Substoichiometry in isotope dilution analysis: Automation of the process with reference to mercury.

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by

Brian Geoffrey Cooksey.

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S U M M A R Y.

Substoichiometry is a radiochemical technique which greatly improves the sensitivity of trace metal analysis by solvent extraction procedures. The basis of the technique is the use of a smaller amount of reagent than the stoichiometric amount required by the metal. In this way the same amount of metal is always extracted. This is convenient in isotope dilution analysis because the activity of the organic phase is then proportional to the specific activity. There is no need to measure the amount of metal actually extracted and a reagent can be used at a low concentration which cannot be measured by conventional techniques.

A method of determining mercury by substoichiometric solvent extraction, which has previously been described by Růžička and Stary (R1), has been automated and its limitations investigated and compared with those of the manual method (B5).

During the course of this investigation chloride was found to interfere by forming a ternary complex, mercuric chloride dithizonate. The reactions and properties of this substance have been studied and its stability constant has been determined (B6).
Several methods of overcoming this chloride interference have been examined. Whilst exploring one of these methods, the addition of ethylene-diamine-tetra-acetic acid, another ternary complex, mercuric chloride

ethylene-diamine-tetra-acetate, was recognised and its stability constants have also been measured.

Two papers have been published reporting this work (B5, B6) and a third is being prepared.

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THE DETERMINATION OF MERCURY BY SUBSTOICHIOMETRIC ISOTOPE DILUTION ANALYSIS.

Summary.

In this chapter a general description is given of the substoichiometric method for the determination of mercury with dithizone. The factors which limit the precision, sensitivity and selectivity are discussed. It is concluded that the precision falls from ± 2% for 10^{-5} g. of mercury to ± 50% for 10^{-8} g of mercury and that gold, platinum and palladium are the only interfering metals.

1.1.1. The Demand for Improved Trace Metal Analysis.

In industry at the present time there is a great demand for trace metal analysis. Recent legislation requires that effluents discharged into inland waterways contain less than 1 p.p.m. of heavy metals. Trace amounts of metals are undesirable impurities in many industrial products :- Electroplating solutions, oil additives, foodstuffs, semiconductors. The analysis of all these materials for trace metals is required.

In the semiconductor field, such very small amounts of impurity affect the conductivity that it is quite impossible to detect them by conventional techniques. As industry advances these greater sensitivities will inevitably be required in other fields. Once 1.4 p.p.m. was considered a conservative upper limit for arsenic in phosphoric acid (a foodstuff additive), recently phosphoric acid with a maximum arsenic content of 0.1 p.p.m. has become commercially available. This limit presents a difficult problem to the analyst. Substoichiometric isotope dilution analysis, which combines the selectivity of solvent extraction procedures with the sensitivity of radiochemical techniques, represents one solution to such problems.

1.1.2. The determination of mercury by substoichiometric isotope dilution analysis.

The substoichiometric determination of mercury by solvent extraction using dithizone as the organic reagent has been described by Růžička (R1,R7). This method is the starting point for the work described in this thesis and will be used as an example to explain substoichiometric isotope dilution analysis.

In this method two separatory funnels are used, one containing the sample dissolved in 10ml of 0.1M sulphuric acid, and the other containing just 10ml of 0.1M sulphuric acid. Suppose that the sample contains 0.1µg of mercury of normal isotopic composition (30% mercury 202, 23% mercury 200, 17% mercury 199 etc). The first step is to add to each flask exactly 0.1µg of mercury which has been labelled with a radioactive isotope of mercury. Suppose that in this step 1000c/s of radioactivity have been added to each funnel. The second step is to react the mercury in each funnel with 4ml of a 10^{-7}M solution of dithizone in carbon tetrachloride. This amount of dithizone is equivalent to 0.04µg of mercury, this is less mercury than is present in either funnel hence the name - substoichiometry. Because each funnel contains excess mercury, the dithizone in each case will be completely converted to primary mercuric dithizonate, in both funnels

0.04µg of mercury will be transferred to the organic phase. In this step isotopic equilibrium will be maintained and some radioactivity will also be transferred to the organic phase. The final step in the analysis is to separate these organic phases and to measure this activity. In the case of the sample in the first funnel, the activity will be :-

$$\frac{0.04}{0.2} \times 1000 = 200c/s.$$

but in the case of the standard in the second funnel :-

$$\frac{0.04}{0.1} \times 1000 = 400c/s.$$

It can be seen that the organic phase from the sample contains less activity than that from the standard because of the greater amount of inactive mercury present in the sample. The specific activity of the mercury isolated from the sample is less than that isolated from the standard. Isotope dilution has occurred.

This reasoning may be applied to the general case of a sample containing an unknown amount of mercury.

Let

W_s = the weight of mercury in the sample.

W_a = the weight of mercury added in the first step.

W_e = the weight of mercury extracted in the second step.

A = the activity added in the first step.

A_a = the activity isolated from the standard in the final step.

A_s = the activity isolated from the sample in the final step.

then

$$A_a = \frac{A.W_e}{W_a}$$

and

$$A_s = \frac{A.W_e}{(W_a + W_s)}$$

$$\therefore \quad \frac{A_a}{A_s} = \frac{W_a + W_s}{W_a} \qquad \text{----------1/1}$$

$$W_s = W_a \left(\frac{A_a}{A_s} - 1 \right) \qquad \text{----------1/2}$$

In this derivation neither A nor W_e appear in equation 1/2, neither the exact reagent concentration nor the specific activity of the isotope used affect the analytical results provided they are the same for both the sample and the standard.

Equation 1/2 is the fundamental equation used in substoichiometric isotope dilution analysis. The normal equation for isotope dilution analysis is :-

$$W_s = W_a \left(\frac{S_a}{S_s} - 1 \right)$$

$$= W_a \left(\frac{A_a}{W_{ea}} \cdot \frac{W_{es}}{A_s} - 1 \right) \qquad \text{----------1/3.}$$

where

S_a = the specific activity of the isotope added.

S_s = the specific activity of the material isolated from the sample.

W_{es} = the weight of mercury extracted from the sample in the second step.

W_{ea} = the weight of mercury extracted from the standard in the second step.

In substoichiometry an equal amount of the element is isolated from the standard and the sample ($W_{ea} = W_{es}$) and specific activities in the isotope dilution equation become activities in the substoichiometric equation.

For a substoichiometric separation, a graph of A_s versus W_s is a displaced rectangular hyperbola. The equation for a rectangular hyperbola referred to its asymptotes as axes is :-

$$xy = C$$

Where C is a constant. Displacing this graph along the x-axis by a distance, a, and referring to a new variable, X.

$$X = x-a$$

so that the equation for the displaced hyperbola is

$$yX + ya = C.$$

let $X = W_s$, $y = A_s$, $a = W_a$, $C = W_a A_a$

$$A_s W_s + W_a A_s = W_a A_a.$$

or $$W_s = W_a \left(\frac{A_a}{A_s} - 1 \right)$$

this is equation 1/2 again proving that the graph is a rectangular hyperbola displaced along the W_s axis so that when $W_s = 0$, $A_s = A_a$.

1.1.3. The advantages of substoichiometric isotope dilution analysis.

(a) The substoichiometric method of analysis is more sensitive than the conventional spectrophotometric method because the substoichiometric reagent can be so dilute that it is not possible to measure the colour of the organic layer. The substoichiometric method is also more sensitive than conventional isotope dilution analysis. The sensitivity of normal isotope dilution analysis could possibly be improved by using modern techniques, such as square wave polarography, to measure the weights of element isolated from the sample and standard, but if this were done the sensitivity would be limited by adsorption just as it is in substoichiometry.

(b) The substoichiometric method is more selective than conventional methods employing organic reagents because such methods use an excess of reagent which can react with an interfering metal. For example in the determination of mercury with dithizone, copper interferes in the spectrophotometric method but not in the substoichiometric one.

(c) As in normal isotope dilution analysis, the substoichiometric method has the advantage

that the element to be determined need not be quantitatively isolated from the sample. All that is necessary is that enough is obtained to completely consume the reagent.

(d) An important consequence of (c) is that adsorption of the metal on to the surface of the glass vessels used in the dissolution and subsequent processing of the sample does not affect the result of a substoichiometric analysis, only adsorption of the metal complex from the organic phase after the substoichiometric separation can do this. This adsorption is the most serious source of error in conventional methods of analysis of high sensitivity, (e.g., square wave polarography). Methods which do not involve chemical treatment of the sample also avoid this difficulty, (e.g., mass spectrometry, X-ray flouresence or neutron activation analysis).

1.1.4. The disadvantages and limitations of substoichiometry.

(a) Substoichiometry is a radiochemical technique which requires special equipment to handle and measure radioisotopes, and laboratory personnel trained in the safety precautions needed in such work.

(b) A suitable reagent must be available. Such reagents are usually available only for those metals which form the strongest complexes. For a large spectrum of reagents these metals are similar. Thus dithizone, diethyl-dithio-carbamate, di-alkyl-dithiophosphates, cupferron and oxine, all form strong complexes with gold, mercury, palladium and copper. Methods for these metals are easy to devise but methods for the alkali, alkaline earth, or rare earth metals are never very selective. (R2. and C4).

(c) Suitable isotopes with a long half-life (> 10 hrs) and a high specific activity (> 10mCi/gm) may not be available, (e.g., Al, B, Li, Si, Ni, Mo, etc.).

(d) Many metals form ternary complexes with organic reagents when the metal is in excess. When such complexes are formed the sensitivity and selectivity are reduced. (see chapter 3).

1.2. Precision and Accuracy.

In this section a statistical treatment of the precision with which mercury can be estimated by solvent extraction and substoichiometric isotope dilution will be attempted. The solution of the sample and any pre-treatment required to ensure that all the mercury is in the same chemical state will be common to all methods of chemical analysis and may be neglected when comparing substoichiometry with other methods.

1.2.1. The coefficient of variation and its components.

The results of a large number of repeat analyses of the same sample will vary among themselves. The precision is a measure of this variation. The mean of all these results will differ from the true result. This difference is the accuracy of the analytical method.

The coefficient of variation will be used as a measure of the precision; it is the standard deviation expressed as a percentage of the mean. The standard deviation is the root mean square deviation from the mean of a large number of results. When estimating the standard deviation experimentally only a small number (less than thirty) of results are usually available and equation 1/4 is used to calculate the best estimate of the standard deviation.

$$(N - 1)\, s^2 = \sum_{i=1}^{i=N} x_i^2 - \Big(\sum_{i=1}^{i=N} x_i \Big)^2 \Big/ N \qquad \text{--------1/4}$$

s = the estimate of the standard deviation.

N = the number of experimental results.

x_i = the i'th experimental result.

This equation together with several other statistical techniques used in this section are described in standard text books of statistics (D1, D2, N1).

It is usually found that the deviations follow the normal distribution. If this is the case and if the coefficient of variation is one per cent, then two thirds of the results will be within one per cent of the mean and all but one twentieth within two per cent.

Errors occur at each step in the analysis and each error contributes a certain amount of variation to the final result. In this section the way in which these errors contribute to the precision of the whole analysis is elucidated, and an experimental estimate of each error is given. In this way it is easy to identify those steps which must be improved if greater precision is required.

1.2.2. The combination of coefficients of variation.

The coefficient of variation of the final result cannot be obtained by adding together the individual coefficients of variation of each step. This combination must be accomplished by using equation 1/5.

$$V(x) = V(a)\left\{\frac{\partial x}{\partial a}\right\}^2_{b,c--} + V(b).\left\{\frac{\partial x}{\partial b}\right\}_{a,c---} + V(c)\left\{\frac{\partial x}{\partial c}\right\}_{a,b---}$$

$$+ \text{--------} \qquad \text{--------} \quad 1/5.$$

where

$$x = F(a,b,c\ \text{-----}).$$

$V(x)$ is the variance of x and $V(a)$ the variance of a etc. The variance is related to the standard deviation ($S(x)$, $S(a)$ etc.)., and the coefficient of variation ($v(x)$, $v(a)$ etc.)., by the following equations :-

$$V(x) = s^2(x)$$

$$v(x) = \frac{s(x)}{x} \cdot 10^2$$

$$V(x) = 10^{-4}(x.v(x))^2$$

Unfortunately equation 1/5 is only applicable when there is no correlation between a,b,c, etc., that is when there is no reason to suspect that a positive error in a is always associated with a positive error in b (or always associated with a negative error in b). As will be shown

below there is such a correlation in the case of substoichiometry and an expedient must be adopted to avoid this difficulty.

As an example in the use of this equation suppose a sample of 250mg is dissolved, diluted to 250ml and a 25ml aliquot pipetted out, and also suppose that the standard deviation of the weighing is 0.1mg, of the dilution 0.1ml and of the pipetting 0.01ml, that is each step has a coefficient of variation of 0.04%. The coefficient of variation of the weight of sample in the final aliquot can be calculated as follows.

Let W_f gm be the weight of sample in the final aliquot of volume V_1 ml taken from a total volume of V_2ml in which the whole of the sample (Wgm) is dissolved. Then :-

$$W_f = \frac{W.\ V_1}{V_2}$$

$$\left(\frac{\partial W_f}{\partial W}\right) = \frac{V_1}{V_2}\ ,\quad \left(\frac{\partial W_f}{\partial V_1}\right) = \frac{W}{V_2}\ ,\quad \left(\frac{\partial W_f}{\partial V_2}\right) = -\frac{W V_1}{V_2^2}$$

so that

$$V(W_f) = V(W).\ \frac{V_1^2}{V_2^2} + V(V_1).\ \frac{W^2}{V_2^2} + V(V_2).\ \frac{W^2 V_1^2}{V_2^4}\ .$$

$$= V(W).\ \left(\frac{W_f}{W}\right)^2 + V(V_1).\ \left(\frac{W_f}{V_1}\right)^2 + V(V_2).\left(\frac{W_f}{V_2}\right)^2$$

$$10^4 \cdot \frac{V(W_f)}{W_f^2} = 10^4 \cdot \frac{V(W)}{W^2} + 10^4 \cdot \frac{V(V_1)}{V_1^2} + 10^4 \frac{V(V_2)}{V_2^2}$$

$$v^2(W_f) = v^2(W) + v^2(V_1) + v^2(V_2).$$

$$= (0.04)^2 + (0.04)^2 + (0.04)^2$$

$$v(W_f) = \sqrt{3} \times (0.04)$$

$$= \underline{0.07\%}$$

An examination of this example will show that equation 1/5 will reduce to the simpler equation 1/6 when the condition 1/7 is satisfied.

$$v^2(x) = v^2(a) + v^2(b) + v^2(c) \quad \text{--------1/6}$$

when

$$\frac{\partial x}{\partial a} = \pm \frac{x}{a}, \quad \frac{\partial x}{\partial b} = \pm \frac{x}{b}, \quad \frac{\partial x}{\partial c} = \pm \frac{x}{c} \text{ etc.} \quad \text{--------1/7}$$

In substoichiometry equation 1/2 is used to calculate the result, i.e.,

$$W_s = W_a \left(\frac{A_a}{A_s} - 1 \right) \quad \text{--------1/2}$$

Any errors in W_a, A_a or A_s will contribute to the errors in W_s. In this case equation 1/6 cannot be used because the condition 1/7 is not satisfied. The reason for this will be clear

whenit is realised that when the sample contains very small amounts of mercury A_a will be very nearly equal to A_s and small relative errors in A_a or A_s will make large relative errors in the term $\left(\frac{A_a}{A_s} - 1\right)$. The coefficient of variation of W_s will then be much larger than that of A_s (or A_a). Under these circumstances equation 1/5 itself must be used.

Whichever equation (1/5 or 1/6) is used the variances of W_a, A_a and A_s must be independent, and this independence is only achieved when measuring very small amounts of mercury, with very small amounts of activity. Under these circumstances $V(A_a)$ and $V(A_s)$ will be due largely to the difficulties of measuring very small amounts of activity. $V(W_a)$ will also be an error of measurement because W_a must be estimated by reverse substoichiometry (R2) (when W_s is known and W_a is estimated from the experimental values of A_a and A_s). These three different errors of measurement are entirely independent and equation 1/5 will be accurate.

In normal circumstances, however, the amounts of activity involved are large enough for accurate measurements to be made and $V(A_a)$ and $V(A_s)$ are much

larger than the error of measurement (see TABLE 1/5B). The additional contributions to $V(A_a)$ and $V(A_s)$ must be due, either to variations in the amount of mercury counted or to variations in its specific activity. It is the additional variations in A_s which are correlated with the variations in W_a. This can be appreciated if an examination is made of the way in which $V(A_a)$, $V(A_s)$ and $V(W_a)$ contribute to $V(W_s)$.

Let an active mercury solution contain mercury having a specific activity of F c/s/g. An aliquot of this solution containing W_a g of active mercury, of activity Ac/s, is added to a sample containing W_s g of inactive mercury. V_o ml of a solution of the organic reagent are added and when the extraction is complete W_e g of mercury, of activity A_o c/s are transferred to the organic phase. V_c ml of this organic phase containing W_c g of mercury, activity A_s c/s, are pipetted into a counting vial and the activity measured. (N.B. These equations differ from those derived in section 1/1 because in the previous section it was assumed that all the organic phase was counted.).

$$A = F.\ W_a$$

$$A_o = \frac{A.\ W_e}{(W_s + W_a)} = \frac{F.\ W_a.\ W_e}{(W_s + W_a)}$$

$$A_s = \frac{V_c}{V_o} . A_o = \frac{V_c.\ W_e}{V_o} \cdot \frac{W_a.\ F}{(W_s + W_a)}$$

$$W_c = \frac{V_c}{V_o} . W_e \qquad \text{--------1/8}$$

$$A_s = \frac{F.\ W_a.\ W_c}{(W_s + W_a).} \qquad \text{--------1/9}$$

In the standard $W_s = 0$

$$A_a = F'.\ W_c'. \qquad \text{--------1/10}$$

$$\frac{A_a}{A_s} = \frac{F'.\ W_c'.}{F\ .\ W_c} \cdot \frac{(W_a + W_s)}{W_a.} \qquad \text{--------1/11}$$

Nominally $F'W_c' = F\ W_c$ but in practice these will differ because of experimental errors due to adsorption, pipetting etc. If these two factors cancel, equation 1/11 reduces to equation 1/1.

The fraction $(W_a + W_s) / W_a$ is identical in equations 1/9 and 1/11. Any error (δW_a) in W_a will be identical in both equations and will contribute to the variation of A_s via equation 1/9 and to the variation of W_s via equation 1/11.

These two contributions are merely different forms of the same error (δW_a). If equation 1/5 is used to calculate $V(W_s)$ by differentiating equation 1/2, this error will be counted twice, once under $V(A_s)$ and once under $V(W_a)$. These two variances are not independent. The crux of this argument is the identical value of δW_a to be used in equations 9 and 11. A similar argument could be applied to W_c or F and might lead one into believing that A_s and A_a are also correlated, but in this case two different extractions are involved and δW_c will take different values for the standard and sample.

