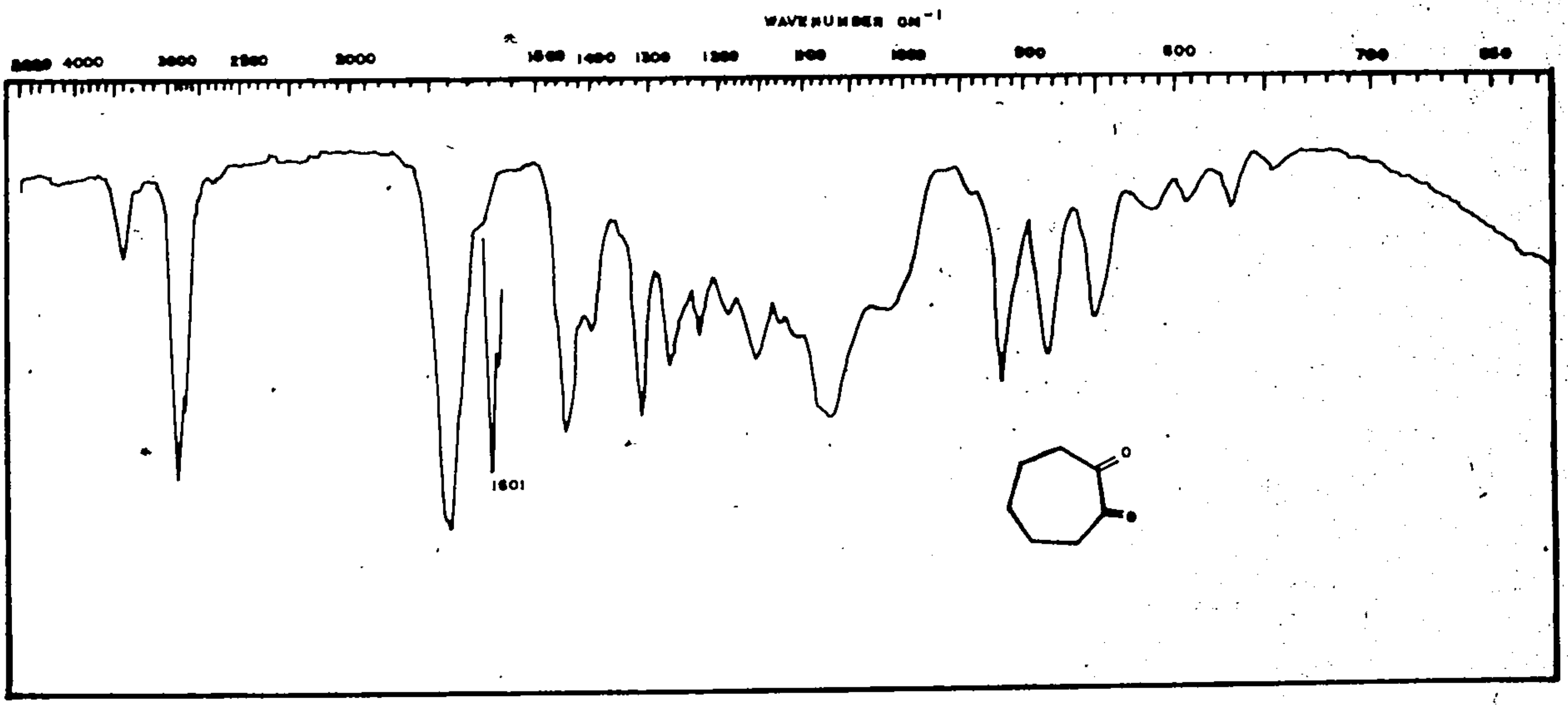


Figure.(A3). Infra red spectrum of 1,2-cycloheptanedione.



Infra red spectrum of 1,2 cycloheptanedione

S

APPENDIX II

A. Tables of data for the kinetic studies

B. Tables of data for the coprecipitation of cobalt with nickel cycloheptanedionedioximate

C. Tables of data for the coprecipitation of copper with nickel cycloheptanedionedioximate

D. Tables of data for the particle counting experiments

Table (A1)

Observed nickel recoveries during the precipitations of nickel cycloheptanedionedioximate at various pH values

pH	Ni found	Δ mg
2.35	4.099	-5.73
2.37	4.974	-4.86
2.67	5.944	-3.89
3.41	7.555	-2.28
3.42	8.438	-1.39
4.15	9.689	-0.14
5.30	9.832	±0.00
5.74	9.837	+0.01
5.97	9.856	+0.03
6.02	9.842	+0.01
7.05	9.822	+0.01
7.12	9.817	-0.01
7.17	9.826	-0.01
7.21	9.812	-0.01
7.63	9.508	-0.32
9.05	9.508	-0.32
10.1	9.543	-0.29

Initial conditions

Initial nickel = 9.831 mg
CHDO/Ni = 2X
HX/CHDO = 10X
Digestion time at 80-90°C = 2.5 hours

Table (A2)

Effect of temperature on the nickel heptoximate precipitation reaction

Reaction time (hour)	Percentage nickel recovered 75°C	23°C	15°C
0.25	93.8		
0.50	88.9	66.6	8.68
0.75			17.8
1.00	98.0	87.4	27.1
1.50	94.9		39.0
2.00	97.9	93.6	52.8
2.50	97.4		61.9
3.00	97.8	94.2	69.3
3.50	98.2		

Initial conditions

Nickel = 5.045 mg

CHDO/Ni = 2X

HX/CHDO

Table (A3)

Studies of reagents excess ratios for the nickel heptoximate reaction

Reaction	CHDO HX pH Temp.(°C)	2X 10X 6.25 23	2X 2X 6.75 23	2X 2X 7.25 23	2X 2X 7.25 15
0.25				0.524	
0.50		2.83	3.36	1.30	0.318
0.75					0.771
1.00		4.81	4.11	2.80	1.32
1.50					2.04
2.00		4.91	4.72		2.42
3.00		4.66	4.75	4.95	3.55
4.00		4.92		4.93	3.97
5.00		4.91		4.96	4.31
6.00		4.93	4.54		4.63

Initial nickel = 5.018 mg

Table (A 4)

Date for kinetic plots

System and temperature	$\ln\left[\frac{\{[HX]^{\circ}-4Ni\ ppt\}}{\{[CHDO]^{\circ}-2Ni\ ppt\}}\right]$	Reaction time (hour)	k'	c'*
Nickel alone 15°C	1.811	0.58	0.207 ±0.04	1.69±0.04
	1.823	0.66		
	1.847	0.75		
	1.877	0.83		
	1.892	1.0		
	1.925	1.1		
Nickel + cobalt 15°C	1.819	0.58	0.0486 ±0.008	1.684 ±0.002
	1.835	0.67		
	1.840	0.75		
	1.867	0.83		
	1.873	0.92		
	1.921	1.0		
Nickel + copper 5°C	1.762	1.6	0.169 ±0.03	1.720 ±0.003
	1.766	1.3		
	1.777	1.8		
	1.781	2.0		
	1.790	2.2		
	1.804	2.4		

*Theoretical $c' = 1.728$

Initial conditions

$[Ni] = 2.03 \times 10^{-3}$ mole l^{-1}

$[Cu] = 1.65 \times 10^{-5}$ mole l^{-1}

$[Co] = 6.93 \times 10^{-7}$ mole l^{-1}

$[CHDO]^{o} = 6.13 \times 10^{-3}$ mole l^{-1}

$[HX]^{o} = 3.45 \times 10^{-2}$ mole l^{-1}

pH = 7.25

Table (A5)

