

Studies in Solvent Extraction of Inorganic
Complexes

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INTRODUCTION

The phenomenon of solvent extraction has been known for a considerable time, for as early as 1892 Rothe showed that ferric chloride could be extracted into ether from an aqueous solution. Nevertheless the utilisation of solvent extraction as a tool in inorganic chemistry has been exceedingly slow in developing and, indeed, it is only in recent years that it has been generally accepted as a technique in pure and applied chemistry.

One of the reasons for this must undoubtedly be the lack of theoretical understanding of the subject which has made it impossible to predict what to expect from a particular system.

However, during recent years such knowledge has been steadily increasing, and, as a result, the use of solvent extraction has been quickly spreading.

In this theses use is made of solvent extraction in both applied and pure analytical chemistry, and some new aspects of solvent extraction are investigated from

the theoretical point of view.

The work carried out in deriving a method for the determination of silver in trade effluent at a concentration of 1 part in 10^8 is divided up into three distinct sections, 1) the concentration of the silver, 2) the separation of the silver from elements that might interfere in the final analysis, and 3) the determination.

Although several methods were investigated it was finally found that concentration by solvent extraction, which at the same time provided a preliminary separation, separation by a suitable choice of sequestering reagents, which back extracted solely the silver, and finally a colorimetric finish, which involved extraction of a chelated silver complex into an organic solution, provided the most convenient and efficient method of analysis.

The determination of the stability constants of a metal ML_n by the normal titration technique, is not possible if it is insoluble in an aqueous phase. If the complex is soluble in an organic phase, however, it is often possible to determine a mixed stability constant K_f' where

$$K_f' = \frac{[ML_n]_o}{[M^{n+}]_w [L^-]_w^n}$$

(the subscripts o and w referring to the organic and aqueous phases respectively) which involves a partition coefficient.

This is not altogether satisfactory since comparison of the changes in stability constant observed going from one compound to another in a series of closely related complexing agents, involve concomitant changes in the partition coefficients p_x and p_c of the reagent HL and of the complex ML_n respectively.

A method is derived from theoretical principals which enables the true formation constant K_f of ML_n

$$K_f = \frac{[ML_n]}{[M^{n+}]_w [L^-]_w^n}$$

to be obtained if the metal M is labelled with a radioactive isotope.

An added complication is the possible presence of lower complexes ML , ML_2 ... in the aqueous phase. A full theoretical study of the equilibrium between a solution containing metal complexes ML_j ($j = 0$ to N) in the aqueous phase, in equilibrium with an immiscible

organic phase, into which only the formally neutral species ML_n is extracted, shows that, a) the relative concentrations of the intermediate species is lower than for a single phase system, and b) the overall degree of formation is higher. It has also been shown that Job's method of continuous variations applies equally to a two phase system, and enables the composition of the extracted species to be determined with greater reliability than in the case of a one phase system. If the radioactive isotope of L is available so that the total concentration of the metal in the aqueous phase ($\sum_{j=0}^n [ML_j]$) and in the organic phase ($[ML_n]_o$) is known, then the stability constants β_n of all of the intermediate complexes may be calculated, where $\beta_n = \frac{[ML_n]}{[M^{n+}]_w [L^-]_w^n}$.

By use of radioactive silver, the solubility of some substituted dithizones in water and several organic solvents is obtained in order to calculate the partition coefficients.

Also the two-phase method of continuous variations is applied to the indium-dithizone system, and the

extinction coefficient and the overall formation constant of indium dithizonate calculated.

THE DETERMINATION OF TRACE-QUANTITIES OF SILVER IN TRADE EFFLUENTS.

Introduction

Silver adversely effects the anerobic bacterial reactions in sewage treatment and there are indications that this inhibition of natural processes may have instigated outbreaks of poliomyelitis. It is also toxic to fish and other aquatic life. A need has therefore arisen for the determination of small amounts of silver in water which may have become contaminated with trade effluent, since local authorities may require a limit on the amount discharged. Any proposed method must be capable of determining trace amounts of silver down to 0.1 p.p.m.

Many methods have been proposed for the determination of small amounts of silver, but few of these are reliable in the presence of organic material or at the concentration levels now imposed. Interference from common metals such as copper, lead and iron has not always been overcome.

For example in Jelly's method¹, said to be sensitive to 50 µg. in a 50 ml. sample, silver is reduced in an

ammoniacal solution in the presence of gelatine, and the colloidal metal determined colorimetrically; copper, cobalt, nickel, cadmium and iron interfere. Members of the Analytical Methods Committee who have investigated this method found it insufficiently sensitive and adversely affected by organic matter and foreign metals².

Procedures for determining silver down to 0.5 and even 0.1 p.p.m. have been claimed involving absorptiometry of its complexes with dithizone or p-diethylaminobenzylidene rhodanine³. As will be shown later these procedures fail where organic material and substantial amounts of other metals are present. In any case some measure of concentration by a factor of 10 to 100-fold would be required before the method could be applied to water containing only 10 µg. per litre.

Heller, Kuhla, and Machek have described the construction and operation of a still designed to concentrate trace metals in several litres of natural waters prior to their determination polarographically or otherwise⁴. Caldwell and McLeod recovered 3.06 mg.

from a total of 3.29 mg. of silver in a 40 litre sample (concentration about 0.1 p.p.m.) by 'occlusion' on the gelatinous precipitate obtained by adding ammonia, mercuric chloride, hydrochloric acid, and magnesium metal: the element was determined gravimetrically in the form of metal after cupellation⁵. There are obvious reasons for avoiding methods of this kind which demand, inter alia, large volumes of sample, and in the absence of special apparatus and dust free rooms, sample volumes of greater than 1 litre would appear to be excessive.

Preliminary Investigations.

A considerable amount of work had been undertaken at the request of the Analytical Methods Committee of The Society for Analytical Chemistry, and some early methods thought to show promise were reinvestigated.

For example :-

1. Preliminary separation of silver, with or without previous destruction of the organic matter, was attempted by chromatography on Zeocarb resin, silica gel, aluminium oxide and on paper, followed by subsequent elution with various combinations of organic solvents and aqueous acids, or ammonia⁶.

2. Aldridge's method for the separation of silver as the cyanide followed by indirect determination of the silver⁷. The cyanide is converted to cyanogen bromide by the addition of bromine water and, after the removal of excess bromine with sodium arsenite, the amount of cyanogen bromide present is estimated by the intensity of the orange-red colour obtained upon adding a dilute solution of benzidine in dilute pyridine. The colour concentration depends, amongst other things, upon the

water content of the pyridine and the time of standing of the solution.

3. Colorimetric determination of the silver after reduction with aldehyde or sucrose⁸. This method has been reported to produce a detectable colour when the silver is present in a concentration of only 1 part in 25,000,000. The colour deepens upon standing.

4. Separation as silver iodide followed by liberation of iodine and its determination absorptiometrically in carbon tetrachloride.

5. Reduction of silver salts to metallic silver on a paper fibre⁹ and comparing the quantity of hydrogen peroxide decomposed catalytically under standardised conditions with the amount decomposed by a series of standard samples. The degree of decomposition depends upon the surface area of the silver film, and therefore its thickness must always be the same for all analyses.

6. Coagulating and separating the silver rhodanine lake at the interface of an immiscible solvent.

Some of these methods had a limited success but a

very serious difficulty was encountered in the readiness with which silver is absorbed on and not subsequently removed from glass (both soft and Pyrex), porcelain, silica and possibly calcium sulphate⁶. Hamence has confirmed the absorption of silver on calcium sulphate and emphasised the need for solubilising any such solid residue from wet oxidation before proceeding with the final determination¹⁰.

Nakamura and Fukami¹¹ have observed considerable losses during the cupellation of silver in amounts of less than 2 mg. and, using $\text{Ag}^{110\text{m}}$ as tracer, found that most of the loss was due to absorption in the cupel. The loss increased with decreasing amounts of silver.

Gorsuch has recently shown that up to 47% of silver can be retained on ignition of its nitrate at 500° for 16 hours in a silica crucible,¹² but his data (loc. cit. Table XX) points to a maximum loss of 5% in wet oxidations involving a total weight of 10 $\mu\text{g.}$ of the element. However it is important to realise that if such a loss were due simply to adsorption on the reaction vessels the actual weight of silver adsorbed might be of the

same order when only a total of 1 $\mu\text{g.}$ of the metal is involved, in which event the total loss could amount to as much as 50%. Such losses have been confirmed in reality when quantities of 1 $\mu\text{g.}$ or less of silver are manipulated in ordinary laboratory glassware and it has been shown that they can be significantly reduced by giving all glassware a water repellant coating of silica by treatment with a suitable reagent (see later).

It is worth noting that ordinary untreated Pyrex glassware, in which a dilute silver solution has been evaporated to dryness, retains the silver so firmly, that even boiling with concentrated nitric acid for a considerable period of time fails to redissolve the silver.

Sherrat⁶ has examined Sandell and Neumayer's method¹³ for the determination of silver after wet oxidation of organic matter with a mixture of sulphuric and nitric acids, he established the conditions for preparing reproducible standard curves for minute amounts of silver in distilled water using a solution of rhodanine in acetone and alcohol as a colour forming reagent. Interference by common metals and especially by excess of reagent could be suppressed by controlling the acidity. Nitric acid was found to be preferable to sulphuric acid

for this purpose but it must be freshly prepared by distillation from urea to remove all traces of nitrous acid.

The extraneous colour from 1 ml. of 0.1% rhodanine could be suppressed by using 4 ml. of freshly prepared N-nitric acid diluted to 50 mls. with distilled water. The limitations of the method for the present purposes are clearly shown by the results given in Table I¹⁴

Table I

Recovery of silver from 100 mls. of drinking water* to which 0.05 g. of Quebracho Tannin had been added

Metal added μg	A	B	C	D	E	F	G
Silver	0	5	20	0	5	10	20
Lead	0	0	0	100	100	100	100
Mercury	0	0	0	100	100	100	100
Iron	0	0	0	100	100	100	100
Optical Density	0.015	0.032	0.087	0.030	0.032	0.048	0.102
O.D. corrected for blank	-	0.017	0.072	-	0.002	0.018	0.072
Silver found	-	2.5	11.2	-	0.2	2.7	11.2

* Hardness of drinking water was 120 p.p.m. calcium (as CaCO_3) and 44 p.p.m. magnesium (as MgCO_3)

The calibration curve, using a 1 cm. cell and a No. 604 filter, was prepared for 0 - 25 μg . silver in a final volume of 25 mls.

Some work has been carried out, as will be seen later on the determination of silver by the rhodanine method but it was not found to be sufficiently reliable at the concentration levels required. The results appear to be very sensitive to changes in the acidity of the final solution.

Scope of the present Work.

In the view of the proved inadequacy of the present procedures a new approach was called for. The alternatives would appear to be a search for a new procedure of adequate sensitivity or a study of concentration techniques which would enable some well tried analytical procedure to be used as a finish.

It would be unjustifiably optimistic to hope to improve the sensitivity of existing absorptiometric procedures by the necessary factor of between 10 and 100 times, except by fortuitous discovery of an entirely new type of reagent. On the other hand neutron activation analysis would appear to provide the required sensitivity in that a sample of only 1 ml. should suffice if the

estimated ultimate sensitivity of 5×10^{-9} g. could be realised¹⁵. This would, however involve irradiation in a nuclear reactor for a period of a month, and although the subsequent chemistry could be greatly simplified or indeed replaced by δ -ray spectrometry it was felt that a speedier and less specialised technique would be more generally acceptable.

The problem thus resolves itself into an examination of three separate stages viz. (i) concentration, (ii) separation from interfering elements, and (iii) final determination. Several possibilities were examined in each case and the final procedure which is given in full in Appendix A represents a compromise between acceptable accuracy and general convenience.

Use of radioactive Silver.

In addition to the preliminary trials of a new method for determining traces of silver radiometrically, of which account is given later, extensive use has been made of radioactive silver to investigate the completeness of concentration and separation procedures, and especially to follow the losses of silver that may occur at all

stages, more especially through absorption.

Previous investigations have had limited success because the silver may be assayed by conventional means only when substances likely to interfere have been removed, that is to say at the final stage of an analytical determination and no check is possible on the efficiency of any of the intermediate steps.

Since radioactivity is a nuclear property, not only can each step involving a radioactive tracer be examined for loss, but the actual position of the radioactivity may be accurately followed, which is of great value when there is surface adsorption.

An essential requirement in using radio tracer procedures is that the added metal must be in the same chemical form and valency state as that in solution. Where any doubt exists about completeness of exchange due note must be taken when interpreting results; nevertheless the method does hold considerable advantages over normal procedures.

If practicable neutron activation followed by γ -ray spectrometry would be a more satisfactory method, but, as mentioned earlier, the inconvenience of this procedure precluded its use.

Concentration Procedures

If physical concentration by distillation⁴ is to be rejected, the possibilities presented by co-precipitation, the use of ion-exchange resins, and the technique of solvent extraction must be explored. Studies have been made in each of these fields using 'labelled' silver throughout. It will be obvious that if the concentration stage can also be made selective, or ideally specific, for silver, the second stage, that of removing elements likely to interfere in the final determination, will be greatly simplified and overall losses may be greatly reduced.

The absorption of silver on amino-mercuric chloride⁵ has already been mentioned. Sandell and Neumayer recommend the collection of silver on tellurium¹³ and the same procedure has been used recently by Hamaguchi and Kuroda¹⁶.

The low solubility of silver sulphide suggests its possible collection on a suitable carrier sulphide. If this were a sulphide of Group II the precipitation in acid solution would have the additional advantage of breaking down the most soluble complexes of silver with

proteins and their degradation products, and also of minimising surface absorption on glassware.

Co-precipitation by mixed crystal formation is preferable since this could provide the separation from other metals which has already been mentioned as desirable. Lead, copper and mercury have all been used effectively as collectors and the use of all these metals was examined using thioacetamide and well washed hydrogen sulphide gas as precipitants.

From Table II it can be seen that recoveries of better than 99% are easily attainable. The main disadvantage of scavenging with a sulphide in this manner is that it will collect all Group II metals and thus the preliminary separation of metals which was hoped for, has not been achieved.

Sandell and Neumayer's method was also investigated: in this the silver is co-precipitated on tellurium produced by adding first sodium tellurite and then stannous chloride to a sample of the water, containing silver, made 2N with hydrochloric acid.

It was found that the tellurite solution was more effective if added in several small quantities rather

than one large addition, and if the solution was stirred in between additions until coagulation was complete. The method also appeared to work well if large quantities of organic material were present (tannin was used to simulate organic matter) but it was noted that at very high tannin concentrations the precipitate did not settle due to the viscose solution.

The method is reported to be efficient down to 0.5 p.p.m. and the present radiochemical measurements confirmed this. Iron, cobalt, nickel and zinc may be separated from silver in this way, but lead is precipitated as the chloride and the tellurium precipitate was found to carry down both copper and mercury.

This is inconvenient since, as will be seen later, it appeared that dithizone (diphenyl thiocarbazone) was the most acceptable reagent for the final determination, and these metals strongly interfere in the absorptiometric determination of silver by dithizone. Also using Te^{129} as tracer Mabuchi has found evidence that a $1.8 \times 10^{-3}\text{M}$ solution of dithizone in carbon tetrachloride will extract tellurium at pH 1, the same pH region as is used for the extraction of silver dithizonate¹⁷.

However it was not possible to confirm this unequivocally.

It is therefore possible that whilst co-precipitation may be used as a quick and convenient method for collecting small quantities of silver from solution, it must be followed by an extensive separation procedure if interfering metals are to be removed. Nevertheless it is likely that the method would prove useful as a preliminary stage when the effluent contained substances which reacted with the other, more selective, concentration reagents mentioned later.

Table 2

The efficiency of various metals for collecting silver by co-precipitation

Carrier	Acid used	Percentage Precipitated
HgS	$\leq 4N$ HCl	≥ 98.5
CuS	$\leq 4N$ HCl	> 99
PbS	$0.1N$ HCl	> 95
Te	$\leq 4N$ HCl	> 99
Te	$\leq 4N$ HCl [*]	> 99

* Containing up to 5 g. per litre of tannin.

The use of ion-exchange resins¹⁸.

There would appear to be nothing to be gained from the point of view of selectivity by attempting to concentrate the metals present in polluted water by means of a cation exchange resin. On the other hand the use of anion-exchange resins presents some interesting possibilities. This silver is known to be absorbed by such a resin in the chloride-ion form with values of the distribution coefficient K_D , ranging from about 1000 in neutral solution to zero in 10M hydrochloric acid¹⁸. These differences are sufficient to permit its separation from palladium which is retained firmly even in 10M acid¹⁹. Marcus reports values of $\log K_D$ ranging from 5.15 to 0.95 for the absorption of silver on to Amberlite IRA-400 from 0.004M to 5.50M solutions respectively of sodium thiosulphate²⁰.

Extraction from a cyanide medium should have many advantages since the high stability of this ion would ensure that the silver would be absorbed irrespective of the form in which it might be originally held as a complex in aqueous solution.

The danger of losses by adsorption on containers would also be reduced. Furthermore, since comparatively few metals form stable complex cyanides the process of concentration would also achieve useful separation.

Using radio-silver and Amberlite IRA-400 in its cyanide form the following values were found for the distribution coefficient at various concentrations of cyanide in the aqueous phase.

* This work was done by Mr. G.L. Reed but for the sake of completeness is inserted here.

Molarity of cyanide in aq. phase	0.25	0.50	1.00	1.50	2.00	3.00	4.00	5.00
$\log K_D$	4.04	3.53	3.03	2.70	2.42	1.87	1.44	0.95

These figures imply that if 100 mls. of water containing 1 μ g. of silver were to be equilibrated with 10 grams of cyanide resin such that the concentration of the cyanide ion in the aqueous phase was 0.25M or less, 99.0% of the silver or better would be absorbed. This was confirmed by experiment, using radio-silver, and excellent decontamination from a number of other elements

was shown to be possible without significant loss of silver. For example copper, lead, and mercury were found to be eluted by 20 column volumes of 2M potassium cyanide.

The removal of silver quantitatively from a cyanide resin was found to present unexpected difficulties. Elution with 6M potassium cyanide was effective but the resulting solution contained large amounts of ions which seriously interfered with the subsequent determination of silver, quite apart from the unpleasant nature of the eluant. Strong ammonia and 5% hydrochloric acid were ineffective and large volumes of acetone-hydrochloric acid mixture were needed to effect a quantitative elution. Dry ashing of the resin lead to considerable loss of silver. Wet ashing with concentrated sulphuric acid induced carbonisation but the use of a mixture of concentrated nitric and perchloric acids was very effective. The most convenient method of removing the silver quantitatively was found to be by warming it with concentrated nitric acid in an evaporating basin. The contents of the basin are then taken to dryness under an infra-red lamp and the residue treated with

molar sulphuric acid, any remaining resin being removed by centrifugation.

Silver was found to be quantitatively absorbed on an anion-resin in the chloride ion form from a solution containing a large excess of lead, copper, iron, mercury and tannin. Elution was readily carried out using 2M ammonium hydroxide. This procedure appeared to be more suitable than the cyanide method for it produced the desired concentration of silver and provided a solution containing no heavy concentrations of salts or interfering ions. Since, however, the value of K_D is rather critically dependent upon the concentration of chloride ion, which reduces the percentage absorbed by the resin when present in even quite low concentration, this procedure could not be recommended for natural effluents of unknown and variable halide ion concentration.

Solvent Extraction

The immense advantages of this technique for purposes of concentration and separation hardly need emphasising. The apparatus is inexpensive, being

limited to a few separating funnels; the separations may be carried out quickly, thus the technique lends itself to use in laboratories which have a need for frequent routine analysis. Although in practice it is not usually possible to obtain a sensitive reagent specific for one metal only, by judicious control of pH and the use of competitive complexing reagents which will withhold either the required metal or the unwanted ones, a very fair degree of separation may be obtained.

Experiments can conveniently deal with volumes of up to a litre, and if the partition coefficient of the complex is high (ca. 10^4) over 99% of it may be extracted into 10 mls. of an organic phase, effecting a concentration of 10^2 in one pass. Consequently solvent extraction not only offers the advantages of concentration, but at the same time a chance of preliminary separation.

In order to extract ionic silver it is first necessary to convert it into an uncharged complex by coordination with a suitably charged ligand. The chemistry of silver suggests that chelation through sulphur would be preferable to chelation through

nitrogen, and that phosphorus or arsenic would be even better as donor atoms²¹. Few suitable chelating agents based on phosphorus or arsenic have been examined and the choice between the sulphur compounds BAL (2,3-dimercaptopropanol) and dithizone (1,5-diphenyl-3-mercaptotetrazan) was made on the basis of the difficulty of removing silver from its complex with the former, and greater selectivity of the latter.

If the dissociation constant of the acid conjugate to the ligand L is given by

$$\frac{[H][L]}{[HL]} = K_r \quad 1$$

and the stability constant of the complex ML_n is

$$\frac{[ML_n]}{[M][L]^n} = \beta_n \quad 2$$

and the partition coefficient of the reagent is

$$P_r = \frac{[HL]}{[HL]}^o \quad 3$$

and the chelate

$$P_c = \frac{[ML_n]}{[ML_n]}^o \quad 4$$

assuming that the metal forms no appreciable amounts of hydrolysis or anion coordination complexes, and that the concentrations of the intermediate species are negligible, then the distribution ratio q , where

q - The total concentration of metal in the organic phase

The total concentration of metal in the aqueous phase is given by

$$q = \frac{[ML_n]_o}{[M^{n+}] + [ML_n]} \quad 5$$

and from 1,2,3,4 and 5

$$q = \frac{\beta_n p_o K_r^n}{P_r^n} \frac{[HR]_o^n}{[H]^n} \quad 6$$

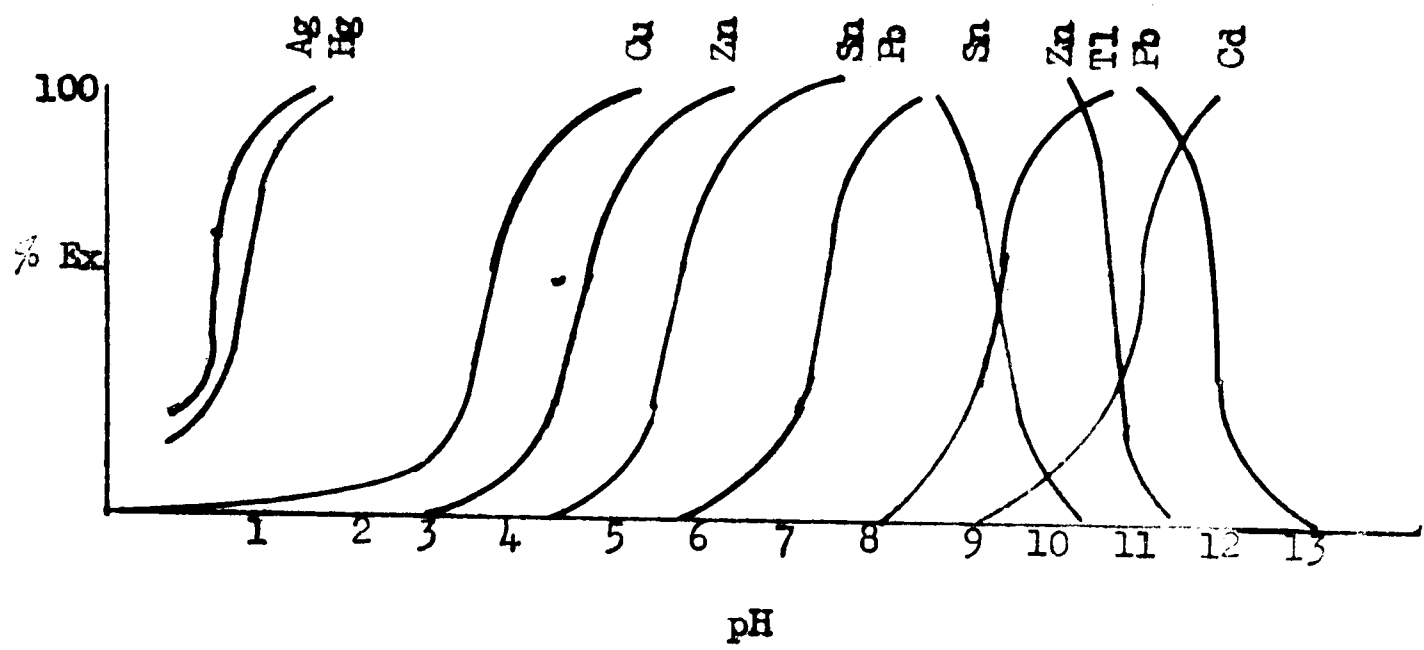
so

$$q = K \left\{ \frac{[HR]_o}{[H]} \right\}^n \quad 7$$

Since, therefore, the distribution of the metal between the aqueous and organic phases is determined for the weakly acidic reagent dithizone (HDZ) by the equilibrium

GRAPH 1

The extraction curves of some metal dithizonates into
chloroform



given in equation 7 considerable selectivity may be imposed upon the concentration stage by the appropriate choice of pH.

Graph 1 shows typical extraction curves of the metal dithizonates from chloroform. It can be seen that this reagent provides silver complexes which are very stable in acid solution. In the presence of excess of the reagent this stability appears to be even more strongly pronounced, with extraction not falling below 98% until the acidity of the aqueous phase is greater than 12 normal.