In practice $V(A_s)$ is estimated from the variation between repeat tests in which the same active mercury solution is used. Those variations in W_a associated with the standardisation of the active mercury solution will not contribute to this experimental variation. The variance corresponding to these standardisation errors will be called $V(MW_a)$. Those variations associated with the pipetting of the active mercury solution and the adsorption of this active mercury will contribute to the experimental variation and will be combined with $V(A_s)$. This procedure is arbitrary but convenient and allows

the use of equation 1/5 because $V(MW_a)$ and $V(A_s)$ are not correlated. Equation 1/5 now becomes :-

$$V(W_s) = V(MW_a).\left(\frac{\partial W_s}{\partial W_a}\right)^2 + V(A_a).\left(\frac{\partial W_s}{\partial A_a}\right)^2 + V(A_s).\left(\frac{\partial W_s}{\partial A_s}\right)^2 \qquad \text{--------1/12}$$

Differentiation of equation 1/2 gives

$$\left(\frac{\partial W_s}{\partial W_a}\right) = \frac{A_a - A_s}{A_s} = \frac{W_s}{W_a}$$

$$\left(\frac{\partial W_s}{\partial A_a}\right) = \frac{W_a}{A_s} = \frac{W_s}{A_a - A_s} = \frac{W_s}{A_a}\left(\frac{A_a}{A_a - A_s}\right)$$

$$\left(\frac{\partial W_s}{\partial A_s}\right) = -\frac{W_a \cdot A_a}{A_s^2} = -\frac{W_s \cdot A_a}{A_s(A_a - A_s)}$$

now

$$\frac{A_a}{A_a - A_s} = \frac{1}{\left(1 - \frac{A_s}{A_a}\right)} = \frac{1}{\left(1 - \frac{W_a}{(W_a + W_s)}\right)} = \frac{W_a + W_s}{W_s.}$$

let $q = \dfrac{W_s}{W_a}$ --------1/13

then

$$\frac{A_a}{A_a - A_s} = \frac{1 + q}{q}$$

thus

$$V(W_s) = V(MW_a)\cdot\left(\frac{W_s}{W_a}\right)^2 + \left(\frac{1+q}{q}\right)^2 \left\{V(A_a)\cdot\left(\frac{W_s}{A_a}\right)^2 + V(A_s)\cdot\left(\frac{W_s}{A_s}\right)^2\right\}$$

or

$$v^2(W_s) = v^2(MW_a) + \left(\frac{1+q}{q}\right)^2 \left\{v^2(A_a) + v^2(A_s)\right\}$$

--------1/14

Equation 1/14 relates the coefficient of variation of the final result (W_s) to the coefficients of variation of W_a, A_a, and A_s.

1.2.3. The sources of error contributing to $V(A_a)$.

The variance $V(A_a)$ can be subdivided in a similar manner to $V(W_s)$ by differentiating equation 1/10 and substituting in equation 1/5, but in addition to the variations associated with F and W_c which are given by this procedure, there are also those variations associated with the measurement of radioactivity. If these are called $V(MA_a)$ equation 1/5 becomes :-

$$V(A_a) = V(MA_a) + V(W_c).\left(\frac{\partial A_a}{\partial W_c}\right)^2 + V(F).\left(\frac{\partial A_a}{\partial F}\right)^2$$

Differentiating equation 1/10 shows that condition 1/7 is satisfied, so that :-

$$v^2(A_a) = v^2(MA_a) + v^2(W_c) + v^2(F)$$

--------1/15

The variance $V(MA_a)$ is composed of three parts; that due to the random nature of nuclear disintegrations which obeys the Poisson distribution law, $V(PA_a)$; that due to the deficiencies of the measuring instrument (i.e., E.H.T. drifts due to poor voltage stabilisation, variation in the gain of the amplifiers due to ageing components etc.), V(I); and a part associated with the dead time correction $V(DA_a)$. Thus :-

$$v^2(MA_a) = v^2(PA_a) + v^2(I) + v^2(DA_a)$$

--------1/16

The mean and variance of the Poisson distribution are equal, so that if the activity A_a is counted for a time T and the total number of counts accumulated is C_a

$$C_a = A_a . T. \quad \text{and} \quad V(C_a) = A_a . T.$$

by equation 1/5

$$V(PA_a) = \frac{A_a T}{T^2}$$

$$v^2(PA_a) = 10^4 . \frac{V(PA_a)}{A_a^2} = \frac{10^4}{A_a . T.} \qquad \text{--------1/17}$$

So that $v(PA_a)$ can be reduced without limit by increasing the counting time T.

If the instrument has a dead time of τ sec/pulse and has counted $A_m T$ pulses in time T sec when the true count rate should be A_t c/s, then

total time for which pulses were not counted $= A_m . T. \tau.$ sec.

variance of this time

$$= A_m T. \tau^2$$

(because τ is a constant and $A_m T$ has a Poisson distribution).

Total lost counts $= A_t . A_m . T. \tau .$

this quantity would have a Poisson distribution), but for the variations in the time $A_m.T.\tau$ so that the actual variance of the lost counts is

$$= A_m.A_t.T.\tau. + A_m.T.\tau^2.A_t^2$$

$$\therefore\ v^2(DA_a) = \frac{10^4}{A_t^2.T^2} \cdot \left(A_m.A_t.T.\tau + A_m.T.\tau^2.A_t^2 \right)$$

$$= \frac{10^4\tau}{T} \cdot \left(\frac{A_m}{A_t} + A_m\tau \right)$$

now $A_t = \frac{A_m}{1 - A_m\tau}$ so that

$$v^2.(DA_a) = \frac{10^4\tau}{T}$$

Comparing $v(DA_a)$ with $v(PA_a)$ it can be seen that

$$v^2(DA_a) > v^2(PA_a) \quad \text{if } \tau > \frac{1}{A_m}$$

Such a high count rate as this ($A = 1/\tau$) could not be used in practice because the dead time correction would be nearly the whole of the true count rate. In all the experiments described in this thesis the dead time correction was less than 10% of the true count rate, often very much less, so that

$$v^2(DA_a) < v^2(PA_a)/10 \text{ and } v^2(DA_a)$$

can be neglected with complete safety.

In this treatment it has been assumed (wrongly) that the dead time correction is accurately known and that the only source of variation is that caused by the random disintegration of atomic nuclei which makes the actual dead time uncertain. In order to account for the errors which occur in measuring the instrumental dead time, another variance (V(MD) must be allowed to contribute to $V(W_s)$ because if these errors are allowed to contribute separately to $V(A_s)$ and (VA_a) a correlation is produced between A_a and A_s, and invalidate the use of equation 1/5. This correlation is apparent when it is appreciated that a dead time correction which is too high will cause both A_a and A_s to be too high. The experimental estimates of $V(A_a)$ and $V(A_s)$ will not be in error by this procedure because in any one series of repeat analyses the same dead time correction will be used. This procedure modifies equation 1/12 to

$$V(W_s) = V(MD) + V(MW_a).\left(\frac{\partial W_s}{\partial W_a}\right)^2 + V(A_a).\left(\frac{\partial W_s}{\partial A_a}\right)^2 + V(A_s).\left(\frac{\partial W_s}{\partial A_s}\right)^2 \qquad \text{--------1/18}$$

and equation 1/14 to

$$v^2(W_s) = v^2(MD) + v^2(MW_a) + \left(\frac{1+q}{q}\right)^2 \left(v^2(A_a) + v^2(A_s) \right)$$

--------1/19

The dead time correction is $A^2\tau$ so that equation 1/2 must be modified to :-

$$W_s = W_a \left(\frac{A_a + A_a^2\tau}{A_s + A_s^2\tau} - 1 \right)$$

$$\frac{\partial W_s}{\partial \tau} = W_a \left(\frac{A_a^2}{(A_s + A_s^2\tau} - \frac{(A_a + A_a^2\tau)\, A_s^2}{(A_s + A_s^2\tau)^2} \right)$$

If the dead time correction is small this reduces to :-

$$\left(\frac{\partial W_s}{\partial \tau} \right) = W_a \left(\frac{A_a (A_a - A_s)}{A_s} \right)$$

$$= W_s \cdot A_a$$

$$V(MD) = V(\tau) \cdot W_s^2 A_a^2$$

$$\frac{V(MD)}{W_s^2} = \frac{V(\tau)}{\tau^2} \cdot \tau^2 \cdot A_a^2$$

or $v^2(MD) = v^2(\tau) \cdot \tau^2 \cdot A_a^2$. --------1/20.

where $v(\tau)$ is the coefficient of variation due to the error of measuring the dead time.

The variance (V(I)) cannot be calculated; it must be measured. Equation 1/21 can now be obtained by substituting for $v^2(PA_a)$ into equation 1/16 from equation 1/17 and neglecting $v^2(DA_a)$.

$$v^2(MA_a) = \frac{10^4}{A_a T} + v^2(I). \quad \text{--------1/21.}$$

A_a will vary considerably from experiment to experiment so that it is usually more convenient not to state the Poisson error explicitly, this gives equation 1/22

$$v^2(MA_a) = v^2(PA_a) + v^2(I) \quad \text{--------1/22.}$$

$V(W_c)$ is due to several causes and three contributions can be measured; a variance V(Cl) due to variations in the amount of adventitious chloride causing variations in the amount of mercuric chloride dithizonate formed (see chapter 3); a variance V(R) due to variations in the strength of the organic reagent caused by oxidation, adsorption or by evaporation of the organic solvent or formation of secondary mercuric dithizonate; and a variance $V(V_c)$ due to variations in the volume of organic phase pipetted into the counting vial. These give :

$$v^2(W_c) = v^2(Cl) + v^2(R) + v^2(V_c) \text{ ------1/23.}$$

The variance V(F) is due to two causes, the variation in the amount of mercury present as a blank in the reagents and the variation in the amount of isotopic exchange which occurs between mercuric dithizonate dissolved in the organic phase and that adsorbed on the walls of the separating funnel. Both of these errors will be treated more fully below (sections 1.2.6. and 1.3.7.).

Substituting for $v^2(MA_a)$ from equation 1/22 and for $v^2(W_c)$ from equation 1/23 into equation 1/15 gives equation 1/24.

$$v^2(A_a) = v^2(I) + v^2(PA_a) + v^2(Cl) + v^2(R)$$

$$+ v^2(V_c) + v^2(F_a) \text{ --------1/24.}$$

The subscript a added to $v^2(F)$ is to distinguish the variance due to the variation in the specific activity of the standard from that of the sample ($v^2(F_s)$)(see next section.).

1.2.4. The sources of error contributing to $V(A_s)$.

The variance $V(A_s)$ is very similar to the variance $V(A_a)$. The variances V(I), V(Cl), V(R), $V(V_c)$ will be identical in magnitude in the two cases. However $V(PA_s)$ will be greater than $V(PA_a)$ because the activity A_s will be less than the activity A_a. (It is not usually worth the extra trouble to count the activity A_s for a longer time particularly when automatic counting equipment is used). $v^2(PA_s)$ is given by equation 1/25 analogous to equation 1/17 for $v^2(PA_a)$.

$$v^2(PA_s) = \frac{10^4}{A_s T} \qquad \text{--------1/25.}$$

The variance $V(F_s)$ will be smaller than $V(F_a)$ because the amount of mercury in solution will be greater than in the case of the standard and the effect of changes in the blank or changes in the amount of mercury adsorbed will be smaller. However the larger amount of mercury also lowers the specific activity and in most cases the coefficient of variation $v(F_s)$ is greater than the coefficient of variation $v(F_a)$ (see section 1.3.7.).

In the case of the sample there is an additional source of error associated with the term $I_d = W_a / (W_a + W_s)$. This isotope dilution

variance $V(I_d)$ is due to errors in pipetting the standard and sample solutions. If $V(V_a)$ is the variance associated with the pipetting of the standard active mercury solution and $V(V_s)$ that associated with the pipetting of the sample solution, then equation 1/5 will give :-

$$V(I_d) = V(V_a)\left(\frac{\partial I_d}{\partial V_a}\right)^2 + V(V_s)\cdot\left(\frac{\partial I_d}{\partial V_s}\right)^2.$$

$$M_a = \frac{W_a}{V_a} \quad , \qquad M_s = \frac{W_s}{V_s}$$

Where M_a, M_s are the concentrations of the active standard solution and the sample solution respectively

$$\frac{\partial V_a}{\partial W_a} = \frac{1}{M_a} = \frac{V_a}{W_a}$$

$$\frac{\partial V_s}{\partial W_s} = \frac{1}{M_s} = \frac{V_s}{W_s}$$

$$\frac{\partial I_d}{\partial W_a} = \frac{1}{W_a + W_s} - \frac{W_a}{(W_a + W_s)^2}$$

$$\frac{\partial I_d}{\partial W_s} = \frac{- W_a}{(W_s + W_a)^2}.$$

from equation 1/13

$$\frac{\partial I_d}{\partial W_a} = \frac{W_a}{W_a + W_s} \cdot \frac{1}{W_a} \cdot \left(1 - \frac{W_a}{W_a + W_s} \right)$$

$$= \frac{I_d}{W_a} \cdot \left(\frac{q}{1 + q} \right)$$

$$\frac{\partial I_d}{\partial W_s} = \frac{W_a}{W_a + W_s} \cdot \frac{1}{W_s} \cdot \left(\frac{W_s}{W_a + W_s} \right)$$

$$= \frac{I_d}{W_s} \cdot \left(\frac{q}{1 + q} \right)$$

$$\frac{\partial I_d}{\partial V_a} = \frac{\partial I_d}{\partial W_a} \cdot \frac{\partial W_a}{\partial V_a}$$

$$= \frac{I_d}{V_a} \cdot \left(\frac{q}{1 + q} \right)$$

$$\frac{\partial I_d}{\partial V_s} = \frac{I_d}{V_s} \cdot \left(\frac{q}{1 + q} \right)$$

so that

$$V(I_d) = \left(V(V_a) \cdot \frac{I_d^2}{V_a^2} + V(V_s) \cdot \frac{I_d^2}{V_s^2} \right) \left(\frac{q}{1 + q} \right)^2$$

$$v^2(I_d) = \left(\frac{q}{1 + q} \right)^2 \left(v^2(V_a) + v^2(V_s) \cdot \right)$$

by analogy with $v^2(A_a)$

$$v^2(A_s) = v^2(I) + v^2(PA_s) + v^2(Cl) + v^2(R) + v^2(V_c)$$

$$+ v^2(F_s) + \left(\frac{q}{(1+q)}\right)^2 \left\{ v^2(V_a) + v^2(V_s) \right\}$$

--------1/26.

1.2.5. A discussion of the magnitudes of the various sources of error and how they contribute to the precision of the analysis.

Using equations 1/24 and 1/26 to substitute for $v^2(A_a)$ and $v^2(A_s)$ in equation 1/19 gives

$$v^2(W_s) = v^2(MD) + v^2(MW_a) + v^2(V_a) + v^2(V_s)$$

$$+\left(\frac{1+q}{q}\right)^2 \left\{ 2.\, v^2(I) + 2\, v^2(Cl) + 2\, v^2(R) \right.$$

$$+ 2.\, v^2(V_c) + v^2(PA_a) + v^2(PA_s) + v^2(F_a)$$

$$\left. + v^2(F_s) \right\}$$

-------- 1/27.

This final equation shows how the various sources of error mentioned above contribute to the precision of the final result. All twelve of these partial coefficients of variation have been measured experimentally and these estimates will now be compared in order to decide the most important sources of error.

v (MW_a). The errors involved in the standardisation of the active mercury solution are very small when strong solutions ($> 10^{-6}$M) are used and the solution is prepared by labelling an inactive solution of a mercury salt which has been standardised by conventional gravimetric or volumetric procedures. Typical results are given in TABLE 1/1 obtained from replicate standardisations. If dilute solutions are prepared by direct dilution of the commercially available isotope, the standardisation will be by reverse substoichiometry and will be repeated several times until the error in the mean result is much smaller than the error in the sample.

v (MD). The dead time correction arises from the inadequate frequency response of the measuring instruments. During the course of this study the instrumentation was greatly improved. The equipment first used (made by Research Electronics Ltd., Cleckheaton) had a dead time mainly due to the response time of the fast Decatron counting tubes. This time is definite and easily measured. The Research Electronics equipment was replaced by more sophisticated electronics (made by Nuclear Enterprises Ltd., of Edinburgh) in

which the limiting factor was the response time of the transistors used in the amplifier and discriminator. This is much less definite and the measured values appeared to increase at low count rates. This greatly increased the magnitude of $v(\tau)$ and, as v(MD) is calculated from $v(\tau)$ via equation 1/20, the increase in precision due to the smaller dead time of the new equipment was not as great as anticipated. Table 1/2 shows the experimental values of τ, $v(\tau)$, and v (MD).

v(I). The improvement in instrumentation is most noticeable in v(I). The voltage stabilisation used for the Nuclear Enterprises equipment was so good that this variation could only be approximately measured for this equipment. The results of several experiments designed to estimate v(I) are recorded in Table 1/4. During long counting times the peak voltage corresponding to the energy of the radiation being measured tends to drift out of the discriminator channel and to reduce the counting efficiency. The drift in the peak voltage occurs because small drifts in the E.H.T. voltage cause large changes in the gain of the photomultiplier tube. This

effect can be minimised by choosing the upper and lower limits of the discriminator channel so that (if the peak voltage drifts upward) the counts lost above the upper limit are just compensated by the counts gained as the Compton scattering peak moves above the lower limit. This procedure minimises the short term value of v(I) but as the counting time increases the drifts become larger, the compensation becomes less satisfactory, and v(I) increases with time.

$v(PA_a)$ and $v(PA_s)$. As mentioned above, these variations can be reduced by increasing the counting time. In the experiments described in this thesis, this time was selected so that $v(PA_s)$ was less than 1%, in most cases it was less than 0.2% (TABLE 1/5B.).

$v(MA_a)$ and $v(MA_s)$. The precision with which A_a and A_s can be measured can be estimated from the sum of $v^2(PA_a)$ and $v^2(I)$ (see equation 1/16). Increasing the counting time decreases $v(PA_a)$ but increases v(I) so that for the greatest accuracy a compromise is necessary and the counting time should be such that $v(PA_a)$ and v(I) are approximately equal. It is possible to reduce v(I) by counting each vial for a short period and

when every vial has been counted, repeating the whole procedure. Any desired precision can be reached if enough repeat counts are accumulated. The total time for which each vial was counted will govern $v(PA_a)$ but $v(I)$ will be reduced, corresponding only to those variations which occur within the time required to count all the vials once. This procedure is an example of the use of randomised blocks and for the best results the order in which the vials are counted should be chosen at random with the aid of a table of random numbers (D1). In substoichiometry it is usually unnecessary to take these precautions because $v(MA_a)$ and $v(MA_s)$ contribute very little to the overall error $v(W_s)$. (TABLE 1/5B).

$v(V_a)$, $v(V_s)$ and $v(V_c)$. Conway (C1) has given a treatment of pipetting errors which will not be repeated here because the errors are of very small magnitude. TABLE 1/3 gives the experimental results obtained by weighing replicate deliveries of water (V_a and V_s) or carbon tetrachloride (V_c).

$v(A_a)$, $v(A_s)$, and V(Cl). In all experiments

the standard was replicated in order to obtain an estimate of the experimental error and the values obtained in this way are shown in TABLE 1/5. There are two kinds of experiments; in the first no precautions were taken against chloride interference and in these v(Cl) contributed to $v(A_a)$; in the second E.D.T.A. was added to overcome chloride interference and in these v(Cl) did not contribute to $v(A_a)$. From the difference between the squares of these results an estimate of v(Cl) has been obtained as shown in TABLE 1/5A. Most of the terms contributing to $v(A_a)$ also contribute to $v(A_s)$ (compare equation 1/24 with equation 1/26) so that a separate estimate of $v(A_s)$ is not necessary, provided the differences between $v(PA_a)$ and $v(PA_s)$, and $v(F_a)$ and $v(F_s)$ are taken into account. A comparison of equation 1/17 with equation 1/25 shows that, if the same counting time is used for both, $v(PA_a) = \sqrt{\frac{A_a}{A_s}} \cdot v(PA_s)$. With moderately strong solutions these two terms ($v(PA_a)$ and $v(PA_s)$) contribute very little to $v(W_s)$ and can be neglected. With very dilute solutions and very low activities this difference could be important, but in practice it is not because adsorption prevents the use of substoichiometry

at such dilutions (see sections 1.3.5. where a treatment is given of the dilute solution case and section 1.3.8. where this is compared with the limit of sensitivity due to adsorption.

$v(R)$, $v(F_a)$ and $v(F_s)$. The coefficient of variation $v(A_a)$ found in the presence of E.D.T.A. is due to the sum of the variations corresponding to the two coefficients of variation $v(R)$ and $v(F_a)$, that is $v^2(A_a) = v^2(R) + v^2(F_a)$. An attempt has been made to estimate $v(R)$ separately by measuring the variation in the colour of the organic phase with the results given in TABLE 1/6. Unfortunately, the estimate of $v(F_a)$ obtained by difference using this estimate of $v(R)$ and $v(A_a)$ in the absence of E.D.T.A., in the above equation is so inaccurately known that it could well be zero, although it is large in comparison with many of the coefficients of variation discussed above. Another estimate of $v(F_a)$ will be given in section 1.3.7. where adsorption is treated, also in this section an attempt will be made to compare $v(F_a)$ and $v(F_s)$ (equations 1/41 and 1/42). The contribution of variations in the blank to $v(F_a)$ and $v(F_s)$ is negligible because the blank

itself is too small to measure even with 0.01 µg standards.