Rate of nickel heptoximate precipitation as a function of percentage of carrier precipitated

System and temperature	% precipitation of nickel	Rate x 10^4 (mole $l^{-1}hr^{-1}$)
Ni + Cu 5°C	0.484	2.17
	1.37	2.15
	2.24	2.14
	3.12	2.12
	4.82	2.09
	6.51	2.05
	8.17	2.02
	9.79	1.99
	11.4	1.96
	13.0	1.93
	14.6	1.90
	16.1	1.87
	17.6	1.84
	19.1	1.82
	20.6	1.79
	22.0	1.76
	26.3	1.69
	30.3	1.62
	37.9	1.48
Ni + Co 15°C	2.34	11.1
	6.79	10.7
	11.1	10.3
	15.2	9.85
	19.1	9.11
	22.9	9.11
	26.5	8.77
	30.0	8.45
	33.4	8.14
	39.8	7.57
	45.8	7,04
	51.3	6.57
	59.0	5.94
	65.9	5.38
	74.1	4.74
	81.4	4.20
	87.9	3.73
	96.2	3.15
	99.9	2.90

Table (B1)

Coprecipitation of cobalt with nickel cycloheptanedione-dioximate at 23°C

Run No.	Percentage precipitation of nickel	λ	D
1	30.9	0.22	0.19
	49.9	0.14	0.10
	69.1	0.083	0.046
	89.8	0.032	0.078
	91.7	0.024	0.053
	94.0	0.031	0.058
2	45.4	0.23	0.18
	54.4	0.14	0.087
	62.7	0.088	0.079
	70.4	0.077	0.054
	88.1	0.046	0.014
3	95.8	0.028	0.041
	98.6	0.022	0.014
	98.5	0.017	0.012
	99.2	0.020	0.0010
	99.4	0.016	0.00049
	99.6	0.019	0.00057

Initial conditions:

$[Ni] = 2.40\times10^{-3}$ mole ℓ^{-1}

$[Co] = 6.79\times10^{-3}$ mole ℓ^{-1}

$[CHDO]/[Ni] = 2x$

$[HX]/[CHDO] = 1.5x$

pH = 7.25

Table (82)

Primary observables in coprecipitation of cobalt with nickel cycloheptanedionedioximate.

(0.5 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in solution (mole l^{-1}) $\times 10^3$	[Co] in solution (mole l^{-1}) $\times 10^7$	[Co] in precipitate (mole l^{-1}) $\times 10^8$
1	0.667	1.48	2.98	4.17
	0.833	1.44	3.09	3.07
	1.00	1.22	3.10	2.93
	1.33	0.933	2.98	4.11
	1.50	0.820	2.99	4.08
	2.00	0.563	2.85	5.49
2	0.667	1.70	3.20	1.94
	1.00	1.34	3.11	2.85
	1.17	1.11	3.07	3.23
	1.33	1.10	3.11	2.85
	1.50	1.04	3.02	3.70
3	0.833	1.39	3.11	2.87
	1.00	1.22	3.11	2.82
	1.17	1.07	2.95	4.43
	1.33	0.913	3.05	3.46
	1.50	0.713	3.04	3.57
4	2.00	0.523	2.95	4.50
	0.667	1.59	3.11	2.84
	0.750	1.57	3.09	3.03
	0.833	1.47	3.13	2.63
	0.916	1.45	3.10	2.89
	1.08	1.28	3.12	2.78
5	0.667	1.58	3.12	2.77
	0.750	1.44	3.07	3.23
	0.866	1.38	3.10	2.92

Table (B3)

Coprecipitation of cobalt with nickel cycloheptanedionedioxímate
(0.5 μg tracer present)

Run No.	Reaction time (hour)	% Precipitation of Nickel	λ	D
	0.667	27.5	0.407±0.04	0.369±0.04
	0.833	29.3	0.274±0.03	0.240±0.03
	1.00	40.4	0.174±0.04	0.139±0.03
1	1.33	54.3	0.165±0.01	0.116±0.01
	1.50	59.8	0.1403±0.006	0.0916±0.005
	2.00	72.4	0.1368±0.003	0.0734±0.003
	0.667	16.6	0.322±0.07	0.302±0.06
	1.00	34.2	0.209±0.03	0.176±0.02
2	1.17	45.6	0.164±0.02	0.125±0.01
	1.33	46.3	0.141±0.02	0.106±0.01
	1.50	49.2	0.170±0.02	0.126±0.01
	0.833	32.0	0.228±0.03	0.194±0.02
	1.00	40.2	0.168±0.02	0.134±0.01
	1.17	47.6	0.216±0.01	0.165±0.01
3	1.33	55.3	0.133±0.01	0.092±0.01
	1.50	65.1	0.1056±0.008	0.063±0.01
	2.00	74.4	0.1030±0.007	0.0518±0.004
	0.667	22.3	0.344±0.06	0.316±0.02
	0.750	23.3	0.351±0.06	0.321±0.02
4	0.833	28.2	0.243±0.05	0.213±0.02
	0.916	29.2	0.257±0.05	0.225±0.01
	1.08	37.3	0.183±0.03	0.150±0.01
	0.667	22.7	0.330±0.07	0.302±0.03
5	0.750	29.4	0.280±0.05	0.252±0.01
	0.866	32.6	0.228±0.04	0.194±0.01

Initial conditions

[Ni] = 2.04×10^{-3} mole l^{-1}

[Co] = 3.40×10^{-7} mole l^{-1}

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 15°C

Table (B4)

Primary observables in coprecipitation of cobalt with nickel cycloheptanedionedioximate.

(1.0 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in solution (mole l^{-1}) $\times 10^3$	[Co] in solution (mole l^{-1}) $\times 10^7$	[Co] in precipitate (mole l^{-1}) $\times 10^8$
1	0.833	1.36	6.46	3.26
	1.00	1.27	6.44	3.48
	1.17	1.07	6.34	4.42
2	0.667	1.71	6.38	4.02
	0.750	1.57	6.04	7.45
	0.833	1.45	6.43	3.57
	1.17	0.833	6.65	2.28
3	0.667	1.52	6.30	4.87
	0.750	1.48	6.32	4.62
	1.00	1.28	6.45	3.29
	1.17	1.06	6.33	4.48
4	0.450	1.78	6.39	3.32
	1.00	1.44	6.54	2.22
	1.25	1.09	6.46	3.18
	1.50	0.578	6.30	5.19
	2.50	0.804	6.25	5.23
5	0.667	1.73	6.36	4.19
	1.00	1.50	6.42	3.61
	1.17	1.39	6.49	2.96
	1.33	1.32	6.69	0.948

Table (B5)

Coprecipitation of cobalt with nickel cycloheptanedionedioximate
(1 μg cobalt present)

Run No.	Reaction time (hour)	% Precipitation of Nickel	λ	D
1	0.833	33.3	0.122±0.03	0.1012±0.008
	1.00	37.7	0.111±0.03	0.0889±0.007
	1.17	47.8	0.103±0.02	0.0759±0.004
2	0.667	16.1	0.348±0.07	0.330±0.03
	0.750	16.3	0.343±0.07	0.330±0.03
	0.833	29.1	0.157±0.03	0.135±0.01
	1.17	59.2	0.038±0.01	0.0239±0.001
3	0.667	25.8	0.249±0.07	0.222±0.03
	0.750	27.5	0.219±0.06	0.193±0.02
	1.00	37.3	0.106±0.04	0.085±0.01
	1.17	48.0	0.104±0.03	0.0765±0.004
4	0.450	13.0	0.43±0.1	0.345±0.07
	1.00	29.7	0.103±0.02	0.080±0.01
	1.25	46.9	0.0766±0.007	0.0560±0.003
	1.50	71.1	0.0206±0.002	0.0024±0.001
	2.50	60.6	0.0849±0.007	0.0543±0.003
5	0.667	15.5	0.378±0.07	0.358±0.07
	1.00	26.5	0.177±0.01	0.097±0.04
	1.17	32.0	0.116±0.02	0.146±0.02
	1.33	35.4	0.0323±0.003	0.0258±0.002

Initial conditions

[Ni] = 2.04×10^{-3} mole l^{-1}

[Co] = 6.79×10^{-7} mole l^{-1}

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 15°C

Table (B6)

Primary observables in coprecipitation of cobalt with nickel cycloheptanedionedioximate.