If equation 6 is applied to silver dithizonate (AgDz) and copper dithizonate (CuDz_2) we get

$$q_{\text{AgDz}} = \frac{\beta_{\text{AgDz}} P_{\text{AgDz}} K_r}{P_r} \frac{[\text{HR}]_o}{[\text{H}]} \quad 8$$

and

$$q_{\text{CuDz}} = \frac{\beta_{\text{CuDz}_2} P_{\text{CuDz}_2} K_r^2 [\text{HR}]_o^2}{P_r^2 [\text{H}]} \quad 9$$

and dividing 8 by 9

$$S = \frac{q_{\text{AgDz}}}{q_{\text{CuDz}_2}} = \frac{\beta_{\text{AgDz}} P_{\text{AgDz}} P_r}{\beta_{\text{CuDz}_2} P_{\text{CuDz}_2} K_r} \frac{[\text{H}]}{[\text{HR}]} \quad 10$$

where S is the separation factor. Taking approximate values of 10^{18} for $\beta_{\text{AgDz}} \text{ } P_{\text{AgDz}}$, 10^{27} for $\beta_{\text{CuDz}_2} \text{ } P_{\text{CuDz}_2}$, 10^4 for p_r and 10^{-5} for K_r and inserting in equation 10, S is found to be 10^4 , thus affording considerable separation.

The solvent extraction of very dilute solutions of silver in sulphuric acid (down to 0.01 p.p.m.) was studied with the aid of labelled silver. Over a wide range of acidities the extraction of silver was effectively quantitative in a single extraction, and tannic acid, used to simulate organic matter present in trade effluent, was found to have no adverse effect in concentrations of up to 5 grams per litre. Over 95% of the silver was removed at one pass from such a solution containing 20 $\mu\text{g.}$ of silver per litre.

At any given pH the extraction of silver takes place in preference to that of mercury, copper, zinc, lead etc., and if the extraction is continued until a further portion of (diluted) dithizone remains green, the removal of silver will certainly have been complete. The high stability of the silver dithizone complex and

the favourably high distribution coefficient in strongly acidic media has the further important advantage that the metal can be extracted from aqueous solutions in which it may be present as complexes with amino-acids or other breakdown products of proteins. Considerable concentrations of chloride ions were not found to inhibit the extraction.

By using a synthetic effluent containing, besides silver tannin, mercury, lead, copper, and iron dissolved in ordinary tap water it was shown that after acidification with sulphuric acid to approximately 0.5N, three extractions with 5 ml. portions of dithizone solution (10 mg/l.) were sufficient for the quantitative removal of silver from up to 500 mls. of sample.

The procedure is therefore admirably suited for the primary concentration of silver by a factor of 10 or better and it has the added advantages of speed, the use of readily accessible apparatus and reagents, and the immediate separation of silver from much organic matter and from the alkaline earth metals which, in any wet ashing procedure, provide a bulky residue of solids on which the silver is readily and strongly adsorbed.

In a few experiments with synthetic effluents, a solid sometimes separated at the water-carbon tetrachloride interface. Measurements of its activity showed it to contain appreciable quantities of silver. Whenever such a scum appears it should be transferred with the organic phase for further treatment.

The separation stage

The choice of method to be used in the final determination of silver will, of course, decide the extent to which a preliminary separation of interfering elements will be necessary, and it will influence equally the choice of the primary method of concentration.

After some experience with the rhodanine method for silver it was decided to use an absorptiometric finish for silver with dithizone as colour developing reagent.

The red-coloured product formed by p-diethylamino-benzylidene-rhodanine with silver is insoluble, so that the determination with this reagent is based upon the photometry of a colloidal suspension. The colour is reported to vary with the time of standing and the pH,

the optimum acidity being 0.05 N.

The relation between the colour of the colloidal suspension and the silver concentration is linear only up to 1 p.p.m., but as little as 0.05 p.p.m. can be detected. Gold, mercury, and palladium also react in acid solution. Measurements showed that 0.05 N acid solution indeed provided the maximum colour intensity, but upon increasing the acidity to 0.08N the optical density of the solution dropped from 0.096 to 0.076.

The definite instability of the colloidal precipitate and its sensitivity to acidity changes made rhodanine a much less convenient reagent to work with than dithizone.

"Merkupral" (tetraethylthiouram disulphide) has recently been recommended for the determination of silver in its ores and is said to be specific for this element²². This procedure depends upon the bleaching by silver ions of the colour of the merkupral copper complex and the sensitivity does not appear to be so great as that of the dithizone method, which can be made as specific by a suitable choice of reaction conditions.

Exhaustive extraction by dithizone of an aqueous phase 0.5N with respect to sulphuric acid will remove varying amounts of mercury, copper, and palladium in addition to the whole of the silver. The presence of large amounts of palladium is not anticipated in trade effluents and up to a 10-fold excess will not invalidate the final determination of silver.

Using radioactive silver we confirmed that when an organic solution containing the dithizonates of silver, mercury, and copper was shaken with an acidified solution of ammonium thiocyanate the silver is reverted into the aqueous phase, and that the process is quantitative for ammonium thiocyanate, provided that the concentration of the (sulphuric) acid was below 2N. Other experiments showed that copper and mercury remained in the organic phase. The acidified ammonium thiocyanate was also found to dissolve any interfacial scum containing silver, presumably as an anionic complex.

Before the final absorptiometric determination of silver it was necessary to remove all thiocyanate ions. This was most conveniently done by adding sulphuric acid and taking down to fuming under an infra red lamp. The

residue could then be taken up quantitatively in a little nitric acid to which urea and hydroxylamine were added to prevent any oxidation of the dithizone by nitrous fumes in the final stage.

As previously stated, radioactive silver was used to study the completeness of every stage and combination of stages in the proposed procedure. It was soon discovered that losses of silver by adsorption on the walls of the vessel could be very serious. For example losses of up to 50% occurred from simply shaking a solution of silver nitrate (1 p.p.m.) in a clean stoppered Pyrex tube. This adsorption was most troublesome when a dilute silver solution was evaporated to dryness and considerable difficulty was experienced in devising a method to recover all the silver after fuming with sulphuric acid. Porcelain, pyrex and even polythene surfaces all adsorbed silver in the cold and the amount always increased upon heating. However it was found that absorption on a fused silica surface was very small and even losses sustained during evaporation could be made negligible if heating were carried out by means of infra-red heaters.

The importance of using fused silica vessels in conjunction with infra-red heaters for evaporations, and of coating all glassware with a silicone surface cannot be emphasised too much, since if these precautions are not taken there can be no hope of carrying the silver all the way through the analysis.

The absorptiometric determination of silver

The final stage can be carried out by

1. Measuring the absorption due to the yellow silver dithizonate complex at 462 μ
2. By measuring the decrease in absorption of a standard dithizone solution at its maxima of 620 μ or 450 μ .
3. By a reversion procedure.
4. By observing the colour change that occurs when silver, due to its superior complexing power with dithizone, replaces copper from a solution of copper dithizonate.

Determination of silver in the range 0 - 1 μ g. was studied using a dilute solution of dithizone in carbon

tetrachloride (5 mg/l.). In order to obtain adequate sensitivity when tiny quantities of silver were present, only a limited volume of extract was available and it was necessary to use micro-cells with a light path of 10 mm. and holding about 0.5 ml.

When using a 'Spekker' absorptiometer the Ilford Spectrum Orange No. 607 filters (with maximum transmission near 600 μ u.) were found to be the most suitable for measuring the concentration of the residual dithizone (method 2), but the mixed colour determination of silver dithizonate ($\lambda_{\text{max}} = 462 \mu$ u) in the presence of excess dithizone (method 1) was found to be very unreliable owing to the closeness of this maximum absorption to the secondary absorption peak (450 μ u) of dithizone. Under these circumstances any increase in the absorption at 462 μ u. due to the formation of more silver dithizonate will be offset to a certain extent by the decrease in concentration of the dithizone itself. Since the extinction coefficient of dithizone at 462 μ u is about 18×10^3 , and that of silver dithizonate at the same wavelength 30.5×10^3 the sensitivity of measurements

carried out would be the same as that achieved with a monocolour determination when the extinction coefficient had the relatively low value of 12.5×10^3 .

Moreover the best Ilford filter available in this case had a comparatively low transmission and the overall sensitivity was poor. It was not considered satisfactory to rely upon a mono-colour method which would entail stripping excess of dithizone from its extraction mixture with silver dithizonate with alkali, since, although the keto dithizonate is reported to be stable to alkali, a red solid, (supposedly a polymeric keto form²³) irreversibly separates upon standing.

If the final silver solution to be determined still contained comparable amounts of copper or mercury the reversion method could be used to advantage. For if C_s , C_c , C_m and C_d are the concentrations and ϵ_s , ϵ_c , ϵ_m and ϵ_d are the molecular extinction coefficients of silver dithizonate, copper dithizonate, mercury dithizonate, and the dithizone excess respectively, the total absorbancy A_M and A_R before and after shaking with acidified thiocyanate (which will revert only silver dithizonate to an equivalent amount of dithizone) will be given by

$$A_M = \sum_s C_s + \sum_o C_o + \sum_m C_m + \sum_d C_d$$

and

$$A_R = \sum_d C_s + \sum_o C_o + \sum_m C_m + \sum_d C_d$$

whence the reversion value $A = (A_R - A_M) = C_s(\sum_d - \sum_s)$

As predicted the reversion curve (the plot of A against the concentration of silver taken) was linear over the range 0 - 2 μg . The reversion method has the advantage that the slope of the calibration curve can be readily checked by carrying out the reversion procedure with a single known concentration of silver, since the calibration curve passes through the origin. A greater advantage in practice is due to the circumstance that the position of the calibration curve does not depend upon the actual concentration of dithizone used, so that problems involved in preparing or maintaining solutions of this notoriously unstable reagent are largely circumvented.

In preliminary work during which anion exchange resins were considered as a means of concentrating silver it was anticipated that the final determination of silver might have to be made in the presence of small

amounts of copper.

The method recommended by Leopoldi²⁴ was therefore re-examined, which makes use of the fact that silver will displace copper from the violet cupric keto-dithizonate to give a series of mixed colours ranging from violet to yellow. This method was found to be excellent for the determination of silver in the presence of copper but the simple method, 2, or the reversion procedure, 3, was preferred because (a) the colour changes are more definite if visual matching is used (b) the standard solution of copper dithizonate appeared to be quite photosensitive and needed frequent restandardisation and (c) absorptiometric determination of the optical density of the mixed colour solutions involved the use of the Ilford Spectrum Blue filter and the sensitivity and reproducibility were less satisfactory than in the other methods examined.

If no photoelectric instrument is available it is possible to assess the colour intensity of the final dithizone solution by visual comparison, although it is much more satisfactory to use an absorptiometer, or better a spectrophotometer for the final determinations.

The aqueous phase containing the silver, after destruction with thiocyanate, is placed in a micro-testtube, a dilute dithizone solution is added and the two phases mixed by agitating with a glass rod flattened at one end.

The final colour of the organic phase is then compared with a series of standards made up previously. If the quantity of silver in the standards is varied by about 0.2 μg . the final determination should be accurate to within $\pm 0.1 \mu\text{g}$.

The final procedure for the determination of silver using solvent extraction to concentrate the element, selective reversion to separate it from interfering elements, and an absorptiometric determination with dithizone is fully described in the Appendix. Over the range 0 - 1 μg . in the final solution an accuracy of $\pm 10\%$ was achieved under optimum conditions which would appear to be adequate for the proposed lower limit of 1 part in 10^8 when using a 100 ml. sample. With higher concentrations of silver there is an appreciable increase in accuracy.

Flame Photometry

It has been reported¹⁶ that by the use of arc spectrographic methods, silver may be estimated down to 0.03 p.p.m. by comparing the 328 mu. silver line with the 325.6 line of an indium standard.

Clearly a time consuming spectrographic method would not find favour for frequent routine analysis but it is possible that laboratories with flame photometers could use them with advantage for the determination of silver if the method proved adequately sensitive.

Using a Beckman flame photometer with a natural gas-oxygen flame a detection sensitivity of down to 2 p.p.m. has been reported²⁵ but this may be increased under favorable conditions. The sensitivity may be compared with that of other elements by dividing the detection sensitivity into one hundred. Some values are given below, the wavelengths in mu. to which these figures refer are given in brackets after the sensitivities

Ag		Cu		Pb	Na
7	(328.1)	100	(324.8)	0.2	(368.3)
50	(338.3)	90	(327.4)	0.3	(405.8)
					10,000 (589)

The relative positions of the more common lines are shown in Graph 2.

It is unlikely that a flame photometer could be used directly for the analysis of the sample of effluent because of interferences due to both anions and cations present.

The second most persistent silver line (338 mμ) is known to decrease in intensity with added anions in the order nitrate, acetate and sulphate and although the first persistent line 328 mμ. remains unaltered copper (327 mμ) is likely to interfere at this wavelength.

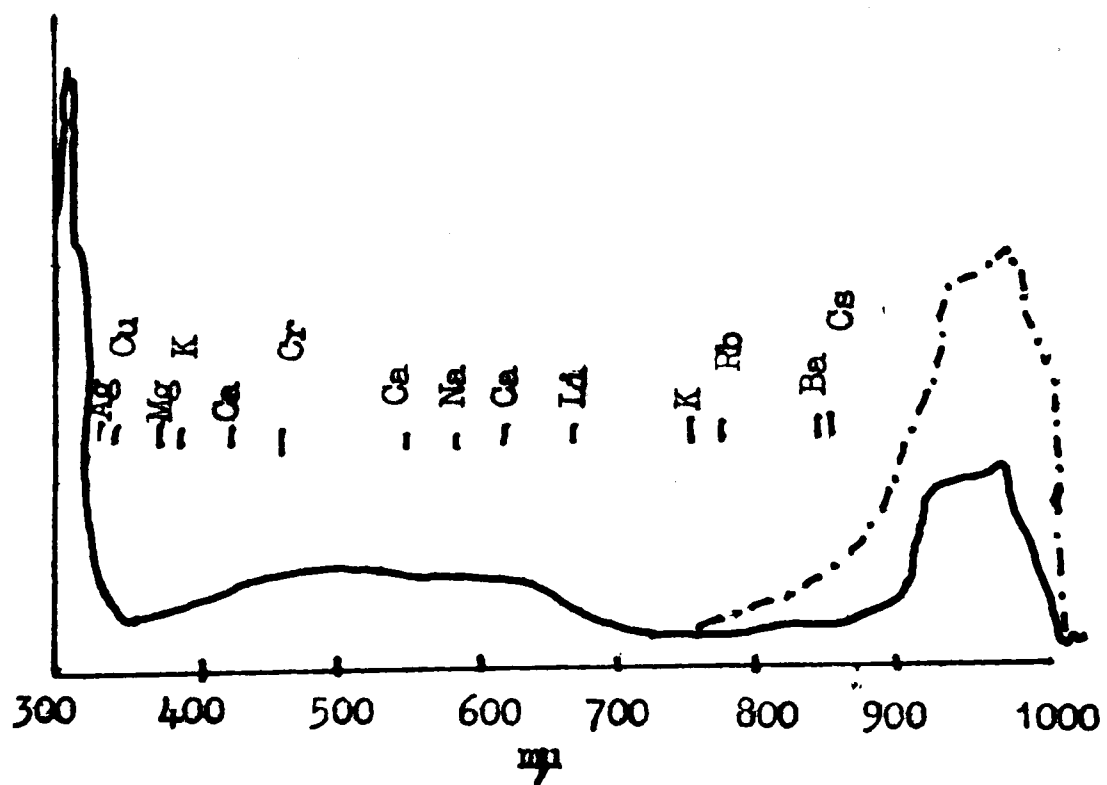
It is not feasible to introduce dilution techniques to reduce interference, due to the initial low concentration level of the silver, neither can radiation buffers be used, since the nature of the interfering substances is not likely to be known and will vary from determination to determination.

Consequently if flame photometric analysis is to be used it must be preceded by concentration and separation stages in order to obtain a final solution suitable for measurement.

As can be seen the lines for silver (328.1 and 338.3

GRAPH 2

Background produced by hydrogen - oxygen and gas -
oxygen flames



----- hydrogen - oxygen

_____ gas - oxygen

mu) fall on a region of high water background and it is important, in order to get good accuracy, to measure as narrow a band width as is feasible. This gives the best signal to background ratio.

By courtesy of Messers Unicam Limited it was possible to carry out measurements of the S.P.900, a new direct reading prism flame photometer of high resolution, incorporating an oxy-acetylene burner. Solutions containing between 1 and 50 p.p.m. of silver in sodium perchlorate solution were measured by scanning the silver bands, using the narrowest band width.

It was found that the silver peaks do not appear to stand out well above the water background, even with relatively large quantities of silver, and, in addition, the sensitivity leaves much to be desired.

From the results quoted below in Table 3 it appears that less than 5 p.p.m. may not be determined with this instrument and at higher concentrations considerable errors may be involved

Table 3

Ag p.p.m.	Scale reading (0-10)
50	3.6
25	1.7
10	0.8
5	0.43

It appears that no advantage will be gained by substituting flame photometry for the more conventional methods of absorptiometric analysis.

From the foregoing data a method for analysis of silver in trade effluent was proposed in the form to be found in Appendix A at the end of this section. The method has been devised bearing in mind the simplicity of equipment and convenience of handling. Solutions were made up as in Table 1 to simulate effluent conditions, and varying amounts of silver added.

Table 4

Silver added	Quantity of solution	Parts per 10^8	Silver found
15.0 μg	100 mls.	15	13.3 μg .
10.0	100	10	8.5
5.0	100	5	4.3
0.95	100	0.95	0.85
0.70	100	0.70	0.60
0.50	100	0.50	0.40
0.50	200	0.25	0.42
0.20	100	0.20	0.20
0.50	500	0.10	0.25

An independent series of experiments were carried out at the laboratories of British Drug Houses Limited and the results obtained are in Table 5 below

Table 5

Silver Added	Silver recovered
1 μ g.	0.85 μ g.
3	2.80
5	4.70
10	9.70

A number of measurements were also carried out at the laboratories of Boots Limited and efficiencies achieved varied between 67% and 90%.

Radiometric methods

Although it was considered preferable to develop a method which did not involve the use of radiometric measurements in its final form, some experiments have suggested that a new method for the determination of silver could be developed from the following considerations.

Let us suppose that a solution of silver keto-dithizonate in an organic solvent is prepared from radioactive silver and completely freed from excess of unreacted silver or dithizone.

If this solution is equilibrated with an aqueous solution containing a much smaller amount of inactive silver

the isotopes will exchange and the amount of the radioactivity in the aqueous phase will be a measure of the amount of silver originally present there. If the specific activity of the silver available is sufficiently high, a very sensitive method becomes available for the determination of traces of silver.

If the equilibrium constant for the reaction



is given by

$$K = \frac{[\text{AgDz}][\text{H}^+]}{[\text{Ag}^+][\text{HDz}]} \quad 11$$

and making use of equations 1, 2, 3 and 11

$$\frac{[\text{AgDz}]_o [\text{H}^+]}{[\text{Ag}] [\text{HDz}]_o} = \frac{K p_o}{p_r} = K' \quad 12$$

Specifically let

S_a = number of moles of radioactive silver originally
in the organic phase

S_i = number of moles of inactive silver originally
present in the aqueous phase

x_1 = the number of moles of silver which, at equilibrium, have gone from the organic to the aqueous phase

$[H^+]$ = the concentration of acid in the aqueous phase

V_0 and V = the volumes of the aqueous and organic phases

From the above $[AgDs]_0 = (S_a - x_1)/V_0$

$[Ag^+] = (S_1 + x_1)/V$

$[HDz]_0 = x/V_0$

whence

$$\frac{S_a - x_1}{x_1(S_1 + x_1)} = K' / [H^+] V = K'' \quad 13$$

at constant hydrogen ion concentration.

The total amount of activity in the system is proportional to S_a . The total amount of silver in all forms is $S_a + S_1$ and the amount present in the aqueous phase at equilibration will be $S_1 + x_1$. The activity of the aqueous phase will thus be proportional to the quotient $(S_1 + x_1)/(S_a + S_1)$.

If the specific activity of the silver is a_s c.p.m. per gm. mole. the radioactivity of the aqueous phase will be given by

$$R_w = \frac{a_s(S_1 + x_a)}{(S_a + S_1)} \quad 14$$

at constant hydrogen ion concentration equation 13 gives

$$K''x_1^2 + (S_1K'' + 1)x_1 - S_a = 0 \quad 15$$

Applying the general solution of a quadratic equation to equation 15

$$x_1 = \frac{-S_1K'' + 1 \pm \sqrt{(S_1K'' + 1)^2 + 4K''S_a}}{2K''} \quad 16$$

and substituting the value of x_1 from 16 into 14

$$R_w = a_s \left(\frac{S_1 + \frac{-S_1K'' + 1 \pm \sqrt{(S_1K'' + 1)^2 + 4S_aK''}}{2K''}}{S_a + S_1} \right) \quad 17$$

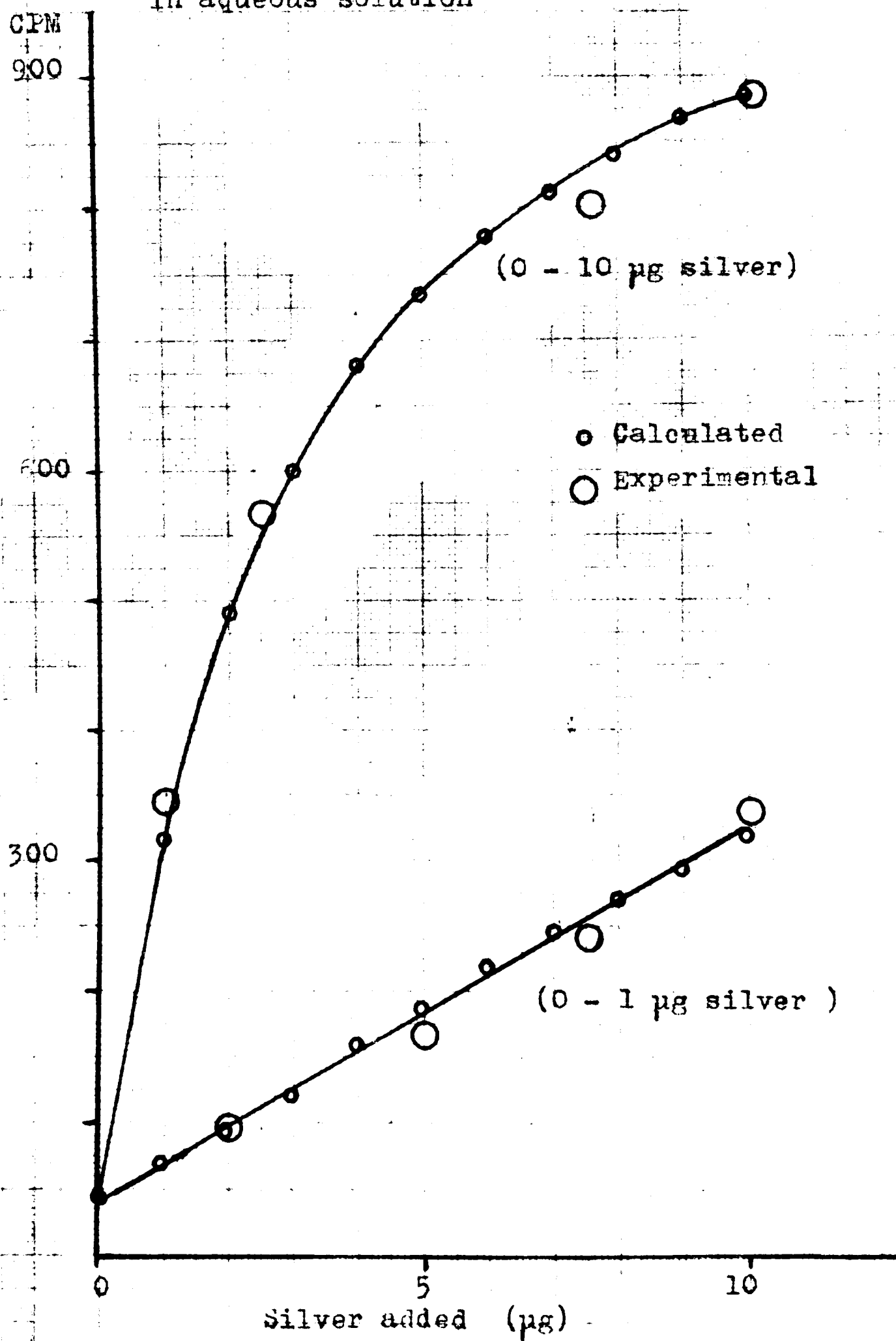
If S_1 is small compared with S_a , and since K'' is large compared with 1 equation 17 becomes

$$R_w = \frac{a_s}{S_a} \left(S_1 - \frac{S_1^2}{S_a} \right)$$

A linear relationship between the count of the aqueous

GRAPH III

Calculated and experimental points for the equilibrium between radioactive silver dithizonate solution and inactive silver in aqueous solution



phase and small amounts of added silver would therefore be expected so long as the assumptions made in deducing equation 18 were valid.