$v(W_s)$. By comparing the estimates given in TABLES 1/1 to 1/6, for the coefficients of variation which contribute to $v(W_s)$ it can be seen that v(Cl) is by far the largest source of error. If this is removed by adding E.D.T.A. $v^2(R)$ and $v^2(F)$ become the biggest terms in equation 1/27. It will be shown in section 1.3.7. that v(F) increases drastically at low reagent concentrations and decreases at high concentrations, so that if high reagent concentrations are used v(R) will predominate but at low reagent concentrations v(F) will predominate. These conclusions must be modified when very small quantities of radioactivity are used when the Poisson error will predominate, this case is discussed in section 1.3.5.

In all cases the final value for $v(W_s)$ depends on q , the ratio of the weight of mercury in the sample to that added to the standard. The amount of mercury in the sample will not normally be known so that it is useless to give a precise value to q but any value of $q > 1$ is acceptable provided results of the highest

accuracy are not required. If the highest possible accuracy is desired and if the amount of mercury in the sample is known, then W_a can be chosen so that the smallest possible value of $v(W_s)$ is obtained when this value of $q = W_s/W_a$ is substituted in equation 1/27. The value of q obtained in this way will depend on the relative magnitudes of the terms inside and outside the brackets in equation 1/27 and also on the magnitude of $v(PA_s)$ which depends upon A_s which in turn depends upon q . Examples of this procedure are given in sections 1.3.5. and 1.3.7.

TABLE 1/1. The experimental estimation of v (MA).

Solution	Method of analysis	result	v(MA)
I1	gravimetric as periodate	11.130 g/l	
	" " "	11.146 g/l	
(Exp. A25)	volumetric versus thiocyanate.	11.146 g/l	0.04%
	" " "	11.146 g/l	
I171	Weight of mercuric oxide used to prepare the solution	0.10000M	
(Exp. 171)	Volumetric versus chloride	0.09967M	0.09%
	" " "	0.09997M	
	volumetric versus E.D.T.A.	0.09960M	
	" " "	0.09962M	

TABLE 1/2. The experimental estimation of v (MD).

Apparatus	dead time (τ)	v (τ)	* v (MD)
Research Electronics single channel γ-ray spectrometer (Exp. 54).	52.5 μs.	4.7%	0.25%
Research Electronics strip chart γ-ray spectrometer (Exp. 54).	16.0 μs.	10.2%	0.16%
Nuclear Enterprises single channel γ-ray spectrometer (Exp. 132).	2.0 μs.	37%	0.08%
Nuclear Enterprises fully automatic γ-ray spectrometer (Exp. 132).	2.4 μs.	48%	0.12%

* A_a = 1000 c/s.

TABLE 1/3. Pipetting errors.

Volume of pipette	$v(V_a)$ and $v(V_s)$ (H_2O)			$v(V_c)$ (CCl_4)
	Exp.102	Exp.128	Exp.132	
5 cm^3		0.059%	0.060%	
2 cm^3			0.015%	0.050%
1 cm^3	0.115%	0.041%	0.036%	
0.25 cm^3		0.144%	0.161%	
0.02 cm^3			0.29%	

TABLE 1/4. Instrumental errors.

Apparatus	Experiment	v (I).
Research Electronics	60	0.20%
Research Electronics	75	0.16%
Research Electronics	102	0.65%
Nuclear Enterprises	132	0.033%
Nuclear Enterprises	275	0.021%

TABLE 1/5A. Experimental values of $v(A''_a)$ in the presence and absence of chloride interference.

Conditions	$v(A''_a)$	ϕ
chloride interference present		
E.D.T.A. absent	2.28%	58
chloride interference absent		
E.D.T.A. present	1.00%	42

v^2 (Cl) = $2.28^2 - 1.00^2$ = 4.19.

v (Cl) = 2.05

N.B. after taking adsorption errors into account

v^2 (Cl) = 3.50 - 0.47 = 3.03, v (Cl) = 1.74

(see section 1.3.7.).

TABLE 1/5B. A comparison of $v(A_a)$ and $v(MA_a)$.

Exp.	Chloride interference	$v(A_a)$	$v(PA)$	$v(A''_a)$
58	present	3.70%	0.25%	3.69%
60	"	2.60%	0.15%	2.57%
61	"	2.00%	0.22%	1.96%
75	"	2.60%	0.38%	2.57%
117	"	0.95%	0.18%	0.89%
119	"	3.00%	0.07%	3.00%
120	"	0.60%	0.17%	0.49%
121	"	1.57%	0.19%	1.53%
122	"	0.73%	0.19%	0.64%
124	"	1.04%	0.19%	0.98%
133	"	1.96%	0.32%	1.91%
138	"	2.02%	0.20%	1.98%
144	"	2.75%	0.71%	2.64%
147	"	3.03%	0.50%	2.96%
148	"	3.15%	0.51%	3.10%
248	absent	0.91%	0.16%	0.90%
250	"	1.01%	0.17%	1.00%
251	"	0.65%	0.18%	0.62%
252	"	0.57%	0.21%	0.53%
253	"	1.31%	0.13%	1.30%
254	"	1.60%	0.10%	1.60%
255	"	0.29%	0.12%	0.27%
256	"	1.45%	0.11%	1.44%

N.B. (a) $v^2(MA_a) = v^2(I) + v^2(PA)$.

(b) $v^2(I)$ assumed 0.20%.

(c) $v^2(A''_a) = v^2(A_a) - v^2(MA_a)$

(d) $v(MA_a)$ = that part of the coefficient of variation of A_a which is due to the errors of measurement.

(e) $v(A''_a)$ = that part of the coefficient of variation of A_a which is due to other sources of variation.

TABLE 1/6 v(R) and v(F)

The experimental estimate of v(R) is 0.75% (ϕ = 4) when no chloride is present.

$$v^2(A''_a) = v^2(R) + v^2(F_a)$$

$$1.01 = 0.56 + v^2(F_a)$$

$$v(F_a) = 0.67\%.$$

TABLE 1/7 Summary.

Coefficient of variation.		Notes
v(Cl) =	2.05%	Removed by adding E.D.T.A.
v(R) =	0.75%	
$v(F_a)$ =	0.67%	Higher at low mercury concentrations.
v(I) =	0.20%	For Research Electronics.
=	0.03%	For Nuclear Enterprises.
v(MD) =	0.20%	For Research Electronics
=	0.10%	For Nuclear Enterprises.
$v(V_a)$ =	$v(V_s)$	Higher if very small pipettes are used.
= $v(V_c)$ =	0.05%	
v(MA) =	0.05%	
v(PS) =	v(PA)	
=	0.20%	Reduced by long counting times.

1.3. Sensitivity.

The sensitivity of the substoichiometric technique is limited by four factors :-

(1) the completeness of the reaction.

(2) the specific activity of the isotope available

(3) the stability of the reagent.

(4) the adsorption of the metal complex on to the walls of the separating funnel.

1.3.1. The completeness of the reaction.

The reaction which occurs in the solvent extraction of mercury as the dithizonate is :-

$$Hg^{2+} + 2\ H_2Dz_{(org)} \rightleftharpoons Hg(HDz)_{2\ (org)} + 2H^+$$

The extraction constant corresponding to this reaction is :-

$$E_{Hg(HDz)_2} = 10^{26.66} = \frac{[Hg(HDz)_2]_{org.}\ [H^+]^2}{[Hg^{2+}]\ [H_2Dz]^2_{org.}}$$

To estimate the sensitivity this equation must be modified to obtain a new equation connecting the minimum reagent concentration $[Hg(HDz)_2]_{org.}$

(N.B. The reagent at equilibrium will be completely converted to primary mercuric dithizonate) and the acidity $[H^+]$. Two additional equations are required to eliminate the concentration of mercuric ions in the aqueous phase $[Hg^{2+}]$, and the concentration of reagent remaining unreacted, $[H_2Dz]_{org.}$ These equations will be obtained by considering the conditions normally used in substoichiometric solvent extraction.

In substoichiometry the analyst adjusts the reagent concentration so that about half the mercury in the standard is extracted into the organic phase; if too little is extracted the sensitivity is lowered because only a little activity is available for measurement, if too much is extracted the selectivity is lowered and other metals might interfere.

Thus :-

$$[Hg^{2+}] = [Hg(HDz)_2]_{org.}$$

In order to apply equation 1/1 the amount of mercury in the organic phase must be independent of the amount of mercury in the sample. This is accomplished by ensuring that virtually all the reagent is converted to primary mercuric dithizonate, for any dithizone remaining in the organic phase of the standard might, in the organic phase of the sample, be converted to mercuric dithizonate

by the additional mercury present in the sample. It is not usually possible to measure the activity of the organic phase more accurately than $\pm$ 0.1%. No appreciable error will be incurred if 0.1% of the reagent remains unreacted or if :-

$$[H_2Dz]_{org} = 10^{-3} [Hg(HDz)_2]_{org}$$

Substituting these two conditions into equation 1/28 gives

$$E_{Hg(HDz)_2} = \frac{10^6 [H^+]^2}{[Hg(HDz)_2]^2_{org.}} \qquad 1/29.$$

This equation gives the minimum reagent concentration which can be used at a given pH or the minimum pH required for a given reagent concentration.

At pH=0 for example

$$[Hg(HDz)_2] = \sqrt{10^{-26.6} \times 10^6 \times 10^0}$$

$$= \underline{\underline{10^{-10.3}}}$$

or at a reagent concentration of 10^{-5}M

$$[H^+] = \sqrt{10^{26.6} \times 10^{-6} \times 10^{-10}}$$

$$= \underline{\underline{10^{5.3}}}$$

These conditions are so wide that the sensitivity is limited by other factors. In the absence of interfering agents the reaction is always complete.

Equation 1/29 suggests that if the sensitivity is low due to an incomplete reaction (for example, in the presence of an interfering ion forming complexes with mercury soluble in the aqueous phase - (see section 1.4.2.), the remedy is to increase the pH.

There are two upward limits to this due to the formation of (a) secondary mercuric dithizonate in the organic phase and (b) hydroxy complexes of mercury in the aqueous phase.

1.3.2. The formation of secondary mercuric dithizonate.

Secondary mercuric dithizonate is formed by the reaction :-

$$Hg^{2+} + Hg(HDz)_{2\,(org)} \rightleftharpoons 2HgDz_{(org)} + 2H^{+}$$

The extraction constant corresponding to this reaction is (B1) :-

$$E_{HgDz} = 10^{-3} = \frac{[HgDz]^{2}_{org.}\,[H^{+}]^{2}}{[Hg^{2+}]\,[Hg(HDz)_{2}]_{org.}}$$

using similar conditions to those imposed in the previous section viz.,

$$[Hg^{2+}] = [Hg(HDz)_2]_{org.}$$

$$[HgDz]_{org.} = 10^{-3} [Hg(HDz)_2]_{org.}$$

gives :-

$$E_{HgDz} = 10^{-6} [H^+]^2 \quad \text{--------1/30}$$

Thus the amount of interference does not involve the reagent concentration.

This gives

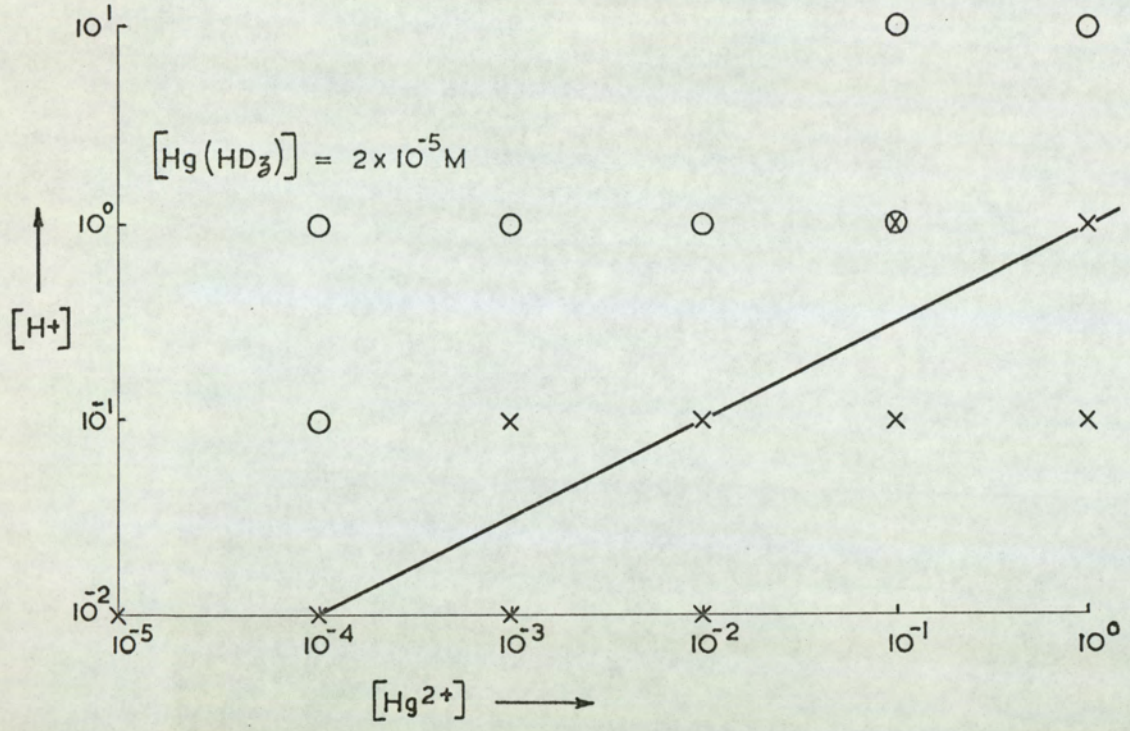
$$[H^+] = 10^{1.5} = 70M.$$

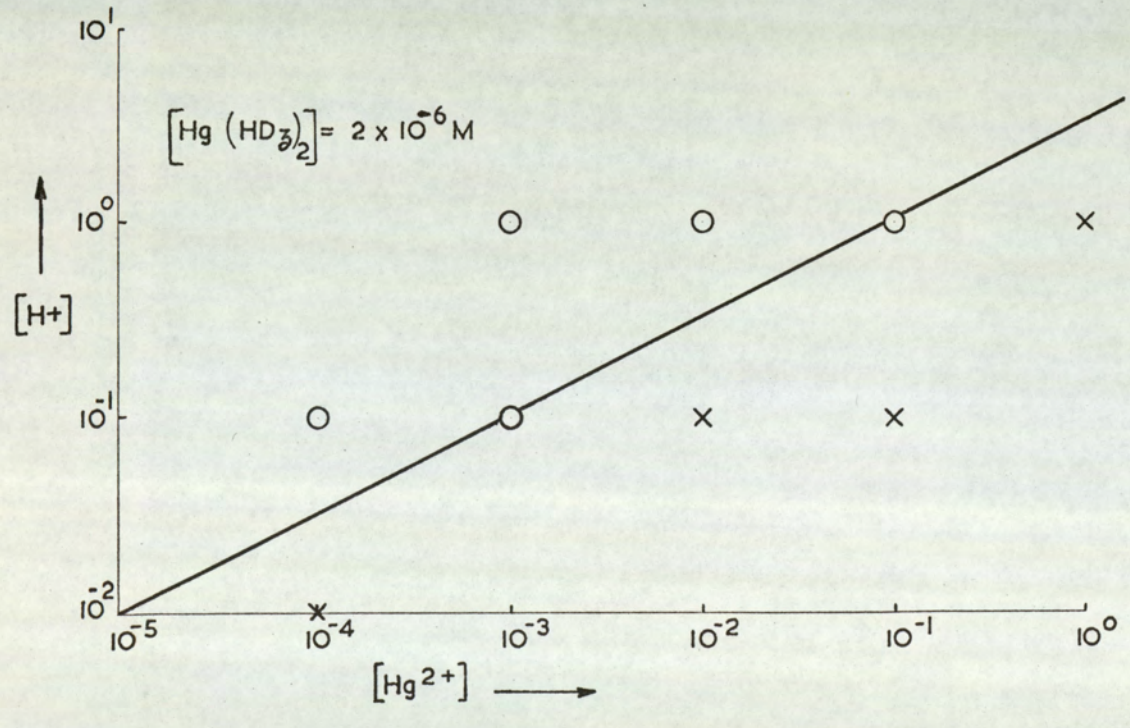
substituting this value in equation 1/29 gives

$$[Hg(HDz)_2]_{min} = 10^{-8.8}$$

which is the smallest reagent concentration which can be employed if no more than 0.1% of secondary mercuric dithizonate or 0.1% dithizone are to be formed. In order to work at this limit however 70M acid must be used which is quite impossible. If this equation represented the true situation it would be impossible to determine mercury substoichiometrically with dithizone and this thesis would never have been written, for at lower acidities even more

FIG. 1/1


10^{1}
10^{0}
10^{-1}
10^{-2}
[H+]
$[Hg(HD_3)]$ = 2×10^{-5}M
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
$[Hg^{2+}]$ ⟶


10^{1}
10^{0}
10^{-1}
10^{-2}
[H+]
$[Hg(HD_3)_2]$ = 2×10^{-6}M
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
$[Hg^{2+}]$ ⟶

secondary dithizonate would be formed.

This conclusion is based upon the work of Mylene Breant (B1) who determined the value of E_{HgDz} used above. In determining this constant Breant encountered difficulties because of the instability of the secondary dithizonate and she concludes that "....the constant is of the order of 10^{-3}." In view of the importance of this conclusion several attempts have been made to improve upon these measurements but with very little success.

The results of the first series of qualitative experiments are shown in Fig. 1/1. The circles represent tests in which the organic phase was orange, i.e., predominantly primary mercuric dithizonate. The crosses represent tests in which the organic phase was violet, i.e., predominantly secondary mercuric dithizonate. The straight line represents an extraction constant

$$E_{HgDz} = 2 \times 10^{-5}$$

when

$$[HgDz] = [Hg(HDz)_2]$$

The next series of experiments were quantitative ones. The concentrations of secondary mercuric

dithizonate and primary mercuric dithizonate in the organic phase were estimated by solving the simultaneous equations resulting when the absorbance of this phase was measured at two wavelengths; the absorption maxima of the two complexes. The results are shown in Table 1/8. These results are unreliable for three reasons.

(1) The time allowed for the reaction was only one minute. This certainly does not represent complete reaction, but upon further shaking the secondary dithizonate begins to decompose, and after shaking for 18 hours a completely colourless organic phase is obtained.

(2) In every case the total amount of reagent present in the organic phase, computed from the concentrations of primary and secondary dithizonate found, was less than that initially added, because a precipitate of secondary mercury dithizonate was formed. The concentration of secondary dithizonate however was always less than its solubility in carbon tetrachloride (6×10^{-5}M) and the loss was experienced even when the initial reagent concentration was only one tenth of the solubility. This is a clear indication that equilibrium had not been reached in these experiments. It is probable that the secondary mercuric dithizonate is formed in the

aqueous phase by the reaction :-

$$Hg^{2+} + Dz^{2-} \rightleftharpoons HgDz$$

This precipitates secondary mercuric dithizonate from the aqueous phase which dissolves only slowly in the organic phase, and equilibrium is not reached before decomposition begins. The higher the initial reagent concentration the greater the amount of secondary dithizonate precipitated, the larger the surface area of solid exposed to the organic solvent and the higher the concentration of secondary dithizonate found in the organic phase. Table 1/9 illustrates this, the concentration of secondary dithizonate approaches saturation at high reagent concentrations. This table also shows that the amount of primary dithizonate remaining increases with initial reagent concentration, proving that the formation of secondary dithizonate in the aqueous phase is also incomplete for at equilibrium the concentration of the primary dithizonate should be a function of the concentration of the secondary complex in the aqueous phase, which is a constant because the aqueous phase will be saturated.

(3) In the quantitative experiments the ionic strength was maintained at 5.0M by the addition of sodium perchlorate. Later investigations showed that the apparent extraction

constant varied drastically with ionic strength. This is almost certainly connected with the incompleteness of the reaction.