(5.0 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in solution (mole l^{-1}) $\times 10^3$	[Co] in solution (mole l^{-1}) $\times 10^6$	[Co] in precipitate (mole l^{-1}) $\times 10^7$
1	0.667	1.61	3.24	1.47
	0.833	1.39	3.23	1.62
	1.17	1.13	3.15	2.46
	1.50	0.847	3.14	2.45
	2.00	0.475	3.12	2.76
2	0.583	1.81	3.27	1.01
	1.00	1.44	3.17	2.26
	1.17	1.37	3.22	1.68
	1.50	1.27	3.23	1.62
3	0.583	1.67	3.20	1.91
	0.750	1.49	3.21	1.84
	1.00	1.31	3.22	1.77
	1.17	1.08	3.18	2.11

Table (B7)

Coprecipitation of cobalt with nickel cycloheptanedionedioximate (5 μg tracer present)

Run No.	Reaction time (hour)	% Precipitation of Nickel	λ	D
	0.667	21.3	0.188±0.03	0.170±0.01
	0.833	32.2	0.127±0.02	0.106±0.02
1	1.17	34.5	0.128±0.01	0.096±0.01
	1.50	58.5	0.0853±0.008	0.055±0.01
	2.00	76.7	0.0582±0.001	0.0269±0.001
2	0.583	11.5	0.313±0.02	0.284±0.03
	1.00	29.4	0.135±0.02	0.111±0.04
	1.17	32.9	0.1274±0.009	0.106±0.04
	1.50	37.6	0.1038±0.005	0.0832±0.007
	0.583	18.3	0.286±0.05	0.265±0.04
3	0.750	27.3	0.175±0.02	0.153±0.03
	1.00	35.6	0.122±0.01	0.10±0.02
	1.17	47.2	0.1003±0.005	0.074±0.01

Initial conditions

[Ni] = 2.04×10^{-3} mole l^{-1}

[Co] = 3.40×10^{-6} mole l^{-1}

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

$[NH_4Ac]$ = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 15°C

Table (B8)

Primary observables in coprecipitation of cobalt with nickel cycloheptanedionedioximate.

(10.0 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in solution (mole l^{-1}) $\times 10^3$	[Co] in solution (mole l^{-1}) $\times 10^6$	[Co] in precipitate (mole l^{-1}) $\times 10^7$*
1	0.667	1.52	6.31	4.82
	1.33	0.941	6.31	4.75
	1.50	0.720	6.22	5.66
	2.00	0.509	6.14	6.44
2	0.833	1.47	6.41	3.71
	0.910	1.06	6.37	4.21
	1.17	1.02	6.39	3.99
	1.33	0.972	6.42	3.66
	1.50	0.758	6.34	4.44
3	0.667	1.54	6.18	5.97
	0.750	1.44	6.22	5.71
	0.833	1.22	6.37	4.13
	1.00	1.29	6.27	5.18
	1.17	1.08	6.44	3.50

Table (B9)

Coprecipitation of cobalt with nickel cycloheptanedionedioximate (10 μg tracer present)

Run No.	Reaction time (hour)	% Precipitation of nickel	λ	D
1	0.667	25.8	0.246±0.01	0.219±0.02
	1.33	53.9	0.0935±0.003	0.064±0.01
	1.50	64.7	0.0834±0.003	0.0495±0.004
	2.00	75.1	0.0717±0.002	0.0347±0.003
2	0.833	28.2	0.170±0.02	0.148±0.01
	0.91	47.9	0.0982±0.004	0.072±0.01
	1.17	50.3	0.0865±0.007	0.062±0.01
	1.33	52.4	0.0747±0.006	0.0518±0.004
	1.50	62.9	0.0682±0.005	0.0411±0.003
3	0.667	24.8	0.326±0.01	0.295±0.08
	0.750	29.6	0.25±0.1	0.236±0.02
	0.833	40.1	0.122±0.01	0.097±0.01
	1.00	36.8	0.173±0.03	0.142±0.02
	1.17	46.9	0.0834±0.005	0.0614±0.004

Initial conditions

$[Ni] = 2.04 \times 10^{-3}$ mole l^{-1}

$[Co] = 6.79 \times 10^{-6}$ mole l^{-1}

$[CHDO] = 6.13 \times 10^{-3}$ mole l^{-1}

$[HX] = 3.45 \times 10^{-2}$ mole l^{-1}

$[NH_4Ac] = 2.4 \times 10^{-2}$ mole l^{-1}

pH = 7.25

Temperature = 15°C

Table(B10)

Primary observables in coprecipitation of cobalt with nickel cycloheptanedionedioximate

(100.0 μg tracer present)

Run No.	Reaction time (hr)	[Ni] in solution x 10^3 (mole ℓ^{-1})	[Co] in solution x 10^5 (mole ℓ^{-1})	[Co] in precipitate x10^6 (mole ℓ^{-1})
1	0.58	1.79	6.46	3.31
	0.67	1.73	6.47	3.32
	0.75	16.0	6.44	3.42
	0.83	15.8	6.51	2.76
	0.91	15.7	6.34	4.49
	1.00	13.3	6.54	2.50
2	0.58	1.88	6.63	1.56
	0.67	1.85	6.60	1.83
	0.71	1.77	6.57	5.09
	0.78	1.65	6.22	5.63
	0.95	1.59	6.18	6.04
3	0.67	1.56	6.13	6.52
	0.75	1.50	5.89	8.94
	0.83	1.49	6.09	6.99
	0.91	1.45	6.30	4.87
	1.00	1.44	6.08	7.26

Initial conditions

[Ni] = 2.04×10^{-3} mole ℓ^{-1}

[Co] = 6.79×10^{-5} mole ℓ^{-1}

[CHDO] = 6.13×10^{-3} mole ℓ^{-1}

[HX] = 3.45×10^{-2} mole ℓ^{-1}

[NH_4AC] = 2.4×10^{-2} mole ℓ^{-1}

pH = 7.25

Temperture = 15° C

Table (B11)

Coprecipitation of cobalt with nickel cycloheptanedione-dioximate

(100 μg tracer present)