A strong solution of radioactive silver dithizonate in carbon tetrachloride was shaken with twelve times the volume of aqueous phase made 0.5 N with respect to sulphuric acid containing varying amounts of silver. The aqueous phase was then counted. Independent measurements making use of the optical density of the silver dithizonate solution, its extinction coefficient and count provided a value for a_s hence the value for R_w could be calculated. It is clear from Graph 3 that the experimental data conforms to that theoretically predicted, and the calibration graph is linear over the range 0 - 1 μg . It should be quite possible to determine quantities of silver as low as 0.01 μg . by this method.

The only difficulty with the method, apart from the need to silicone all glassware, was the inaccuracies produced by a red solid which separated out from the silver dithizonate solution on standing. To avoid any inaccuracies that its formation might incur, the silver dithi-

zionate solution must be freshly made up before use.

If no inactive silver be added equation 13 reduces to

$$K' = \frac{(S_a - x_1) H^+ V}{x_1^2} \quad 19$$

By measuring the activity of the aqueous phase and knowing a_s , a series of values for x_1 may be obtained for varying hydrogen ion concentration, and hence K' may be calculated.

Values of K' varied between 1.73×10^7 in 6.34N sulphuric acid to 5.57×10^7 in 0.63 N sulphuric acid.

Values cited in the literature obtained by more conventional methods are 1.5×10^7 for 6 N sulphuric acid²⁷ and 4.7×10^7 for ionic strength 0.1²⁸.

Radiochemical check on the efficiency of analysis.

It is possible, in spite of losses during an analytical assay, to carry out an exact analysis by means of an isotope dilution method.

Suppose that a solution contains x $\mu\text{g.}$ of silver which is unknown, and which is to be determined, and to this is added a known amount y $\mu\text{g.}$ of active silver, of known specific activity a_s c.p.m. per gm. mol.

After passing through the analytical process the total quantity of silver is found (say colorimetrically as silver dithizonate) and the amount of activity present is also measured. Let us assume that the final volume of silver solution upon which the assay takes place is V mls. and for the final determination only a fraction of the initial silver T remains.

The total amount of silver initially is

$$\frac{(x + y) 10^{-6}}{A_g} \text{ mols}$$

where A_g is the atomic weight of silver and the final concentration is

$$\frac{(x + y) 10^{-3} T}{A_g V}$$

The absorbency of the silver dithizonate at the absorption maximum (462 mμ) will be

$$A = \frac{(x + y) 10^{-3} T}{Ag V} \epsilon_{462} \quad 22$$

If ϵ_{462} is the extinction coefficient of silver dithizonate at 462 mμ and 1 cm. cells are used.

Now the activity of the added silver solution will be

$$R_1 = \frac{y 10^{-6} a_s}{Ag} \text{ c.p.m.}$$

For the final count the specific activity will now be

$$\frac{Y}{x + y} \cdot a_s$$

so the final count should be

$$R_f = \frac{Y}{x + y} \cdot a_s \cdot \frac{x + y}{Ag} \cdot 10^{-6} = R_1$$

Any difference between R_f and R_1 therefore is a measure of the loss of active silver in the solution and if this exchanges with the inactive silver it is a measure of the total loss of silver during analysis.

$$\text{i.e. } T = \frac{R_f}{R_1} \quad 23$$

So from 22 and 23

$$x = \frac{A_{Ag} \cdot V \cdot R_1}{10^{-3} R_f \epsilon_{462}} - y \quad 24$$

In practice it is more convenient, as was mentioned earlier, to measure the decrease of the optical density at 620 mμ due to the formation of the silver dithizonate.

When no silver is present, if 1 cm. cells are used,

$$A_1 = \epsilon_{HDz} c_1 \quad 25$$

$$A_2 = \epsilon_{HDz} c + \epsilon_{AgDz} c_2 \quad 26$$

The extinction coefficients referring to 620 mμ

Subtracting 25 from 26

$$A_1 - A_2 = \Delta A = \epsilon_{HDz} (c_1 - c) - \epsilon_{AgDz} c_2$$

But since silver dithizonate is a 1:1 complex $c_1 - c = c_2$

so
$$\Delta A = c_2 (\epsilon_{HDz} - \epsilon_{AgDz}) \quad 27$$

From 21, 23 and 27 we then get.

$$x = \frac{A_{Ag} \cdot V \cdot R_1}{10^{-3} R_f (\epsilon_{AgDz} - \epsilon_{HDz})} - y \quad 28$$

Thus equations 24 and 28 provide a method for the calculation of x.

SOME THEORETICAL INVESTIGATIONS INTO THE APPLICATION OF SOLVENT EXTRACTION TO COMPLEX CHEMISTRY

The Determination of acid dissociation constants.

It would be of considerable value if the utility of a particular analytical reagent could be assessed from theoretical principles. Much work has been done in an attempt to make this possible, data has been accumulated, and many valuable deductions have been made²⁹.

The methods used consisted of comparing the acid dissociation and metal stability constants of a number of closely allied compounds, having previously determined these constants by titration, with either hydrogen or glass electrodes as hydrogen ion concentration indicators.

This method has been used extensively for substances which are soluble in water but, unhappily, it may not be applied directly to compounds which are soluble in an organic phase but only slightly soluble in water. Although measurements have been made in mixed solvents, the interpretation of results to make them comparable with those obtained in purely aqueous media is difficult, and there has been a general tendency to quote a mixed

stability constant of the type K' in equation 12^{30, 31}.

Since this involves the partition coefficient of both the acid and the metal chelate, clearly any difference in the value of K' obtained when altering the chelating agent will reflect, not only changes in the stability constant, but also variation in the partition coefficients involved in the constant K' .

In order to obtain a clearer picture of these changes attempts have been made to obtain true acid dissociation constants for such substances as dithizone in which the partition coefficient is very much in favour of the organic phase.

Thus measurements of the distribution of a weak acid between water and an immiscible organic solvent lead to values of a 'mixed' dissociation constant K'_r where

$$\frac{[H][L]}{[HL]_o} = \frac{K_r}{p_r} = K'_r$$

from which, value of the true acid dissociation constant K_r may be calculated, provided that the partition coefficient p_r has been determined from a subsidiary series of experiments³².

Dyrssen has obtained values for the true stability constant of dithizone by making use of solubility measurements³³, and for cupferron and oxine by means of a two phase titration technique³⁴. The last method is likely to prove the most convenient, since a series of experiments are replaced by a single titration. Consequently some time was given to the problem of applying a two phase titration to the measurement of the acid dissociation constants of dithizone and its related compounds.

Let us assume that a solution of dithizone in carbon tetrachloride, in contact with an aqueous phase, is titrated with strong caustic soda from a micrometer syringe, so that there is no appreciable change in volume of either phase.

Applying the condition of electroneutrality

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{L}^-] \quad 29$$

or
$$[\text{L}^-] = [\text{Na}^+] + [\text{H}^+] - K_w / [\text{H}] \quad 30$$

If, therefore, the hydrogen ion concentration of the solution is known, the free ligand ion concentration L^- may be calculated from the known concentration of added alkali.

If the volume of the organic phase is V_o , that of the aqueous phase V_w , and the initial concentration of the ligand $[HL]_T$

$$[HL]_T V_o = [HL]_o V_o + ([L^-] + [HL]) V_w \quad 31$$

and inserting values from equations 3 and 1 into equation 31 we get

$$\frac{1}{[L^-]} = \frac{[H]}{[HL]_T V_o K_r} \frac{V_o p_r + V_w}{V_o} + \frac{V_w}{[HL]_T V_o} \quad 32$$

If $V_o p_r \gg V_w$ which is likely since V_o will be of the same order as V_w and p_r will be large, equation 31 reduces to

$$\frac{1}{[L^-]} = \frac{[H]}{[HL]_T} \frac{p_r}{K_r} + \frac{V_w}{[HL]_T V_o} \quad 33$$

For dithizone p_r/K_r will have a value of the order 10^9 for the carbon tetrachloride water system, $[HL]_T$ will be of the order of 10^{-4} , so if $V_w = V_o$ the following related values for the hydrogen ion concentration and the reciprocal of the free ligand ion concentration are obtained

$[H^+]$	$1/[L^-]$
10^{-11}	1.01×10^{-4}
10^{-10}	1.1×10^{-4}
10^{-9}	2.0×10^{-4}
10^{-8}	1.1×10^{-5}
10^{-7}	1.01×10^{-6}

The significance of these figures is that if the free ligand ion concentration $[L^-]$ is to be calculated from equation 30 its value is likely to be too small to be determined accurately in solution more acid than pH 8, and the differences likely to be met with are likely to be very small at pH's in excess of 9. Hence significant pH measurements are limited to those obtained from solutions of acidities varying between pH 8 and 9, a difficult region to work with in unbuffered solutions.

It is, however, possible to carry out titrations in the presence of a buffer, making work in the pH range 8 to 9 practicable.

If the acid dissociation constant of the buffer is given by

$$K_b = \frac{[H][B]}{[HB]}$$

then equation 29 becomes

$$[\text{Na}^+] + [\text{H}^+] = [\text{OH}^-] + [\text{L}^-] + [\text{B}^-] \quad 35$$

now

$$[\text{HB}]_T = [\text{HB}] + [\text{B}^-] \quad 36$$

assuming that neither species $[\text{HB}]$ or $[\text{B}^-]$ appreciably partitioned into the organic phase.

Thus combining 36 with 34

$$[\text{B}^-] = \frac{K_b [\text{HB}]_T}{[\text{H}^+] + K_b} \quad 37$$

Inserting the value of $[\text{B}^-]$ from 37 into 35 we get

$$[\text{L}^-] = [\text{Na}^+] + [\text{H}^+] - \frac{K_w}{[\text{H}^+]} - \frac{K_b [\text{HB}]_T}{[\text{H}^+] + K_b} \quad 38$$

and this value may be inserted into equation 33.

A number of titrations were carried out to test the validity of these equations, using dithizone as the ligand and acid HL. but results were not found to be satisfactory due to the time taken to achieve equilibrium after adding alkali. It was found that immediately after addition of alkali the aqueous phase became more alkali than the

equilibrium value, but as the phases were well mixed the equilibrium value was slowly achieved.

The method of stirring is quite clearly of prime importance but it was found that even when a most efficient centrifugal stirrer was used, which forced one phase through the other at high speed, between five and ten minutes were needed to obtain a stable state. The time required for a titration was therefore likely to be considerable, and so, for the sake of convenience, values of p_r/K_r were obtained from a series of individual equilibration experiments, and p_r found independently by measurements to be described later.

The determination of metal stability constants for complexes which are insoluble in water

It was mentioned earlier, that when the chelating agent, HL, and the metal chelate ML_n are only slightly soluble in water, but favour an immiscible organic phase, it was common practise to define a mixed constant of the type K' in equation 12.

It would appear possible, however, to find the true

stability constants for stepwise equilibria, even when equilibrium between 2 phases is involved, if use is made of the additional information which can be obtained by using a metal 'labelled' with a radioactive isotope.

Let us assume that an aqueous solution containing a total amount of metal C_M (added as perchlorate), is in contact with an equal volume of immiscible organic phase, containing a total amount of ligand C_L . Concentrated alkali, say caustic soda, is added from a micrometer syringe, so that there is no appreciable increase in volume during the process of titration.

If the metal is divalent and only a neutral species is extracted, we have

$$C_M = [M] + [ML] + [ML_2] + [ML_2]_o \quad 39$$

and

$$C_L = [HL] + [L] + [ML] + 2[ML_2] + 2[ML_2]_o + [HL]_o \quad 40$$

Applying the condition of electroneutrality

$$\begin{aligned} [H^+] + 2[M^{++}] + [Na^+] + [ML^+] &= [L^-] + [OH^-] + 2[ClO_4^-] \\ &= [L^-] + [OH^-] + 2C_M \end{aligned} \quad 41$$

Substituting for C_M from 39 into 41

$$[\text{Na}] + [\text{H}] - [\text{OH}] = [\text{L}] + [\text{ML}] + 2[\text{ML}_2] + 2[\text{ML}_2]_0 \quad 42$$

and substituting from equation 40

$$[\text{Na}] + [\text{H}] - [\text{OH}] = c_L - [\text{HL}] - [\text{HL}]_0 \quad 43$$

and from 1 and 3 equation 43 becomes

$$L = \frac{c_L - [\text{Na}] - [\text{H}] + [\text{OH}]}{(1 + p_r)[\text{H}] / K_r} \quad 44$$

Thus provided that the partition coefficient and the acid dissociation constant of the acid conjugate to the ligand $[\text{L}^-]$ are known, it is possible to calculate the free ligand ion concentration $[\text{L}^-]$.

The normal procedure to complete calculation for a one phase system would be to combine equations 39, 42 and 2, ($p_r = p_c = 0$), giving an equation of the type

$$[\text{Na}] + [\text{H}] - [\text{OH}] = [\text{L}] + c_M \left(\frac{\beta_1 L + 2(1 + p_c)\beta_2 L^2}{1 + \beta_1 L + (1 + p_c)\beta_2 L^2} \right) \quad 45$$

and by substituting the values for $[\text{L}]$ from 44 into 45, for different quantities of added alkali, a number of equations may be obtained which may be solved for β_1 and β_2 .

Unfortunately if this procedure is carried out for a system for which p_o and p_r are not negligible compared with 1, then on solving equation 45, values for β_1 and $\beta_2 p_o$ would be obtained; but it would be impossible to find the individual values of β_2 and p_o without additional information.

If, however, the metal is radioactive, its distribution ratio, q , may be measured.

Now $q = \frac{\text{total amount of metal in the organic phase}}{\text{total amount of metal in the aqueous phase}}$

$$\text{so } q = \frac{p_o \beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2} \quad 46$$

It will be obvious that in equation 46 the term β_2 is not multiplied by $(1 + p_o)$ as in equation 45.

If, therefore, in addition to measuring the hydrogen ion concentration of the aqueous phase, upon adding alkali to the two-phase system containing metal and chelate, the distribution ratio of the metal between the two phases is determined, a further equation relating p_o , β_1 , β_2 and $[L]$ is obtained from which can be calculated β_1 , β_2 , $\beta_2 p_o$ and hence p_o .

From the purely practical aspect it should be remembered that experiments of this type may be carried out as a continuous titration or as a series of separate extractions.

Provided that equilibrium between the two phases is quickly established, the former is the more convenient, but in this case the titration vessel must be modified to allow assay of the activity of the two phases after each addition of alkali.

The stability constants found in this way are true stability constants and may be directly compared with those obtained from measurements carried out in a single aqueous phase, provided that the two phases are immiscible. In practice, of course, the system is not made up of two completely separate solvents, but two solutions of one solvent saturated with the second.

If there is any effect due to the miscibility of the two solvents, it might be expected to make itself apparent in two different ways. It might affect the hydrogen ion concentration reading or the value obtained for the partition coefficient.

Since the partition coefficient of the ligand between

an aqueous organic-solvent pair should be equal to the ratio of the solubilities in these two phases (see later) it is possible to determine the partition coefficient by this means when the two phases are separate and when they are in contact.

It was found that there was little difference in the two values for the partition coefficients of dithizone between water and carbon tetrachloride so measured.

In addition, the curves for the titration of a water soluble acid and base were exactly superposable, whether the aqueous phase was in contact with a carbon tetrachloride phase or not, suggesting that the effect of miscibility of the two phases could be considered to be negligible.

For many purposes it is not necessary to know the stability constants of the intermediate complexes, provided that the formation constant of the uncharged complex, ML_n , is known.

Unfortunately, many methods used to carry out these calculations have, quite wrongly, assumed that intermediate complexes are present in negligible proportions. It is,

however, possible, as will be seen in the next section, to approach this condition more nearly by taking advantage of the particular properties of a two phase system and applying them to Job's method of continuous variations.

OBSERVATIONS ON JOB'S METHOD OF CONTINUOUS VARIATIONS
AND ITS EXTENSION TO TWO-PHASE SYSTEMS.

The method of continuous variations, first enunciated by Job³⁵ and treated in great detail by Vosburgh and Cooper³⁶, is one of the most widely used procedures for determining the composition of a soluble metal complex formed in solution from a metal M and ligand L (charges are omitted for the sake of generality). To facilitate the subsequent discussion the basic procedure will be recapitulated.

Mixtures of M and L are prepared in various proportions subject to the condition that the total molecular concentration of the two components should remain constant. For each mixture some property characterising the complex ML_n (e.g. its optical absorbency) is determined and from this is subtracted the corresponding quantity calculated on the assumption that no complex formation has taken place. A plot of the resulting value (the Job ordinate, A_j) against the mole fraction of one component will have an extremum from which the actual composition of the complex is readily calculable.

Thus for the reaction:



$$xC \quad (1 - x)C \quad 0$$

(ii) at equilibrium

$$(x - \alpha)C \quad (1 - x - n\alpha)C \quad \alpha C$$

47

The value of the characteristic ordinate, A_j , is then given by

$$A_j = \{(x - \alpha)C \epsilon_M + (1 - x - n\alpha)C \epsilon_L + \alpha C \epsilon_C\} - \frac{x C \epsilon_M}{48} + (1 - x)C \epsilon_L = (\epsilon_C - \epsilon_M - n\epsilon_L)\alpha C$$

where ϵ_M , ϵ_L , and ϵ_C are the molecular extinction coefficients of the species M, L, and ML_n respectively, and a light-path of 1 cm. is assumed. It follows that:

$$\begin{aligned} \partial A_j / \partial x &= C(\epsilon_C - \epsilon_M - n\epsilon_L)(\partial \alpha / \partial x) \\ &= \text{Constant} \times (\partial \alpha / \partial x) \end{aligned}$$

and that the position of the extremum in the Job plot will be most readily determined when ϵ_C is large compared with

ξ_M and ξ_L . If the stability constant for the complex is defined by $\beta_n = [ML_n] / [M][L]^n$, logarithmic differentiation and insertion of the condition $\partial\alpha/\partial x = 0$ leads at once to the desired result:

$$x = 1/(1 + n), \text{ or } n = (1 - x)/x \quad 49$$

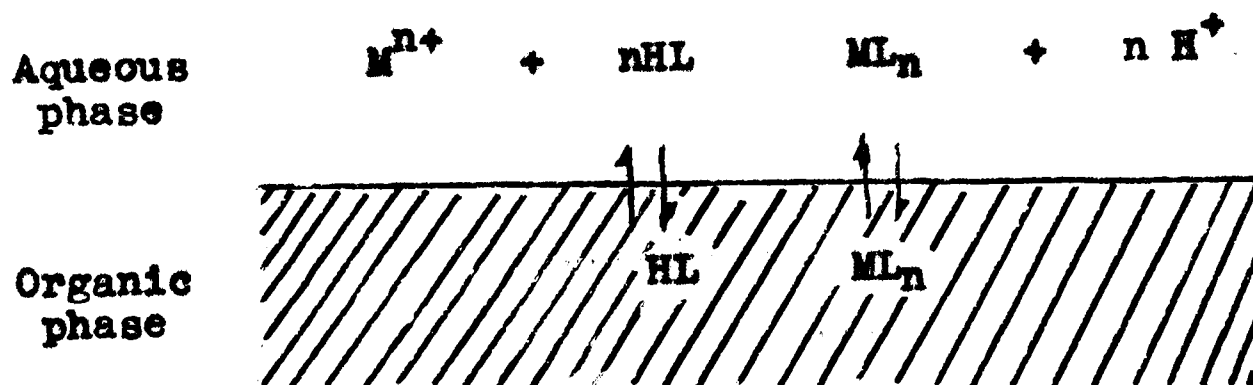
at the turning point.

Extension to a Two-phase System.

One essential requirement of the procedure outlined above is that the system should be homogeneous. In many cases this is impracticable. For although the metal cation will be soluble in water but not in organic solvents, the reverse is often true of the ligand, more especially when this is a large organic molecule: many metal inner complexes are very sparingly soluble in water though soluble in organic solvents. To overcome these difficulties mixtures of solvents (e.g. water-methanol-chloroform) have been used to provide a single phase, but the low solubility of the metallic inner complex has often proved the limiting factor³⁷. It would clearly be of considerable general value if Job's method could

be applied to a two-phase system. Although this has been tried practically and with apparent success³⁸ no theoretical justification for the procedure has yet been put forward.

Consider a reagent, HL (e.g. oxine or dithizone), capable of partition between water and an organic solvent: allow it to react with a metal cation, M, to give an uncharged complex, ML_n , which can itself be extracted into the organic phase. At equilibrium the system can be represented diagrammatically thus:



Partition coefficients for the reagent (p_r) and uncharged metal complex (p_c) are defined by:

$$p_r = [HL]_o / [HL] \text{ , and } p_c = [ML_n]_o / [ML_n]$$

where the subscript o distinguishes the organic from the aqueous phase. We assume that the system as a whole

contains αC moles of metal and $(1 - \alpha)C$ moles of the reagent, HL, which is the acid conjugate to the ligand ion, L^- . The reagent may be added initially in the form of a solution in the organic solvent. The metal ion will, of course, be present initially in the aqueous phase which must be buffered to ensure constancy of pH and should preferably have a constant salt background to preserve constant ionic strength, in default of which the application of the law of mass action to the system may be invalidated³⁹. For simplicity we postulate that the solvents are completely immiscible and that the volumes of aqueous and organic phases are equal.

Provided that there are no intermediate step-complexes³⁹ such as ML_j ($j \neq n$), or more complex species such as $H_n M L_1$ and their hydrolysis products⁴⁰, the concentration of the unique extractable complex ML_n in the aqueous phase after equilibration will be denoted by αC . The concentration in the organic phase will then be $[ML_n]_o = \alpha C_k$. Considerations of mass balance lead to the following equations:

$$\alpha C = [M^{n+}] + [ML_n] + [ML_n]_o \quad 50$$

and

$$(1 - x)C = [HL] + [HL]_o + n[ML_n] + n[ML_n]_o \quad 51$$

$$\text{whence } [M^{n+}] = xC - \alpha C(1 + p_o) \quad 52$$

and

$$[HL] = \{(1 - x)C - \alpha C(1 + p_o)\} / (1 + p_r) \quad 53$$

If the equilibrium constant for the reaction taking place in the aqueous phase is defined by:

$$K_e = [ML_n] [H^+]^n / [M^{n+}] [HL]^n \quad 54$$

then by substituting $[ML_n] = \alpha C$, and values for $[M^{n+}]$ and $[HL]$ from equations (52) and (53) we obtain:

$$K_e = \frac{\alpha C (1 + p_r)^n [H^+]^n}{\{xC - \alpha C(1 + p_o)\} \{(1 - x)C - \alpha C(1 + p_o)\}^n} \quad 55$$

Differentiation gives:

$$\left(\frac{\partial \log K_e}{\partial x} \right)_{pH} = \frac{d\alpha}{dx} \left\{ \frac{1}{\alpha} + \frac{(1 + p_o)}{x - \alpha(1 + p_o)} + \frac{n^2(1 + p_o)}{1 - x - \alpha(1 + p_o)} \right\} \\ - \frac{1}{x - \alpha(1 + p_o)} + \frac{n}{1 - x - \alpha(1 + p_o)} \quad 56$$

If A_j is the absorbency of the complex ML_n in a 1 cm. layer of the organic phase, then:

$$A_j = [ML_n] \epsilon_c = \alpha C v_c \epsilon_c \quad 57$$

whence

$$dA_j/dx = C_p \epsilon_c (d\alpha/dx) \quad 58$$

Maximum absorbency will occur when $dA/dx = 0$, whence $d\alpha/dx = 0$ at the extremum. Inserting this condition into equation (56) gives:

$$x = 1/(1 + n) \quad \text{or} \quad n = (1 - x)/x \quad 49$$

as before. Hence with 1:1, 1:2, and 1:3 complexes the extremum will occur when $x = 0.5$, 0.33 and 0.25 respectively, just as in the familiar method of continuous variations applied to a homogeneous system^{35, 36, 39}. In this extension of Job's method the most sensitive wavelength at which to carry out measurements will be that for which ϵ_c is greatest.

Measurements at High pH and with a Coloured Reagent.

If the pH of the aqueous phase is high enough a substantial proportion of the reagent may be transferred from the organic to the aqueous phase and it will be

necessary to take into account the concentration of the free ligand ion, L^- . Equations (51) and (53) now take the form:

$$(1 - x)C = [HL] + [HL]_o + n[ML_n] + n[ML_n]_o + [L^-] \quad 51a$$

and

$$[HL] = (1 - x)C - n\alpha C(1 + p_o) / \{1 + p_r + (K_r/[H^+])\} \quad 53a$$

where $K_r = [H^+][L^-] / [HL]$.

The reagent itself may be coloured (with a molecular extinction coefficient of ϵ_r) and it is necessary to examine what effect this will have on the condition for the extremum. The actual absorbency in a 1 cm. layer of the organic phase will be given by:

$$\begin{aligned} A &= [ML_n]_o \epsilon_c + [HL]_o \epsilon_r \\ &= \alpha C p_c \epsilon_c + \left\{ \frac{(1 - x)C - n\alpha C(1 - p_o)}{1 + p_r + (K_r/[H^+])} \right\} p_r \epsilon_r \end{aligned}$$

And by subtracting the contribution

$$(1 - x)C p_r \epsilon_r / \{1 + p_r + (K_r/[H^+])\}$$

which would have been given by the reagent had no complex formation taken place, we arrive at:

$$A_j = \alpha C [p_c \epsilon_c - n(1 + p_c) p_r \epsilon_r / \{1 + p_r + (K_r / [H^+])\}] \quad 57a$$

Thus, as before, $\partial A_j / \partial x = \text{constant } x(\partial \alpha / \partial x)$.