Because this reaction is slow it is impossible to estimate the amount of secondary dithizonate from equilibrium considerations, and empirical investigation is essential. In all the following experiments the organic phase was examined spectrophotometrically for secondary dithizonate; only in the case of solutions above pH2 was any detected.

A further reason why the formation of secondary mercuric dithizonate is unimportant is that it is completely prevented by the small traces of chloride usually present in the distilled water used as a solvent (see below 1.4.2.).

TABLE 1/8. Experimental estimates of E_{HgDz}.

$[H^+]$	$[Hg^{2+}]$						
	5×10^{-3}	1×10^{-2}	2×10^{-2}	5×10^{-2}	1×10^{-1}	2×10^{-1}	5×10^{-1}
5.0				5.74	3.68	4.60	6.19
2.0				5.48	3.80	4.08	5.11
1.0	3.66	4.03	4.07	4.25,4.57	4.58	3.96	5.10
0.5	3.92	4.66	4.17	4.35,4.52	4.89	4.84	5.28
0.2	4.40	4.35	5.00,4.82	5.18,5.03	6.42	5.80	6.00
0.1			4.92				
0.05			6.10				

The results are quoted as $-\log E_{HgDz}$ and omitting those values which are $\simeq$ 6.0 the mean is 4.53 on 29 results.

$[Hg(HDz)_2]$ in. = 1×10^{-5}.

TABLE 1/9. Variation of E_{HgDz} with initial primary mercuric dithizonate concentration.

$[Hg(HDz)_2]$		$[HgDz]$	E_{HgDz}	$E' = \frac{E_{HgDz}}{[HgDz]^2}$
INIT.	FINAL.			
3.3×10^{-4}	5.6×10^{-5}	2.8×10^{-5}	7×10^{-5}	0.9×10^{5}
2.0×10^{-4}	4.7×10^{-5}	1.1×10^{-5}	1.3×10^{-5}	1.1×10^{5}
6.0×10^{-5}	2.0×10^{-5}	1.2×10^{-5}	3.6×10^{-5}	2.5×10^{5}
3.6×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	6.6×10^{-5}	3.9×10^{5}
1.6×10^{-5}	6.9×10^{-6}	4.2×10^{-6}	1.3×10^{-5}	7.3×10^{5}
6.3×10^{-6}	3.0×10^{-6}	1.0×10^{-6}	1.7×10^{-6}	1.7×10^{5}
2.8×10^{-6}	1.4×10^{-6}	2.6×10^{-7}	2.4×10^{-7}	3.6×10^{5}

1.3.3. The formation of hydroxy complexes.

In alkaline solutions the sensitivity is reduced by the formation of undissociated mercuric hydroxide in the aqueous phase. This is governed by the reaction :-

$$Hg^{2+} + 2H_2O \rightleftharpoons Hg(OH)_2 + 2H^+$$

for which the equilibrium constant is (A1) :-

$$K = 10^{-6.3} = \frac{[Hg(OH)_2][H^+]^{2.}}{[Hg^{2+}]} \text{ ---------- } 1/31$$

using equation 1/31 to substitute for $[Hg^{2+}]$ in equation 1/28 gives :-

$$10^{32.9} = \frac{[Hg(HDz)_2]_{org.}}{[H_2Dz]^2_{org.}[Hg(OH)_2]}$$

corresponding to the reaction

$$Hg(OH)_2 + 2H_2Dz = Hg(HDz)_2 + 2H_2O.$$

making the usual assumptions

$$[Hg(OH)_2] = [Hg(HDz)_2]_{org.}$$

$$[H_2Dz]_{org.} = 10^{-3}[Hg(HDz)_2]_{org.}$$

gives :-

$$[Hg(HDz)_2]^2_{org.} = 10^{-26.9}$$

$$[Hg(HDz)_2]_{org.} = 10^{-13.45} \text{ ----------} 1/32$$

This is the lowest possible reagent concentration, below which more than 0.1% of the reagent remains unconsumed, providing that the formation of hydroxy complexes is the only limiting factor. This is much lower than that found for secondary mercuric dithizonate. The formation of the secondary dithizonate is a more serious limitation than the formation of the hydroxide.

Equation 1/32 contains no terms involving $[H^+]$. The sensitivity is independant of pH providing :-

$$[Hg(OH)_2] > [Hg^{2+}]$$

from equation 1/31, this is true when :-

$$[H^+]^2 < 10^{-6.3}$$

$$[H^+] < 10^{-3.15}.$$

i.e. above pH 3.2.

However if the pH is maintained by buffers, these will almost certainly be composed of anions which form stronger complexes with mercury than the hydroxide ion, and so will limit the sensitivity more severely (section 1.4.2.).

Upon hydrolysis, mercury also forms the anionic complex, $Hg(OH)_3^-$, and the polynuclear complexes, $Hg_2(OH)_2^{2+}$ and Hg_2OH^{3+}. These do not affect the previous conclusions however for the

former is only formed in strongly alkaline solutions and the latter are only formed at very high mercuty concentrations.

$$\frac{[Hg(OH)_3][H^+]}{[Hg(OH)_2]} = 10^{-14.85} \quad (G1)$$

$\therefore [HgOH)_3] > [Hg(OH)_2]$

if $[H^+] < 10^{-14.85}$ i.e., above pH 14.85.

$$\frac{[Hg_2OH]}{[HgOH][Hg^{2+}]} = 10^{-0.9} \quad (A1)$$

$\therefore [Hg_2OH] > [HgOH]$

if $[Hg^{2+}] > 10^{-0.9}$

$$\frac{[Hg_2(OH)_2]}{[Hg(OH)_2][Hg^{2+}]} = 10^{1.05} \quad (A1)$$

$\therefore [Hg_2(OH)_2] > [Hg(OH)_2]$

if $[Hg^{2+}] > 10^{-1.05}$

Similarly the complex $Hg(OH)^+$ is formed in acid solutions where hydrolysis will be of even less importance than with the dihydroxy complex.

$$\frac{[HgOH^+]}{[Hg(OH)_2][H^+]} = 10^{2.7} \quad (A1)$$

$$[\,HgOH^{+}\,] > [\,Hg(OH)_2\,]$$

if $[\,H^{+}\,] > 10^{-2.7}$ i.e., below pH 2.7.

1.3.4. The stability of the reagent.

Very dilute solutions of dithizone are unstable. If the reagent decomposes appreciably between the time it is pipetted into the separating funnel and the time it is converted to the more stable mercuric dithizonate, differences may occur between the amounts of mercury extracted from the sample and the standard. The amount of mercuric dithizonate formed is not, by itself, important, but differences between the sample and the standard must be avoided.

These differences may arise for several reasons; 1) because the greater concentration of mercury in the sample effects a speedier conversion to mercuric dithizonate; 2) because the reagent in one test is allowed to decompose whilst reagent is being added to the next; 3) because there are catalysts present in the sample which are absent from the standard or 4) because the sample and standard are at different temperatures.

These effects are small and the reagent will be allowed to decompose, at the most, for a few minutes. Only reagent solutions which are decomposing very rapidly will affect the results.

Unfortunately the decomposition of dithizone solutions is not a reproducable phenomenon. It is

due to the presence of minute amounts of oxidising agents in the organic solvent and varies greatly between one batch of solvent and another. In practice solutions as dilute as 10^{-8}M have been used occasionally but sometimes even 10^{-6}M solutions cannot be used. If zinc dithizonate is used instead of dithizone, a greatly increased stability is obtained and if most of the oxidising agents in the organic solvent are destroyed by the prior addition of a slight excess of reagent, 10^{-7}M solutions can be used for several weeks. Under these circumstances the stability of the reagent does not limit the sensitivity of the method.

There are two considerations to be born in mind when using zinc dithizonate. Firstly, it reacts more slowly with mercuric ions than dithizone. Secondly, the zinc ions liberated by the reaction compete with mercury for the dithizone and the sensitivity is lowered. Neither of these is important. The reaction is slowed down much more drastically if E.D.T.A. is added to overcome chloride interference (chapter 4) and zinc forms such a weak complex with dithizone that its affect on the sensitivity is undetectable. (see section 1.4.3.).

1.3.5. The limitations placed upon the sensitivity by the specific activity of the isotope used.

When determining very small quantities of mercury, the precision of the method will be limited by the difficulty of measuring very small amounts of radioactivity. In order to calculate the sensitivity of the method, if this were the only factor to limit the sensitivity, a minimum permissible precision must be decided upon and then the amount of radioactivity necessary to give this precision calculated.

The following argument is often used in designing tests of a certain accuracy. Imagine a sample (A) containing a certain amount of mercury (x). The results of the analysis of this sample will vary around x because of the difficulty of measuring the small amount of activity used. If the distribution of these results is normal with a standard deviation σ then 95% of these results will lie between $x \pm 2\sigma$. If a single analysis is carried out the probability of the result lying within this range is 0.95. Similarly if the analysis of another sample (B) gives the result y, then the true result will lie between $y \pm 2\sigma$

FIG 1/2

$2\sigma = 0{\cdot}1x$

THE PROBABILITY THAT y IS LESS THAN $(x + 2\sigma)$ IS 50% (THE SHADED AREA)

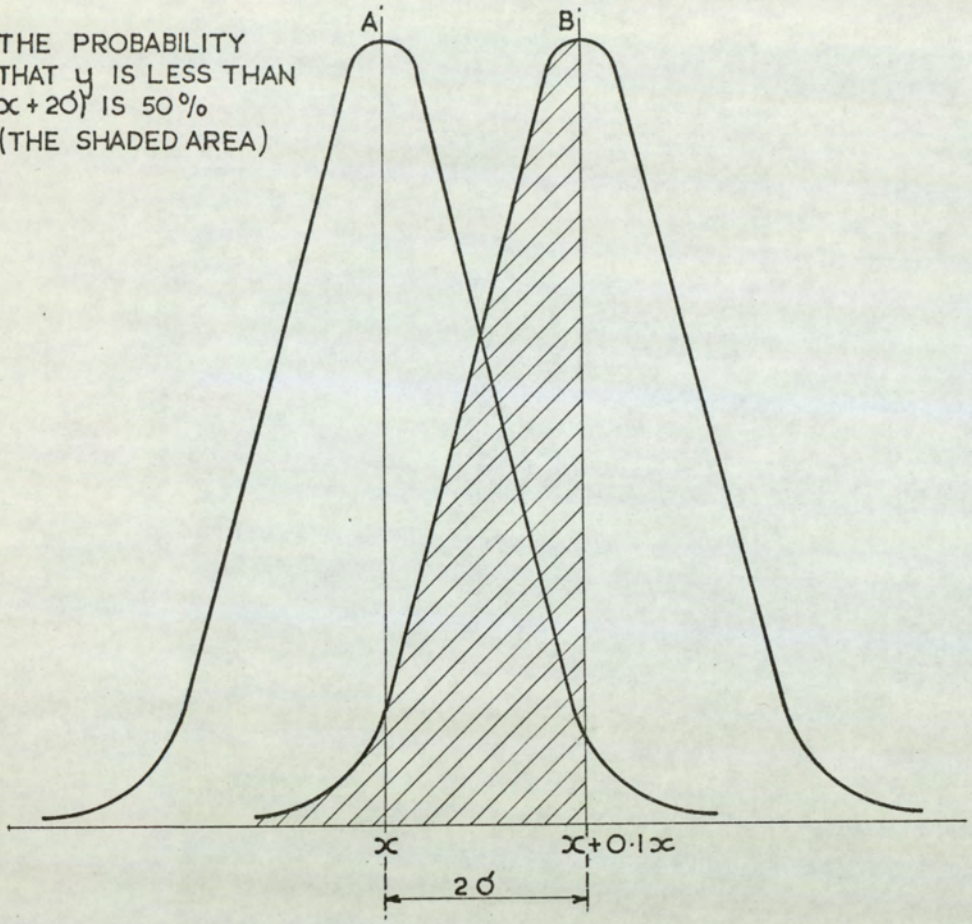
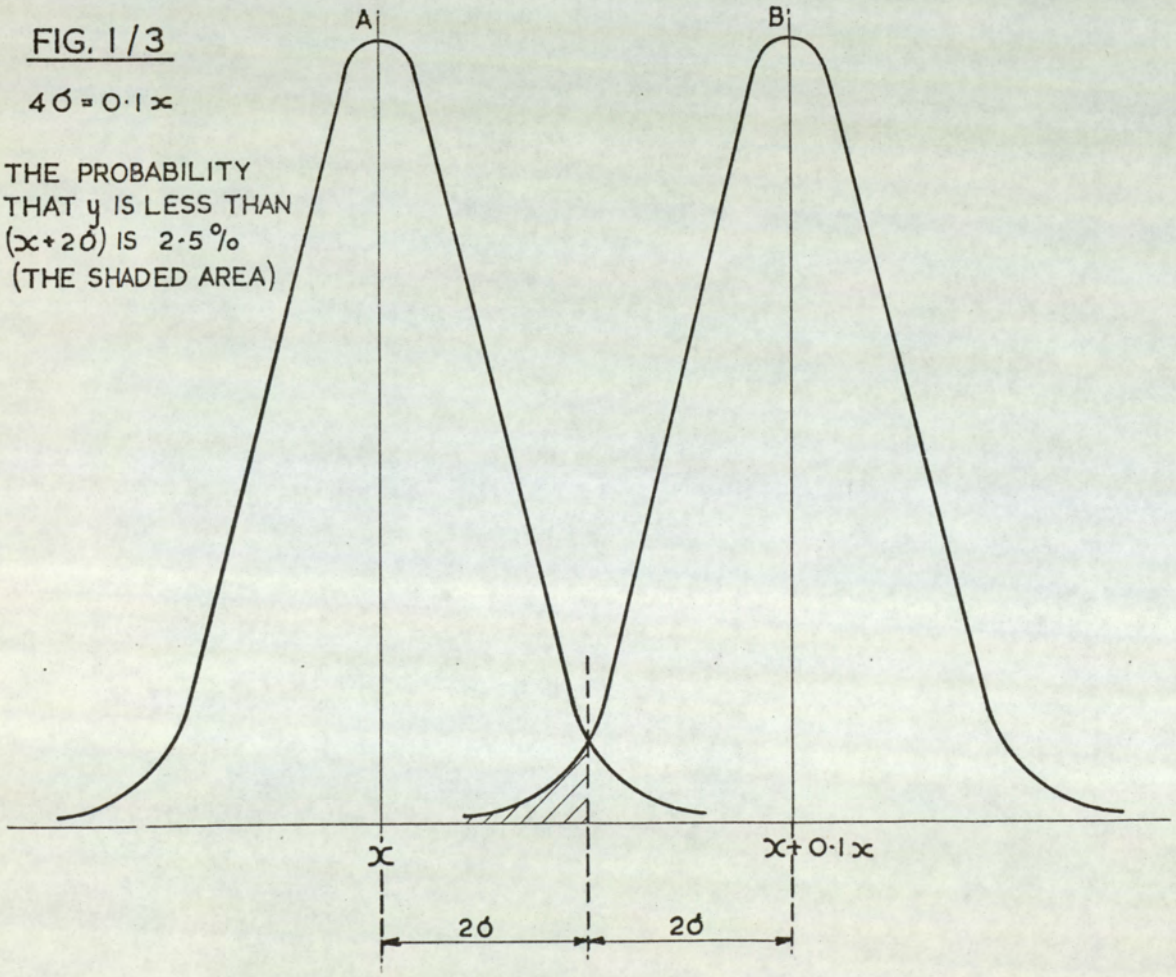


FIG. 1/3

$4\sigma = 0{\cdot}1x$

THE PROBABILITY THAT y IS LESS THAN $(x + 2\sigma)$ IS 2·5% (THE SHADED AREA)



with a probability of 0.95. Now a probability of 0.95 may be considered near enough certainty so that if it is desired to know the true result to within $\pm$ 0.1x, then enough radioactivity must be added so that

$$2\sigma = 0.1x \qquad \text{----------1/33}$$

This argument is quite satisfactory providing the statistics used are understood. However analysts often believe that these 95% confidence limits represent the smallest difference which can be detected with certainty; that if the true result for sample B is x + 0.1x then an analysis will always reveal the difference between A & B, providing equation 1 is satisfied. This is untrue. There is, in fact, a chance of 50% that y is less than $x + 2\sigma$ as can be seen from FIG.1/2. In order to reduce mistakes of this type (known as errors of the second kind) a smaller value of σ must be obtained by increasing the amount of radioactivity used. If the limit shown in FIG.1/3 is used viz :-

$$4\sigma = 0.1x \qquad \text{--------1/34}$$

then the probability of making such a mistake is reduced from 0.5 to 0.025.

As an example suppose that x is the maximum permissible limit for the amount of mercury in wheat to be used for cereal

manufacture. Then, if the manufacturer rejects all batches which upon analysis show more than 0.9x, he will be certain of satisfying this limit if he adds sufficient radioactivity to satisfy equation 1/33. If, however, he has analysed a competitor's product and obtained the result x, and wishes to be certain of selling a cereal containing less mercury than his competitors by selling only material analysing at 0.9x, he must use equation 1/34 to choose a suitable activity.

These limits are completely arbitrary and almost any relationship between x and σ could be chosen. Two other important limits should be mentioned, the two limits of detection.

If a result, y, is obtained, this result is significantly greater than zero if y is greater than y_d and

$$y_d = 2\sigma$$

This is a limit of detection often suggested but if the sample actually contains x and $x = y_d$ there will only be a 50% chance of y being greater than y_d. A better limit is x_d

$$x_d = 4\sigma$$

The smallest amount of mercury which can be detected with certainty is x_d, and if $x = x_d$ there is only a 2.5% chance that y will be less than y_d.

TABLE 1/9 summarizes these relationships in terms of the coefficient of variation (v) used in section 1/2.

Having decided upon a minimum permissible precision the smallest amount of mercury which can be determined with this precision must be calculated. The general equation for the precision of the substoichiometric method was given in section 1/2 as :-

$$v^2(W_s) = v^2(MD) + v^2(MW_a) + v^2(V_a) + v^2(V_s) + \left(\frac{1+q}{q}\right)^2 \left\{ 2\,v^2(I) + 2\,v^2(Cl) + 2\,v^2(R) + 2\,v^2(V_c) + v^2(PA_a) + v^2(PA_s) + v^2(F_a) + v^2(F_s) \right\} \qquad \text{----------1/27.}$$

Amongst the terms included in this equation only $v^2(PA_a)$ and $v^2(PA_s)$ depend upon the specific activity of the isotope used. The coefficients of variation $v(F_a)$ and $v(F_s)$ are affected by the specific activity indirectly but are primarily functions of the adsorption of primary mercuric dithizonate on the walls of the separating

funnel (see section 1.3.7.). In this section only the effect of specific activity is being considered and $v(F_a)$ and $v(F_s)$ will be both assumed to have the value of $v(F_a)$ calculated in TABLE 1/6. Substituting the numerical values given in section 1/2 to the other terms in equation 1/27, but assuming $v(Cl) = 0$ (i.e., E.D.T.A. present) gives the equation :-

$$v^2(W_s) = \left(\frac{(1+q)}{q}\right)^2 \left(2.02 + v^2(PA_a) + v^2(PA_s) \right)$$

In this equation $v(MD)$, $v(MW_a)$, $v(V_a)$ and $v(V_s)$ have been neglected because they are too small to affect the final result.

In order to relate this equation to the specific activity it is necessary to substitute for $v(PA_a)$ and $v(PA_s)$ from equations involving the amount of activity used in the analysis. Equations 1/17 and 1/25 used in section 1/2 are, however, not applicable here because the activities to be measured are comparable in magnitude to the background activity. Indeed the background must be included because it has a direct effect upon the sensitivity.