Run No.	Reaction time (hour)	% precipitation of nickel	λ	D
1	0.58	12.5	0.373 0.008	0.359±0.07
	0.67	15.2	0.290±0.07	0.284±0.08
	0.75	21.7	0.212±0.1	0.192±0.1
	0.83	22.7	0.159±0.05	0.143±0.04
	0.91	23.3	0.258±0.1	0.227±0.1
	1.00	34.9	0.087±0.04	0.071±0.05
2	0.58	8.01	0.296±0.07	0.287±0.06
	0.67	9.83	0.28 ±0.1	0.269±0.08
	0.71	13.5	0.22 ±0.1	0.21 ±0.1
	0.78	19.5	0.352±0.008	0.329±0.07
	0.95	22.2	0.372±0.009	0.345±0.08
3	0.67	23.7	0.374±0.005	0.344±0.004
	0.75	26.4	0.46 ±0.1	0.43 ±0.1
	0.83	27.1	0.34 ±0.1	0.31 ±0.1
	0.91	29.1	0.21 ±0.1	0.188±0.09
	1.00	29.6	0.312±0.2	0.27 ±0.1

Table (B 12)

Variation of homogeneous distribution coefficient D with rate of nickel heptoximate precipitation

Cobalt present	Rate x 10^4 (mole l^{-1} hr^{-1})	D	ln D	λ
0.5 μg	8.51	0.2403	-1.426	0.2738
	7.43	0.1391	-1.972	0.1742
	6.09	0.1160	-2.155	0.1649
	5.56	0.09162	-2.390	0.1403
	4.34	0.07338	-2.612	0.1368
	9.73	0.3021	-1.197	0.3218
	8.03	0.1755	-1.740	0.2087
	6.93	0.1253	-2.077	0.1641
	6.87	0.1063	-2.241	0.1411
	6.58	0.1257	-2.074	0.1698
	8.24	0.1953	-1.633	0.2281
	7.45	0.1343	-2.007	0.1683
	6.74	0.1650	-1.802	0.2162
	6.00	0.09162	-2.390	0.1334
	5.05	0.06303	-2.764	0.1056
	4.15	0.05180	-2.960	0.1030
	9.18	0.3162	-1.151	0.3444
	9.08	0.3208	-1.137	0.3506
	8.61	0.2129	-1.547	0.2425
	8.51	0.2249	-1.492	0.2570
	7.77	0.1500	-1.897	0.1831
	9.15	0.3022	-1.197	0.3302
	8.50	0.2521	-1.378	0.2802
	8.89	0.2388	-1.432	0.2067
	8.19	0.1942	-1.639	0.2276
1.0 μg	8.12	0.1012	-2.291	0.1218
	7.69	0.08890	-2.420	0.1109
	6.71	0.07590	-2.578	0.1034
	6.66	0.07670	-2.568	0.1330
	9.79	0.3304	-1.108	0.3483
	8.52	0.1347	-2.005	0.1566
	5.62	0.02390	-3.734	0.03810
	8.84	0.2215	-1.507	0.2487
	8.68	0.1926	-1.647	0.2192
	7.73	0.08549	-2.459	0.1063
	6.70	0.07647	-2.571	0.1043
	10.1	0.3451	-1.064	0.4257
	6.82	0.05600	-2.882	0.07660
	2.53	0.03240	-3.442	0.05812

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Cobalt present	Rate x 10^4 (mole l^{-1} hr^{-1})	D	ln D	λ
	9.84	0.3579	-1.028	0.3777
	9.50	0.4038	-0.9068	0.4293
	8.77	0.09660	-2.337	0.1769
	8.24	0.1456	-1.927	0.1155
	6.61	0.08240	-2.496	0.1132
5.0 μg	9.28	0.1701	-1.772	0.1879
	8.23	0.1063	-2.242	0.1267
	7.69	0.1062	-2.243	0.1293
	5.68	0.05522	-2.896	0.08530
	3.92	0.02686	-3.617	0.05820
	10.2	0.2844	-1.257	0.3129
	8.50	0.1114	-2.195	0.1345
	8.16	0.1064	-2.241	0.1264
	7.70	0.08317	-2.287	0.1038
	9.57	0.2651	-1.328	0.2855
	8.70	0.1531	-1.877	0.1754
	7.90	0.09990	-2.304	0.1221
	6.78	0.07400	-2.604	0.1003
10.0 μg	8.84	0.2190	-1.519	0.2460
	6.12	0.06417	-2.746	0.09359
	5.08	0.04948	-3.006	0.08343
	4.08	0.03474	-3.360	0.07188
	8.61	0.1478	-1.912	0.1703
	6.71	0.07185	-2.633	0.09816
	6.48	0.06160	-2.787	0.08654
	6.28	0.05180	-2.960	0.07471
	5.26	0.04112	-3.191	0.06820
	8.94	0.2952	-1.220	0.3261
	8.48	0.2357	-1.445	0.2498
	7.46	0.09660	-2.337	0.1223
	7.79	0.1417	-1.954	0.1728
	6.80	0.06135	-2.791	0.08340

Table (B13)

Variation of logarithmic distribution coefficient λ with rate of precipitation I and number of crystals N

Cobalt present	λ	$\frac{I}{N}(\lambda-1) \times 10^{11}$	$k_2 \times 10^{11}$	$k_1 \times 10^{11}$
0.5 μg	0.407	16.6	82.9±4	12.3±0.3
	0.322	21.2		
	0.351	18.1		
	0.280	14.9		
	0.344	19.4		
	0.331	14.4		
	0.274	4.40		
	0.174	1.67		
	0.189	0.926		
	0.165	0.664		
	0.140	0.513		
	0.137	0.290		
	0.209	1.73		
	0.164	1.02		
	0.141	0.770		
	0.170	0.587		
	0.228	4.53		
	0.168	1.68		
	0.216	0.926		
	0.133	0.678		
	0.106	0.485		
	0.103	0.289		
	0.242	4.64		
	0.257	2.93		
	0.183	1.55		
	0.228	3.46		
1.0 μg	0.348	20.5	56.6±3	2.75±0.04
	0.343	15.6		
	0.249	11.4		
	0.426	14.1		
	0.378	19.7		
	0.219	16.5		
	0.122	5.07		
	0.111	1.86		
	0.103	1.06		
	0.157	5.11		
	0.0381	0.947		
	0.106	1.88		
	0.104	1.06		

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Cobalt present	λ	$\frac{I}{N}(\lambda - 1) \times 10^{11}$	$k_2 \times 10^{11}$	$k_1 \times 10^{11}$
	0.103	2.06		
	0.0766	1.04		
	0.0206	0.266		
	0.0849	0.237		
	0.177	1.96		
	0.116	1.28		
	0.0323	1.00		
5.0 μg	0.313	70.6	32.6±17	33.9±1
	0.127	1.25		
	0.104	0.740		
	0.286	68.7		
	0.175	17.5		
	0.122	1.88		
	0.100	1.07		
	0.188	24.2		
	0.135	2.00		
	0.128	1.08		
	0.0853	0.558		
	0.0582	0.287		
10.0 μg	0.246	21.4	88.3±5	6.67±0.4
	0.0935	0.725		
	0.0834	0.500		
	0.0717	0.294		
	0.170	5.09		
	0.0982	1.06		
	0.0865	1.04		
	0.0747	0.758		
	0.0682	0.527		
	0.326	19.4		
	0.250	15.5		
	0.122	4.66		
	0.117	1.87		
	0.0864	1.09		

Table (B14)

Values of rate of nickel heptoximate precipitation and corresponding values of natural logarithm of observed homogeneous distribution coefficients