If the corrected value for $[HL]$ from equation (53a) is introduced into equation (54), differentiation and insertion of the condition for an extremum, $\partial \alpha / \partial x = 0$ leads at once to equation (49), showing that the theory of the simple Job method is equally applicable to these more complicated systems.

Since both p_c and $p_r \gg 1$, equation (57a) may be simplified to:

$$A_j = \alpha C p_c [\epsilon_c - n \epsilon_r / \{1 + (K_r / p_r [H^+])\}]$$

which suggests the possibility of working at wavelengths such that $\epsilon_c \gg \epsilon_r$ or $\epsilon_r \gg \epsilon_c$ for maximum sensitivity in locating the extremum.

Location of the Extremum Radiometrically

As already stated, the value of the Job ordinate, A_j , is derived from some convenient and distinctive property

of the complex ML_n whose composition is under investigation. Optical absorbeney has been most often used and it is essential to choose a wavelength for which $\epsilon_c \gg \epsilon_M$, ϵ_L , ϵ_{HL} , and $\epsilon ML_j (j \neq n)$. Even so, the contribution to the total absorbeney from intermediate complexes, $ML_j (j \neq n)$ may be appreciable when the mole fraction of metal is large compared with that of the ligand. This adverse feature is absent from the two-phase modification of Job's procedure since only the formally neutral complex ML_n is present in the organic phase. Moreover, advantage can be taken of the great gain in sensitivity in locating the extremum secured by labelling the metal with a highly radioactive nuclide. (Graph 4) shows how the activity in the two phases varies with x .

Graph 4 shows that the activity of the aqueous phase increases very slowly at first with x since most of the metal is being extracted into the organic phase as the radioactive complex, ML_n . Once the value of x exceeds $1/(1 + n)$, the activity rises rapidly, as shown in curve B. On the other hand the activity of the organic phase rises steeply with x until the extremum at $x = 1/(1 + n)$ and then falls steeply as shown by curve C. The maximum is well defined and its location can be ascertained

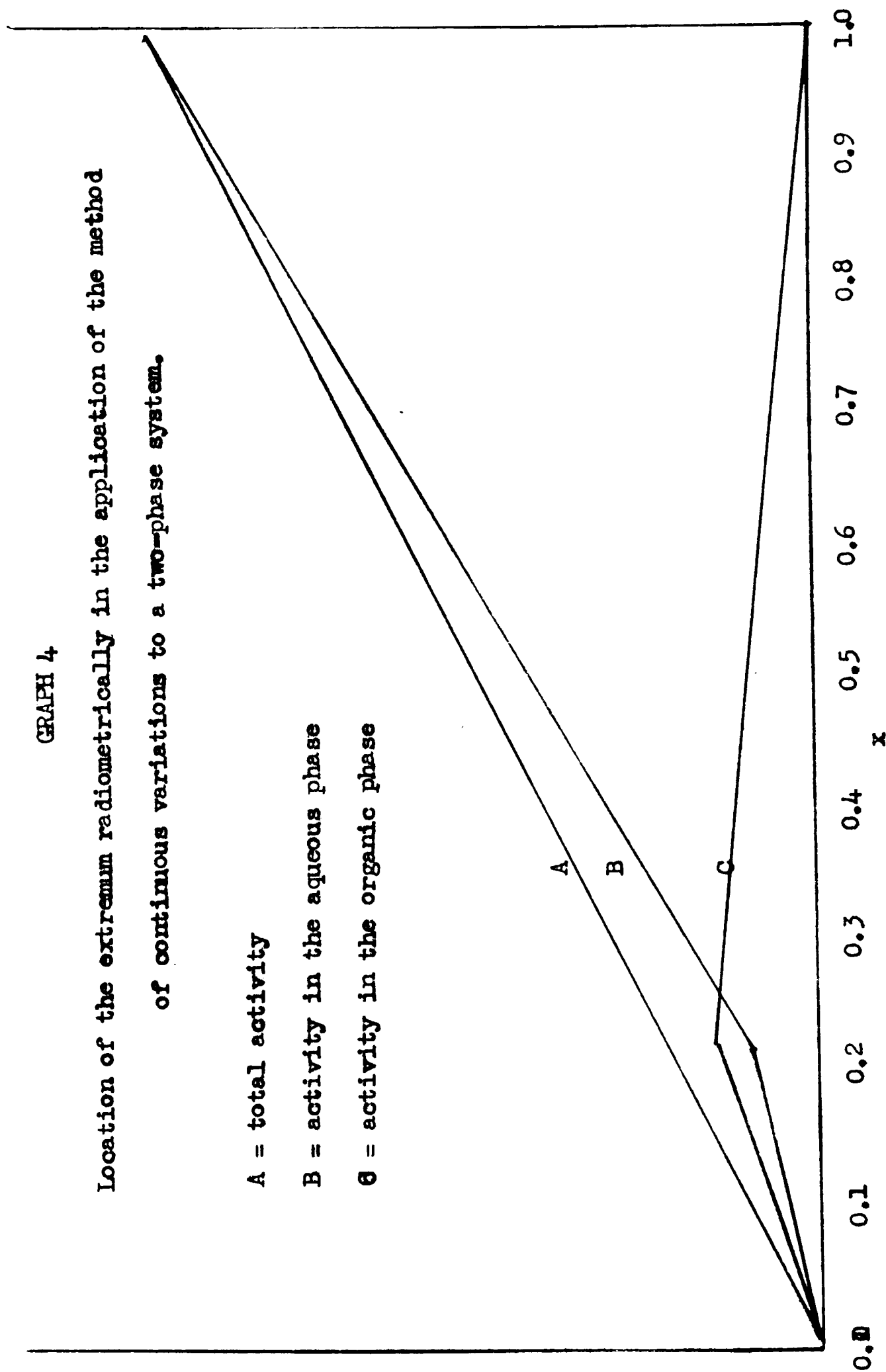
GRAPH 4

Location of the extremum radiometrically in the application of the method
of continuous variations to a two-phase system.

A = total activity

B = activity in the aqueous phase

C = activity in the organic phase



independently of the optical absorption of the possible components of the system. Indeed, by this modification Job's method of continuous variations can be applied to systems in which all the reactants and products are optically transparent.

Errors in Concentration Measurements.

A fundamental postulate in the method of continuous variations is that the total molar concentration of metal and ligand should remain the same while x is varied. This is usually met by examining mixtures prepared from xV ml. of a stock solution of metal with $(1 - x)V$ ml. of a stock solution of ligand of exactly the same molarity. We now propose to consider what errors will be introduced if these two stock solutions are not equimolar, but of concentrations C and C' respectively.

In a one-phase system, where the concentration of the complex at equilibrium is assumed to be given by $[ML_n] = \alpha C'$, it is easily shown that:

$$\beta_n = [ML_n] / [M][L]^n = \alpha C' / (xC - \alpha C') \{ (1 - x)C' - n \alpha C' \}^n \quad 59$$

By differentiation and insertion of the condition, $\partial \alpha / \partial x$

= 0 for the extremum, we find:

$$\begin{aligned} n &= (1 - x) / \left\{ x - \alpha (C' - C) / C \right\} \\ \text{or } x &= \frac{1}{(1 + n)} + \frac{n}{(1 + n)} \frac{(C' - C)}{C} \alpha \end{aligned} \quad 49a$$

Similarly, in the two-phase system, if $[ML_n] = \alpha C'$

and $[ML_n]_0 = p_c \alpha C'$, then :

$$n = (1 - x) / \left\{ x - \alpha (1 + p_c) (C' - C) / C \right\}$$

or

$$x = \frac{1}{(1 + n)} + \frac{n}{(1 + n)} (1 + p_c) \frac{(C' - C)}{C} \alpha \quad 49b$$

Equations (49a) and (49b) reduce to equation (49) when $C = C'$. In the single-phase system $\alpha \gg 1$. In the two-phase system the partition coefficient $p_c \gg 1$, but the product $\alpha (1 + p_c)$ cannot exceed unity. In both cases the error in the position of the extremum will therefore be determined by the product $\left\{ n / (n + 1) \right\} \alpha \left\{ (C' - C) / C \right\}$. If a 10% error in the concentration of one of the supposedly equimolecular stock solutions is assumed, the maximum range of x values for the extremum could lie between 0.55 and 0.45 for a 1:1 complex, between 0.40

and 0.27 for a 2:1 complex, and between 0.325 and 0.175 for a 3:1 complex. Thus, even with a systematic error of 10% in making up one of the stock solutions there is little chance of wrongly identifying a 1:1 complex from the position of the extremum in a Job plot. But incorrect conclusions might easily be drawn when 2:1 or 3:1 (or higher) complexes are involved, depending on which of the two stock solutions was the stronger.

The Effect of Intermediate Complexes.

Up to this point we have assumed that the complex ML_n is in direct equilibrium with M and L, i.e. that intermediate step-complexes ML_j ($j = 1, 2, \dots, (n - 1)$) or higher complexes ($j = n + 1, n + 2, \dots$) are present only in negligible concentrations. By a careful choice of wavelengths it has been possible in some cases to establish the composition of more than one step-complex in an equilibrium mixture^{36, 39}. An obvious restriction is that each step-complex must have a sufficiently wide range of existence; more explicitly, the concentration of metal and ligand must be such that the range of values of the free-ligand concentration covered by the Job curve (and more particularly in the neighbourhood of the extremum)

should be such that the corresponding value of the degree of formation of the system $\bar{n}$, should approximate to that of n in the formula ML_n of the complex under investigation. In brief, the relevant values of $[L]$ should correspond with a plateau or at least a gently rising portion of the formation curve ($\bar{n}$ against pL) where ML_n is the predominant species. Failure to realise this condition has led a number of previous workers to draw erroneous conclusions from experimental Job curves³⁹.

It will be obvious that errors due to ignoring the presence of intermediate complexes will be greatest when the complex under investigation is extensively dissociated and where the lower complexes are of comparable stability, i.e. when the successive stability constants $K_1, K_2, \dots$ are of comparable size and not too large. Although it is impossible to formulate explicit equations for the errors caused by neglecting the effect of lower complexes, even in the simple case where $n = 2$, some insight may be gained by considering particular cases.

Consider the application of the method of continuous variations to a homogeneous system in which the complexes ML_2 coexists with ML , M and L . If the total concentration of reactants, $C = 10^{-3}M$, and $K_1 = [ML]/[M][L] = 10^5$ and

$K_2 = [ML_2] / [ML] [L] = 10^3$, it is possible to calculate conjugate values of $[L]$, $\bar{n}$, and x from the following equations:

$$\frac{\beta_1[L] + 2\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2} = \bar{n} = \frac{C_L - [L]}{C_M} = \frac{(1-x)C - [L]}{xC} \quad 60$$

Differentiation of equation (60) yields:

$$dx/d[L] = - \{1 + xC(d\bar{n}/d[L])\} / C(\bar{n} + 1)$$

from which it is clear that as x increases, since $d\bar{n}/d[L]$ is always positive, both L and $\bar{n}$ will decrease monotonically (cf. Graph 5, curve E).

The actual concentration of the complex ML_2 is given by:

$$\begin{aligned} [ML_2] &= \beta_2 M [L]^2 \\ &= K_1 K_2 [L]^2 \cdot xC / (1 + K_1[L] + K_1 K_2 [L]^2) \end{aligned}$$

and, with an optimum choice of wavelength, the value of the Job ordinate, A_j , will be proportional to this.

The results of such calculations are presented diagrammatically in Graph 5 (Curve A). As might have been expected, even on the ligand-rich side of the graph

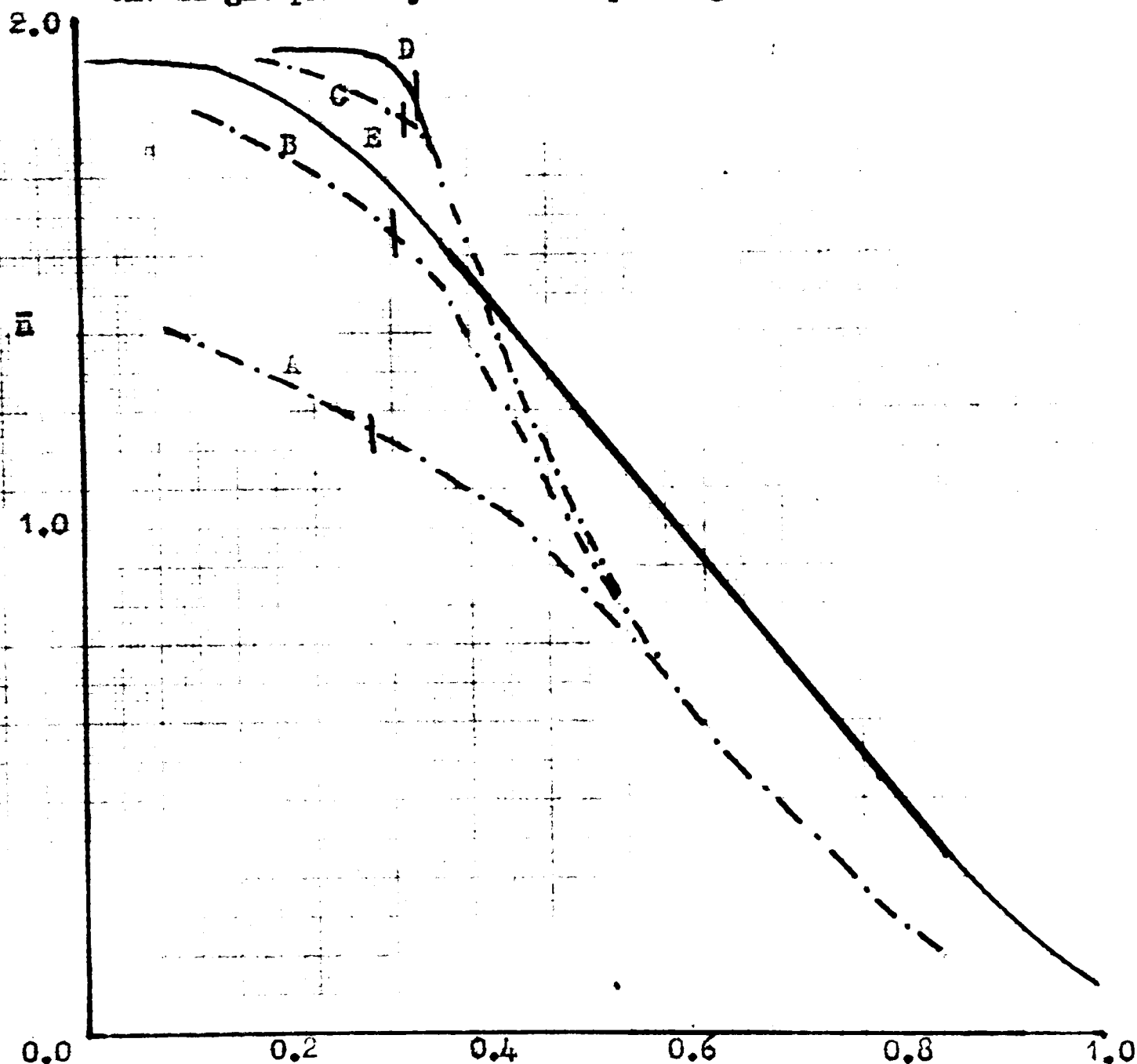
($x < 1/3$), the degree of formation of the system is very

Calculated degrees of formation, $\bar{n}$, as a function of the mole fraction, x , of metal in systems for which $\log \beta_1 = 5$ and $\log \beta_2 = 8$.

The total concentration of metal and ligand for curves A, B, and C is 10^{-3} , 10^{-2} and 10^{-1} respectively.

Curve D presents the data for a two phase system at a total concentration of 10^{-3} M where the partition coefficient of the species ML_2 is 999.

Curve E is the formation curve ($\bar{n}$ versus $pL = -\log_{10} L$) for the single phase system corresponding to curve A.



The vertical lines cutting curves A, B, C and D show where the extrema would have occurred in a Job plot.

much below 2 and the concentration of lower complex ML and of free metal ions M cannot validly be neglected. When the metal is in excess ($X \longrightarrow 1$) the degree of formation, $\bar{n}$, falls off steeply and the Job curve is markedly distorted. But of greater significance is the striking result that the maximum of the Job plot occurs when $X = 0.27$, from which the erroneous conclusion would be drawn that the complex had the composition ML_3 and not ML_2 .

If the method of continuous variations had been applied to the same system with solutions ten times as strong ($C = 10^{-2}M$), calculations on similar lines lead to the data plotted as curve B in Graph 5. Here the degree of formation is much higher (about 1.67) in the neighbourhood of the extremum; but, although this occurs at a higher mole fraction of metal ($x = 0.301$), this fraction lies between the values expected for a 1:2 complex ($x = 0.333$) and a 1:3 complex ($x = 0.250$) and the choice in practice would be still harder owing to the inevitable experimental uncertainty in measuring absorbencies.

One way of raising the proportion of ML_2 in the equilibrium mixture is to increase the concentration.

Curve C in Graph 5 is based on data obtained by calculations for the same system as before with solutions of total concentration, $C = 10^{-1}M$. In this case the extremum is found at $x = 0.321$, pointing unequivocally to a 1:2 complex. At this point the degree of formation is as high as 1.88 and about 90% of the total metal is present as the complex ML_2 .

We now consider the application of the method of continuous variations to the same system of metal complexes but postulating that the uncharged species ML_2 can be solvent extracted into an organic phase.

If V , V_0 are the volumes of the aqueous and the organic phase respectively, and C , x , and β_0 are defined as before, considerations of mass balance lead to the following equations:

$$(1 - x)CV = ([L] + [ML] + 2 [ML_2])V + 2 [ML_2]_0 V_0$$

and

$$xCV = ([M] + [ML] + [ML_2])V + [ML_2]_0 V_0$$

for the case where ML_2 is the extractable complex.

Similar equations may be written for more complex systems.

For equal phase volumes, $V = V_o$, and it follows that:

$$\begin{aligned} \bar{n}_T &= \frac{\text{Total concentration of bound ligand}}{\text{Total concentration of bound metal}} \\ &= \frac{(1 - x)C - [L]}{xC} = \frac{\beta_1 [L] + 2(1 + p_o)\beta_2 [L]^2}{1 + \beta_1 [L] + (1 + p_o)\beta_2 [L]^2} \quad 60a \end{aligned}$$

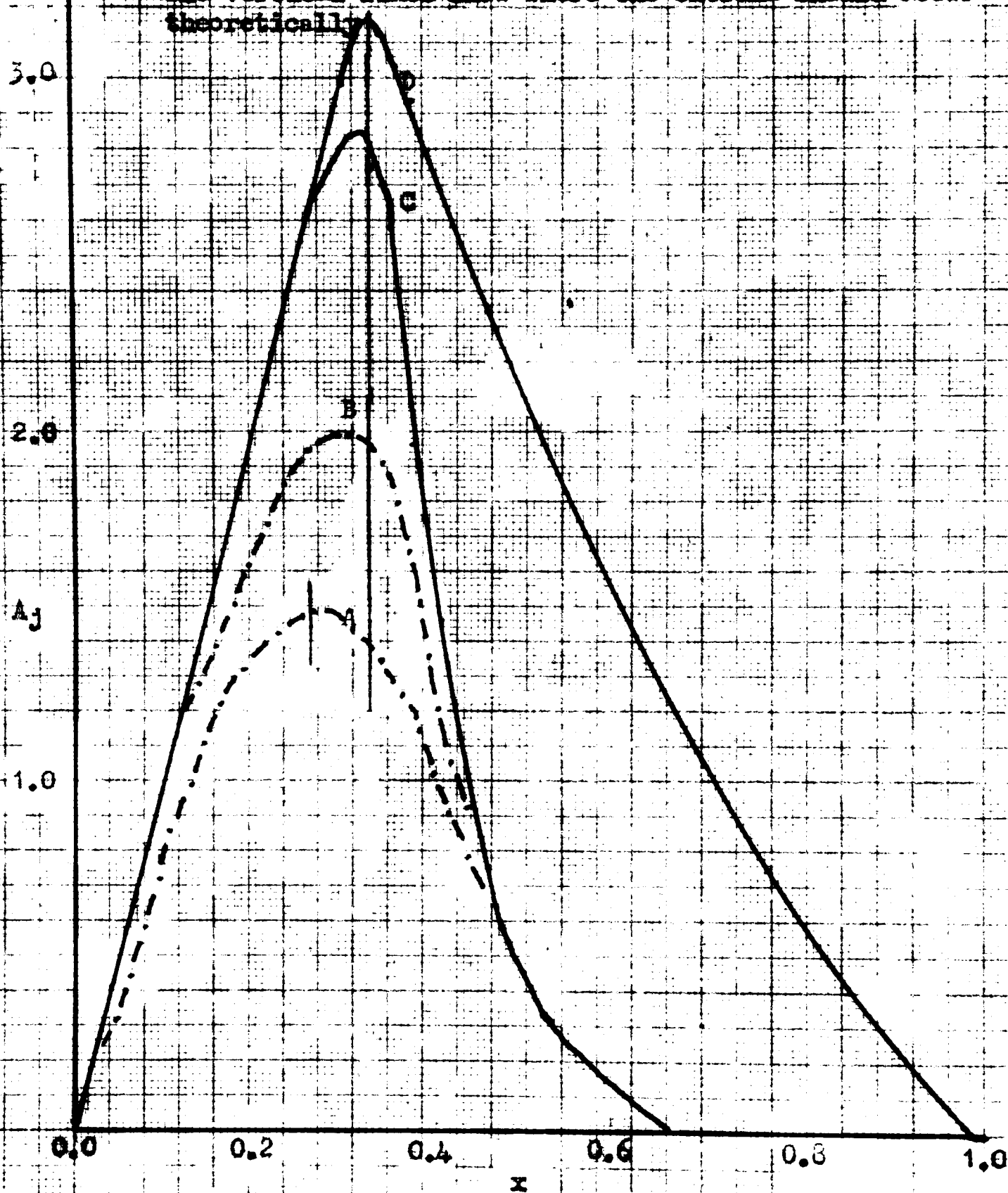
Equation (60a) is identical in form with equation (60), the only difference is that β_2 has been replaced by $\beta_2(1 + p_o)$. In other words, the degree of formation of the system as a whole corresponds to that which would result had the stability constant of the highest complex been increased by a factor $(1 + p_o)$. Since the percentage of any complex, ML_j , is given by the quotient $\beta_j [L]^j / (1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n)$, the effect of increasing the value of β_n (relative to those of β_1, β_2 , etc.) is to decrease the proportion of lower complexes ML_j ($j < n$) relative to that of ML_n itself, so that such systems approach more and more closely to the ideal case postulated in the simplified treatment of the method of continuous variations and represented by equation (47). Since the effect of solvent extraction is equivalent to increasing the important overall constant

β_n for the complex ML_n by the factor $(1 + p_o)$, the extension of Job's method to two-phase systems should have the further advantage that the position of the extremum should correspond more closely to the theoretical value, so that the possibilities of incorrect deductions should be diminished.

We illustrate this for calculations for a two-phase system with $\beta_1 = 10^5$, $\beta_2 = 10^8$, and $C = 10^{-3}M$, assuming the reasonable value of $p_o = 999$ for the partition coefficient of the complex ML_2 . The results are plotted as curve D in Graph 6. The extremum is well defined and corresponds exactly with the formation of a 1:2 complex. It will be recalled that the Job curve for this system at the same concentration in a single phase (Graph 6, A) would have suggested a 1:3 complex. At the extremum the degree of formation of the system (as a whole) is 1.94, appreciably higher than in the case of solutions even 100 times as strong (Graph 6, curve C) in a monophasic. However, since the unique extractable species has the formula ML_2 , the degree of formation in the organic phase is always two, so that the effective degree of formation in the aqueous phase is actually decreased in consequence of

GRAPH 6

The method of continuous variations applied to the metal complexes treated in graph 5. Curves A, B, and C apply to systems with total concentrations of 10^{-3} , 10^{-2} and 10^{-1} M. Curve D refers to a two phase system at a total concentration of 10^{-3} M. The vertical lines show where the extrema should occur theoretically.



solvent extraction which always removes twice as much ligand as metal.