Let C_s be the number of counts accumulated in time T by the counter when counting the sample vial and let A_b be the

background activity.

$$C_s = T(A_s + A_b)$$

$$V(C_s) = T(A_s + A_b)$$

$$A_s = \frac{C_s}{T} - A_b.$$

$$V(A_s) = V(C_s) \left(\frac{\partial A_s}{\partial C_s}\right)^2 + V(A_b) \left(\frac{\partial A_s}{\partial A_b}\right)^2$$

$$= \frac{T.(A_s + A_b)}{T^2} + \frac{A_b T}{T^2}$$

where $V(A_b) = \frac{A_b T}{T^2}$ analogous to the

equations (1/17 and 1/25) developed for A_a and A_s in section 1/2. assuming the background is also counted for T sec.

$$10^4. \frac{V(A_s)}{A_s^2} = v^2(PA_s) = \frac{(A_s + 2A_b.).\ 10^4}{T.A_s^2}$$

similarly

$$v^2(PA_a) = \frac{(A_a + 2A_b)\ 10^4}{T.A_a^2}$$

let $A_a = n.A_b.$ ---------- 1/35

$$v^2(PA_a) = \frac{A_b.\ (n + 2).\ 10^4}{T.A_b^2\ n^2}$$

$$v^2(A_b) = \frac{V(A_b).\ 10^4}{A_b^2} = \frac{10^4}{TA_b}$$

by manipulating equation 1/13 it can be shown that

$$\frac{A_a}{A_s} = \frac{W_s + W_a}{W_a} = 1 + q$$

$$\therefore \quad A_s = \frac{nA_b}{1 + q}$$

$$v^2(PA_s) = \frac{A_b\left(\frac{n}{1+q} + 2\right).\ (1+q)^{2}.\ .10^4}{T.\ n^2.\ A_b^{2.}}$$

Thus

$$v^2(PA_a) = v^2(A_b).\ \frac{(n+2)}{n^2}$$

$$v^2(PA_s) = v^2(A_b).\ \frac{(1+q)\ (n+2+2q)}{n^2.}$$

For the measurements of background activity used in this thesis, 10^4 counts were allowed to accumulate so that $v(A_b) = 1\%$. This value can be reduced by employing longer counting times. It will be shown below (section 1.3.8.) that the sensitivity of the substoichiometric determination of mercury is not limited by the specific activity available but by the amount of adsorbed mercuric dithizonate on the walls of the separating funnel. Using a smaller value of $v(A_b)$ would increase the sensitivity calculated in this section and would

not change this conclusion. For some other metal it is possible that the specific activity is the factor which limits sensitivity; in this case the minimum value of $v(A_b)$ should be determined experimentally. In this section, however, the value $v(A_b) = 1\%$ will be used giving an estimate of the sensitivity that could be attained with the technique actually employed.

This gives :-

$$v^2(W_s) = \left(\frac{1 + q)^2}{q} \right) \left(2.02 + \frac{n(2 + q) + (2q^2 + 4q + 4)}{n^2} \right)$$

--------- 1/36

In order to obtain an equation relating the precision ($v(W_s)$) to the amount of mercury in the sample (W_s) an equation is required relating W_s to n and q. This equation is obtained as follows.

From the definition of q (equation 1/13)

$$W_s = q.W_a.$$

let

$$W_a = \frac{W_e}{S}$$

$$W_s = \frac{q.W_e.}{S}$$

but from equation 1/8

$$W_e = \frac{V_o.\ W_c.}{V_c}$$

$$W_S = \frac{q\ V_o.}{S\ V_c}\ W_c.$$

and from equation 1/10

$$W_c = \frac{A_a}{F}$$

$$W_s = \frac{q \cdot V_o \cdot A_a}{S. V_c. F.}$$

from the definition of n (equation 1/35)

$$A_a = n A_b$$

$$W_s = \frac{q \cdot V_o \cdot n. A_b.}{S. V_c. F.}$$

now F is the specific activity in c/s/g, so that

$$F = 3.7 \times 10^{10} \eta C$$

where η is the counting efficiency of the nucleonic equipment used and C is the specific activity in curies per g. of the isotope used.

so that

$$W_s = \frac{n\ q}{3.7 \times 10^{10}} \cdot \frac{A_b}{\eta} \cdot \frac{1}{C} \cdot \frac{V_o}{V_c.S.} \text{ -------1/37.}$$

In equation 1/37, n and q depend upon the precision, $\frac{A_b}{\eta}$ depends upon the quality of the instrumentation, $\frac{V_o}{V_c S}$ depends upon the skill of the analyst, and the remaining variable is C the specific activity available.

An examination of equation 1/37 shows that W_s is proportional to the product nq. For any particular value of $v(W_s)$ it is possible to select several pairs of values (n,q) which satisfy equation 1/36. By plotting a graph of nq versus q , that pair of values which give the minimum value of the product (n.q.) can be found. This calculation has been carried out for all four values of $v(W_s)$ given in TABLE 1/10 and gave the results quoted in TABLE 1/11.

In TABLE 1/11 it is assumed that

$$V_o = 10 \text{ ml}, \quad V_c = 5 \text{ ml}, \quad S = 0.5$$

these are the conditions most often used in isotope dilution analysis. This can be improved upon by increasing V_c and S to the limit where $\frac{V_o}{V_c S} = 1.$

How near this limit can be approached depends upon how much liquid is absorbed by the filter paper when separating the organic and aqueous phases and upon how accurately the strength of the reagent can be adjusted so that, in the standard, only a very small excess of mercury remains in the aqueous phase. In neutron activation analysis where strong solutions are used this factor has been decreased to 1.5. Also in this table $\frac{A_b}{\eta}$ has been assumed

to be 1 5c/s. Typical values of this ratio, for the equipment used in this work, are given in TABLE 1/12. The value of C used in TABLE 1/11 was 0.5 curies per g of mercury, which is the specific activity of the commercially available isotope.

TABLE 1/10. The minimum permissible precision.

Type of analysis	Only errors of the first kind controlled.	Errors of both the first and the second kind controlled.
Qualitative.	$2\sigma = x.$ $v(W_s) = 50\%.$	$4\sigma = x.$ $v(W_s) = 25\%.$
Quantitative.	$2\sigma = 0.1x.$ $v(W_s) = 5\%.$	$4\sigma = 0.1x.$ $v(W_s) = 2.5\%.$

TABLE 1/11. The smallest amount of mercury determinable. ($W_s(min)$).

$v(W_s)$	nq	q	m	A_a/η	A_s/η	M reag.	$W_s(min)$	W_a
2.5	11.5	2.0	5.75	86.3c/s	28.8c/s	4.6×10^{-9}	0.0368µg	0.0184µg
5.0	1.74	0.6	2.88	43.2c/s	27.0c/s	2.4×10^{-9}	0.0057µg	0.0092µg
2.5	0.125	0.13	1.00	15.0c/s	13.3c/s	8.0×10^{-10}	0.0004µg	0.0032µg
5.0	0.046	0.08	0.58	8.6c/s	8.0c/s	4.6×10^{-10}	0.0015µg	0.0018µg

TABLE 1/12. Efficiencies and backgrounds of the counting equipment.

Equipment	A_b c/s.	η	A_b/η c/s
Research Electronics*	15	0.40	37
Nuclear Enterprises single channel	2.4	0.17	14
Nuclear Enterprises Gammamatic	4.0	0.31	13
Nuclear Enterprises single channel *	9.0	0.34	26
Nuclear Enterprises Gammamatic *	7.0	0.46	15

In the unmarked cases the mercury 203 peak at 278 kev was measured, all the activity between 230 kev and 380 kev being included. Where the suffix * is present, the thallium X-ray was also included, all the activity above 30 kev being counted.

1.3.6. A comparison of the sensitivity of substoichiometric isotope dilution and neutron activation analysis.

It is the specific activity which limits the sensitivity of neutron activation analysis. This limit may be calculated in a similar manner to that adopted in the previous section for isotope dilution analysis.

The equation :-

$$W_s = W_a \cdot \frac{A_s}{A_a}$$

is the fundamental equation for substoichiometric neutron activation analysis analogous to equation 1/2 for isotope dilution analysis. Differentiation of this equation shows that condition 1/7 is satisfied, so that

$$v^2(W_s) = v^2(W_a) + v^2(A_s) + v^2(A_a)$$

This expression can be modified in the same way as the analogous isotope dilution expression (equation 1/14). Including only the most important terms gives the equation

$$v^2(W_s) = 2\,v^2(R) + 2\,v^2(F) + v^2(PA_s)$$

(N.B. $v(PA_a)$ will be very small because in neutron activation analysis the standard will have a

large, easily measured, activity).

Substituting the values of $v^2(R)$ and $v^2(F)$ given in section 1/2 gives :-

$$v^2(W_s) = 2.02 + v^2(PA_s)$$

but

$$\frac{v^2(PA_s)}{10^{-4}} = \frac{V(PA_s)}{A_s^2} = \frac{(A_s + 2A_b)}{T.A_s^2}$$

let $A_s = mA_b$.

$$v^2(PA_s) = v^2(A_b).\left(\frac{m+2}{m^2}\right)$$

$$v^2(W_s) = 2.02 + \left(\frac{m+2}{m^2}\right) \text{ ----------1/38.}$$

if $v(A_b)$ = 1% as in section 1.3.5.

This equation is analogous to equation 1/36 for isotope dilution. Following the same argument as used for isotope dilution instead of equation 1/37, one obtains the equation :-

$$W_s = \pm \frac{m}{3.7 \times 10^{-10}} \cdot \frac{A_b}{\eta} \cdot \frac{V_o}{V_c.S} \cdot \frac{1}{C}$$

Solving equation 1/38 for the minimum value of m, using the values of $v(W_s)$ given in TABLE 1/10 gives the results reproduced in TABLE 1/13. It can be seen from this table that neutron activation analysis is more sensitive than isotope dilution

analysis even when the difficulties due to adsorption, which bedevil isotope dilution analysis, are overcome. If accurate quantitative analysis of a small amount of mercury is required neutron activation analysis is greatly superior. In this argument the same specific activity has been assumed for both methods of analysis. In practice, if the metal has one radioactive isotope with a long half-life, the commercially available isotope will be more active, giving some advantage to isotope dilution analysis, but if the metal has an isotope with a short half-life, the advantage lies with neutron activation analysis because such isotopes are inconvenient for isotope dilution. However, these minor differences are not important because it is not specific activity but adsorption which limits the sensitivity of isotope dilution analysis. The very great advantage of neutron activation analysis is the complete avoidance of this error so that the full sensitivity calculated in TABLE 1/13 can be obtained. The claim made by Růžička and Stary (R2) that the sensitivity of isotope dilution analysis rivals that of neutron activation analysis cannot be upheld.

TABLE 1/13. A comparison of the sensitivity of neutron activation and isotope dilution analysis.

$v(W_s)$ %	Sensitivity of isotope dilution analysis n q (a)	Sensitivity of neutron activation analysis m. (b)
2.5	11.5	0.815
5.0	1.74	0.318
25	0.125	0.0575
50	0.046	0.0283

(a) $$W_s(\text{min}) = n\,q.\,\frac{A_b.}{\eta}\,\frac{V_o}{V_c}\cdot\frac{1}{S}\cdot\frac{10^{-10}}{3.7C}\ (g)$$

(b) $$W_s(\text{min}) = m.\,\frac{A_b.}{\eta}\,\frac{V_o}{V_c}\cdot\frac{1}{S}\cdot\frac{10^{-10}}{3.7C}\ (g)$$

where $W_s(\text{min})$ is the smallest amount of mercury which can be determined and C is the specific activity of the isotope. The other symbols (A_b, η V_o, V_c and S) are constants whose meaning is given in the text.

1.3.7. The influence of adsorption on the sensitivity and accuracy.

Adsorption may occur from either the aqueous or the organic phase. Adsorption from the aqueous phase does not affect the accuracy or the precision providing sufficient mercury remains in the aqueous phase to react with all the reagent. The estimate of W_s does not depend upon the amount of mercury present but upon the isotope dilution law (equation 1/3). The radiochemically labelled mercury must, of course, be added before the adsorption takes place for this to be true. The amount of mercury adsorbed from the aqueous phase varies from 0.01 to 1.0µg ; figures which show that adsorption from the aqueous phase can limit the sensitivity. The amount of mercury adsorbed in any particular case depends upon the complexity of the pretreatment and the surface area of the glassware used.

Adsorption of mercuric dithizonate from the organic phase is a much more serious source of error. This has two effects corresponding to (a) the amount of mercury adsorbed and (b) the specific activity of the mercury adsorbed.

If the concentration of the reagent is so low that adsorption accounts for an appreciable part of the mercury in the organic phase, then it is very unlikely that the same amount of mercury will be removed from (or added to) the

sample as is removed from the standard. If the final concentration of mercuric dithizonate is not identical in the sample and standard errors will occur because equation 1/11 (section 1.2.2.) will not reduce to equation 1/1 (section 1.1.2.); W_c' will not equal W_c.

Mercury will be transferred from the walls of the separating funnel to the organic phase if the separating funnel has previously adsorbed a large amount of mercury from a test in which the reagent is stronger than the test under consideration. Conversely, clean funnels, or funnels previously used for weaker reagents will remove mercury from the organic phase. This is a consequence of the laws of adsorption. The classical adsorption law :-

$$W_w = K\,[Hg(HDz)_2]^{1/n}, \quad n > 1 \text{ -------1/39.}$$

will be used in this section. It has no theoretical significance but has been found to apply to a wide variety of adsorption phenomena from dilute solution (G2). In equation 1/39, W_w is the weight of mercury on the walls of a separating funnel in equilibrium with a mercuric dithizonate solution of concentration $[Hg(HDz)_2]$ mole/litre, and n and K are constants (n must not be confused with the same symbol used

in section 1.3.5.).

When carrying out routine analysis by substoichiometry it is convenient to use a different set of separating funnels for each reagent concentration. If this is done adsorption does not alter the concentration of the organic phase because the mercuric dithizonate on the separating funnel walls is in equilibrium with that in solution, thus eliminating this source of error. This equilibrium is a dynamic one, however, and some mercury is always exchanged between the walls and the solution. The mercury on the walls will have a different specific activity to that in solution, the final specific activity of the organic phase will then be in error. As the magnitude of this effect will not be the same in the sample and standard, equation 1/11 will again not reduce to equation 1/1, because F' does not equal F, and if the results are calculated from equation 1/2, they will be wrong. It is this specific activity effect which is most troublesome in substoichiometric analysis.

Let W_t be the amount of mercury exchanged in time t and let F_w be the specific activity of the mercury on the

walls of the vessel. Let W_e be the total amount of mercury in the organic phase; F_e be the specific activity of this mercury before the exchange and F_f the final activity after the exchange. If the separating funnels have always been used with reagents of the same concentration the total amount of mercury transferred to the walls from the organic phase will equal the amount transferred from the organic phase to the walls. Thus :-

$$F_f = \frac{F_e (W_e - W_t)}{W_e} + F_w \frac{W_t}{W_e} \qquad \text{--------1/40}$$

$$\frac{dF_I}{dF_w} = \frac{W_t}{W_e}, \qquad V(F_f) = V(F_w) \cdot \frac{W_t^2}{W_e^2}$$

because all the variations in F_f are due to the variations in F_w (F_e, W_e are constants, W_t is also a constant if t is constant).

In the case of the standard $F_e = F_a$ and $V(F_f) = V(F_a)$.

$$\frac{V(F_a)}{F_a^2} = F(F_w) \cdot \frac{W_t^2}{F_a^2 \cdot W_e^2}$$

$$v^2(F_a) = \frac{10^4 \cdot W_t^2}{F_a^2 \cdot W_e^2} \cdot V(F_w) \qquad \text{---------1/41}$$

In the case of the sample

$$F_e = F_s = \frac{F_a \cdot W_a}{W_a + W_s} = \frac{F_a}{(1 + q)}, \qquad \text{and } V(F_f) = V(F_s)$$

so that

$$\frac{V(F_s)}{F_s^2} = V(F_w) \cdot \frac{W_t^2 \ (1+q)^2}{W_e^2 \ F_a^2}$$

$$v^2(F_s) = \frac{10^4 \cdot W_t^2 \cdot (1+q)^2}{W_e^2 \cdot F_a^2} \cdot V(F_w) \qquad \text{---------1/42}$$

These equations assume that $V(F_w)$ is the same for both the standard and sample. This is true because the separating funnels used for both will be selected at random from the same set of funnels.

If $v^2(F_a)$ and $v^2(F_s)$ are the predominant terms in equation 1/27 (section 1.2.5.), which will often be the case at low concentrations (see below), then :-

$$v^2(W_s) = \frac{(1+q)^2}{q^2} \left(v^2(F_s) + v^2(F_a) \right) \qquad \text{---------1/43}$$

substituting for $v^2(F_s)$ and $v^2(F_a)$ from equations 1/41 and 1/42 gives

$$v^2(W_s) = \frac{(1+q)^2}{q^2} \cdot \frac{10^4 \cdot W_t^2 \cdot V(F_w)}{W_e^2 \cdot F_a^2} \cdot \left((1+q)^2 + 1 \right) \qquad \text{---------1/44}$$

Amongst the terms in this equation only W_t and W_e vary with reagent concentration. The variations of F_w are due to the accumulated variations in the specific activity of the tests for which the funnel has previously been used, and are independant of

the reagent concentration, i.e., $V(F_w)/F_a^2$ does not vary with reagent concentration.

The isotopic exchange of mercury between solutions of mercuric dithizonate in carbon tetrachloride and mercury adsorbed on to glass surfaces is the sum of two first order reactions corresponding to exchange with primary mercuric dithizonate on the glass (rate constant $1/k = 1$ hr) and with mercuric chloride on the glass (rate constant $1/k = 30$ hr). During the time allowed for the extraction ($t = 10$ mins. for tests without E.D.T.A. and $t = 30$ mins. for tests with E.D.T.A.) only a small part of the mercury on the walls is exchanged and this part will mostly be primary mercuric dithizonate. Thus

$$\ln\left\{\frac{W_w}{W_w - W_t}\right\} = kt = \frac{t}{60} \quad (t \text{ in mins.})$$

$$\frac{W_t}{W_w} = 1 - e^{-kt}$$

but from equation 1/39

$$W_w = K\,[Hg(HDz)_2]^{1/n}$$

$$\therefore \quad W_t = K\,[Hg(HDz)_2]^{1/n}\left\{1 - (\ln^{-1} kt)^{-1}\right\}$$

also

$$W_e = V_o\,[Hg(HDz)_2]$$

substituting these relationships in equation 1/44 gives

$$v^2(W_s) = 10^4 \cdot \frac{V(F_w)}{F_a^2} \cdot \frac{K^2 \left[Hg(HDz)_2 \right]^{2/n} \left(1 - (\ln^{-1} kt)^{-1} \right)^2}{V_o^2 \left[Hg(HDz)_2 \right]} \cdot \left(\frac{(1+q)^2}{q^2} \cdot ((1+q)^2 + 1) \right)$$

$$v^2(W_s) = v^2(F_w) \cdot \left[Hg(HDz)_2 \right]^{(2/n - 2)} \cdot \left(\frac{(1+q)^2}{q^2} \cdot ((1+q)^2 + 1) \right) \qquad \text{--------1/45}$$

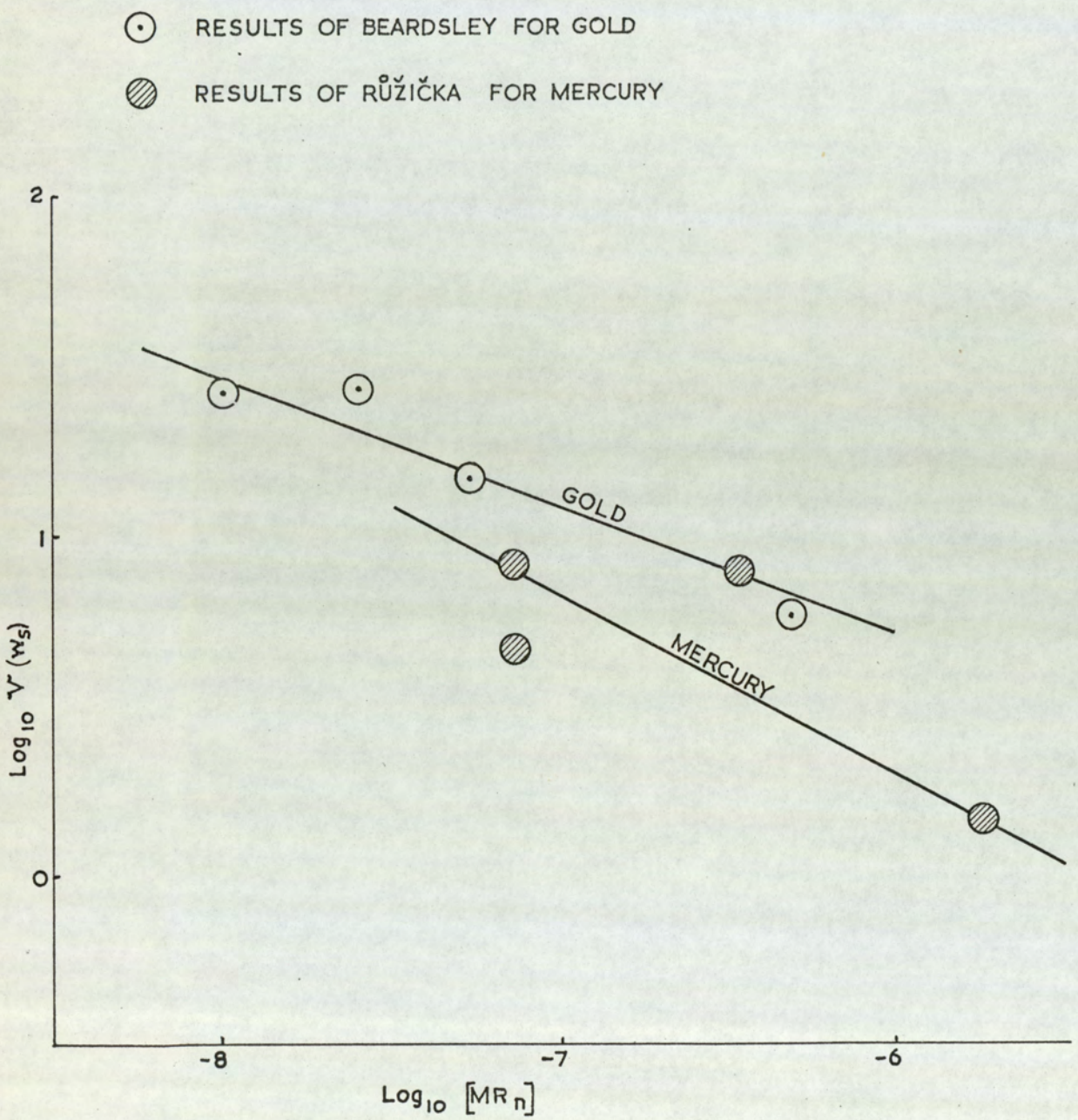
where

$$v^2(F_w) = 10^4 \cdot \frac{V(F_w)}{F_a^2} \cdot \frac{K^2}{V_o^2} \cdot \left(1 - e^{-kt} \right)^2 \qquad \text{--------1/46}$$

which is a constant.