Rate x 10^4 (moles $litre^{-1}$ $hour^{-1}$)	ln D
8.51	-1.43
7.43	-1.97
6.09	-2.15
5.56	-2.39
4.34	-2.61
9.73	-1.20
8.03	-1.74
6.93	-2.08
6.87	-2.24
6.58	-2.07
8.24	-1.63
7.45	-2.01
6.74	-1.80
5.99	-2.39
5.05	-2.76
4.15	-2.96
9.18	-1.15
9.08	-1.14
8.61	-1.55
8.51	-1.49
7.77	-1.90
9.15	-1.20
8.50	-1.38
8.89	-1.43
8.19	-1.64

Initial conditions

[Ni] = 2.03×10^{-3} mole l^{-1}

[Co] = 3.46×10^{-7} mole l^{-1}

Temp. = 15°C

pH = 7.25

Table (C1)

Primary observables in coprecipitation of copper with nickel cycloheptanedionedioximate
(2.5 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in precipitate mole ℓ^{-1} $\times 10^4$	[Cu] in Solution mole ℓ^{-1} $\times 10^6$	[Cu] in precipitate mole ℓ^{-1} $\times 10^6$
1	1.33	1.58	1.31	0.334
	1.50	2.02	1.26	0.262
	1.67	2/79	1.14	0.463
	1.87	2.85	1.28	0.456
	2.17	4.72	1.15	0.433
	3.0	4.73	0.967	0.587
2	1.33	1.52	1.34	0.256
	1.50	1.70	1.38	0.199
	1.67	2.24	1.23	0.270
	1.83	2.14	1.29	0.253
	2.00	2.31	1.31	0.263
	2.83	3.07	1.08	0.438

Initial Conditions

Total [Ni] = 2.04×10^{-3} mole ℓ^{-1} (relative value)

Total [Cu] = 1.57×10^{-6} mole ℓ^{-1} (relative value)

[CHDO] = 6.13×10^{-3} mole ℓ^{-1}

[Hx] = 3.45×10^{-2} mole ℓ^{-1}

$[NH_4AC]$ = 2.4×10^{-2} mole ℓ^{-1}

pH = 7.25

temperature = 5°C

Table (C2)

Coprecipitation of copper with nickel cycloheptanedionedioximate
(2.5 μg tracer present)

Run No.	Reaction time	% Precipitation of nickel	λ	D
	1.33	7.42	2.07±0.9	2.4±1
	1.50	8.30	1.45±0.4	1.59±0.9
	1.67	10.9	2.08±0.4	1.8±1
2	1.83	10.4	1.79±0.5	1.68±0.7
	2.00	11.2	1.52±0.4	1.58±0.6
	2.83	15.1	2.3±1	2.3±1
	1.33	7.72	2.25±0.7	3.05±0.6
	1.50	9.87	2.12±0.5	1.90±0.8
1	1.67	13.7	2.1±1	2.6±1
	1.87	14.0	1.36±0.7	1.35±0.9
	2.17	23.1	1.21±0.3	1.28±0.2
	3.0	23.2	1.85±0.3	2.03±0.3

Initial conditions

[Ni] = 2.04×10^{-3} mole l^{-1}

[Cu] = 1.57×10^{-6} mole l^{-1}

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 15°C

Table (C3)

Primary observables in coprecipitation of cooper with nickel cycloheptanedionedioximate (5 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in precipitate mole ℓ^{-1} $\times 10^4$	[Cu] in solution mole ℓ^{-1} $\times 10^6$	[Cu] in precipitate mole ℓ^{-1} $\times 10^6$
1	1.50	1.897	2.68	0.644
	1.67	2.710	2.42	0.666
	1.83	2.547	2.52	0.642
	2.00	2.587	2.41	0.690
	2.17	3.278	2.26	0.700
	3.50	4.856	2.09	1.01
2	1.37	1.401	2.78	0.574
	1.50	1.852	2.62	0.606
	1.67	2.098	2.21	0.904
	2.00	2.763	2.53	0.457
	2.17	3.516	2.57	0.958
	2.75	4.489	1.75	1.263
3	1.50	1.798	2.50	0.630
	1.67	2.409	2.39	0.667
	1.92	2.218	2.47	0.691
	2.33	3.877	2.10	0.863
	2.67	3.708	2.07	1.26

Total [Ni] = 2.04×10^{-3} mole ℓ^{-1} (relative value)

Total [Cu] = 3.15×10^{-6} mole ℓ^{-1} (relative value)

[CHDO[= 6.13×10^{-3} mole ℓ^{-1} pH = 7.25

[Hx] = 3.45×10^{-2} mole ℓ^{-1} temperature = 5°C

[NH_4AC[= 2.4×10^{-2} mole ℓ^{-1}

Table (C4)

Coprecipitation of copper with nickel cycloheptanedionedioximate

(5.0 μg tracer present)

Run No.	Reaction time(hr.)	% Precipitation of nickel	λ	D
1	1.50	9.28	1.63 ± 0.4	2.34 ± 0.6
	1.67	13.2	1.84 ± 0.3	1.80 ± 0.07
	1.83	12.4	1.66 ± 0.3	1.79 ± 0.4
	2.00	12.6	1.97 ± 0.4	1.75 ± 0.5
	2.17	16.0	1.90 ± 0.3	1.62 ± 0.7
	3.50	23.7	1.52 ± 0.2	1.56 ± 0.2
3	1.50	8.79	2.49 ± 0.7	2.61 ± 0.2
	1.67	11.7	2.19 ± 0.5	2.09 ± 0.2
	1.92	10.8	2.11 ± 1	2.3 ± 1
	2.33	18.9	1.93 ± 0.4	1.76 ± 0.6
	2.67	18.1	2.10 ± 0.3	2.74 ± 0.4
2	1.37	6.85	1.8 ± 1	2.81 ± 0.4
	1.50	9.10	1.9 ± 1	2.32 ± 0.4
	1.67	10.2	3.28 ± 0.7	3.58 ± 0.4
	2.00	13.5	1.51 ± 0.6	1.16 ± 0.5
	2.17	17.2	1.08 ± 0.1	1.56 ± 0.3
	2.75	21.9	2.37 ± 0.2	2.57 ± 0.3

Table (C5)

Primary observables in coprecipitation of copper with nickel cycloheptanedionedioximate (10 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in precipitate mole l^{-1} x 10^4	[Cu] in solution mole l^{-1} x 10^6	[Cu] in precipitate mole l^{-1} x 10^6
	1.67	2.85	5.39	0.900
	1.92	2.75	5.01	1.29
1	2.00	4.06	3.87	2.42
	2.17	3.78	4.21	2.08
	2.33	5.31	4.34	1.95
	1.50	2.38	5.08	1.21
	1.67	2.82	5.11	1.18
2	1.83	2.73	4.14	1.45
	2.00	2.91	4.01	2.29
	2.17	3.69	4.18	2.11
	3.25	5.46	3.50	2.80
	1.50	2.70	4.66	1.64
	1.67	1.95	4.68	1.62
3	1.83	2.49	5.13	1.16
	2.00	3.32	4.16	2.14
	2.33	3.92	3.62	2.68

Initial conditions

Total [Ni] = 2.04×10^{-3} mole l^{-1} (relative value)

Total [Cu] = 6.30×10^{-6} mole l^{-1} (relative value)

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole^{-1}

pH = 7.25

Temperature = 5°C

Table (C6)

Coprecipitation of copper with nickel cycloheptanedionedioxímate
(10 μg tracer present)