That curves obtained by applying the method of continuous variations to a two-phase system may yet lead to the correct conclusions even though the degree of formation is very low can be illustrated by the rather extreme case presented by the solvent extraction of a metal complex (e.g. a metal-dithizone complex) for which we postulate $\beta_1 = 10^6$, $\beta_2 = 10^{10}$, and $\beta_3 = 10^{12}$. The total concentration of reactants is assumed to be as low as $10^{-4}M$ and the partition coefficient of the complex, $p_c = 7 \times 10^5$, and that of the reagent, $p_r = 7 \times 10^4$, both strongly favour the organic phase. We further postulate that the acid, HL, conjugate to the ligand is a weak one with $K_r = 10^{-4}$, and that the aqueous phase is buffered at pH 5. The equations characterising this system will be:

$$\frac{(1 - x)C - [L] \left\{ 1 + (1 + p_r) \frac{[H^+]}{K_r} \right\}}{xC} = \bar{n} =$$

$$\frac{\beta_1 [L] + 2\beta_2 [L]^2 + 3\beta_3 [L]^3 (1 + p_c)}{1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 (1 + p_c)}$$

and

and

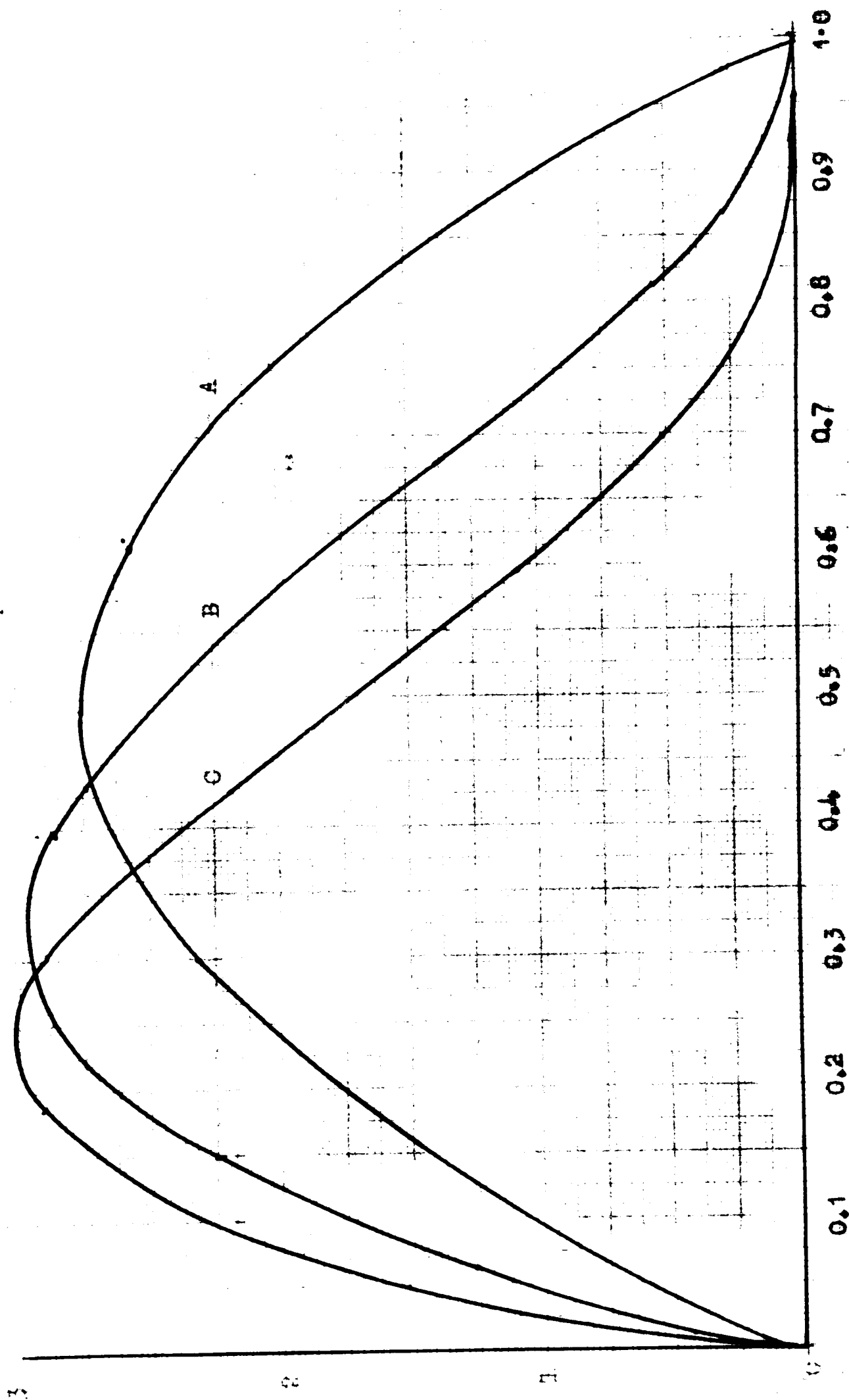
$$[ML_n] = xC_{\beta_n} [L]^n / [1 + \beta_1 [L] + \beta_2 [L]^2 + \beta_3 [L]^3 \times (1 + p_o)]$$

Since $pH = pK_r + 1$, 90% of the uncomplexed ligand acid in the aqueous phase will be in the form of free ions, L ; but the actual concentration will be very low because p_r is so large, in consequence of which the bulk of the uncomplexed reagent remains in the organic phase. Notwithstanding, the results calculated and plotted in Graph 7 indicate clearly that the maximum concentration of the species ML_3 in the organic phase does occur when $x = 0.33$.

It is of interest that if one of the intermediate species had been coloured it would have been possible to apply the ordinary Job procedure to the aqueous phase at the same time in order to establish its composition.

In the two-phase systems, the decrease in free ligand concentration due to the extraction of the ligand acid into the organic phase is compensated by the apparent increase in the stability constant from its true value β_3 to its "effective" value $\beta_3(1 + p_o)$ which produces a great increase in the degree of formation of the species

GRAPH 7



The variation in the concentration of the species ML, ML₂ and ML₃ in the aqueous phase of a two phase system. The ordinates of curves A, B and C must be multiplied by 0.77×10^7 , 10^{11} and 10^{17} respectively to give the actual concentrations of the species ML, ML₂ and ML₃.

ML_3 (relative to that in a mono-phase with the same free-ligand concentration) and causes the system to approach more closely to the ideal case postulated in equation (47).

Had the equilibria discussed above been established in a monophasic (so that $p_o = p_r = 0$ in the relevant equations) the degree of formation in the aqueous phase at equal values of x would be found to be higher than that in the aqueous phase of the preceding case. However, the way in which the concentrations of the species ML , ML_2 , and ML_3 now vary with x is shown in Graph 8, and it is clear that if the method of continuous variations had been used to ascertain their composition the species ML_3 could have been identified as a 5:1 complex and the species ML_2 as a 2:1 complex.

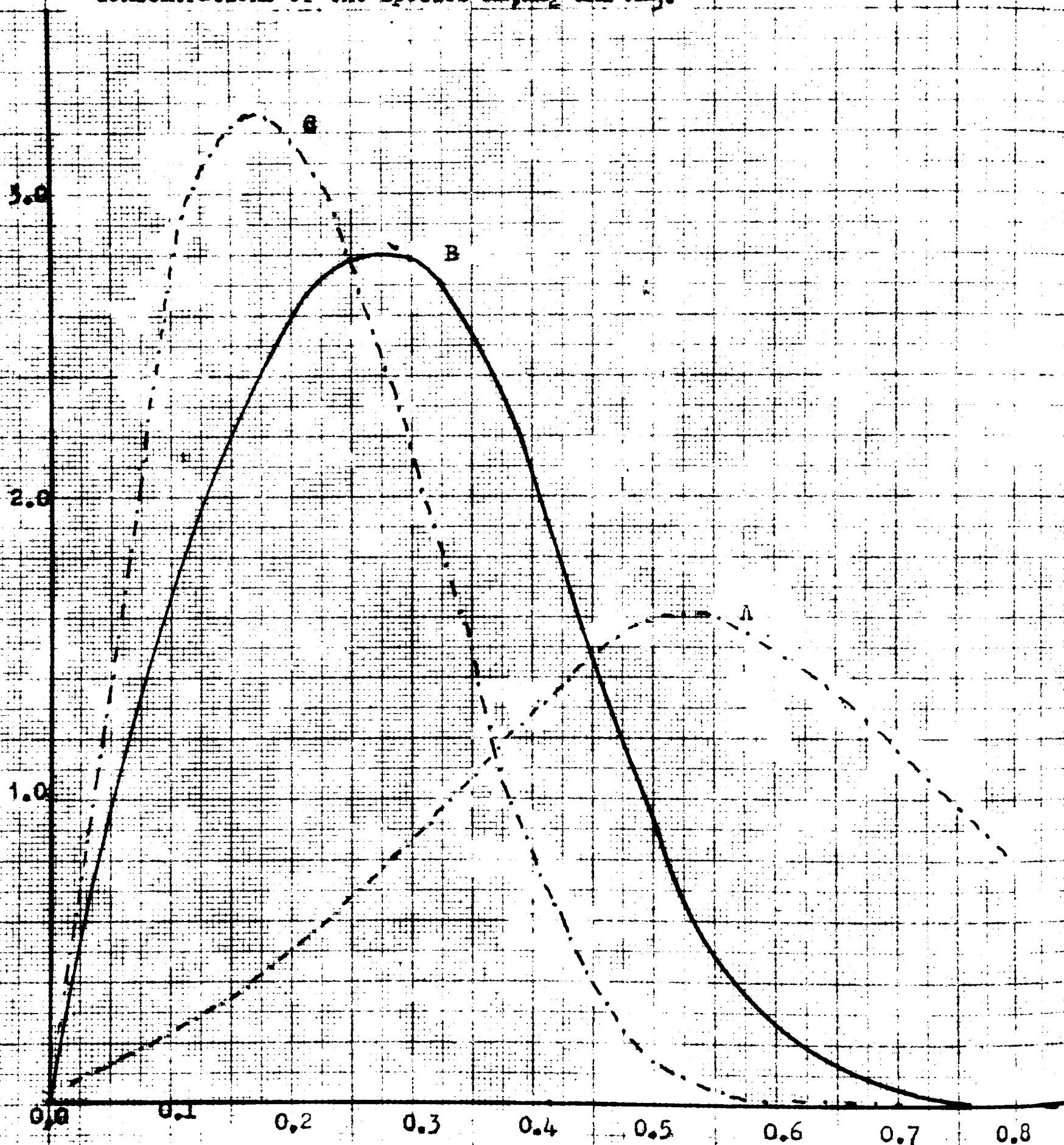
Calculation of Stability Constants from Job Curves.

The Job curve for a 1:1 complex has its extremum when $x = 0.5$, and the degree of flattening in this neighbourhood is a measure of the extent of its dissociation into the components M and L . Indeed the ratio of the measured value of A_j at the extremum to the value

GRAPH 8

The method of continuous variations applied in a monophasic to the system treated in graph 7.

The ordinates of the curves A, B and C must be multiplied by 2.5×10^{-5} , 2.5×10^{-6} and 10^{-8} respectively to give the actual concentrations of the species ML , ML_2 and ML_3 .



obtained by the intersection of the tangents at $x = 0$ and $x = 1$ forms an accurate measure of the concentration term $[ML]$, whence $[M] = [L]$ can be calculated and thence the stability constant⁴¹. Although this treatment is rigorous when applied to systems in which only a 1:1 complex is formed it should be obvious from the foregoing discussion that it cannot validly be extended to calculations of the stability of higher complexes ML_2 , ML_3 , etc. unless it is possible to demonstrate that lower complexes do not contribute materially to the equilibrium mixture, i.e. unless $\beta_1, \beta_2, \dots \ll \beta_n$. The geometric construction needed to obtain the value of the Job ordinate corresponding to no dissociation (e.g. by drawing tangents to the curve at $x = 0$ and $x = 1$) may be subject to considerable error, especially on the ligand-rich side of the diagram (cf. Graphs 6 and 8). Confronted with this difficulty some authors have identified the "theoretical" value of A_1 , corresponding to no dissociation of the complex ML_n , with the point of intersection of the tangent to the Job curve at $x = 0$ (since this is usually well defined) and the ordinate through $x = 1/(1 + n)$. Unless the extremum of the Job curve also coincides with

this value of x , the ratio of the experimental to the calculated value of A_j will not give a correct measure of the concentration of the species ML_n . In any case, for any value of β_n computed from this ratio alone tacitly it is assumed that all lower complexes are of negligible stability. These objections do not appear to be generally appreciated, as may be seen from a number of publications in recent years³⁹.

CALCULATION OF EXTINCTION COEFFICIENTS FROM PARTITION

DATA

Making the same assumptions as in the method of continuous variations we may define the distribution coefficient q by

$$q = \frac{[ML_n]_o}{[ML_n] + [M^{n+}]} \quad 61$$

From equation 52 and assuming p_o to be large compared with 1

$$\frac{1}{q} = \frac{x_c - \alpha C p_o}{\alpha C p_o} \quad 62$$

If besides measuring the radioactivity of both phases the optical absorbancy of the species ML_n in the organic phase is measured

$$A = \alpha C p_o \epsilon d \quad 63$$

where A is the absorbancy of the organic phase, ϵ is the extinction coefficient and d is the cell length in cms.

From 62 and 63

$$\frac{1}{q} = \xi \frac{xC}{A} d - 1 \quad 64$$

So that the plot of $1/q$ against xC/A should give a straight line of slope ξd , or, if $d = 1$ of slope ξ .

Determination of the formation constant K_f

The formation constant of a metal complex ML_n may be defined as

$$K_f = \frac{[ML_n]}{[M^{n+}][L^-]^n} \quad 65$$

Hence

$$\frac{[ML_n] + [M^{n+}]}{[ML_n]_0} = \frac{K_f [M^{n+}][L^-]^n + [M^{n+}]}{[ML_n]_0} \quad 66$$

Making use of equations 1 and 61

$$\frac{1}{q} = [M^{n+}] \left[\frac{\frac{K_f^n [HL]^n}{[H^+]^n} \cdot K_f + 1}{[ML_n]_0} \right] \quad 67$$

Finally from equations 52, 53 and 67

$$\frac{1}{q} = [xC - \alpha C(1 + p_0)] \left[\frac{K_f K_f^n (1 - x)C - n\alpha C(1 - p_0) n[H^+]^n}{[H^+]^n \alpha C_T} \right] \quad 68$$

Since αC_p may be found from optical measurements, provided p_r and K_r are known, K_f may be calculated.

The Determination of partition coefficients.

The investigation of certain aspects of solvent extraction from the theoretical point of view has led, as has been seen in the previous section, to a possible method for the determination of the true acid dissociation and stability constants of chelates which are only slightly soluble in water, but which are appreciably soluble in an organic phase.

From the foregoing equations it can be seen that before K_f may be found the partition coefficient and acid dissociation constant of the complexing agent must be determined.

The measurement of the partition coefficient is likely to prove very difficult experimentally and so an attempt was first made to devise a method by which this quantity could be determined.

A concentration partition coefficient, defined by

$$p_r = \frac{\text{Concentration of chelating agent in the organic phase}}{\text{Concentration of chelating agent in the aqueous phase}}$$

should be determinable by any method which will allow the measurement of the concentration of chelating agent in both phases. Unfortunately, however, although their solubility in an organic phase is reasonably large, often in excess of 1 gram per litre, the partition coefficient of many chelating agents is very large, and measurement of the low concentration in the aqueous phase is a particularly difficult matter. If the substance has a high extinction coefficient, separation of the aqueous phase followed by extraction into a much smaller volume of organic phase may provide sufficient colour to enable accurate spectrophotometric measurements to be made. This has been done for tropolone with satisfactory results⁴².

A saturated aqueous solution of diphenyl thio-carbazone, ϵ_{max} of the order of 3×10^4 , will have a concentration of the order of only 10^{-7} moles per litre, so if 4 cm. cells are used for measurement after a 10 fold concentration, an optical density of 0.12 will be found. This is still a very low value and little confidence can be placed upon results obtained from solutions of higher transmittancies than this.

A method likely to provide greater sensitivity may be devised using a radioactive isotope.

After equilibration, the two phases are separated, and each treated with an isotope of the metal, which forms a complex with the particular chelating agent being investigated.

If the chelating agent in the aqueous phase is completely converted into chelate by adding excess of metal, and this is then extracted quantitatively into an organic phase, assay of the radioactivity of this solution will give a measure of the concentration of the metal chelate, and hence that of the original chelating agent in the aqueous phase.

Similarly if the organic half of the equilibrium mixture is shaken with an aqueous solution containing excess metal, metal chelate will be formed. If all the chelating agent is converted to complex and this is quantitatively extracted into the organic phase, assay of the activity of the organic phase will enable the original concentration of the chelating agent in the organic phase to be calculated.

If the aqueous phase has been concentrated m times and if a_s is the specific activity of the metal under given conditions of counting, c is its concentration and Λ the absorption factor of the organic phase, the count of the organic phase will be given by

$$N_1 = a_s c_1 \Lambda \quad 69$$

For the solution containing the chelate, which was originally in the aqueous phase, after a m fold concentration will be

$$N_2 = a_s c_2 m \Lambda \quad 70$$

Hence from 61 and 62

$$\frac{N_1}{N_2} = \frac{c_1}{c_2} m$$

If the stoichiometry of the complex is $1:n$, the ratio of the metal concentrations c_1/c_2 in the two phases will be equal to that of the ligand $nc_1/nc_2 = p_r$

$$p_r = \frac{A_1}{A_2} \cdot m \quad 71$$

Thus direct radiochemical assay and knowledge of the concentration factor m will enable p_r to be found. If the specific activity, a_s , of the metal is high a very sensitive method is available for the determination of the concentration of the chelating agent. The apparent value of a_s may be increased by using a radiation detector of high sensitivity, and the overall sensitivity of the method is enhanced by making λ as low, and m as high as possible.

Due to the very low concentration of ligand in the aqueous phase it will facilitate measurement if the system is as near saturation as is possible, since at saturation the concentration of the ligand in the aqueous phase is at its maximum.

The partition coefficient obtained in this way for a solute distributed between two immiscible phases should be similar to the solubility ratio. This however is only true if, in the first place, the ratio of the activity coefficients of the solute remains in the two phases unchanged as the total solute concentration increases and in the second place there is no appreciable miscibility of

the solvents. Serious discrepancies may occur if there is actual complex formation between the solvent and the complex but compounds of this type were not expected to occur between substituted dithizones and the solvents used.

Since the concentration of the ligand in the organic phase is likely to be of the order of 10,000 times that in the aqueous phase, a major source of error in these partition measurements is likely to be that caused by incomplete separation of the phases, because very small quantities of organic phase entrapped in the aqueous phase will make an appreciable difference in its apparent ligand concentration. It would therefore appear preferable to calculate the partition coefficient from the ratio of solubilities, since solubility measurements can be carried out in the absence of the second phase.

Whilst measurement of the solubility of the ligand acid in the organic phase is unlikely to present much difficulty, Sandell has pointed out that equilibrium is established exceedingly slowly between an aqueous acid

and solid dithizone and the overall results are more satisfactory if a little organic phase such as carbon tetrachloride is present. Experiments were carried out which verified this. Sandell also noted that equilibrium was attained more quickly from the supersaturated side as opposed to the unsaturated side, the comparative times being a few minutes and an hour respectively.

From the foregoing discussion two points become evident. In the first place the system must be as near saturated as possible to give the maximum concentration of ligand acid in the aqueous phase. Secondly, in order to establish equilibrium, an organic phase must be present. Consequently partition coefficients of dithizone and its related compounds were found from solubility measurements, making sure when determining the solubility in an aqueous phase, that the organic solvent present did not appreciably alter the solubility of the dithizone in water⁴³.

Optical methods were used wherever possible to determine the actual solubility of the chelating agents in the various solvents used, and to do this the

extinction coefficients of the ligands had to be found.

This was done in one of two ways; either by the standard titration method⁴⁴ or by a new radiochemical method.

The absorbancy of any solution is given by $A = \epsilon cd$. Thus if the absorption of a solution of complex in an organic phase of known extinction coefficient, is measured, the concentration of the solution will be given by

$$c_1 = \frac{A_1}{\epsilon d}$$

If this is converted to the complex ML_n by adding excess of a radio-isotope in an aqueous solution, then c/n will be the concentration of the metal and

$$\frac{c_1}{n} = \frac{A_1}{\epsilon, dn} \quad 72$$

From equation 69 the count obtained under given counting conditions will be given by

$$N_1 = a_s \frac{c_1}{n} \Lambda \quad 73$$

Combining 64 and 65

$$a_s = \frac{N_1 \epsilon_1 d_1 n}{A_1} \quad 74$$

If the same procedure is carried out for a second ligand also forming a $n:1$ complex for which ϵ_2 the extinction coefficient is not known then

$$a_s \Lambda = \frac{N_2 \epsilon_2 d_2 n}{A_2} \quad 75$$

And from 74 and 75

$$\epsilon_2 = \frac{A_2}{A_1} \frac{N_1}{N_2} \frac{d_1}{d_2} \epsilon_1 \quad 76$$

All quantities except ϵ_2 are known thus ϵ_2 may be calculated.

The disadvantage of this method over a titration method is that standardisation measurements must be made using a ligand whose extinction coefficient is accurately known.

The advantages are that the radiochemical method is more sensitive and may be used to provide accurate

results for very dilute solutions. Also the strength of the metal solution is not important provided that excess is present, which obviates errors that might occur due to absorption of metal on glassware from the exceedingly dilute solutions often needed for titrations.

Solubilities of some dithizonates

Table 19

Solvent	Water $\times 10^{-7}$	Carbon tetra- chloride $\times 10^{-3}$	Chloroform $\times 10^{-3}$	benzene $\times 10^{-3}$
Dithizone	2.82	2.00	69.53	4.84
Di(p-fluorophenyl) dithizone	1.36	0.22	4.83	1.36
Di(p-chlorophenyl) dithizone	1.79	0.39	5.89	
Di(p-bromophenyl) dithizone	1.39	0.18	1.19	
Di(p-tolyl) dithizone	3.23	10.3	50.7	

The determination of the formation constant of Indium

Dithizonate.

Indium dithizonate, in common with most metal dithizonates is only very slightly soluble in water, but appreciably soluble in organic solvents. Investigations have been limited by its unstable character (stable between pH 5 and 6 when extracted into carbon tetrachloride) but it is reported to be a 3:1 complex³⁸ with an extinction coefficient of 87×10^3 and a (mixed) formation constant

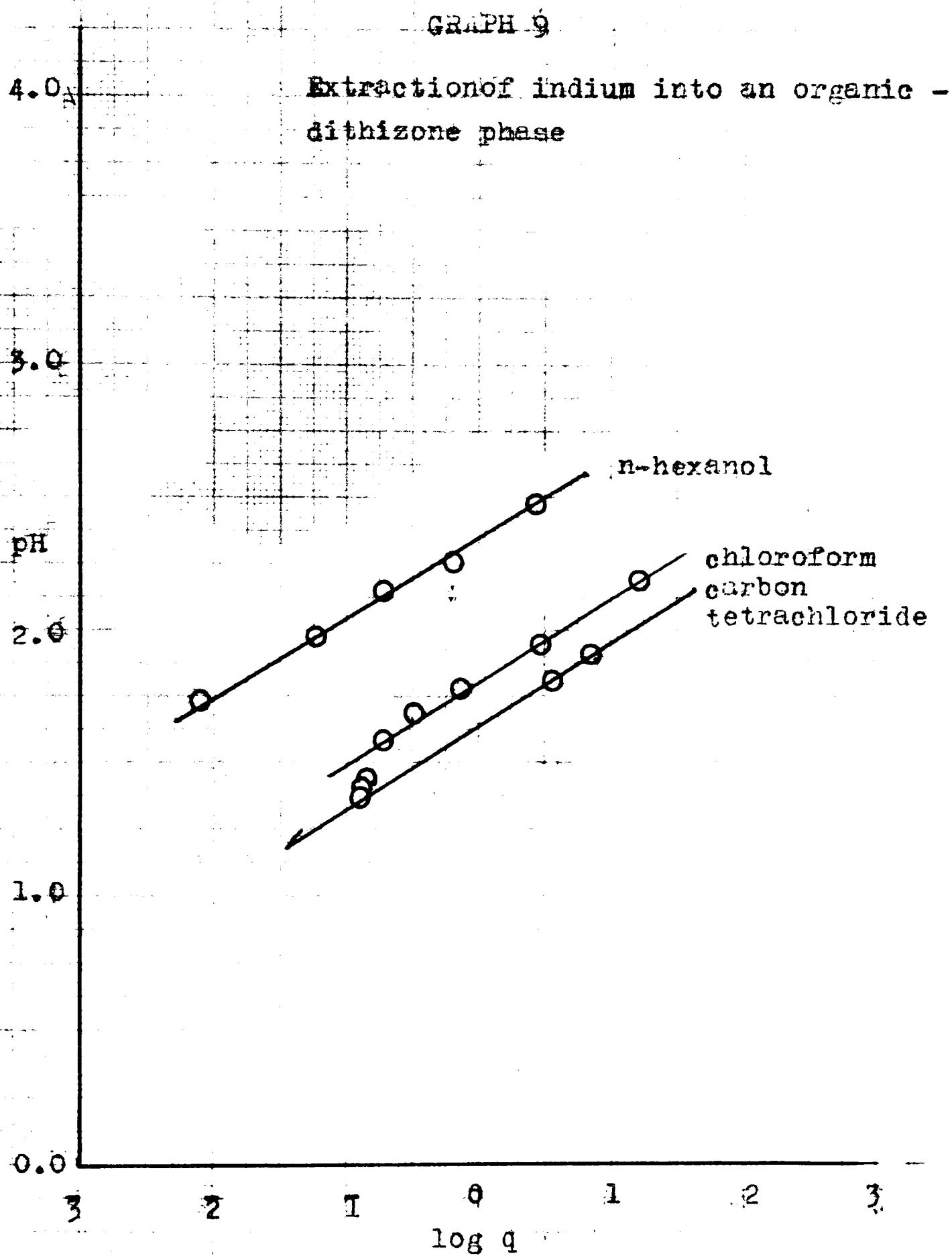
$$K_f = \frac{[\text{InDz}_3]_o}{[\text{In}^{3+}] [\text{Dz}]^3} = 8.62 \times 10^{30}$$

It was decided to investigate indium dithizonate by means of the method of continuous variations in a two phase system, and since the method was being used for the first time, the stoichiometry was checked by a second solvent-extraction method.