Examination of equation 1/45 shows that a graph of log $v(W_s)$ versus log $\left[Hg(HDz)_2 \right]$ should give a straight line with a slope $(1/n - 1)$. Unfortunately

FIG. 1/4


RESULTS OF BEARDSLEY FOR GOLD
RESULTS OF RŮŽIČKA FOR MERCURY
GOLD
MERCURY
2
1
0
-8
-7
-6
Log10 V (Ws)
Log10 [MRn]

no data suitable for such a graph has been obtained in this study. In most of the work the reagent concentration has been so high that other terms in equation 1/27 (section 1.2.5.) are comparable with $v^2(F_a)$ and equation 1/43 does not hold. As a test of the hypothesis in general, n has been calculated from the data given by Růžička (R1) for mercury and Beardsley (B3) for gold. The results are given in Table 1/14 and the graph is shown as Fig. 1/4. The results for gold are quite good but those for mercury are poor. It is extremely difficult to determine standard deviations accurately and many of these results are based on too few degrees of freedom. The values of 'n' found (2.5 for gold, 2.2 for mercury) do not differ significantly from 2 and in the subsequent treatment this value will be assumed. (See also "The quantity of mercury adsorbed" Section 1.5.7.). It gives the simple relationship :-

$$v^2(W_s) \propto [Hg(HDz)_2]^{-1}$$

(N.B. When the adsorption occurs from aqueous solution n usually takes a value between 2 and 4, but no figures are available for adsorption from carbon tetrachloride. (G2)).

There is no proof in these figures that the changes in $v(W_s)$ with reagent concentrations are due to adsorption. Other explanations are possible, for example, greater instability of the reagent or the greater effect of variations in the blank. However the hypothesis is reasonable; the value of n obtained is reasonable; the reagent concentration at which $v(W_s)$ becomes very large is a concentration at which adsorption is known to be very important; and, finally, calculations based on the value n = 2 are in reasonable agreement with the entirely independent estimate of $v(F_a)$ given in section 1.2.6.

To calculate the contribution of adsorption to $v^2(W_s)$ at the high concentrations used in this work it is necessary to assume that only this adsorption contribution varies with reagent concentration and also that this variation follows some known law. The law assumed here is that derived above from the results of Beardsley (B3) and Růžička (R1), i.e., equation 1/39 is assumed to hold with n = 2.

In section 1.2 all the values of

$v(A_a)$, determined in the absence of E.D.T.A. were combined to give a single value regardless of reagent concentration. If these values are divided into groups with closely similar reagent concentrations TABLE 1/15 is obtained. This table reveals a clear trend of increasing experimental error with decreasing reagent concentration. The calculations which follow ascribe this trend to adsorption.

By comparing equation 1/44 with equation 1/45 it can be seen that, when n = 2 :-

$$v^2(F_w) = \frac{10^4 . W_t^2 . V(F_w) [Hg(HDz)_2]}{W_e^2 . F_a^2}$$

This equation can be confirmed by substituting the values given above for K, k, and V_o into equation 1/46 which defines $v^2(F_w)$. Substituting this value of $v^2(F_w)$, which as explained above does not vary with reagent concentration, into equation 1/41, gives the dependance of $v^2(F_a)$ upon reagent concentrations, viz :-

$$v^2(F_a) = v^2(F_w) [Hg(HDz)_2]^{-1} \quad \text{--------1/47}$$

substituting this value of $v^2(F_a)$ into equation 1/24 gives

$$v^2(A_a) = v^2(I) + v^2(PA_a) + v^2(Cl) + v^2(R) + v^2(V_c) + v^2(F_w) [Hg(HDz)_2]^{-1}$$

let

$$v^2(x) = v^2(I) + v^2(PA_a) + v^2(Cl) + v^2(R) + v^2(V_c) \quad \text{------ 1/48}$$

and assuming that $v^2(x)$ does not vary with reagent concentration, equation 1/49 is obtained to describe the way in which $v(A_a)$ varies with reagent concentration.

$$v^2(A_a) = v^2(x) + v^2(F_w)\,[\,Hg(HDz)_2\,]^{-1} \text{ -------1/49.}$$

This equation must be used rather than equation 1/45 for two reasons; (a) the data in TABLE 1/15 refer to $v(A_a)$ not $v(W_s)$ as does the data of Beardsley and Růžička and (b) the concentrations of the reagent given in TABLE 1/15 are so high that $v^2(F_a)$ no longer dominates equations 1/24 and 1/27 as assumed in the derivation of equation 1/45 (i.e. $v^2(x)$ cannot be neglected).

Substituting the figures for the highest and lowest reagent concentrations from TABLE 1/15 into equation 1/49 give a pair of simultaneous equations.

$$8.54 = v^2(x) + v^2(F_w) \,/\, 1.4 \times 10^{-6}$$

$$4.02 = v^2(x) + v^2(F_w) \,/\, 1.3 \times 10^{-5}$$

Solving these equations give $v^2(x) = 3.50$ and $v^2(F_w) = 0.71 \times 10^{-5}$ litre mole $^{-1}$. There are two checks on these values. Firstly, calculating $v(A_a)$ at the remaining reagent concentration in TABLE 1/15 gives $v(A_a) = 2.22$ which agrees with the value 2.57 given in the table. Secondly, it is possible to compare

the value of $v^2(F_a)$ obtained in section 1.2.5. from the variation in the colour of the organic phase with that calculated from equation 1/47. The reagent concentration used in these experiments was 1.3×10^{-5}M so that $v^2(F_a) = 0.54$ from equation 1/47 is in good agreement with the value 0.45 given in section 1.2.5.

From this information it is possible to estimate $v(W_s)$ at any reagent concentration, and by equating these values of $v(W_s)$ to those limiting values suggested in section 1.3.5. (TABLE 1/10), the sensitivity of substoichiometric isotope dilution analysis, when limited only by adsorption, can be calculated.

Neglecting the terms, $v^2(MD)$, and $v^2(MW_a)$, which were shown in section 1.2.5. to be very small, in equation 1/19 gives

$$v^2(W_s) = \left(\frac{1+q}{q}\right)^2 \left(v^2(A_s) + v^2(A_a)\right)$$

Neglecting the terms $v^2(V_a)$ and $v^2(V_s)$ in equation 1/26, as suggested by the results given in section 1.2.5., and comparing the resulting equation with equation 1/48 it can be seen that

$$v^2(A_s) = v^2(x) + v^2(F_s)$$

so that

$$v^2(W_s) = \left(\frac{1+q}{q}\right)^2 \left(2\,v^2(x) + v^2(F_a) + v^2(F_s)\right)$$

also by combining equations 1/42 and 1/41

$$v^2(F_s) = (1 + q)^2 \; v^2(F_a)$$

and from equation 1/47

$$v^2(W_s) = \left(\frac{1 + q}{q}\right)\left(2\,v^2(x) + \frac{[1 + (1 + q)^2]\; v^2(F_w)}{[Hg(HDz)_2]}\right)$$

--------1/50

To calculate the sensitivity (W_s) from the precision ($v(W_s)$) a further equation is required relating W_s to the reagent concentration $[Hg(HDz)_2]$.

$$W_e = V_o\,[Hg(HDz)_2] \times 10^{-3} \times 200 \text{ g}$$
$$= 0.2\,V_o\,[Hg(HDz)_2]$$

$$\frac{W_s}{W_a} = q \quad , \quad \frac{W_e}{W_a} = S \quad , \quad \frac{W_s}{W_e} = \frac{q}{S}$$

$$\therefore \quad W_s = 0.2\frac{q}{S} \cdot V_o \cdot [Hg(HDz)_2]$$

Substituting this into equation 1/50 gives

$$v_2(W_x) = \left(\frac{1 + q}{q}\right)^2 \left(2\,v^2(x) + \frac{q.V_o\,v^2(F_w)\,(2 + 2q + q^2)}{5S\,W_s}\right)$$

--------1/51.

To obtain the greatest possible precision it is best to work in the presence of E.D.T.A. so as to reduce $v^2(Cl)$ to zero. This will not change $v^2(F_w)$ but will reduce $v^2(x)$. All the results given in TABLE 1/5A in the presence of E.D.T.A. were

obtained at a reagent concentration of 1.3×10^{-5}M whence $v^2(F_a) = 0.54$ from equation 1/47. Thus in the presence of E.D.T.A.:-

$$v^2(A_a) = 1.01 \quad \text{(see TABLE 1/5A)}$$

$$= v^2(x) + v^2(F_a)$$

$$v^2(x) = 1.01 - 0.54$$

$$= 0.47.$$

also $V_o = 10$ ml and $S = 0.5$ (both values commonly used for this work), and $v^2(F_w) = 0.71 \times 10^{-5}$ as shown above. Substituting these values into equation 1/51 gives :-

$$v^2(W_s) = \left(\frac{1+q}{q} \right)^2 \left(0.94 + \frac{0.71 \times 10^{-5}}{W_s} (8q + 8q^2 + 4q^3) \right)$$

This equation can be used to calculate the smallest quantity of mercury which can be determined with any given degree of precision. In the same way as in section 1.3.5., the smallest values of W_s which could possibly be estimated with each of the values of $v^2(W_s)$ given in TABLE 1/10 were estimated from graphs of W_s versus q. The results of these calculations are recorded in TABLE 1/16. It can be seen that the sensitivity obtained in this way is much less than those calculated in the previous sections (1.3.1. - 1.3.5.). Adsorption limits the sensitivity more severely than any other factor.

The figures in TABLE 1/16 must not be taken too literally. The estimate of $v(F_w)$ upon which they are based is a high one. The results were obtained with old separating funnels which had often been cleaned and had a glass surface with a high adsorption coefficient (K in equation 1/39). New untreated glass surfaces adsorb very little mercury whereas old separating funnels which have been treated with alkalies or chromic acid or strong detergents can adsorb very large amounts (e.g. 4 µg from 10^{-4}M solutions, 0.2 µg from 10^{-7}M solutions - see section 1.5). In TABLE 1/17 some results are presented which were obtained with dilute solutions and nearly new separating funnels. Much greater precision was obtained than predicted by equation 1/51 using $v^2(F_w) = 0.71 \times 10^{-5}$. However, even these results give a low sensitivity when compared with the values suggested in previous sections. It is now clear that adsorption is the factor which limits the sensitivity of isotope dilution analysis and that this limitation is an indefinite one depending upon the condition of the interior glass surface of the separating funnels used in the analysis. The very great advantage of neutron activation analysis is that the addition of carrier enables much higher reagent concentrations to be employed

so circumventing this difficulty. Only with neutron activation analysis can the full sensitivity of radiochemical methods be achieved.

There is one further aspect of adsorption errors which demands attention. In the above treatment only variable errors have been considered but an examination of equation 1/40 will show that the correct result will only be obtained when the specific activity of the mercury on the walls of the vessel is equal to the specific activity of the mercury in the organic phase (i.e., $F_f = F_e = F_w$). Further this condition must be true of both the standard and the sample if F and F' are to cancel in equation 1/11. As the standard and the sample necessarily have different specific activities both of these conditions are unlikely to be satisfied at the same time, and a bias will be introduced. This bias is clearly shown in the results of Beardsley and Růžička used above to estimate n (Beardsley; 20% high at 2.5×10^{-8}M, 50% high at 1×10^{-8}M; Růžička; 70% high at 7×10^{-8}M - see TABLE 1/14). As in the case of the variable error this bias increases at low reagent concentrations because a greater fraction of the mercury is adsorbed. This bias is the most disturbing aspect of the adsorption error; it

varies with the amount of mercury in the sample and with the previous history of the separating funnel used and so is almost impossible to estimate.

TABLE 1/14 Precision of the determination of Gold and Mercury at low concentrations.

Reagent Concentration	µg added	µg found (mean).	Standard deviation s µg.	q.
(a) Gold.(B3).				
5×10^{-7}	1.00	1.03	0.057	1.0
5×10^{-8}	0.10	0.10	0.016	1.0
2.5×10^{-8}	0.05	0.06	0.013	1.0
1×10^{-8}	0.01	0.015	0.0025*	0.5.
(b) Mercury(R1).				
1.7×10^{-6}	2.78		0.040*	1.6
3.5×10^{-7}	0.28		0.023*	0.8
7×10^{-8}	0.028		0.0012*	0.4
7×10^{-8}	0.0056	0.0095	0.00048*	0.08

* all corrected to a value of q = 1 using the formulae

$$s.(\text{table.}).\sqrt{20} = s_{Exp.}\sqrt{\frac{(1+q)^2}{q^2}(1+(1+q)^2)}$$

TABLE 1/15 Variation of $v(A_a)$ with reagent concentration.

$[Hg(HDz)_2]$	$v(A_a)$	ϕ	Experiments.
1.3×10^{-5}M	2.01%	37	117,119,120,121,122,124,133,138, 144,147,148.
5.0×10^{-6}M	2.57%	12	75
1.4×10^{-6}M	2.92%	7	58, 60,61

TABLE 1/16 Calculated limit of detection due to adsorption.

$v(W_s)$	q	W_s(min).	M(min).
2.5	1.0	230 µg	5.7×10^{-5}
5.0	0.6	2.4µg	1.0×10^{-5}
25	0.4	0.6µg	3.7×10^{-7}
50	0.4	0.16µg	1.0×10^{-7}

TABLE 1/17 Experimental $v(A_a)$ at low reagent concentrations.

Exp.	$[Hg(HDz)_2]$	$V(A_a)$	ϕ	$v(W_s)$(q=1).	$V(W_s)$(calc).+
103	2×10^{-8}M	3.4	3	15%	>100%
258	1×10^{-7}M	2.50	3	11.2%	50%

+ from equation 1/51.

1.3.8. Summary - limits of sensitivity.

In TABLE 1/18, the limitations imposed on the sensitivity by the factors discussed above are compared. The most important of these is adsorption. Under the best possible conditions this limits the sensitivity to 10^{-8} g of mercury, and to 10^{-4} g if the separating funnels are in poor condition and high accuracy is desired.

TABLE 1/18. Comparison of the limits of sensitivity imposed by various factors.

Factor	W_s(min).	Molarity of Reagent
Completeness of reaction - hydroxide complexes	6×10^{-8} µg	3×10^{-14}
Completeness of reaction - sec.mercuric dithizonate	2×10^{-3} µg	1.5×10^{-9}
Specific activity of the isotope *	4×10^{-4} µg	8×10^{-10}
Stability of the reagent solution	2×10^{-2} µg	1×10^{-8}
Adsorption of mercuric dithizonate*	6×10^{-1} µg	4×10^{-7}
* assuming $v(W_s) = 25\%$		

1.4. Selectivity.

1.4.1. The interference of metals.

If the sample contains metals other than mercury these may react with the mercury dithizonate forming some metal dithizonate. The organic phase from the sample would then contain less mercury than the standard and a high result would be obtained.

The amount of metal dithizonate formed is governed by the reaction :-

$$2\,M^{n+} + n\,Hg(HDz)_2 \rightleftharpoons 2\,M(HDz)_n + n\,Hg^{2+}.$$

which has the extraction constant :-

$$E_{M/Hg} = \frac{[M(HDz)_n]^2_{org}\,[Hg^{2+}]^n}{[Hg(HDz)_2]^n_{org}\,[M^{n+}]^2} \qquad \text{-------1/52}$$

$$= \frac{E^2_{M(HDz)_n}}{E^n_{Hg(HDz)_2}} \qquad \text{-------1/53}$$

where n is the charge on the metal ion and :-

$$E_{M(HDz)_n} = \frac{[M(HDz)_n]_{org}\,[H^+]^n}{[H_2Dz]^n_{org}\,[M^{n+}]}$$

In addition to the usual conditions $[Hg^{2+}] = [Hg(HDz)_2]_{org}$ and $[M(HDz)_n] = 10^{-3}\,[Hg(HDz)_2]$ a third condition $[M^{n+}] = 10^3\,[Hg^{2+}]$, must be imposed if a thousandfold excess of metal is to be tolerated. Substituting these conditions into

equation 1/52 gives :-

$$E_{M/Hg} = 10^{-12}$$

However $E_{Hg(HDz)_2} = 10^{26.66}$ (see section 3.3.8.)

so that by equation 1/53

$$E^2_{M(HDz)_n} = 10^{26.66n.} \times 10^{-12}$$

$$E_{M(HDz)_n} = 10^{(13.33n - 6)} \qquad \text{----------1/54}$$

If the metal extraction constant ($E_{M(HDz)_n}$) is less than the value given by equation 1/54, the metal does not interfere. If it is greater than this value then more than one thousandth of the reagent is converted to metal dithizonate. TABLE 1/18 gives all the known extraction constants for metal dithizonates into carbon tetrachloride. From this table it would appear that only palladium interferes seriously and that silver just interferes. In practice gold and platinum also interfere seriously (extraction constants not known) and silver interferes only at high concentrations; copper, bismuth etc., do not interfere.

In section 1.3.4. it was stated that the use of zinc dithizonate in place of free dithizone lowers the sensitivity. This effect can be treated quantitatively. As before $[Hg^{2+}] = [Hg(HDz)_2]_{org}$, also $[Zn^{2+}] = [Hg(HDz)_2]_{org}$ because the zinc dithizonate

initially present in the reagent is converted, at equilibrium, to an equivalent amount of zinc ions and mercuric dithizonate. Substituting these conditions, together with the value $E_{Zn/Hg} = 10^{-48.8}$ into equation 1/52 gives

$$\frac{[\,Zn(HDz)_2\,]}{[\,Hg(HDz)_2\,]} = 10^{-24.4}.$$

This amount of zinc dithizonate will be formed in addition to any free dithizone or secondary mercuric dithizonate, so that if 99.9% of the reagent is to be converted to primary mercuric dithizonate, slightly less dithizone etc., can be tolerated. The sensitivity must be lower, although by an utterly negligible amount.