Run number	Reaction time	Percentage precipitation of nickel	λ	D
1	1.67	13.9	1.03 ±0.3	1.03 ±0.1
	1.92	13.4	1.61 ±0.3	1.66 ±0.1
	2.00	19.8	2.19 ±0.4	2.53 ±0.5
	2.17	18.5	1.99 ±0.2	2.18 ±0.2
	2.33	25.9	1.19 ±0.1	1.28 ±0.1
2	1.50	11.6	1.74 ±0.9	1.80 ±0.8
	1.67	13.7	1.40 ±0.7	1.44 ±0.2
	1.63	13.3	1.84 ±0.7	1.94 ±0.3
	2.00	14.2	2.94 ±0.4	3.45 ±0.4
	2.17	18.0	2.05 ±0.3	2.29 ±0.2
	3.25	26.7	1.88 ±0.02	2.18 ±0.03
3	1.50	13.2	2.12 ±0.5	2.29 ±0.4
	1.67	9.55	2.97 ±0.5	3.29 ±0.3
	1.83	12.1	1.58 ±0.4	1.64 ±0.1
	2.00	16.3	2.29 ±0.3	2.58 ±0.1
	2.33	19.2	2.59 ±0.3	3.12 ±0.2

Table (C7)

Primary observables in coprecipitation of copper with nickel cycloheptanedionedioximate (25 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in precipitate mole l^{-1} x 10^4	[Cu] in solution mole l^{-1} x 10^6	[Cu] in precipitate mole l^{-1} x 10^6
1	1.66	2.01	11.8	3.63
	1.83	2.42	12.2	3.63
	2.00	2.82	10.3	5.00
	2.17	3.01	11.9	3.77
	2.33	3.17	11.3	4.43
2	1.58	1.57	13.8	1.96
	1.83	2.22	13.5	2.25
	2.00	2.40	12.2	3.75
	2.17	2.75	12.4	4.07

Initial conditions

Total [Ni] = 2.04×10^{-3} mole l^{-1} (relative value)

Total [Cu] = 1.57×10^{-5} mole l^{-1} (relative value)

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 5°C

Table (C8)

Coprecipitation of copper with nickel cycloheptanedionedioximate.

(25 μg tracer present)

Run No.	Reaction time (hr)	% Precipitation of nickel	λ	D
1	1.66	9.81	2.77 ±0.3	2.82 ±0.5
	1.83	11.8	2.03 ±0.4	2.22 ±0.2
	2.00	13.9	2.85 ±0.5	3.03 ±0.2
	2.17	14.7	1.74 ±0.4	1.83 ±0.3
	2.33	15.5	1.97 ±0.4	2.13 ±0.3
2	1.58	7.70	1.66 ±0.8	1.70 ±0.8
	1.83	10.9	1.32 ±0.6	1.38 ±0.5
	2.00	11.8	2.02 ±0.2	2.27 ±0.1
	2.17	13.5	1.63 ±0.1	2.11 ±0.06

Table (C9)

Primary observables in coprecipitation of copper with nickel cycloheptanedionedioximate (50 μg tracer present)

Run No.	Reaction time (hour)	[Ni] in precipitate mole l^{-1} $\times 10^4$	[Cu] in solution mole l^{-1} $\times 10^6$	[Cu] in precipitate mole l^{-1} $\times 10^6$
1	1.50	1.21	27.56	3.66
	1.67	1.41	27.81	4.16
	1.83	2.24	26.44	4.27
	2.00	2.35	24.27	6.37
	2.17	2.67	24.55	7.83
	2.33	2.95	24.38	8.04
2	1.50	0.983	28.52	3.49
	1.67	1.51	27.91	3.70
	1.83	1.92	26.52	4.20
	2.00	2.25	25.83	6.79
	2.17	2.12	24.78	7.19
	2.33	2.68	21.49	11.15
3	1.50	1.40	26.59	4.758
	1.58	1.67	26.96	4.587
	1.75	1.95	26.70	4.600
	1.83	1.97	23.08	8.19
	2.00	2.51	24.37	7.48
	2.16	4.21	21.79	8.56

Initial conditions

Total [Ni] = 2.04×10^{-3} mole l^{-1} (relative value)

Total [Cu] = 3.15×10^{-5} mole l^{-1} (relative value)

[CHDO] = 6.13×10^{-3} mole l^{-1}

[HX] = 3.45×10^{-2} mole l^{-1}

[NH_4Ac] = 2.4×10^{-2} mole l^{-1}

pH = 7.25

Temperature = 15°C

Table (C10)

Coprecipitation of copper with nickel cycloheptanedionedioximate
(50 μg tracer present)

Run No.	Reaction time	% Precipitation of nickel	λ	D
	1.50	5.987	2.2 ±1	2.1 ±1
	1.67	6.910	1.88±0.6	2.02±0.5
1	1.83	10.39	1.56±0.3	1.31±0.2
	2.00	11.53	2.12±0.3	2.01±0.2
	2.12	13.10	1.77±0.2	2.11±0.1
	2.33	14.45	1.64±0.2	1.951±0.03
	1.50	4.820	1.99±0.2	2.41±0.1
	1.67	7.420	1.56±0.1	1.66±0.05
2	1.83	9.413	1.73±0.1	1.52±0.04
	2.00	11.01	1.70±0.2	2.12±0.1
	2.17	10.40	2.18±0.2	2.50±0.1
	2.33	13.17	2.70±0.3	3.44±0.3
	1.50	6.827	2.4±1	2.4±1
	1.58	8.203	1.81±0.9	1.52±0.8
3	1.75	9.577	1.63±0.7	1.63±0.6
	1.83	10.11	2.91±0.5	3.3±1
	2.00	12.30	1.95±0.5	2.18±0.4
	2.16	20.61	1.59±0.2	1.51±0.2

Table (C11)

Variation of logarithmic distribution coefficient λ with rate of precipitation I and number of crystals N

Copper present	λ	$\frac{I}{N}(\lambda-1) \times 10^{11}$	$k_2 \times 10^{11}$	$k_1 \times 10^{11}$
2.5 μg	2.07	13.4	6.83±3	9.59±0.9
	1.44	0.666		
	2.08	1.22		
	1.79	0.539		
	1.52	0.227		
	2.27	0.310		
	2.25	15.7		
	2.12	1.70		
	2.10	1.29		
	1.37	0.241		
	1.21	0.0970		
	1.85	0.219		
5.0 μg	1.63	0.950	1.34±0.02	1.74±0.07
	1.84	0.962		
	1.66	0.457		
	1.97	0.471		
	1.90	0.401		
	1.52	0.0834		
	1.74	1.50		
	1.91	1.38		
	3.28	2.68		
	1.89	0.428		
	1.40	0.178		
	2.49	2.25		
	2.19	1.38		
	2.11	0.683		
	1.93	0.314		
	2.10	0.339		
10.0 μg	1.02	0.0279	1.30±0.1	1.79±0.09
	1.61	0.366		
	2.19	0.534		
	1.99	0.431		
	1.19	0.0587		
	1.77	1.13		
	1.40	0.458		
	1.84	0.573		
	2.94	0.925		

....