From equation 7 it may be seen that

$$\log q = \log K + n \log [\text{HR}]_o - n \log [\text{H}]$$

If considerable excess of reagent is present, then a plot of $\log q$ against pH should give a straight line of slope n .



Extraction - pH data was obtained for indium dithizonate with carbon tetrachloride, chloroform, and n-hexanol as organic phases and the resulting plots are given in graph (9).

From this it can be seen that in all three cases $n = 3$.

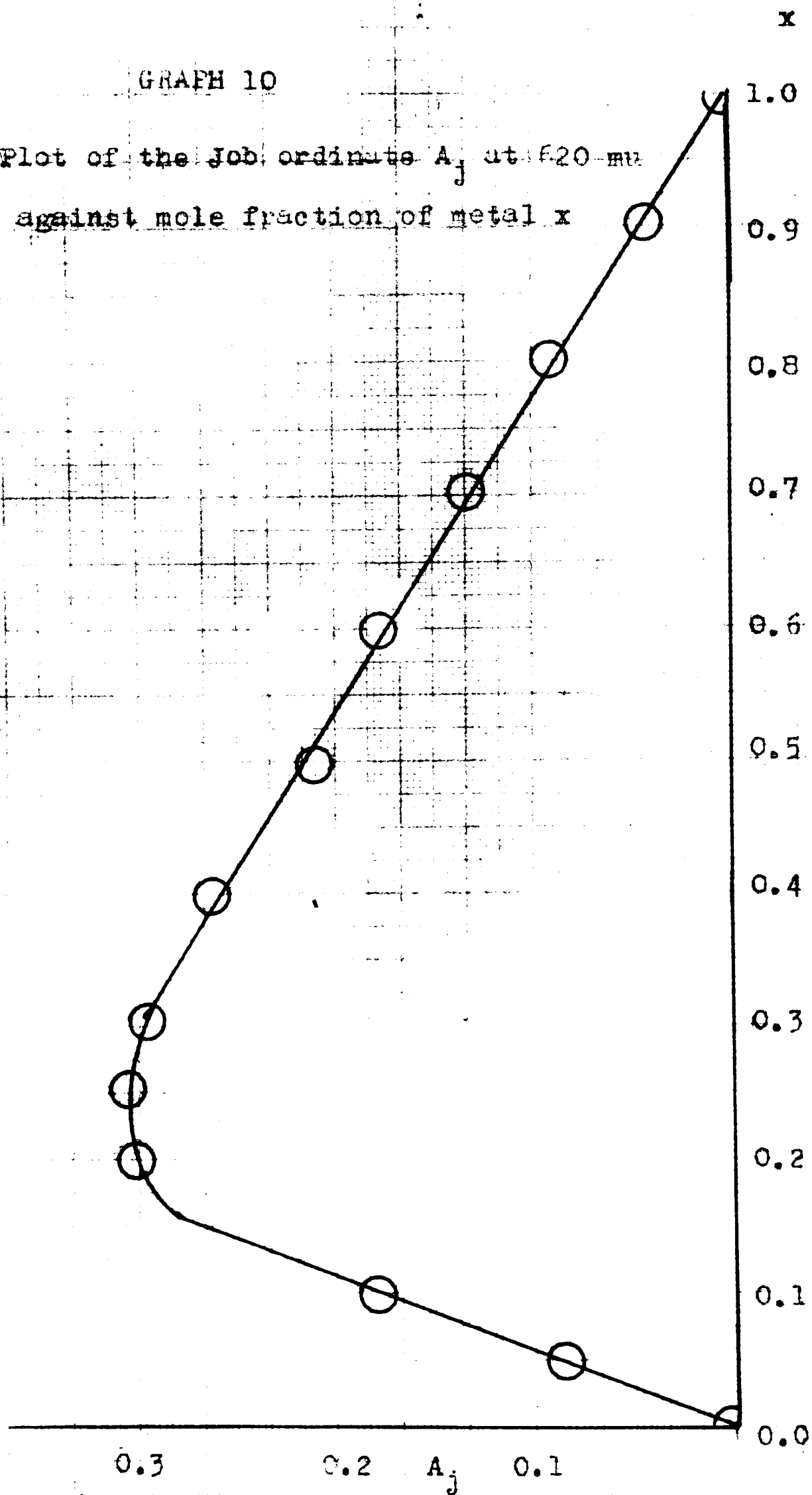
The method of continuous variations was applied to the indium - dithizone - carbon tetrachloride - water system using labelled indium. Full details are given in the experimental section.

The plots of the Job ordinate at 620 mμ and 510 mμ against the mole fraction of indium are given in graphs 10 and 11. It can be seen that the extrema occur at the point where the mole fraction of metal in the system is 0.25, implying a 1:3 complex, in agreement with extraction data already mentioned.

A plot of radioactivity of each of the phases against mole fraction of metal may be seen in graph 12. From the similarity between this graph and graph 4 it is obvious that the experimental results agree with those expected from the theoretical argument deduced earlier. The turning point once more occurs when the mole fraction

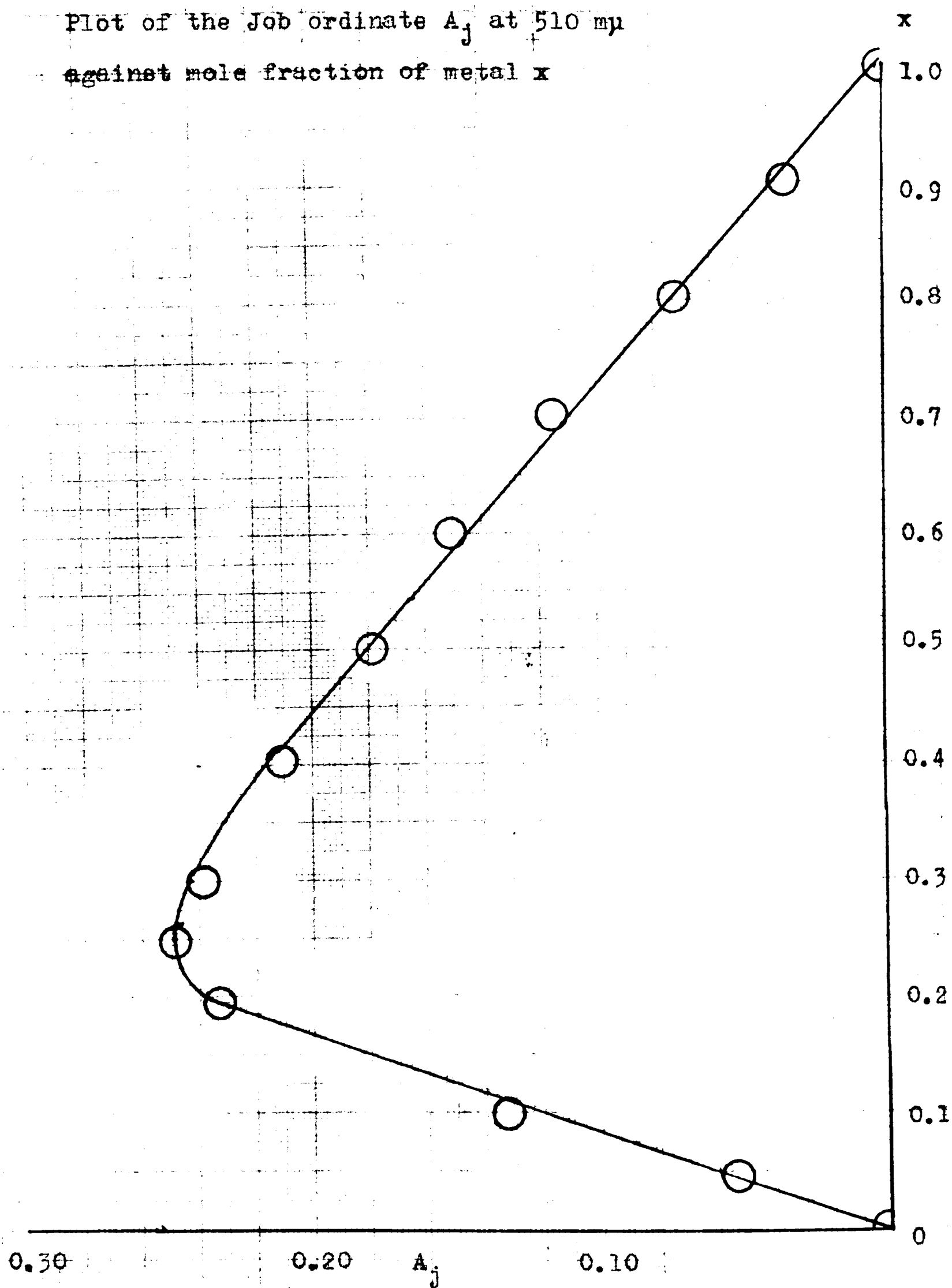
GRAPH 10

Plot of the Job ordinate A_j at 620 m μ
against mole fraction of metal x



GRAPH 11

Plot of the Job ordinate A_j at 510 m μ
against mole fraction of metal x



of the metal is 0.25 indicating a 1:3 complex.

By inserting values in equation (64) the plot of $0x/A$ vs. $1/q$ in graph 13 is obtained, whence the slope gives the value of 86.1×10^3 for the extinction coefficient, in good agreement with Pililenko's value of 87×10^3 .

Finally, by making use of equation (68) the following values of K_f were calculated.

x_C	$10^{26} \times K_f$
0.2	2.35
0.25	1.63
0.3	0.80
0.4	1.26
0.5	1.97
0.6	0.99
Mean	1.5 ± 0.75

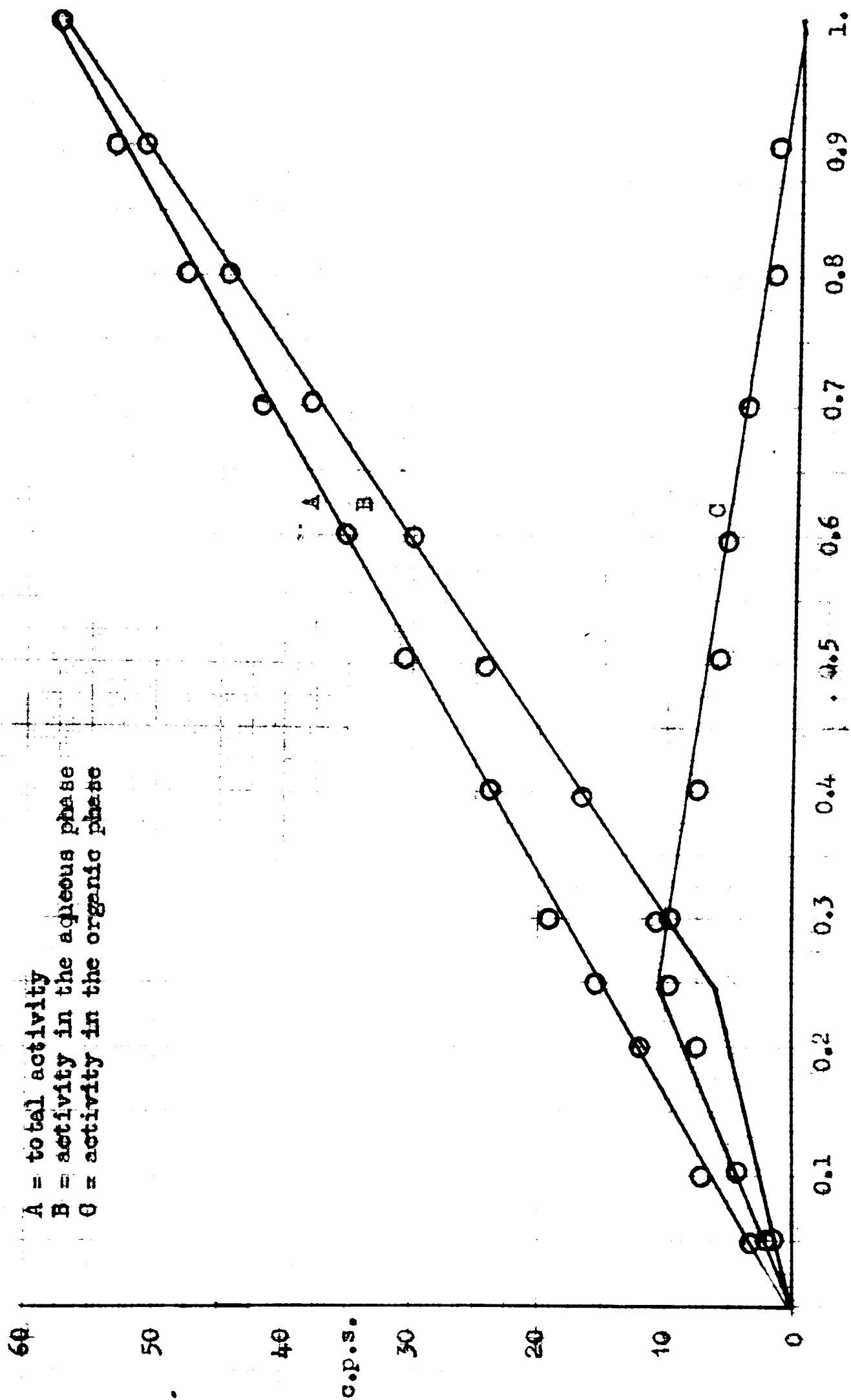
Calculations were not carried out on measurements obtained from solutions of very low ligand or metal content, since under these conditions it is not possible to measure either the distribution ratio or the optical density of the metal complex with sufficient accuracy.

If the value for K_f is taken as 1.5×10^{26} , then by using the value for K_f' already quoted

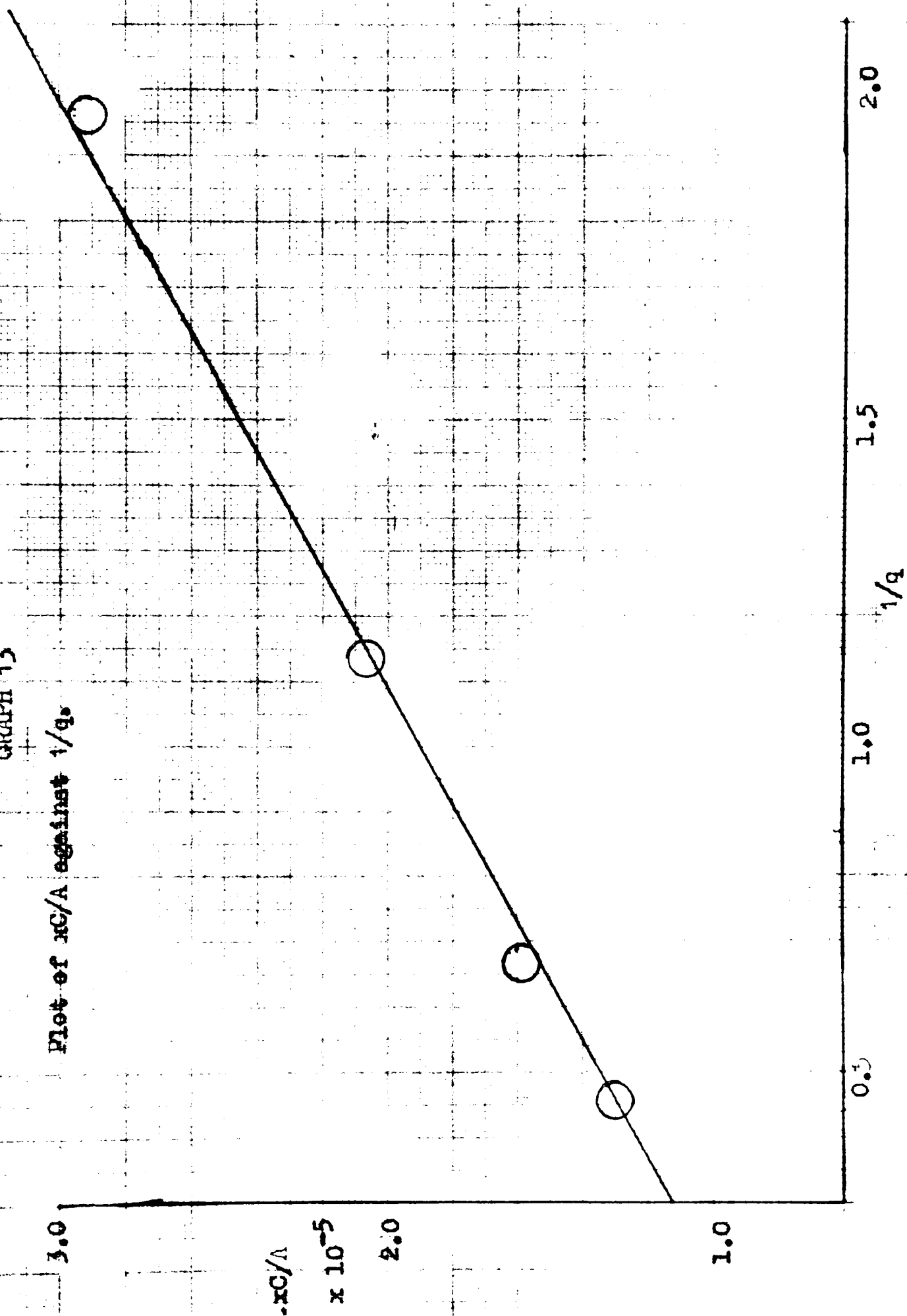
$$p_0 = K_f'/K_f = 5.75 \times 10^4$$

GRAPH 12

Plot of the radioactivity of both phases against the mole fraction of metal.



GRAPH 13

Plot of $\kappa C/\Lambda$ against $1/q$.

EXPERIMENTAL SECTION

General

A series of radiation detectors were available for counting α , β or γ rays, the choice of counter depending upon the radioisotope used. Since most of the activity was γ , and in solution, scintillation counters for counting liquids were most frequently used.

Two different crystals could be incorporated into the counter. One was a well - type crystal $2\frac{1}{2}$ inches in diameter, into which was placed a plastic phial of diameter 0.6 inches, which contained the liquid; the other was a smaller crystal 0.6 inches in diameter, which fitted into the centre of a specially shaped polythene cup. The well-type assembly provided higher geometry and resolution, and only two mls. of liquid were needed. However, since the cups for the smaller crystal held 10 mls. of solution the overall count rate was higher for a given solution in consequence of the increased quantity of liquid, than if the well crystal was used. The crystals were used in conjunction with a wide-band

amplifier, a single-channel pulse-analyser and standard scalars. Provision was made for connecting the scalars in tandem if a high counting rate precluded the use of a mechanical register.

For work with radioactive indium a Geiger counter (20th Century Electronics Type M6) designed for liquid counting was used. Since the liquid container is an integral part of the counter. The absorption of any radioactivity on the walls of the container, which is unavoidable with silver, will increase the apparent background of the counter and eventually make it useless. Consequently metals which are likely to cause contamination must be avoided. With the well crystal set up, only the phials are likely to be contaminated and since these are relatively inexpensive they may be disposed of.

All counts given in the experimental section have had the background deducted and are the average of at least three separate counts. Wherever possible the total number of counts was 10,000, to obtain a statistical accuracy of 1%.

Purification of reagents and cleansing of apparatus.

Due to the sensitivity of dithizone to small amounts

of metals great care must be taken to purify solvents and clean glassware.

In order to remove metals from water it was first distilled from an all-Pyrex still and then passed through an Elgastat mixed-bed deioniser, and accepted only if it had a resistance of more than 4×10^6 ohms per centimeter.

Glassware was soaked in a chromic acid bath, then in a 1:1 nitric acid bath and, after washing with deionised water, it was shaken with a very dilute solution of dithizone.

The glassware was considered clean enough if the dithizone retained its light green colour.

Before use with silver the glassware was treated in the following manner.

1 cc. of "Repelcote" silicone water repellant (Hopkin and Williams) was diluted with a little benzene, and any surface that was likely to come into contact with metal was washed with this solution. The apparatus was then placed in an oven and baked at for 110°C . over night. This treatment provided a most satisfactory silicone coating which reduced to negligible proportions the absorption by

silver on glassware.

Co-precipitation of silver.

With mercuric sulphide.

A series of solutions were made up containing 40 mls. of hydrochloric acid of various concentrations, 1.0 ml. of 0.1 M mercuric chloride solution, 0.4 ml. active silver solution containing approximately 2 μ g of silver per ml. and 2.0 mls. of thioacetamide solution (2.6 g. in 50 mls.). The mixture was placed in a large centrifuge tube (capacity 50 mls.) which in turn was placed in a water bath, and was stirred by a small glass paddle driven by an electric motor.

The water in the bath was gradually brought up to boiling by which time the mercuric sulphide precipitate had formed.

After cooling, the tube and contents were centrifuged, the supernatant liquid withdrawn, its activity counted and the acidity ascertained by titration with standard alkali.

The count was compared with that obtained from a standard made up by adding 0.4 mls. of silver solution to 43 mls. of dilute nitric acid.

A check on the mass balance was made by dissolving the precipitate, after centrifuging, in the minimum of concentrated nitric acid, diluting to 43.4 mls. and counting. The count rate observed can be seen to be in good agreement with the count rate of the standard.

For the most acid solution (experiment A) a second addition of mercury solution was made, but this did not increase the efficiency of the co-precipitation appreciably.

Table 6

Solution	Acid strength	Count of liquid	% Co-precipitated
A	5.30 N	1.57 c.p.s.	92.55 %
B	4.14	0.34	98.4
C	2.79	0.29	98.6
D	1.40	0.23	98.9
E	0.91	0.11	99.5
F	0.54	0.10	99.5
G	0.32	0.08	99.6
H	0.13	0.08	99.6

The average count for a number of different standards was 21.12 c.p.s.

The following solutions had the supernatant liquid decanted and the precipitate dissolved in warm concentrated nitric acid, which was then diluted to 43.4 mls.

Table 7

Solution	Count
A	19.5 c.p.s.
B	20.7
C	20.94
D	20.9

Co-precipitation with copper in a sulphuric acid medium

Exactly the same method was used as for mercury, explained in the previous section except that 1.0 ml. of 0.1 M copper sulphate was added instead of mercuric chloride, and sulphuric acid was used. The value of the standard was the same 21.12 c.p.s.

Table 8

Solution	Acid strength	Count of liquid	% Co-precipitated
A	9.05 N	0.16 c.p.s.	99.25 %
B	6.3	0.12	99.43
C	4.55	0.06	99.72
D	3.21	0.07	99.64
E	2.02	0.11	99.5
F	1.05	0.15	99.3
G	0.52	0.15	99.3

Mercury and sulphuric acid

The method was again the same. The mercury was

added as mercuric sulphate solution

Table 9

Solution	Acid strength	Count of liquid	% Co-precipitated
A	8.5 N	0.13 c.p.s.	99.39 %
B	6.6	0.10	99.53
C	4.4	0.17	99.19
D	2.26	0.01	99.95
E	2.06	0.07	99.97
F	1.04	0.06	99.72
G	0.5	0.05	99.75

Lead and hydrochloric acid

Table 10

Solution	Acid strength	Count of liquid	% Co-precipitated
A	0.001 N	0.132 c.p.s.	99.38 %
B	0.01	0.266	99.87
C	0.02	0.303	99.57

Thallium

A series of experiments were carried out in which thallium was used as carrier in a sulphuric acid medium. There was no evidence from these results, obtained over widely varying acid and thallium concentrations, that thallium would prove an efficient carrier for silver and consequently this line of research was discontinued.

Co-precipitation as telluride.

30 mls. of hydrochloric acid solution were pipetted into a large centrifuge tube. To this was added 1 ml. of tellurium solution (100 mg. Te in 100 ml. of a hydrochloric acid solution containing 10 mls. concentrated hydrochloric acid per 100 mls. of solution) and 0.4 mls. of active silver solution.

As before, after allowing the precipitate to form, the mixture was centrifuged and the count of the liquid ascertained.

Table 11

Solution	Acid strength	Count of liquid	% Co-precipitated
A	8.0 N	0.28 c.p.s.	98.45 %
B	6.1	0.01	99.95
C	4.3	0.06	99.72
D	2.1	0.05	99.78
E	1.4	0.03	99.86
F	0.8	0.04	99.81
G	0.06	0.06	99.72
H	0.01	0.05	99.76

Co-precipitation of silver by means of tellurium in the presence of tannin.

From the previous experiment it can be seen that tellurium provides a suitable method for the collection

of silver from aqueous solution. Since, however, there is likely to be suspended organic matter in effluent, the efficiency of the process must be investigated in the presence of organic material.

Solutions of tannin of varying strengths were made up in 2N hydrochloric acid and 30 mls. of these solutions, together with 10 mls. of stannous chloride solution, and 0.4 mls. of active silver solution, placed in a large centrifuge tube.

After precipitation the mixture was centrifuged and the activity of the aqueous layer determined.