TABLE 1/19. The interference of metals.

Metal M	Valence n	Extraction constant $E_{M(HDz)_n}$	Comments
Thallium	1	$10^{-3.34}$ (P1)	No interference
M^+	1	$10^{7.33}$	Just interferes.
Silver	1	$10^{7.6}$ (T1)	Just interferes.
Tin	2	10^{-2} (P1)	No interference
Nickel	2	$10^{-1.19}$ (K1)	No interference
Lead	2	$10^{0.38}$ (K1)	No interference
Cobalt	2	$10^{1.54}$ (K1)	No interference
Cadmium	2	$10^{1.6}$ (K1)	No interference
Zinc	2	$10^{2.30}$ (K1)	No interference
Copper	2	$10^{10.48}$ (S1)	No interference
M^{2+}	2	$10^{20.66}$	Just interferes
Palladium	2	10^{27} (S2)	Interferes
Gallium	3	$10^{-1.3}$ (P2)	No interference
Indium	3	$10^{4.84}$ (P1)	No interference
Bismuth	3	$10^{9.75}$ (K1)	No interference
M^{3+}	3	$10^{33.99}$	Just interferes

N.B. M^+, M^{2+}, M^{3+} represent theoretical metals which have extraction constants given by equation 1/54.

1.4.2. The interference of complexing agents which form mercury complexes soluble in the aqueous phase.

Ligands which form soluble undissociated complexes with mercury interfere by reducing the concentration of the mercuric ion in the aqueous phase and so reversing the reaction upon which the analysis is based. (see section 1.3.1.).

Consider a ligand (L) which forms complexes of the type, HgL_n, n = 1,2,3, or 4 (4 is the maximum co-ordination number of the mercuric ion). The charge on the complex ion will depend upon n and upon the charge on the ligand, and will not affect the quantitative argument. However if the complex is uncharged (e.g., HgI_2, HgS_2O_3 etc.), it may partition. In such cases the interference is more serious because even a weak complex will change the quantity of mercury extracted into the organic phase but if a large excess of ligand is added further charged complexes (e.g., HgI_4^{2-}, $Hg(S_2O_3)_2^{2-}$) are formed and usually these do not extract. Charged complexes always have low partition coefficients into carbon tetrachloride because the low polarity of this solvent is unfavourable for ion-association complexes.

Suppose that these complexes have a stability

product

$$\beta_n = \frac{[HgL_n]}{[Hg^{2+}]\,[L^-]^n} \qquad \text{----------1/55.}$$

N.B. Polynuclear complexes are more difficult to deal with. If a treatment is desired reference R3 should be consulted. Polynuclear hydroxy complexes have been dealt with in section 1.3.3.

The total concentration of mercury in the aqueous phase (C_{Hg}) is given by :-

$$C_{Hg} = [Hg^{2+}] + [HgL] + [HgL_2] + [HgL_3] + [HgL_4]$$

let

$$\alpha_{Hg(L)} = \frac{C_{Hg}}{[Hg^{2+}]} = 1 + \sum_{n=1}^{n=4} \frac{[HgL_n]}{[Hg^{2+}]}$$

$$= 1 + \sum_{n=1}^{n=4} \beta_n [L]^n$$

Hence a conditional extraction constant ($E'_{Hg(HDz)_2}$) can be defined as

$$E'_{Hg(HDz)_2} = \frac{E_{Hg(HDz)_2}}{\alpha_{Hg(L)}} \qquad \text{----------1/56.}$$

$$= \frac{[H^+]^2\,[Hg(HDz)_2]_{org}}{[H_2Dz]^2_{org} \cdot C_{Hg.}}$$

The treatment given in sections 1.3.1. and

1.3.2. may now be followed with the substitutions

(a) $E'_{Hg(HDz)_2}$ for $E_{Hg(HDz)_2}$ and (b) $C_{Hg} = [Hg(HDz)_2]_{org}$

for $[Hg^{2+}] = [Hg(HDz)_2]$ giving the equations

1/57 and 1/58 analogous to equations 1/29 and 1/30.

$$E'_{Hg(HDz)_2} = \frac{10^6 \ [H^+]^2}{[Hg(HDz)_2]^2} \qquad \text{---------1/57.}$$

$$E'_{Hg\ Dz} = 10^{-6} \ [H^+]^2 \qquad \text{---------1/58.}$$

combining these in the manner used in section 1.3.2.

$$\frac{E'_{Hg(HDz)_2}}{E'_{HgDz}} = \frac{10^{12}}{[Hg(HDz)_2]^2} \qquad \text{---------1/59.}$$

but

$$\frac{E'_{Hg(HDz)_2}}{E'_{HgDz}} = \frac{E_{Hg(HDz)_2}}{\alpha_{Hg(L)}} \cdot \frac{\alpha_{Hg(L)}}{E_{HgDz}} = \frac{E_{Hg(HDz)_2}}{E_{HgDz}}$$

That is to say equation 1/59 is the same condition used in section 1.3.2., $[Hg(HDz)_2] = 10^{-8.8}$. This is the smallest possible reagent concentration if 0.1%

of both free dithizone and secondary mercuric dithizonate are to be present in the organic phase at the same time. This is the sensitivity and is not influenced by the addition of the ligand whatever the stability constant of the complex formed.

The minimum permissible reagent concentration is a function of pH however. At high acidities it is given by equation 1/57. As the pH rises the minimum reagent concentration falls until the limit represented by equation 1/58 is reached. At this pH 0.1% of secondary dithizonate is formed; above this pH more secondary dithizonate is formed and substoichiometry is not possible. Now both equations 1/57 and 1/58 involve $\alpha_{Hg(L)}$, so that the range of pH values over which these changes occur is governed by the concentration of the interfering ligand.

Substituting in equations 1/57 and 1/58 for the conditional extraction constants from equation 1/56 and taking logarithms give equations 1/60 and 1/61.

$$pH = \tfrac{1}{2} \log \alpha_{Hg(L)} - \log [Hg(HDz)_2] - 10.33 \qquad \text{--------1/60}$$

$$pH = \tfrac{1}{2} \log \alpha_{Hg(L)} - 1.5 \qquad \text{--------1/61}$$

These equations clearly reveal the dependance of pH upon the alpha coefficient. If the reagent concentration is above $10^{-8.8}$M, the pH given by equation 1/60

(the lower limit below which free dithizone is formed) is below that given by equation 1/61 (the upper limit above which secondary mercuric dithizonate is formed). Any pH between these two limits will give satisfactory results. As an example consider the interference of 3.5 ppm of chloride ($[L^-] = 10^{-4}M$). At this concentration $\alpha_{Hg(Cl)} = 10^{5.23}$, equation 1/61 gives the highest tolerable pH as 1.12 and equation 1/60 the lowest tolerable pH as -2.71. Any pH between these limits would be suitable; 1M or 0.1M perchloric acid could be used. This calculation shows clearly that a small amount of chloride will prevent the formation of secondary mercuric dithizonate at normal acidities (see section 1.3.2.).

If the reagent concentration is high it is possible to prevent the interference of a ligand even when its exact concentration is not known. If the pH of the test solution is chosen to be that given by equation 1/61 for the lowest concentration of ligand anticipated, any ligand concentration above this will not interfere providing equation 1/60 is satisfied. Using the chloride concentration ($1 \times 10^{-4}M$) of the previous example as the lower limit and working with a $10^{-5}M$ reagent at a pH of 1.12, no interference would be experienced from chloride until its concentration exceeded 0.2M corresponding to an alpha coefficient of $10^{12.90}$.

(N.B. neither of these two examples have taken into account the formation of mercuric chloride dithizonate. In chapter 3 it will be shown that the formation of this substance is a very serious source of error).

Another method of overcoming the interference of a variable and unknown amount of ligand is to add a definite excess of a second ligand which forms stronger complexes with mercury. If two ligands (L_1 and L_2 say) are present the alpha value will be given by :-

$$\alpha_{Hg(L)} = \alpha_{Hg(L_1)} + \alpha_{Hg(L_2)} - 1.$$

The overall alpha coefficient will be dominated by the alpha value of the stronger ligand and the concentration of the weaker ligand will be of no importance. This procedure may cause difficulties however because mercury has a strong tendency to form mixed complexes containing more than one ligand. These will alter the overall alpha coefficient and the pH range. Usually the stability constants of such mixed complexes will not be known (see chapter 4).

When working with strong ligands with large alpha coefficients alkaline solutions must be used. Equation 1/60 however is inaccurate in alkaline solutions because when deriving it, the ionisation of dithizone was neglected. When this ionisation is taken into account equation 1/60 becomes

$$pH = \tfrac{1}{2} \log \alpha_{Hg(L)} - \log [Hg(HDz)_2] - 10.33 - \log \alpha_{H_2Dz}$$

Below pH 8.8 this equation reduces to equation 1/60 ($\alpha_{H_2Dz} \doteq 1$) above pH 8.8 it reduces to equation 1/62.

$$0 = \tfrac{1}{2} \log \alpha_{Hg(L)} - \log [Hg(HDz)_2] - 19.1 \text{ -----1/62.}$$

(N.B. These equations are derived in section 4.2.2. Equation 1/62 is equation 4/10 with $E_{Hg(HDz)_2} = 10^{26.66}$, $E_{H_2Dz} = 10^{-8.8}$, $V_o/V_a = 1$, $C_{H_2Dz} = 10^{-3} [Hg(HDz)_2]$, $C_{Hg} = [Hg(HDz)_2]$.)

Equation 1/62 gives the minimum reagent concentration it is possible to use with a given alpha coefficient when the pH is above 8.8, and this concentration is clearly independent of how high the pH actually is. However the pH must still be below that given by equation 1/61, so that only ligands which can give alpha coefficients above $10^{20.6}$ can be used in such alkaline solutions. To conclude, if the alpha value is below $10^{20.6}$ it is necessary to work below pH 8.8 and the minimum reagent concentration is $10^{-8.8}$ whereas if the alpha value is above $10^{20.6}$ it is possible to work in solutions more alkaline than pH8.8 and the minimum reagent concentration,

which is now given by equation 1/62, will be greater than $10^{-8.8}$.

Finally it must be remembered that dithizone reacts more slowly with undissociated mercury complexes than with free mercuric ions. Whenever the presence of interfering ligands is suspected a check should be made to ensure that the reaction time used is sufficient and that longer shaking times will not extract more mercury.

Reference C4 gives a comprehensive list of stability products for the calculation of alpha coefficients.

1.4.3. B The interference of metals in the presence of a second ligand.

In the spectrophotometric method for determining mercury with dithizone E.D.T.A. is often added to overcome the interference of copper and it was thought possible that a similar method could be used substoichiometricaly. Conditional constants can be used to modify the treatment of metal interference given in section 1.4.1. in the same way they were used in section 1.4.2. to modify the treatment given in sections 1.3.1 and 1.3.2. This gives equation 1/63 in place of equation 1/53.

$$E_{M/Hg} = \frac{\left(E'_{M(HDz)_n}\right)^2}{\left(E'_{Hg(HDz)_2}\right)^n} = \frac{E^2_{M(HDz)_n}}{\alpha^2_{M(L)}} \cdot \frac{\alpha^n_{Hg(L)}}{E^n_{Hg(HDz)_2}} \qquad \text{--------1/63.}$$

substituting (a) C_{Hg} for Hg^{2+} and (b) C_M for M^{n+}) throughout give instead of equation 1/54 - equation 1/64.

$$E_{M(HDz)_n} = \frac{\alpha_{M(L)}}{\alpha^{n/2}_{Hg(L)}} \cdot 10^{(13.33n - 6)} \qquad \text{-------1/64.}$$

In order to improve the selectivity the value of $E_{M(HDz)_n}$ which can be tolerated in the presence of the ligand (given by equation 1/64) must be greater than

the value which can be tolerated in the absence of the ligand (given by equation 1/54). That is

$$\frac{\alpha_{M(L)}}{\alpha^{n/2}_{Hg(L)}}$$

must be greater than one. If the predominant complex formed between the metal and the ligand is ML_p and the predominant complex formed between the ligand and mercury is HgL_q. This inequality becomes

$$\frac{1 + \beta_p [L]^p}{\left(1 + \beta_q [L]^q\right)^{n/2}} > 1$$

As the concentration of ligand is increased this fraction changes from one, at low ligand concentrations, to

$$\frac{\beta_p [L]^p}{\beta_q^{n/2} [L]^{q\,n/2}}$$

at high ligand concentrations. The ratio $\beta_p / \beta_q^{n/2}$ varies much more from one metal to the next than $[L]^{p - q\,n/2}$ and it is convenient to assume that the latter is one. This is in fact the case for E.D.T.A. ($p = q = 1$) and bivalent metal ions ($n = 2$). TABLE 1/20 gives the ratio $\beta_p / \beta_q^{n/2}$ for a large number of E.D.T.A. complexes. It can be seen that in no case is the sensitivity improved. A very similar argument could be applied to the

spectrophotometric method and a similar conclusion would be drawn. However in the absence of E.D.T.A. impossibly high acidities are required to prevent the interference of copper in the spectrophotometric method. Thus, although the addition of E.D.T.A. actually lowers the selectivity by a factor of one thousand, it does enable the analyst to carry out the determination within the pH range 0 - 14.

In section 1.4.1. it was shown that palladium interferes in the substoichiometric determination of mercury, and the possibility of overcoming this interference by the addition of a complexing agent has been examined. TABLE 1/21 compares the stability products of several complexes of mercury and palladium and it can be seen that ethylenediamine offers some promise of improvement. When ethylene diamine was tried in practice, however, a purple aqueous phase was obtained due to the formation of mixed complexes of ethelynediamine, mercury and dithizone.

TABLE 1/20. The effect of adding E.D.T.A. upon the selectivity.

Metal (M)	Valence (n)	Stability constant (Ref.R.3.) ($\log_{10} \beta_p$)	$\log \beta_p - \frac{n}{2} \log \beta_q$	Conclusion
Silver	1	7.3	-3.5	selectivity impaired
Tin (II)	2	22.1	+0.3	selectivity unchanged
Copper	2	18.8	-3.0	selectivity impaired
Nickel	2	18.6	-3.2	selectivity impaired
Lead	2	18.0	-3.8	selectivity impaired
Cadmium	2	16.5	-5.3	selectivity impaired
Zinc	2	16.5	-5.3	selectivity impaired
Cobalt	2	16.3	-5.5	selectivity impaired
Iron (II)	2	14.3	-7.5	selectivity impaired
Manganese	2	14.0	-7.8	selectivity impaired
Iron (III)	3	25.1	-7.6	selectivity impaired
Indium	3	25.0	-7.7	selectivity impaired
Bismuth	3	22.8	-9.9	selectivity impaired
Gallium	3	20.3	-12.4	selectivity impaired

TABLE 1/21. Suppression of palladium interference with various ligands.

	Stability product			
	chloride β_4	bromide β_4	glycine β_2	ethylenediamine β_2
Palladium	12.3 (L1)	13.1 (L1)	17.5 (M2)	26.9 (M3)
Mercury	15.1 (M1)	21.0 (M1)	19.2 (F1)	23.3 (W1)
Conclusion	Selectivity impaired	Selectivity impaired	Selectivity impaired	Selectivity improved

1.5. Experimental.

1.5.1. The determination of the dead time (Section 1.2.).

Various volumes (Vml) of a labelled mercury solution (0.1 to 5.0ml) were diluted to 5.0ml and the activity measured (Ac/s).

A graph was plotted of the measured activity per ml ($y = A/V$) versus the measured activity ($x=A$). The slope of this graph (dy/dx) divided by the intercept on the y axis gave the dead time of the instrument.

This graph should be a straight line. A straight line was fitted by the method of least squares and $v(i)$ was calculated from the variation of the experimental points around this fitted line, (see D1).

1.5.2. The determination of v(I) (Section 1.2.).

A source containing a labelled mercury solution was counted for sufficient time to accumulate a large number of counts (10^6 for the Research Electronics equipment and 10^7 for the Nuclear Enterprises equipment). This count was repeated several times. Let N_i be the count observed in the ith repeat and let there be m observations, then:-

$$v^2_{inst} = \frac{10^4}{\bar{N}^2}\left(\frac{\sum_{i=1}^{i=m}(N_i - \bar{N})^2}{(m-1)} - \bar{N}\right)$$

1.5.3. The determination of $v(A_a)$ in the absence of E.D.T.A. (Section 1.2.).

Ten ml. of labelled mercuric perchlorate solution (either 2.6×10^{-5}M or 2.8×10^{-6}M) in dilute perchloric acid (10^{-2}M to 10^{0}M) was shaken for ten minutes with zinc dithizonate dissolved in carbon tetrachloride (1.3×10^{-5}M or 1.4×10^{-6}M). The organic phase was filtered through a dry No. 41 Whatman paper and the activity of 5ml measured. This procedure was repeated m times. If A_i is the observed count rate in the ith experiment then

$$v^2_{A_a} = \frac{10^4}{\bar{A}^2} \cdot \frac{\sum_{i=1}^{i=m}(A_i - \bar{A})^2}{(m-1)}$$

1.5.4. The determination of $v(A_a)$ in the presence of E.D.T.A. (Section 1.2.).

Ten ml. of a 2.6×10^{-5}M solution of mercuric perchlorate, labelled with Hg - 203, dissolved in 10^{-1}M ammonium acetate, 10^{-1}M acetic acid and 10^{-2}M E.D.T.A. was shaken for thirty minutes with a 1.3×10^{-5}M solution of zinc dithizonate in carbon tetrachloride. The organic phase was filtered through a No. 41 Whatman paper and the activity of 5ml. measured. This procedure was repeated m times.

If A_i is the observed result of the ith experiment then :-

$$v^2_{(A_a)} = \frac{10^4}{\bar{A}^2} \frac{\sum_{i=1}^{i=m} (A_i - \bar{A})^2}{(m-1)}$$

1.5.5. The determination of v(R) (Section 1.2.).

Ten ml of 1×10^{-5}M mercuric perchlorate and 5ml of 0.1M perchloric acid were shaken for three minutes with 5.0ml of 1.3×10^{-5}M zinc dithizonate solution in carbon tetra-chloride. The organic phase was filtered through a No. 41 Whatman paper and the absorbance measured in a 1cm cell at 490 n.m. This procedure was replicated m times and, if A_i is the absorbance of the ith replicate, v(R) was calculated from

$$v^2_{(R)} = \frac{10^4}{\bar{A}^2} \frac{\sum_{i=1}^{i=m} (A_i - \bar{A})^2}{(m-1)}$$

N.B. 490 n.m. is the isosbestic point see chapter 3.

1.5.6. The determination of ^{E} HgDz (Section 1.3.2.).

Five molar perchloric acid and 1M mercuric perchlorate solution were mixed with 5M sodium perchlorate and water to give 10ml of an aqueous phase which had an ionic strength of 5M. The volumes of perchloric acid and mercury solution were chosen to give the desired final acidity and mercuric ion concentration This mixture was shaken 1 minute with 10ml of a 6.2×10^{-5}M solution of primary mercuric dithizonate in carbon tetrachloride. The organic phase was filtered

through a No. 41 Whatman paper and its absorbance measured at 480 n.m. and 540 n.m. with an S.P.600 spectrophotometer.

The final concentrations of primary and secondary mercuric dithizonate were calculated from the equations :-

$$7.3 \times 10^5 [Hg(HDz)_2] = 1.07A_4 - 0.71A_5$$

$$1.9 \times 10^5 [HgD_z] = 0.71A_5 - 0.14A_4.$$

where A_4 and A_5 are the absorbancies in 1cm cells at 480 n.m. and 540 n.m. respectively.

For the qualitative experiments the colour of the organic phase was observed not measured, and for these results and for the results quoted in TABLE 1/8 the concentration of the primary mercuric dithizonate was varied.

1.5.7. Efficiencies of the counting equipment (Section 1.3.5.).

These were determined by counting an aliquot of a standardised radioactive solution of Hg-203 obtained from The Radiochemical Centre, Amersham, Bucks.

1.5.8. The kinetics of adsorption (Section 1.3.7.).

Two separating funnels which had previously been used with radioactive solutions of mercuric dithizonate 1×10^{-5}M were shaken with successive portions of inactive 1×10^{-4}M mercuric dithizonate solutions, until no more radioactivity was extracted from the walls of the glass vessels.