Copper present	λ	$\frac{I}{N}(\lambda-1) \times 10^{11}$	$k_2 \times 10^{11}$	$k_1 \times 10^{11}$
	2.05	0.458		
	1.89	0.174		
	3.75	4.58		
	2.12	1.69		
	2.97	2.35		
	1.58	0.402		
	2.29	0.604		
	2.51	0.508		
25.0 μg	1.66	0.711	1.44±0.02	2.10±0.1
	1.32	0.224		
	2.02	0.496		
	1.67	0.307		
	3.38	3.63		
	2.77	2.09		
	2.04	0.724		
	2.85	0.886		
	1.74	0.333		
	1.97	0.340		
50.0 μg	2.15	1.78	1.08±0.1	1.31±0.05
	1.88	1.07		
	1.56	0.396		
	2.47	2.26		
	1.56	0.396		
	2.12	0.549		
	1.77	0.354		
	1.63	0.225		
	1.56	0.680		
	1.73	0.523		
	1.70	0.343		
	2.18	0.554		
	1.81	0.871		
	1.63	0.499		
	2.91	1.36		
	1.95	0.460		
	1.59	0.253		

Table (C12)

Observed fractional amounts of copper incorporated into nickel cycloheptanedionedioximate

Reaction time	% Ni precipitated	% Cu precipitated
1.33	9.042	20.51
1.50	12.20	30.13
2.00	15.78	25.52
2.25	20.50	26.81
2.58	21.03	37.03
4.00	33.74	28.22
5.50	44.50	40.05
6.50	45.28	46.69
7.50	53.98	52.06
1.58	7.703	12.44
1.83	10.86	14.07
2.00	11.75	22.29
2.17	13.46	21.46
1.70	9.81	24.85
1.83	11.85	22.68
2.00	13.90	34.75
2.17	14.71	24.12
2.33	15.52	28.27

Initial conditions

[nickel] = 0.00203 mole l^{-1} pH = 7.25

[CHDO] = 0.00613 mole l^{-1} Temperature = 5°C

[HX] = 0.0345 mole l^{-1}

copper = 25.0 μg

Table (D1)

Number of particles observed during the precipitation of nickel cycloheptanedionedioximate in the presence of trace amount of cobalt

Reaction time (minutes)	No. of particles x 10^7 (average)	Relative error (percentage)
35	0.10 ± 0.05	54.3
40	0.31 ± 0.04	128
45	0.41 ± 0.09	20.9
50	1.4 ± 0.4	26.0
55	2.2 ± 0.3	15.7
60	3.7 ± 0.5	13.9
65	4.1 ± 0.9	22.0
70	5.7 ± 1.3	22.8
75	6.1 ± 1.4	23.1
80	7.7 ± 3.3	43.1
85	8.0 ± 1.7	21.2

Initial conditions

[Ni] = 2.03×10^{-3} mole l^{-1}

[Co] = 6.93×10^{-7} mole l^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2X

Temperature = 15°C

pH = 7.25

Table (D2)

Number of particles observed during the precipitation of nickel cycloheptanedionedioximate in the presence of trace amount of copper

Reaction time (minutes)	No. of particles x 10^7 (average)	Relative error (percentage)
80	0.16 ± 0.06	38.3
100	1.7 ± 0.3	17.9
120	4.0 ± 0.6	14.5
140	5.4 ± 0.2	3.35
160	6.0 ± 0.006	0.940
180	7.3 ± 0.3	0.409

Initial conditions

[Ni] = 2.03×10^{-3} mole l^{-1}

[Cu] = 1.66×10^{-5} mole l^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2X

Temperature = 5°C

pH = 7.25

APPENDIX III

A. Tables for mass balances

B. Computer programs

Table (A1)

Mass balance of nickel observed in the precipitation of nickel cycloheptanedionedioximate[a]

Reaction time (hour)	Nickel in filtrate sample (mg)	Nickel in precipitate sample (mg)	Mass balance[b] (mg)
0.67	2.65±0.10	0.440±0.024	3.09±0.13
0.83	2.40±0.071	0.529±0.060	2.93±0.13
1.0	2.48±0.054	0.565±0.018	3.05±0.072
1.2	2.28±0.13	0.783±0.056	3.06±0.19
1.3	2.17±0.13	0.896±0.0052	3.07±0.14
2.0	1.74±0.15	1.340±0.042	3.07±0.19
2.5	1.43±0.08	1.547±0.058	3.00±0.14
		Average	3.04±0.052

Initial conditions

[Nickel] = 0.00254 mole l^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2X

pH = 7.25

Temperature = 15°C

[a] The analysis of nickel was carried out by atomic absorption method.

[b] Initial nickel = 3.00 mg (relative amount)

Table (A2)

Mass balance of copper observed during the precipitation with nickel cycloheptanedionedioximate[a]

Reaction time (hour)	Copper in filtrate sample (µg)	Copper in precipitate sample (µg)	Mass balance[b] (µg)
1.5	45.3±0.48	4.94±0.33	50.2±0.81
1.7	44.3±0.56	4.53±0.28	48.8±0.84
1.8	42.1±0.42	6.67±0.20	48.8±0.62
2.0	41.0±0.49	10.8±0.20	51.8±0.69
2.2	39.4±1.3	11.4±0.40	50.8±1.7
2.3	34.1±0.81	11.7±0.42	51.8±1.2
		Average	50.4±0.46

Initial conditions

[Ni] = 2.03×10^{-3} mole l^{-1}

[Cu] = 1.66×10^{-5} mole l^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2.0X

pH = 7.25

Temperature = 5°C

(a) Analysis of copper was carried out by atomic absorption technique

(b) Initial copper = 50.0 µg (relative amount)

Table (A3)

Mass balance of nickel observed in the precipitation of nickel cycloheptanedionedioximate in the presence of cobalt[a]

Reaction time (hour)	Nickel in filtrate sample (mg)	Nickel in precipitate sample (mg)	Mass balance[b] (mg)
0.83	2.53±0.091	0.427±0.012	2.96±0.10
1.0	2.19±0.083	0.661±0.014	2.85±0.097
1.6	2.16±0.071	0.841±0.020	3.00±0.090
2.0	1.71±0.068	1.30±0.024	3.01±0.092
3.5	0.951±0.029	2.12±0.035	3.07±0.064
		Average	2.98±0.051

Initial conditions

[Nickel] = 2.54×10^{-3} mole l^{-1}

[Co] = 6.93×10^{-7} mole^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2X

pH = 7.25

Temperature = 15°C

[a] The analysis of nickel was carried out by atomic absorption method

[b] Initial nickel = 3.00 mg (relative amount)

Table (A 4)

Mass balance of cobalt observed during the precipitation with nickel cycloheptanedionedioximate[a]

Reaction time (hour)	Cobalt in filtrate sample (μg)	Cobalt in precipitate sample (μg)	Mass balance[b] (μg)
0.67	0.974±0.007	0.0233±0.001	0.997±0.008
0.83	0.923±0.007	0.0212±0.001	0.944±0.008
1.0	0.970±0.007	0.0315±0.001	1.002±0.008
1.2	0.947±0.007	0.0404±0.001	0.987±0.008
1.3	0.955±0.007	0.0473±0.001	1.002±0.008
2.0	0.908±0.007	0.0940±0.002	1.002±0.009
3.7	0.832±0.006	0.164±0.002	0.996±0.008
		Average	0.990±0.003

Initial conditions

[Nickel] = 0.00254 mole l^{-1}

CHDO/Ni = 1.5X

HX/CHDO = 2X

pH = 7.25

Temperature = 15°C

[a] The analysis of cobalt was carried out by gamma ray counting technique

[b] Initial cobalt = 1.00 μg (relative amount)