Table 12

Solution	Strength of tannic acid	Aqueous count	% Co-precipitated
A	1 g./l.	0.12 c.p.m.	99.43 %
B	3	0.12	99.43
C	5	0.14	99.33
D	7	0.11	99.48
E	8	0.09	99.57
F	10	0.15	99.29
G	12	0.10	99.53
H	15	0.07	99.67

It was noticed that with strong tannic acid solutions (ca 30 g./l.) although a dark precipitate was formed upon the addition of stannous chloride solution, it did not settle, due to the high viscosity of the solution, and

centrifuging did not appear to help.

Co-precipitation of silver from synthetic effluent by
means of tellurium.

Synthetic effluent was made up containing 100 μg Pb, 100 μg Hg, 100 μg Fe 0.06 g. tannic acid and 8 μg . active silver per 200 mls. of solution.

200 mls. of this synthetic effluent was placed in a 250 ml. beaker and vigorously stirred, whilst 10 mls. of stannous chloride solution were added. At intervals of about three minutes, three further additions of 1 ml. of tellurium solution were made and the whole centrifuged. The aqueous layer was then removed by means of a suction pipette thus leaving the precipitate in the tube. Coagulation of the precipitate was found to occur in the cold and it was not necessary to heat the solution to boiling and keep it there for 0.5 hr. as suggested by Sandell. The 250 ml. beaker was washed with 40 mls. of normal sulphuric acid and the washings transferred to the centrifuge tube, the mixture stirred and finally centrifuged once more. The precipitate was washed again with N

sulphuric acid and then twice with deionised water to remove all the chloride and as much of the organic matter, that might have adhered to the precipitate, as possible.

The centrifuge tube containing the precipitate was then placed in a water bath, three mls. of concentrated nitric acid added, and the water in the bath brought to boiling. The clear liquid was then transferred to a 50 ml. beaker and two more elutions of the precipitate made with three mls. of concentrated nitric acid, when control experiments showed that there was no activity remaining in the centrifuge tube.

Upon evaporation of the nitric acid extracts it was found that the residue contained some organic matter, which had presumably been occluded on the silver tellurium precipitate but this could be easily destroyed by repeated evaporations with concentrated nitric acid.

In a series of experiments the nitric acid extract from the precipitate was diluted to 50 mls. and the count of the solution compared with that obtained from a dilute nitric acid solution containing 8 μg of silver. From these results it appeared that the co-precipitation of

silver from trade effluent, as carried out in the above procedure was better than 99% efficient.

Solvent Extraction

Speed of equilibration

A series of experiments were carried out to ascertain the time required to achieve equilibrium in the silver-dithizone system.

20 mls. of approximately N/10 sulphuric acid containing 0.4 μ g. active silver solution were pipetted into a shaking tube and 20 mls. of a solution of dithizone in carbon tetrachloride added.

The tubes were shaken for varying lengths of time on a mechanical shaker oscillating at approximately 225 cycles per minute, the two phases were then separately withdrawn by means of a suction pipette, centrifuged to remove any of the second phase that might be entrapped, and the activity counted.

From the results obtained, in Table 13, it may be seen that equilibrium is established in less than 10 minutes and therefore at this acidity the time needed for equili-

bration is unlikely to hinder extraction experiments.

Table 13

Equilibration	Time	% extracted
A	10 mins.	99.48 %
B	20	99.41
C	40	99.54
D	60	99.61
E	100	99.52
F	120	99.48
G	200	99.49

Experiments were carried out to determine the range of acidities over which silver may be extracted from aqueous solution by a strong dithizone solution.

20 mls. of a solution of dithizone in carbon tetrachloride (10 mg./l.) were shaken with 20 mls. of sulphuric acid solution containing 0.4 μ g. of silver for 30 minutes, the phases separated, centrifuged, and the activities assayed.

The acidity of the aqueous phase was determined by titration with standard alkali.

Table 14

Experiment	Acidity	% Extraction
A	0.03 N	99.28
B	0.058	99.0

Experiment	Acidity	% Extraction
C	0.118 N	99.3
D	0.17	99.3
E	0.66	99.05
F	0.90	98.9
G	1.50	98.4
H	2.88	98.47
I	4.60	98.2
J	8.40	98.2
K	10.50	97.8
L	12.40	87.38
M	14.70	20.5
N	18.40	2.8

Extraction of silver from an aqueous phase containing
tannic acid by means of solvent extraction

Having found that the silver was extracted by dithi-
zone over a very wide range of acid concentrations, the
effect on extraction of adding tannic acid to the aqueous
phase was investigated.

It was found, during the first series of experiments,
that the mass balance, given by the sum of the activities
of both phases, that of the organic phase being corrected
for absorption of activity, was far from being constant,
and in many cases was under half that expected. This
was traced to a scum of organic material, which separated

at the interface of the two phases and onto which the silver absorbed very firmly. This scum tended to form in larger quantities, the higher the acidity of the aqueous phase, but could be reduced to negligible proportions for all but the most highly concentrated organic solutions, by keeping the acidity of the aqueous phase below 0.1 N.

In the following series of experiments, solutions of 0.1 N sulphuric acid were made up containing 0.8 μ g. of active silver and different amounts of tannic acid. 20 mls. portions of these solutions were shaken at 225 cycles per minute for 30 minutes with a carbon tetrachloride - dithizone solution (8 mg./l.), the phases separated, centrifuged, and the radio-activity assayed.

Table 15

Experiment	Tannic acid strength	% Extracted
A	7 g./l	96.4
B	10	98.3
C	15	97.2
D	18.5	97.2
E	27.5	96.1

Removal of silver from the dithizone phase.

The solution of dithizone in carbon tetrachloride is

likely to contain, in addition to silver, mercury, copper, and organic material, either dissolved from the aqueous phase, or else due to oxidation of the dithizone itself.

Consequently the organic phase is of no use for the determination of the silver and the silver must be removed from it. One method of doing this, much practiced in biochemical analyses, is to destroy the dithizone by heating with acid, to evaporate off the organic solvent and to remove any organic residue by repeated evaporation with nitric acid, sulphuric acid or hydrogen peroxide. After the metal residue has been dissolved its silver content is then determined by a suitable method, which is insensitive to the other metals that may be present.

After trials of this method of destroying the dithizone it was considered that it would be more satisfactory if evaporation of the solvent could be avoided, since it was found that even with much care some loss occurred due to 'spitting'.

Although solutions of dithizone are stable to quite strong solutions of nitric acid, it was found that only a very small quantity of concentrated nitric acid was

needed to decompose quite large quantities of dithizone solution.

Consequently silver was extracted into a solution of dithizone in carbon tetrachloride (10 mg./l.) and varying quantities of nitric acid added. After vigorous shaking the green dithizone solution was seen to be destroyed, whereupon the aqueous phase was made up to 20 mls., the phases separated, centrifuged and the counts assayed. It can be seen from Table 16 that as little as 0.125 ml. of concentrated nitric acid is effective.

Table 16

ml. conc. nitric acid	acid strength after dilution to 25 mls.	% Extraction. into aq. phase
1.0	0.84 N	99.68 %
0.5	0.42	99.55
0.25	0.22	99.56
0.125	0.01	99.04

Back extraction with thiocyanate.

Whilst it does appear that the destruction of dithizone by nitric acid may be carried out effectively with quite small quantities of acid, this is far from being the ideal method of back-extraction, for any metals that happen to have been co-extracted into the organic phase

will find their way into the aqueous phase with the silver. In addition, if, during the preliminary extraction of the silver, an interfacial scum has separated, this will have to be transferred with the organic phase, and complete destruction of the complexed silver will entail destruction of this organic matter which will be a lengthy procedure.

It has been suggested that if a mixture of silver, copper and mercury dithizonates are shaken with a dilute acid thiocyanate solution, only the silver will be extracted. Consequently the efficiency of the thiocyanate extraction was investigated.

25 ml. aliquot portions of 2% ammonium thiocyanate solution in dilute sulphuric acid solution were shaken for 15 minutes at 225 cycles per minute with 25 mls. of a carbon tetrachloride phase, containing a mixture of dithione and silver dithizonate. The phases were separated, centrifuged and the activity of the two phases determined.

Table 17

Experiment	Acidity	% Extraction
A	0.28 N	99.8 %
B	0.57	99.7
C	1.2	99.6
D	2.4	99.49
E	4.1	97.8

Similar experiments were carried out in 0.1 N sulphuric acid for copper and mercury independently in order to ascertain whether the separation of the two metals from silver would be complete.

Since no radioactive copper and mercury was available, the thiocyanate extract was evaporated to dryness, the thiocyanate destroyed with sulphuric acid and the residue dissolved in water. This aqueous solution was made 0.1 N by adding sulphuric acid and then shaken with dilute dithizone solution. If copper and mercury dithizonates had been present they would have formed dithizonates and this complex formation would have been apparent by the drop in absorption at $\lambda_{\max}$ for dithizone i.e. 620 m μ and by the increase in absorbency at the $\lambda_{\max}$ for copper and mercury dithizonates.

The experiments showed that no copper or mercury was back extracted by thiocyanate under these conditions.

Further it was found that treatment with 2% thiocyanate solution removed the silver that had been adsorbed on any interfacial scum, so that the appearance of this scum did not preclude accurate analysis, but merely

meant that the scum had to be transferred with the organic layer, to be extracted with thiocyanate solution.

Prior to the final determination, the thiocyanate had to be destroyed and this was done by the addition of concentrated sulphuric acid to the aqueous solution and subsequently evaporating to dryness. Occasionally a very small amount of organic residue was left at this stage but this was easily destroyed by fuming with a little concentrated nitric acid.

Considerable difficulty was experienced at this stage due to the absorption of silver on the vessel in which the evaporation was being carried out. The silicone surface, which had proved so valuable, up to this point, in preventing the absorption of silver, was decomposed by heating with concentrated acids.

Recoveries after evaporation in porcelain vessels proved little better than those for untreated glass. Eventually it was found that fused silica vessels retained little or no silver if a solution was evaporated to dryness in them, even if the silver solution was very dilute.

Heating of silica vessels was carried out in the first instance by means of a hot-plate, but it was found

that losses due to spitting were high. The most effective way of heating was by infra-red heaters from above and below.

The colourimetric determination of silver.

The use of p-dimethylaminobenzylidene rhodanine as a colorimetric reagent for silver was examined first. The colour was found to be rather unstable, varying a little with time and a great deal with acidity. The dependence of absorbency with acidity may be seen in Table 18. The strength of the rhodanine used was 0.05 g./100 ml. of ethanol.

Table 18

Acidity	Absorbency
0.16 N	0.044
0.08	0.076
0.04	0.096

In light of other experiments (not recorded) it was decided not to carry out further work with this reagent.

A method which has been much recommended for the determination of silver, especially in the presence of copper, uses copper dithizonate as reagent. As silver

replaces the copper, the colour of the solution varies between the reddish-brown colour of copper dithizonate and the yellow colour of silver dithizonate.

A series of experiments were carried out shaking 10 mls. of a solution of copper dithizonate in carbon tetrachloride with 10 mls. of an aqueous solution containing silver, after which the absorbency of the solution was determined by means of a "Spekker" absorptiometer.

It was found that the only suitable filter was an Ilford blue filter, and the light transmittancy of this filter at 550 $m\mu$, the $\lambda_{\max}$ of copper dithizonate, was low thus decreasing the sensitivity of the method.

For visual comparison it was thought that the colour change from red-brown to yellow was less decisive than the change from green to yellow, hence dithimone was considered to be a more satisfactory reagent for silver.

It is desirable to use as little reagent solution as possible in order to get the maximum colour change, and in order to obtain satisfactory equilibration when using these small quantities of liquid, a special micro-separator was made. This is shown in Fig. 1.

An aqueous solution was placed in a micro-separator

MICRO-SEPARATION APPARATUS

(full size)

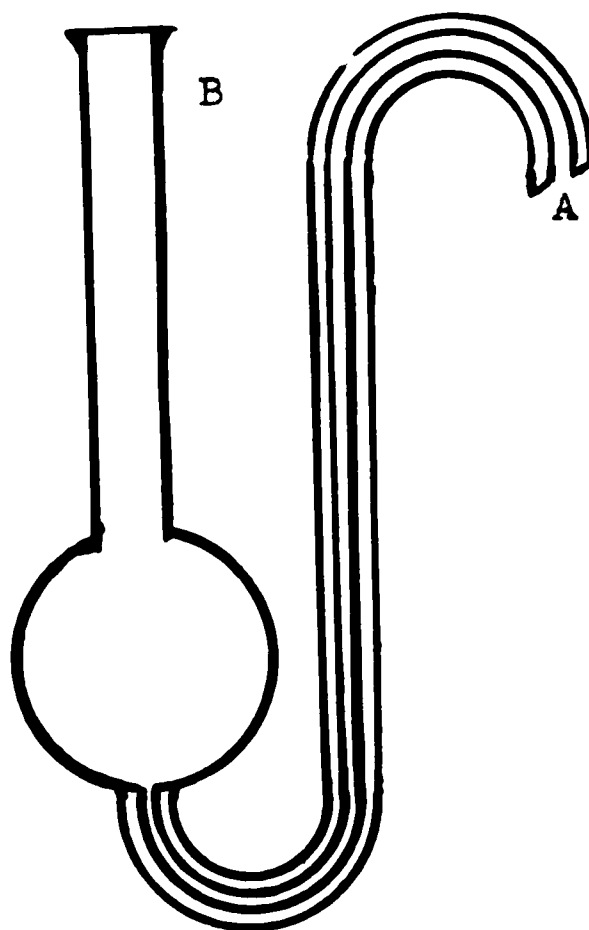


Fig 1

together with 0.5 mls. of a solution of dithizone in carbon tetrachloride and nitrogen, presaturated with the organic phase, passed in at point A to agitate the solution until equilibrium had been established. The nitrogen supply was then disconnected from A and pressure applied at B, whereupon the dithizone-silver dithionate solution was blown out of the micro separator at point A and could be collected in a micro-cell for determination.

Visual comparison may be made, by adding the silver solution after destruction of the thiocyanate to 0.5 mls. of dithizone solution in a micro testtube, and the two phases agitated by a rod flattened at one end. Equilibration of the two phases could also be carried out, as before, in the micro-separator.

Comparisons are made with solutions made up in a similar way but containing known amounts of silver.

Dithizone standards and calibration curves were always obtained from ^{fresh} freshly prepared dithizone solution, immediately before they were required, since it was found that over extended periods of time the results obtained varied.

More consistant results were also found if a reducing

agent was added to the aqueous phase during the final determination.

Absorption factor for silver in carbon tetrachloride.

In order to compare counts obtained from counting carbon tetrachloride solutions with those from an aqueous phase Λ_{CCl_4} for silver had to be found where

$$\Lambda_{CCl_4} = \frac{\text{Count rate of a given amount of silver in org. phase}}{\text{Count rate of a same amount of silver in aq. phase}}$$

For this a solution of silver dithizonate in carbon tetrachloride was made up and the count rate accurately determined. A number of 5 ml. portions were then shaken with an aqueous phase which was 0.2 M with respect to both sulphuric acid and ammonium thiocyanate. The phases were then separated, centrifuged and the radioactivity assayed. From the count of the organic phase it was clear that all the activity had been extracted and direct comparison between the count of the aqueous phase and that of the original organic phase gave a value for Λ .

The value found was 0.976.

DETERMINATION OF K' FOR THE SILVER DITHIZONE
EQUILIBRIUM

A solution of silver dithizonate was made by adding excess of a solution of dithizone in carbon tetrachloride to a solution of silver on 0.5 N sulphuric acid. After equilibration of the two phases the organic phase was separated, and shaken up several times with dilute ammonia (1:1000) in order to remove any excess dithizone present until the ammonia phase showed no sign of yellow colour. The resulting silver dithizonate solution was centrifuged to remove any entrapped water droplets and its absorption measured at 273 m μ . and 462 m μ . The absorption at 620 was also measured to make sure that the solution contained no free dithizone.

5 mls. of the organic phase and 5 mls. of the aqueous phase containing the appropriate strength of acid were then shaken together for 10 mins. at 225 cycles per minute on a mechanical shaker. The mixture was then centrifuged and the phases separated. Results are given below

Table 23

Sulphuric Acid	$10^7 \times K'$
6.34	1.68
5.07	2.11
3.80	2.65
2.54	2.78
1.27	3.60
0.63	5.58

Table 24

Parameters calculated for a two-phase system with $\log \quad_1 = 6$, $\log \quad_2 = 10$, $\log \quad_3 = 12$, $p_c = 7 \times 10^5$, $p_r = 7 \times 10^4$, $K_r = 10^{-4}$, $pH = 5$, and the total concentration of reactants = $10^{-4}M$.

pL	$10^2 \bar{n}$	x	$10^5 [M]$	$10^7 [ML]$	$10^{11} [ML_2]$	$10^{17} [ML_3] \quad w$
9.000	0.0999	0.9291	9.2817	0.9281	0.0928	0.0093
8.699	0.1996	0.8583	8.5656	1.7131	0.3426	0.0685
8.523	0.2992	0.7876	7.8526	2.3558	0.7067	0.2120
8.398	0.3985	0.7174	7.1422	2.8571	1.1429	0.4571
8.301	0.4980	0.6468	6.4356	3.2178	1.6089	0.8045
8.222	0.5965	0.5765	5.7306	3.4383	2.0630	1.2378
8.155	0.6952	0.5065	5.0294	3.5206	2.4644	1.7251
8.097	0.7938	0.4365	4.3303	3.4642	2.7714	2.2171
8.046	0.8943	0.3667	3.6344	3.2710	2.9439	2.6495
8.043	0.9412	0.3319	3.2877	3.1233	2.9672	2.8183
8.000	0.9903	0.2971	2.9411	2.9411	2.9411	2.9411
7.979	1.0393	0.2622	2.5951	2.7249	2.8611	3.0042
7.959	1.0882	0.2275	2.2504	2.4754	2.7230	2.9953
7.921	1.1860	0.1581	1.5624	1.8749	2.2499	2.6999
7.886	1.2836	0.0886	0.8746	1.1369	1.4780	1.9214
7.854	1.3810	0.0197	0.1946	0.2224	0.3813	0.5339

Table 25

Parameters calculated for the same system of metal complexes in a monophasic at $pH = 5$.

pL	$\bar{n}$	x	$10^5 [M]$	$10^5 [ML]$	$10^7 [ML_2]$	$10^8 [ML_3]$
6.301	0.3361	0.7443	4.95392	2.4770	0.1238	0.0006
6.000	0.5075	0.6569	3.26419	3.2642	0.3264	0.0033
5.699	0.6842	0.5807	1.91014	3.8203	0.7641	0.0153
5.523	0.7775	0.5440	1.33010	3.9903	1.1971	0.0359
5.398	0.8372	0.5203	1.00841	4.0334	1.6134	0.0645
5.301	0.8802	0.5026	0.80422	4.0211	2.0106	0.1005
5.000	1.0002	0.4450	0.37080	3.7080	3.7080	0.3708
4.824	1.0689	0.4056	0.22219	3.3328	4.9992	0.7499
4.699	1.1206	0.3678	0.14708	2.9416	5.8832	1.1766
4.602	1.1637	0.3351	0.10385	2.5962	6.4906	1.6226
4.523	1.2012	0.3044	0.00760	2.2813	6.8439	2.0531
4.456	1.2347	0.2752	0.00570	1.9944	6.9806	2.4432
4.398	1.2651	0.2472	0.00433	1.7330	6.9320	2.7728
4.347	1.2929	0.2202	0.00332	1.4939	6.7227	3.0252
4.301	1.3186	0.1941	0.00255	1.2748	6.3739	3.1870
4.260	1.3423	0.1686	0.00195	1.0783	5.9031	3.2467
4.222	1.3645	0.1438	0.00148	0.8875	5.3249	3.1043
4.187	1.3851	0.1195	0.00110	0.7157	4.6518	3.0237
4.155	1.4046	0.0956	0.00079	0.5504	3.8946	2.7262
4.125	1.4228	0.0722	0.00054	0.4083	3.0621	2.2960
4.097	1.4400	0.0492	0.00034	0.2710	2.1637	1.7309
4.046	1.4716	0.0040	0.00023	0.2108	1.8973	1.7076

Two Phase Titrations

In order to test the utility of a two phase titration technique for acid dissociation and stability constant measurements a special piece of equipment was built and a

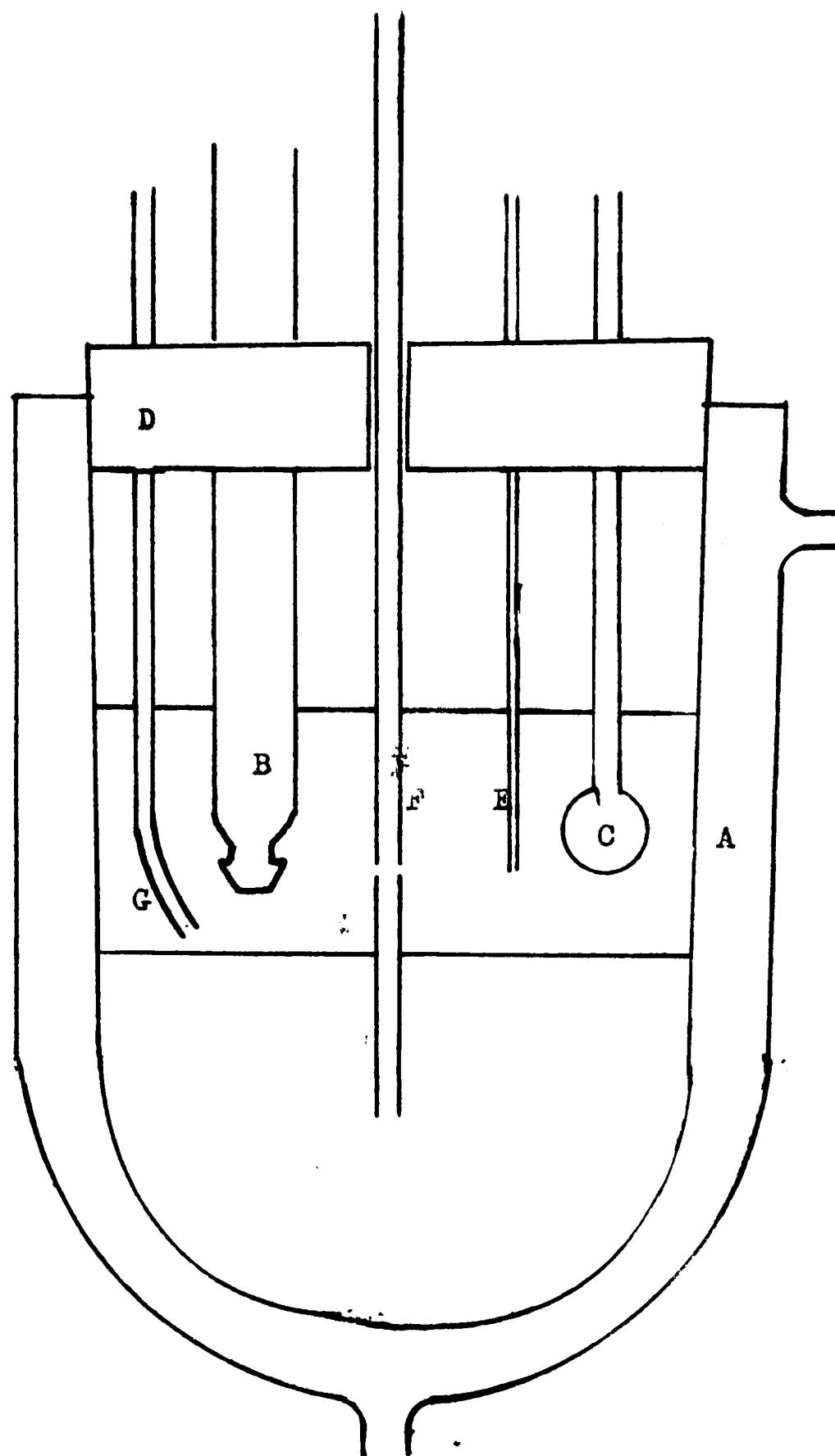


Fig. 2

Two phase titration cell as described in text

sketched diagram is given in Fig. 2.

It consists of a glass vessel of approximately 350 mls. capacity surrounded by a water jacket A, which is kept at a constant temperature with water from a thermostat. It was found that if the intervening piping was well lagged by means of asbestos string, the temperature of the liquid in the vessel was kept to within 0.1° of that set by the thermostat.

The reference electrode B and glass electrode C were positioned in the rubber bung D so that they were immersed in the aqueous phase but not in the organic phase, and the capillary tip of a micrometer syringe, or micro buerette E also dipped into the aqueous phase.

Stirring was found to be of the utmost importance, and the normal propellor type stirrer was not found to be satisfactory.

A stream of nitrogen, passed in to the system through G, could be made to effect efficient stirring, but tended to splash when passing through the solution at a sufficiently high rate, and also lifted globules of the organic phase to the surface, where small quantities remained.

Finally a stirrer of extreme simplicity was designed which provided excellent stirring. It consisted of a glass tube which was rotated at high speed by an electric motor, and had two small holes blown in it about an inch above the bottom. If these holes were placed slightly above the aqueous - organic interface, a stream of droplets of the lower phase were thrown through the upper phase, and violent mixing ensued without splashing, provided that the stirrer was rigidly held.

In order to follow small changes in acidity, a special high stability voltage comparator was built, and full details are given in Appendix B.