B 1 (Program I)

```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C-----LEAST SQUARES PROGRAM.
      DIMENSION X(200), Y(200)
 100  READ 1,N,NN
      IF(N.EQ.0)GOTO 101
 1    FORMAT(2I3)
      PRINT 30,NN
 30   FORMAT(1H1,2HNN,I3,/,10X,1HX,10X,1HY)
      DO 2 J =1,N
      READ 3, X(J), Y(J)
    3 FORMAT(2F10.0)
    2 PRINT 20,J,X(J),Y(J)
   20 FORMAT (1XI5,2F10.6)
      A = N
      SIGX = 0.0
      SGDXY = 0.0
      SGDX2 = 0.0
      SIGY = 0.0
      SIGY2 = 0.0
      SIGXY = 0.0
      DO 4 I = 1,N
    4 SIGX = SIGX + X(I)
      XBAR = SIGX/A
      DO 5 L = 1,N
      DELX = X(L) - XBAR
      SGDXY = SGDXY + Y(L)*DELX
      SGDX2 = SGDX2 + DELX**2
      SIGY2 = SIGY2 + Y(L)**2
      SIGY = SIGY + Y(L)
      SIGXY = SIGXY + X(L)*Y(L)
    5 CONTINUE
      SLOPE = SGDXY/SGDX2
      SYDX2 = (SIGY2 - ((SIGY**2)/A) - SLOPE*SIGXY + (SLOPE*SIGX*SIGY/A)
     1)/(A - 2.0)
      SB = SQRT(SYDX2/SGDX2)
      YBAR = SIGY/A
      CEPT = YBAR - SLOPE*XBAR
      SA = SQRT(SYDX2/A)
      PRINT 6, SLOPE, SB
    6 FORMAT(1H0,4X,8HSLOPE  =,E14.6,5X,20HSTANDARD DEVIATION =,E13.6)
      PRINT 7, CEPT, SA
    7 FORMAT(1H0,12HINTERCEPT  =,E14.6,5X,20HSTANDARD DEVIATION =,E13.6)
      PRINT 8
    8 FORMAT(1H0,15X,10H**********)
   13 READ  (5,10)Q
   10 FORMAT (1F9.4)
      IF(Q.EQ.0.0)  GO TO 14
      P=(Q-CEPT)/SLOPE
      WRITE(6,15)P,Q
   15 FORMAT (2F20.6)
      GO  TO  13
   14 CONTINUE
      DO 9 I=1,N
      CALL PLOTPT (X(I),Y(I),4)
      Y(I)=CEPT+SLOPE*X(I)
      CALL PLOTPT (X(I),Y(I),2)
    9 CONTINUE

      CALL OUTPLT
      GO TO 100
  101 CONTINUE
      STOP
      END
```

B2 (Program II)

```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     ISOL = NO OF SOLUTION
C     IOBS = NO OF OBSERVATION
C     AMEAN = MEAN VALUE
C     VIN = VARIANCE
C     STD = STANDARD DEVIATION
      DIMENSION A(90,10),TOTAL(90),AMEAN(90),DIF(90,10),DIFS(10),
     1SDIFS(90),STD(90),VIN(90)
   10 READ(5,20)ISOL,IOBS
   20 FORMAT(2I5)
      IF(ISOL.EQ.0)GO TO 50
      DO 60 I=1,ISOL
   60 READ(5,70) (A(I,J),J=1,IOBS)
      WRITE(6,10)
   10 FORMAT(1H1,2X,*STANDARD DEVIATION PROGRAM*//)
      DO 90 I=1,ISOL
   90 WRITE(6,71) (A(I,J),J=1,IOBS)
   70 FORMAT(8F10.0)
   71 FORMAT(1X,8F15.5)
      PRINT 27
   27 FORMAT(1H0,1X,*SOLUTIONS*10X,*MEAN*,8X,*VARIANCE*,7X,*STANDARD
     +DEVIATION*,///)
      DO 35 I=1,ISOL
      TOTAL(I)=0.
      DO 30 J=1,IOBS
      TOTAL(I)=A(I,J)+TOTAL(I)
   30 CONTINUE
      AMEAN(I)=TOTAL(I)/IOBS
   35 CONTINUE
      DO 45 I=1,ISOL
      SDIFS(I)=0.
      DO 40 J=1,IOBS
      DIF(I,J)=AMEAN(I)-A(I,J)
      DIFS(J)=DIF(I,J)*DIF(I,J)
   40 SDIFS(I)=SDIFS(I)+DIFS(J)
      VIN(I)=SDIFS(I)/(IOBS-1)
      STD(I)=SQRT(VIN(I))
      PRINT 42,I,AMEAN(I),VIN(I),STD(I)
   42 FORMAT(1X,I5,5X,3E15.6)
   45 CONTINUE
      GO TO 10
   50 STOP
      END
```

B 3 (Program III)

```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     NPR = NO OF PROBLEM
C     NPRS = NO OF SETS IN A PROBLEM
C     TT = TRACER TOTAL
C     TS = TRACER IN SOLUTION
C     CT = CARRIER TOTAL
C     CS = CARRIER IN SOLUTION
C     VTS = VARIANCE IN TRACER IN SOLUTION
C     VCS = VARIANCE IN CARRIER IN SOLUTION
C     VLMD = VARIANCE IN CUMBDA
      READ(5,1) NPR
    1 FORMAT(I10)
      DO 10 I=1,NPR
      READ(5,1) NPRS
      WRITE(6,30)
      DO 50 J=1,NPRS
      READ(5,20) TT,TS,CT,CS,VTS,VCS
   20 FORMAT(8F10.0)
      VLMD=VTS/(TT*ALOG(CT/CS))**2+(ALOG(TT/TS)/(CS*(ALOG(CT/CS))**2
     $))**2*VCS
      WRITE(6,40) J,TT,TS,CT,CS,VTS,VCS,VLMD
   50 CONTINUE
   10 CONTINUE
   40 FORMAT(1X,I10,7E15.7/)
   30 FORMAT(1H1,10X,*I*,6X,*TT*,13X,*TS*,13X,*CT*,13X,*CS*,12X,*VTS*,
     $12X,*VCS*,11X,*VLMD*//)
      STOP
      END
```

B 4 (Program IV)

```
      PROGRAM IST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C     NPR=NO OF PROBLEMS
C     A=TRACER IN PRECIPITATE
C     B=CARRIER IN PRECIPITATE
C     E=TRACWR IN SOLUTION
C     F=CARRIER IN SOLUTION
C     VA=VARIANCE IN TRACER IN PRECIPITATE
C     VB=VARIANCE OF CARRIER IN PRECIPITATE
C     VE=VARIANCE OF TRACER IN SOLUTION
C     VF=VARIANCE OF CARRIER IN SOLUTION
C     DD=VARIANCE OF D
      READ (5,1) NPR
    1 FORMAT (I10)
      DO 10 I=1,NPR
      READ (5,1) NPRS
      WRITE(6,30)
      DO 50 J=1,NPRS
      READ (5,20) A,B,E,F,VA,VB,VE,VF
   20 FORMAT (8F10.0)
      DD=(F/(B*E))**2*VA+(A/(B*E))**2*VF
     2+(A*F/(B*E**2))**2*VE
     3+(A*F/(E*B**2))**2*VB
      WRITE(6,40) J,A,B,E,F,VA,VB,VE,VF,DD
   50 CONTINUE
   10 CONTINUE
   40 FORMAT (1X,I10,9E13.5/)
   30 FORMAT (1H1,10X,*I*,5X,*A*,12X,*B*,12X,
     3*E*,12X,*F*,11X,*VA*,11X,*VB*,11X,*VE*,
     311X,*VF*,11X*DD*//)
      STOP
      END
```

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