With this piece of equipment it was found that potential changes of 0.1 mV could be accurately followed, and satisfactory results were obtained for substances which achieved equilibrium quickly.

For dithizone, however, the speed of equilibrium was too slow to make two phase titrations a satisfactory proposition.

Solubility determinations

It has been pointed out⁴³ that if a solid, whose solu-

bility is to be determined, is shaken with successive portions of solvent, the concentration of solute in the solution so obtained should remain constant until all the solute has been dissolved, whereupon further additions of solvent will decrease the concentration of solute. A method of this type is satisfactory for substances which are moderately soluble in the solvents used, but if the solubility is high, large quantities of solid are needed to saturate the solvent in the successive equilibrations.

A straightforward method of shaking the solvent with solid is likely to provide good results for dithizone with solvents in which it is fairly soluble, but, as Sandell has shown⁴⁵ this method breaks down when applied to aqueous solutions since the speed of equilibration is so slow.

Even if the equilibrium is approached from the supersaturated side it is uncertain whether a true equilibrium is achieved unless an organic phase is present.

Consequently solubility measurements in an aqueous phase were carried out by the following method.

150 mls. of aqueous phase and 2 mls. of carbon tetra-

chloride were placed in a flask and sufficient purified dithizone to saturate the system added. The aqueous phase was supersaturated with the dithizone by making alkali with 1:1000 ammonia and then precipitating with the very minimum (2 drops) of diluted isopiestic hydrochloric acid solution.

The flask and contents were then shaken for at least 24 hours at 20°C the phases separated by centrifugation, and solid suspended in the aqueous phase which was not removed by centrifugation removed by filtration through a fine glass sinter. The dithizone was then extracted from the aqueous phase into a much smaller quantity of organic phase, usually effecting a concentration of about 10 times and the optical density of the organic solution measured. If the colour of this solution was too weak to be accurately measured then the pH of the aqueous phase was brought to approximately 2 and excess active silver added to the aqueous phase, whereupon the dithizone was converted to silver dithizonate and assay of the organic phase gave a measure of the concentration of the dithizone present, if the stoichiometry of the silver complex and the specific activity of the silver is known.

The concentration of the dithizone in an organic phase was obtained by dilution followed by measurement of the optical density of the diluted solution. In cases where the concentration of the solute in the aqueous phase had been measured radiochemically, a portion of this diluted organic solution was converted to the active silver complex and direct comparison of the assays of the activity of the complex derived from the saturated aqueous and organic solutions and a knowledge of the concentration and dilution factors involved gave a measure of the partition coefficient and the solubility of the complexing agent in the aqueous phase.

Determination of pH extraction curves for Indium from an aqueous phase into an organic dithizone phase.

25 ml. of a solution of dithizone in chloroform was pipetted into a shaking tube, together with 25 ml. of active indium solution N/10 sodium perchlorate solution, both solutions being saturated with respect to the other phase to prevent a volume change on mixing. The pH of the solution, which was unbuffered, was altered to that

required by adding drops of hydrochloric acid or ammonia, approximately determining the pH of the solution by means of pH papers.

The shaking tube and its contents were shaken at 225 cycles per minute for 1 hr. and after this the activity of both aqueous and organic phases were counted by pipetting 10 ml. into the polythene scintillation counter cups, the outside of the pipette being carefully cleaned to remove any surplus drops. The pH of the remainder of the aqueous phase was determined by using the Morton electrode system, in conjunction with a glass electrode. Solutions of dithizone in chloroform, carbon tetrachloride, and n-hexanol were all used and found to indicate a 1:3 complex.

The solution of dithizone in n-hexanol was found to be photosensitive, particularly to fluorescent laboratory lighting, and consequently measurements were carried out in subdued lighting, and solutions were only shaken for half an hour.

The n-hexanol - water mixture was found to produce emulsions easily, and all solutions had to be centrifuged

for ten minutes before separation of the phases.

Distribution of active indium between an unbuffered aqueous phase and a solution of dithizone in chloroform. (Table 26). Distribution of active indium between an unbuffered aqueous phase and a solution of dithizone in carbon tetrachloride (Table 27). Distribution of active indium between an unbuffered aqueous phase and a solution of dithizone in n-hexanol (Table 28).

The method of continuous Variations applied to the Indium-dithizone system.

Solutions of Indium perchlorate in an acetate buffer, and of dithizone in carbon tetrachloride were made up, of strength 2.2×10^{-5} moles per litre.

The sodium acetate - hydrochloric acid buffer, which was used gave a pH of 5.49 when measured by means of a glass electrode system. The solutions were made up so that the total amount of metal and ligand present in the system was always the same, and the total volumes of each of the two phases was brought to 20 mls. by the addition of carbon tetrachloride or buffer, as required.

Table 26

Aqueous count c.p.s.	Org. count c.p.s.	Total count c.p.s.	% Ex	pH	log q
237.78	1.98	328.75	0.82	1.72	3.918
204.76	11.57	216.33	5.35	1.97	2.753
189.79	35.14	224.93	15.64	2.17	1.267
145.59	92.98	238.97	38.96	2.22	1.805
63.60	159.91	223.51	71.55	2.46	0.400

Table 27

67.05	8.96	75.01	11.94	1.37	1.126
63.93	8.95	72.88	12.29	1.42	1.139
65.00	9.47	74.47	12.68	1.45	1.164
14.45	56.35	70.80	79.50	1.80	0.591
8.48	62.76	71.24	88.81	1.91	0.869

Table 28

37.12	7.77	44.89	17.32	1.56	1.321
32.47	11.01	43.48	25.32	1.68	1.523
25.12	19.14	44.26	43.24	1.76	1.881
11.37	32.66	43.03	75.90	1.94	0.458
2.40	38.75	41.15	94.20	2.30	1.288

The solutions were placed in a shaking tube and shaken vigorously for ten minutes, the solutions separated by means of a withdrawal pipette and centrifuged to make sure that one phase was completely free from the other. The absorbancy of the organic phase was then measured at the wavelengths 450 mμ, 510 mμ and 620 mμ. on a spectrophotometer and the radioactivity of both phases assayed.

The absorption factor for the indium - carbon tetrachloride system was found to be 0.92.

It was found, that due to the photosensitivity of indium dithizonate, experiments were more satisfactory if carried out in subdued light. Results are given in Table 29.

Table 29.

Expt.	Mole fraction of metal	A _j 510	A _j 620	Organic phase Activity,	Aqueous phase c.p.s.
A	0.0	0.000	0.000	0.0	0.0
B	0.05	0.054	0.082	2.88	1.02
C	0.1	0.133	0.174	5.77	1.94
D	0.2	0.232	0.303	8.53	4.04
E	0.25	0.246	0.305	10.00	6.76
F	0.3	0.220	0.297	9.73	11.11
G	0.4	0.209	0.256	8.20	16.07
H	0.5	0.178	0.210	7.18	24.02
I	0.6	0.151	0.174	5.70	29.64
J	0.7	0.115	0.133	4.32	38.13
K	0.8	0.074	0.082	2.77	44.53
L	0.9	0.032	0.041	0.98	52.20
M	1.0	0.000	0.000	0.01	57.23

DETERMINATION OF SILVER IN TRADE EFFLUENT

Appendix A

Principle of the method.

The silver will be accompanied by other metals in the effluent and in the presence of chloride ions and organic materials it may be largely present in the form of complexes.

The silver, together with a number of other metals, is first extracted into a small volume of concentrated dithizone solution, in carbon tetrachloride, whence it is removed selectively by treatment with an aqueous solution of ammonium thiocyanate. After destruction of this thiocyanate, and re-solution of the silver in dilute nitric acid, the final determination is made colorimetrically.

Range.

For a 100 ml. sample with a silver concentration of 0.2 - 20 micro grams per litre, a visual colour comparison, or an absorptiometric procedure with micro cells holding

0.5 - 1.0 ml. was adopted. If the absorptiometer available has cells holding 4 - 7 mls. a correspondingly larger sample must be taken.

Applicability.

The method is of wide applicability. There is no interference by the presence in each 100 ml. sample of 50 mg. of organic material, tannin, and 50 micro grams each of copper, ferric iron, lead and mercury, in addition to the constituents normally present in this volume of tap water.

A. Preliminary concentration of the Silver.

1. For each 100 ml. sample, contained in a 500 ml. conical separating funnel add 1 ml. of concentrated sulphuric acid.
2. Extract the silver by shaking for 1 minute with 5 ml. of the concentrated dithizone solution (A) collecting the extract in a 20 ml. centrifuge tube.
3. Repeat the extraction twice more with 5 ml. portions of the strong dithizone solution, combining the organic

phases in the centrifuge tube. Reject the aqueous phase.

Note (a)

In the presence of excessively large amounts of organic material, a scum may form at the interface of the two phases. This must be transferred with the organic phase.

Note (b)

If the volume is as high as 500 mls. a further two extractions with 5 mls. of concentrated dithizone (A) should be undertaken using a second centrifuge tube.

4. Spin and remove the aqueous phase with a suction pipette. Add 2 mls. of distilled water, spin, and again reject the aqueous phase. Transfer the solution of silver dithizonate in carbon tetrachloride to a 50 ml. separating funnel.

B. Separation of the Silver from the Organic Solution.

5. Add 4 mls. of 2% ammonium thiocyanate to the centrifuge tube so as to collect any remaining droplets of organic phase and any scum, gently agitate the contents and transfer quantitatively to the separating funnel.

Stopper the funnel, shake the mixture for 1 minute, allow the phases to separate, and, with a suction pipette, transfer as much as possible of the aqueous phase to a 25 ml. silica crucible.

6. Repeat stage 5 twice more. Run off and reject the organic phase from the separating funnel, and add the last few drops of the aqueous phase to the silica crucible.

7. Add 1.5 ml. of concentrated sulphuric acid, evaporate to fuming under an infra-red lamp and then to dryness by radiant heat from below as well as above the crucible. Add 0.3 ml. of 2N nitric acid, and warm until any solid residue is completely dissolved. Add 1 ml. of 10% urea solution, 1 ml. of 20% hydroxylamine sulphate solution, and digest the solution for 5 minutes near its boiling point under the infra-red lamps. Cover the crucible with a watch glass and allow to cool to room temperature.

0. Determination of Silver.

8. Transfer the contents of the silica crucible to the micro separator (Fig. 1) with a suction pipette. Rinse the crucible twice with 2 ml. portions of N/2 sulphuric acid.

9. Add 1 ml. of dilute dithizone solution (B) and mix with the aqueous phase by passing, for two minutes, a stream of nitrogen which had been presaturated by passing through a carbon tetrachloride solution of dithizone.

If the colour of the organic phase has a greenish hue, the amount of silver can be estimated as less than 1.5 micrograms. In this case the determination can be carried out in one of the following ways.

a. Direct visual comparison.

Prepare visual standards by adding to each of 9 micro-testtubes (ignition tubes), of dimensions $7\frac{1}{2}$ cms. x 1 cm. dia., 1 ml. of the dilute dithizone solution (B) followed by 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6 mls. of a dilute standard silver solution and 3.0, 2.8, 2.6 ... mls. of N/2 sulphuric acid.

Extraction of the silver is effected by agitation of the organic and aqueous phases together for 2 mins. with the aid of a thin glass rod flattened at the bottom, starting with the solution poorest in silver. By applying pressure at the top transfer the mixed colour organic phase from the micro separator to a tenth testtube

and wash it in with 3-4 mls. of the aqueous phase. Compare the sample and the standards and estimate the silver content to the nearest 0.1 microgram. Direct sunlight must be avoided.

b. Absorptiometry using micro cells.

After mixing the aqueous and organic phases in the micro separator, transfer the mixed-colour carbon tetrachloride phase to a micro cell and replace the lid. Measure the absorbancy in a Spekker absorptiometer, using an Ilford Orange Filter No. 607, or in a Beckman or Unicam Spectrophotometer at $\lambda = 620$, against a comparison cell filled with the dilute dithizone solution (B). Prepare a standard curve by adding a known amount of silver in the range 0.2 - 1.5 micrograms to 0.3 mls. of 2N nitric acid, 1 ml. of 10% urea solution and 1 ml. of 20% hydroxylamine sulphate, and after the addition of 1 ml. of dilute dithizone solution (B) carry out the whole extraction process from stage 9.

Subtract the blank obtained by carrying 100 mls. of distilled water through the whole process from stage 1 to the final determination.

D. Procedure for Large Quantities of Silver.

If the colour of the organic phase in stage 9 is a clear yellow (showing that there is no excess of dithizone) further 1 ml. portions of the dilute dithizone solution (B) are added and the equilibration repeated until a definite mixed colour is observed. Note the total volume, x , of the dithizone used.

The concentration of the silver can then be determined, either by the visual method (Procedure a.) or on an absorptiometer (Procedure b.), or using an absorptiometer with micro cells if the volume of the organic phase is sufficient.

In each case the number of micrograms of silver is calculated by multiplying the figure obtained in this way by the factor x .

Reagents

Distilled Water

Laboratory distilled water was passed through an Elgastat type B 102 portable deioniser.

Concentrated Sulphuric Acid.

Lab reagent. S.G. 1.838 - 1.844 at 15°C.

N/2 Sulphuric Acid.

Conc. acid diluted with distilled water.

2 N Nitric Acid.

Conc. acid diluted with distilled water.

Carbon Tetrachloride.

For solution A Harrington's Pure. 95% boils between 76 - 78°C.

For solution B it was purified by standing with bromine for two weeks, after which it was refluxed with sodium hydroxide solution, shaken with a solution of hydroxylamine hydrochloride and distilled.

Dithizone.

Solution (A) B.D.H. reagent in carbon tetrachloride (100 mg./l)

(B) " " " " " (5 mg./l)

APPENDIX B

In order to follow the acidity changes likely to occur during a two phase titration, it is necessary to detect changes in potential of ± 0.1 mV. in a glass electrode-reference electrode system.

It is possible to draw only a minute current from this system since a larger current will cause polarisation of the electrode to occur⁴⁶, the effects of which may take more than an hour to wear off. Consequently some form of voltage comparator is needed which may be adjusted so as to provide an equivalent potential to that of the electrode system, and then this potential may be determined by an instrument likely to draw an appreciable current, without any ill effects.

After much experimentation a design was decided the circuit of which is given in the accompanying diagram⁴⁷.

Despite its notorious reputation for instability, the apparatus incorporates an electrometer triode (ET 1) as a sensitive nullpoint indicator, because this particular valve was available when the apparatus was being

made. It was found that, provided certain precautions were taken, (see later) the equipment worked well over long periods of time.

The connection from the glass electrode, is taken from the ceramic switch 82 to the grid of the valve. The potential of the calomel electrode is opposed by a potential derived from the potentiometers P1 and P2 and provided by the battery B. The potentiometer P3 is employed to pre-set the grid bias of the valve between 0 and -2 V. When the system is in balance between P2 and the electrode cell the net potential on the valve grid will be equal to that provided by P3.

The potentiometers P4 and P5 in the anode circuit are used to adjust the voltage at the valve anode to exactly +6 V.; in this condition there will, of course, be no current flow through the galvanometer G. If however the voltage on the valve grid changes the current passed by the valve will correspondingly alter, and so therefore will the current at the anode. The galvanometer G will therefore deflect.

The 500 micro ammeter is used, together with the

operation of P3 to set the current through the valve to a reasonable value. P6 is used to set the filament current through the valve, the power supply is derived from the high capacity accumulator AC. C. The voltmeter V and its associated switch S5 is provided for monitoring purposes.

The operation of the instrument is as follows:-

The batteries were connected by means of switch S4 and the filament current brought to 0.09 A. by means of switch P6.

With P4 and P5 set at their middle point the grid bias was adjusted by P3 to bring the current through the micro-ammeter to 350 μ A. At least an hour was allowed for the electronic circuit to settle down.

The electrode system was now connected and measurements commenced. Balance was attained by altering the potentiometers P1 and P2 until no deflection of the galvanometer occurred on either position of the ceramic switch S2. At this point the potential derived from P3 and the net potential of the electrode-potentiometer systems was then equal. The potentiometers P4 and P5 were required at intervals to set accurately the zero on the galvanometer when S2 is in the first position. In this position also,

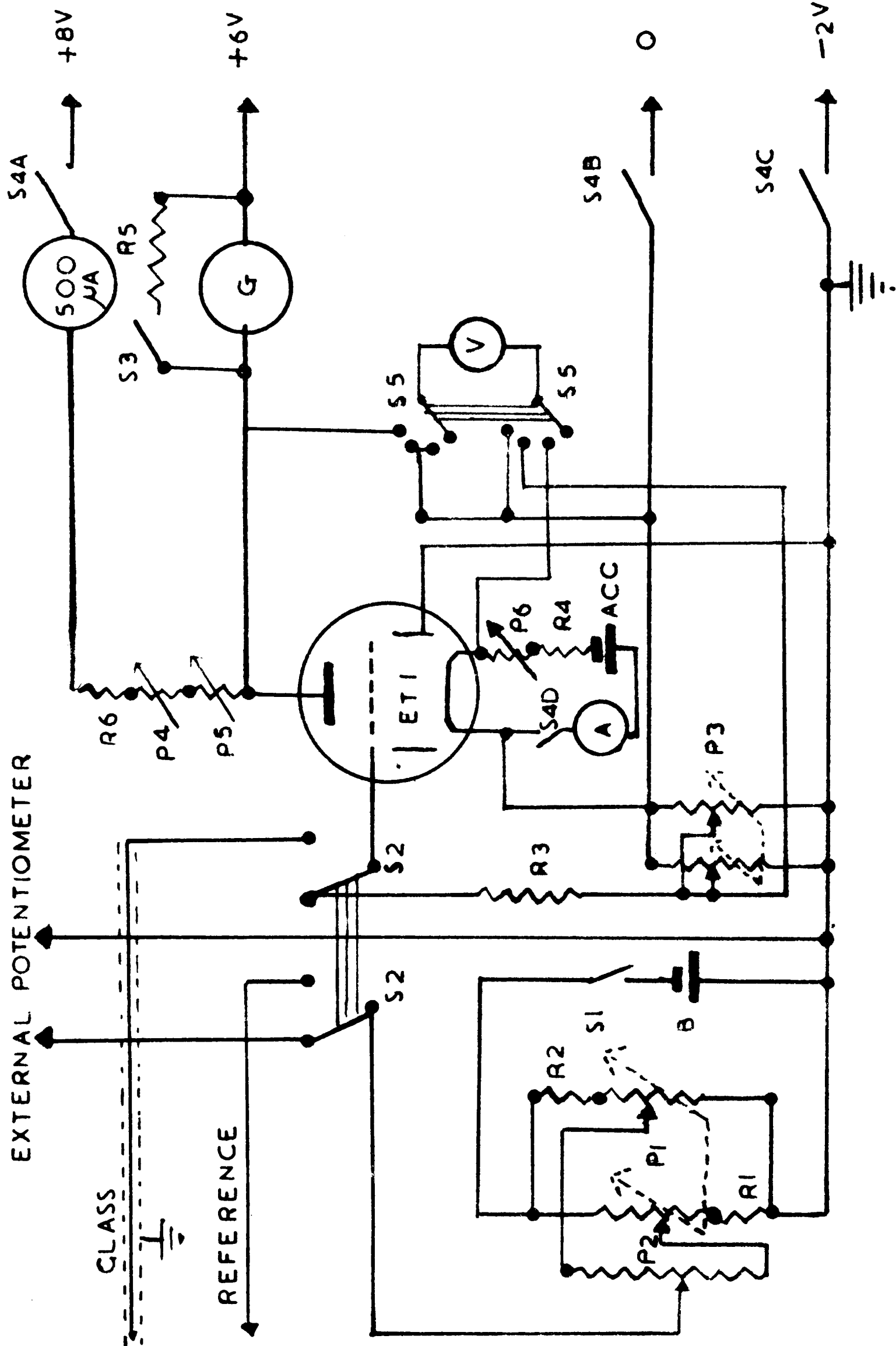
the output of the internal potentiometer system which is of low impedance is made available on terminals, to permit its measurement on an external precision potentiometer.

The switch S2 must make before it breaks. Otherwise the glass electrode acts as a condenser, and upon making a connection between the glass electrode and the FT 1 a pulse is passed which causes an annoying deflection of the galvanometer which must be then allowed to come to rest before proceeding with adjustment.

The FT 1 was mounted on a thick pad of sponge rubber to decrease unsteadiness that might occur due to microphonic noise and all the components were placed in a metal box and were kept dry by means of silica gel. The connecting wire from the glass electrode terminal to switch S2, and from S2 to the FT 1 must not allow any leakage and therefore this part of the circuit was constructed from screened wire.

No screened room was available and it was found that instability was caused by switching apparatus on and off in the same laboratory, and even by bringing clothing made of terylene near the equipment. To avoid trouble of this

type all accumulator leads were made of screened cable and the whole apparatus placed in a cage of perforated zinc.



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ABSTRACT

The solvent extraction of inorganic complexes has been studied in connection with two distinct problems, (i) the determination of small quantities of silver at a level of 1 part in 10^8 in trade effluent, and (ii) the measurement of the stability constants of metal complexes which are very sparingly soluble in water, though soluble in an organic solvent.

(i) The method finally proposed for the determination of small quantities of silver in trade effluent containing organic material in addition to copper, iron, lead, mercury, and calcium, etc. was arrived at after detailed study of

- a) The concentration of the silver
 - b) The separation of the silver from elements likely to interfere in the final determination.
 - c) The absorptiometric determination.
- a) Concentration of silver by co-precipitation was investigated using $\text{Ag}^{110\text{m}}$ as a radioactive tracer. It was found that silver was quantitatively co-precipitated

as sulphide with mercury, copper, and lead. If organic material was present in the solution it was more satisfactory to co-precipitate the silver with elementary tellurium.

Although efficient as a means of concentration, co-precipitation did not provide a satisfactory separation of silver from the metals likely to interfere in the final determination.

The silver complex of dithizone (diphenyl thio-carbazone) is soluble in organic solvents, and its considerable stability to acid solutions suggested that it would provide a very useful method of concentration of silver by a factor of 10 or better, since only mercury and some copper are likely to be co-extracted. These predictions were verified experimentally and, in addition to concentration, a preliminary separation of silver was thus effected.

b) It was shown that a solution of dithizone in carbon tetrachloride would retain copper and mercury even in the presence of aqueous thiocyanate, but that the superior stability of the thiocyanate complex of silver over that of the dithizone complex, permitted its

quantitative back extraction into an acidic aqueous phase. Selective extraction was thus obtained.

After the thiocyanate had been destroyed by wet ashing the whole of the silver was obtained free from metals which could interfere in the final determination.

c) p-Dimethylaminobenzylidene rhodanine, tetraethylthiourea disulphide and dithizone were all considered for the absorptiometric determination of silver.

Dithizone was finally chosen as it was considered to provide the best compromise between overall accuracy and general convenience for the determination of the concentration of silver after destruction of the thiocyanate with sulphuric acid. Both visual and photoelectric determinations were found to be accurate to $\pm 0.1 \mu\text{g}$ in the range from 0 - 10 μg .

It was found that traces of silver are absorbed upon glassware very readily. If, however, all surfaces which are likely to come into contact with the element are given a coating of silica by treatment with a commercial silicone preparation, it was found that the absorption could be reduced to negligible proportions.

(ii) The determination of the stability constant of the metal complex ML_n by the normal titration tech-

nique is not possible if it is insoluble in an aqueous phase. If the complex is soluble in an organic phase, however, it is often possible to determine a mixed stability constant K_f' , where

$$K_f' = \frac{[ML_n]_o}{[M^{n+}]_w [L^-]_w^n}$$

(the subscripts o and w referring to the organic and aqueous phases respectively) which involves a partition coefficient.

This is not altogether satisfactory, since comparison of the changes in this stability constant observed going from one compound to another in a series of closely related complexing agents, involve concomitant changes in the partition coefficients p_r and p_c , of the reagent HL and the complex ML_n respectively.

A method is derived from theoretical principles which enables the true formation constant K_f of ML_n

$$K_f = \frac{[ML_n]_w}{[M^{n+}]_w [L^-]_w^n}$$

to be obtained if the metal M is labelled with a radioactive isotope.

An added complication is the possible presence of

lower complexes ML , ML_2 ... in the aqueous phase. A full theoretical study of equilibrium between a solution containing metal complexes ML_j ($j = 0$ to N) in the aqueous phase, in equilibrium with an immiscible organic phase in to which only the formally neutral species ML_n is extracted, shows that

a) the relative concentrations of the intermediate species is lower than for a single phase system, and b) the overall degree of formation is higher. It has also been shown that Job's Method of Continuous Variations applies equally to a two-phase system and enables the composition of the extracted species to be determined with greater reliability than in the case of a one-phase system. If the radioactive isotope of M is available so that the total concentration of metal in the aqueous phase ($\sum_{j=0}^N [ML_j]$) and in the organic phase ($[ML_n]_o$) is known, the stability constants β_n of all the intermediate complexes may be calculated, where $\beta_n = [ML_n]_w / [M^{n+}]_w [L^-]_w^n$.

By use of radioactive silver, the solubility of some substituted dithizones in water and several organic solvents is obtained, in order to calculate the partition

coefficients.

Also the two-phase method of continuous variations is applied to the indium-dithizone system and the extinction coefficient and the overall formation constant of indium dithizonate calculated.