A graph was plotted of the total activity removed (y=A) versus the rate of removal ($x = dA/dt$). This graph consisted of intersecting straight lines. Further analysis showed these to be due to two first order reactions with very different rate constants, the rate constants for the two funnels being similar, (i.e., 1.1, 1.3 hrs^{-1}, and 30,25 hrs^{-1}).

1.5.9. The quantity of mercury adsorbed.(Section 1.3.7.).

A 100ml separating funnel, which had been shaken with strong mercuric dithizonate solution until no more activity could be extracted, was shaken with carbon tetrachloride for 64 hours to completely remove the adsorbed mercuric dithizonate. This funnel was then shaken with 10^{-7}M labelled mercuric dithizonate for 24 hours. The activity was measured before and after the experiment and from the observed decrease in activity the amount of mercury adsorbed was calculated to be 0.16µg. A similar experiment with 10^{-4}M

solutions gave 3.7µg adsorbed. From these figures an estimate of n in equation 1/39 can be made :-

$$W_w = C^{\frac{1}{n}}.k.$$

$$0.16 = (10^{-7})^{\frac{1}{n}}.k.$$

$$3.7 = (10^{-4})^{\frac{1}{n}}.k.$$

$$\frac{3.7}{0.16} = (10^{3})^{\frac{1}{n}} = 23$$

$$\underline{n = 2.2.}$$

N.B. The separating funnel was very old and had often been cleaned. The surface was in bad condition and adsorbed rather more mercury than normal.

C H A P T E R T W O.

THE AUTOMATIC DETERMINATION OF MERCURY.

Summary.

In this chapter the modification of the technicon Auto-Analyser for automatic radiochemical substoichiometry is described. An account is given of the development of the automatic method for mercury and of the study of the limitations of this method.

2.1.1. Description of the Technicon Auto-Analyser.

The Technicon Auto-Analyser is a commercially available apparatus for automatic chemical analysis. The machine consists of a sampler which places a nozzle in one of forty cups containing the samples. The cups are changed automatically at regular intervals. The sample and reagents are forced, by a peristaltic pump through glass apparatus which carries out the normal chemical operations (mixing, heating, filtering etc.). The final solution is passed through a colorimeter or flame photometer, the electrical output of which is continuously recorded on a strip chart recorder.

This system involves long lengths of tubing which would normally be difficult to wash out between samples. Technicon have overcome this difficulty by breaking up the liquid stream with air bubbles so that no mixing can occur between neighbouring bubbles. This greatly improves the washing and speeds of 120 samples per hour are possible.

2.1.2. Advantages of the Technicon Auto-Analyser.

(i) Skilled personnel are not required to operate the machine. A short training course will enable a junior technician to use it.

(ii) In manual analysis each step; weighing, pipetting, transferring, etc., adds an error which varies with the analyst. These personal errors are eliminated by the Auto-Analyser.

(iii) When using the Auto-Analyser there is no need to wait for a reaction to go to completion: no need to heat to such a temperature that complete reaction occurs. An empirical approach is justified. The only requirement is that a reproducible calibration graph can be constructed. A condition more likely to be fulfilled by the more reproducible machine.

(iv) A machine works continuously and can carry out many more analyses than an individual analyst. Twenty analyses an hour is a very high rate for manual analysis; sixty samples an hour is not unusual with the Auto-Analyser.

(v) The lower limit of sensitivity of trace analysis often depends on the amount of contamination that occurs in the analytical process. Usually it is not the quantity of contamination that matters but how consistent this amount is. In the

colorimetric determination of lead 10 µg may be measured to an accuracy of ± 0.3 µg. If the blank is always 7 µg, 3 µg of lead could be determined with a precision of ± 10%. If however the blank varies from 7 µg to 10 µg, the sample must contain 30 µg of lead to obtain the same precision. The Auto-Analyser always gives more consistent blanks than the manual method, thus increasing the sensitivity.

2.1.3. Disadvantages of the Auto-Analyser.

(i) The Auto-Analyser is expensive, costing about £3,000.

(ii) Because they are expensive, all the machines in one laboratory are always in full use. A breakdown in these circumstances causes a severe dislocation.

(iii) It requires about 30 min to change from one kind of analysis to another and about 15 min for the first result to appear on the strip chart recorder. This means that it is not economical to carry out a wide range of tests on one machine when only a few analyses of any one kind are required. Under these circumstances it is cheaper to employ human labour.

(iv) The colorimetric and flame photometric procedures are not suitable for very accurate analysis. Assay's cannot be carried out on the Auto-Analyser.

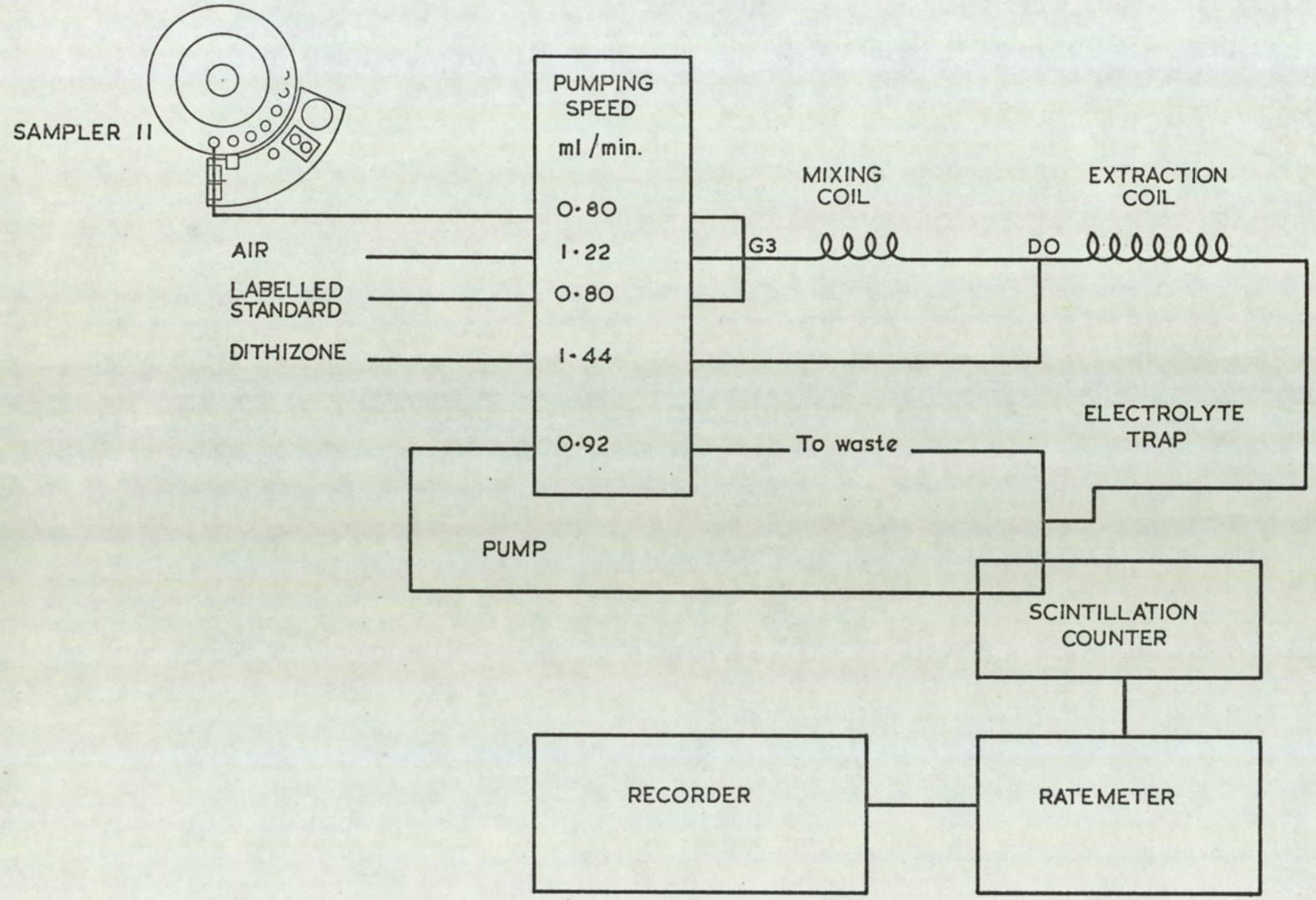

SAMPLER II
PUMPING SPEED ml/min.
0·80
1·22
0·80
1·44
0·92
AIR
LABELLED STANDARD
DITHIZONE
G3
MIXING COIL
DO
EXTRACTION COIL
To waste
ELECTROLYTE TRAP
PUMP
SCINTILLATION COUNTER
RECORDER
RATEMETER

FIG. 2/1

2.2. Development of the method.

2.2.1. The modification of the Auto-Analyser for radioactive isotope dilution analysis.

Technicon instruments were able to supply equipment for automatic solvent extraction and the only modification required for substoichiometric isotope dilution analysis was the replacement of the colorimeter by a scintillation counter fitted with a flow cell and a rate meter.

A flow diagram of the equipment is shown in Fig 2/1. This is the arrangement suggested by Růžička (R4) which originated this line of research. Later this was modified slightly in order to reduce adsorption and stability problems and to increase the sensitivity (Fig 2/2). The operation of this last system will be described in section 2.4.1.

Several difficulties were encountered and the investigation of these and the methods used to overcome them will be described in the subsequent sections (2.2.2. - 2.2.4.).

2.2.2. Matching the Ratemeter and Recorder.

The first strip chart records produced by the newly assembled apparatus were most unsatisfactory showing a large amount of noise which could only be removed by reducing the amplifier gain nearly to zero. When this was done the recorder did not follow the varying signal from the ratemeter accurately. Several possible

faults were investigated but were proven not to be the cause of the trouble: the stability of the voltage supply to the potentiometer wire; the internal resistance of the ratemeter not being matched to the input resistance of the recorder; the use of noisy compressed carbon resistors. An attempt was made to reduce the noise by interposing a two stage resistance capacitance filter with a time constant of six seconds between the ratemeter and the recorder. This reduced the noise but did not remove it, a result which suggested that the ratemeter was the source of the noise.

A trial with several recorders brought to light one which worked satisfactorily. It was found that this recorder had no earth connection. Disconnecting the earth from the other recorders removed the trouble from these instruments also. Reconnecting the earth and shorting the input to the recorder while leaving the ratemeter connected did not stop the noise; clearly the noise was due to a varying voltage between the output terminal of the ratemeter and the earth. Monitering this voltage showed that it was syncronised with the noise, and was very large (100v.). This voltage was leaking through the insulation on the signal transformer when the earth was connected to the amplifier of the recorder.

No further trouble was encountered once the earth was disconnected. Later an instrument was purchased from Nuclear Enterprises which included a matched ratemeter recorder pair. This always gives satisfactory results.

2.2.3. Adsorption problems.

Adsorption problems are particularly severe with the Auto-Analyser. Plastic surfaces adsorb much more strongly than glass and the Auto-Analyser has large plastic surfaces exposed to the reagents; sample cups; flow cells; pump tubing; connection tubing etc.

To reduce the magnitude of these effects as much plastic as possible must be replaced with glass; glass sample cups and flow cell should be used and the glass connections should be butt jointed. This is not always possible. A glass flow cell cannot be employed for an isotope which only emits β -rays. Glass sample cups are expensive and not disposable. However plastic cups can be used provided the solutions are not allowed to stay in the cup for more than an hour because adsorption from the aqueous phase is never very severe. The pump tubing, however, must be flexible and always remains as a source of difficulty.

The worst adsorption occurs in the pump tubing carrying the organic reagent. This reduces the initial concentration of the reagent leaving the pump tubing. As equilibrium is approached this concentration gradually increases finally reaching the concentration of the reagent entering the tube. Analyses cannot be conducted until equilibrium

is reached (see Fig.2/8). This may take several hours with 10^{-8}M solutions, by which time the reagent may well have begun to decompose. This has been overcome by pumping strong zinc dithizonate solution and diluting it "in situ" with carbon tetrachloride. Adsorption is much less severe in strong solutions. (see sections 1.3.7 and 1.5.8.).

Even with glass there is some adsorption. The background activity in the flow cell gradually increases over a period of months and when it becomes too high the cell must be replaced and the activity allowed to decay. Another effect is the gradual building up of mercuric dithizonate in the extraction coil. This causes the trailing edge of the sample peaks to be drawn out because isotopic exchange occurs between mercuric dithizonate adsorbed on the glass coil and that in solution. The peak due to the following sample is then too large because it is built up on the trailing edge of the previous sample. Such contaminated coils must be discarded.

2.2.4. The maximum sampling rate.

Carry over may be defined as the time required for the recorder pen to move 95% of its full deflection. This time should be a constant and should not be influenced by the amount of mercury in the sample or the activity of the standard. This time determines the amount of contamination of one sample by a preceding one and so controls the maximum sampling rate.

With solvent extraction systems this time is controlled by the time required to wash out the electrolyte trap because this has the largest volume through which no air bubbles pass (see 2.1.1.). In the apparatus modified for radiochemical analysis the volume of the flow cell must also be considered because no air bubbles flow through this either.

To calculate the carry over time consider a trap (volume V ml) filled with organic phase containing 'C' gm. mole per litre of mercuric dithizonate. Let an organic phase containing a gm. mole/litre of mercuric dithizonate enter the trap at 'r' ml/min. After a short time, "dt" min., the concentration of the mercuric chloride in the trap changes by dC gm. mole/litre. During dt mins rdt ml of the 'a' gm. mole/litre solution will have entered and 'rdt' ml of the 'C' gm. mole/litre

132.

solution will have left the trap.

The amount of mercury dithizonate added to the trap is therefore

$$(a - c)\, r\, dt \text{ millimole.}$$

and the resulting change in concentration must be

$$dC = r\,dt.\ \frac{(a - C)}{V}$$

or $$\frac{dC}{(a - C)} = \frac{r}{V}\, dt. \qquad \text{--------2/1.}$$

To obtain the carry over time (t_b) this expression must be integrated between the limits

$t = 0,\ C = 0,\ :\quad t = t_b \quad C = 0.95a.$

$$\int_{C=0}^{C=0.95a} \frac{dC}{(a-C)} = \int_{t=0}^{t=t_b} \frac{r}{V}\, dt.$$

$$\text{In } a - \text{In } 0.05a = \frac{r}{V}\, t_b - \frac{r}{V} \cdot 0$$

$$t_b = \frac{V}{r} \cdot \text{In } 20 = \frac{3V}{r}$$

N.B. This derivation assumes that the entering solution is instantly mixed with that present in the trap. This may be true for the electralyte trap but is not true for the flow cell.

To verify the above formulae experiments were conducted at two pumping rates and several different concentrations of mercury. Two estimates of t_b were obtained in each experiment; one on the rising edge and one on the falling edge.

The results are shown in TABLE 2/1, and agree well with an assumed volume V = 0.74 ml. The actual volume of the electrolyte trap was 0.5 ml but this neglects the volume of the flow cell.

In the arrangement used for analysis (Fig.2/2) r = 1.8 ml/min and V = 3.5 ml t_b = 6 min. The maximum sampling rate will be $60/t_b$ = 10 samples per hour. In most cases a rate of 5 samples per hour was used.

This is a lower rate than normal for the Auto-Analyser and is characteristic of solvent extraction procedures. To improve it the flow cell and the electrolyte traps must be made smaller, or the rate at which the organic reagent is pumped must be increased. If the last expedient is followed and the concentration of the reagent is not changed, the amount of radioactivity in the flow cell will not be altered. The rate at which the sample is pumped will be changed in proportion to the rate at which the reagent is pumped; the total volume of sample consumed during the analysis time will be unaltered, and the sensitivity will also be unaltered. The limit in this direction is set by turbulence in the electrolyte trap, which in turn depends upon the size of the trap. Once the maximum pumping rate for a particular trap volume has been reached the sampling speed can only be

increased further by diluting the reagent and decreasing the sensitivity and accuracy.

In the arrangement presented in Fig.2/2 a low sampling rate is used to obtain a high sensitivity. Since the completion of this work Růžička (R5) has designed a new flow cell which does not add to the carry over time. Air bubbles are passed through this flow cell. If many small bubbles are used the recorder chart is hardly altered because the counting statistics prevent a smooth curve being drawn even in the absence of air bubbles. In this way higher speeds and higher sensitivities were achieved.

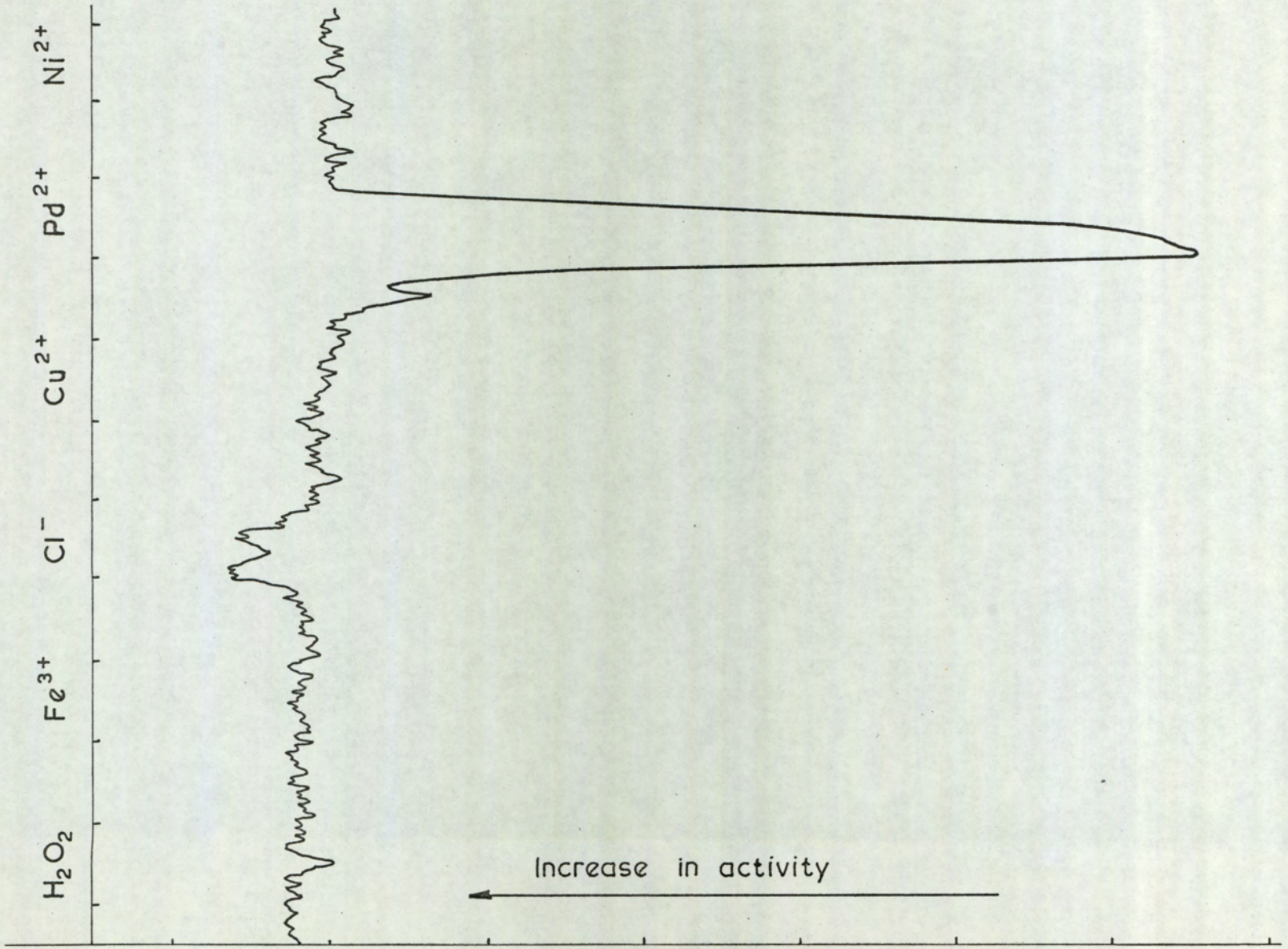

H_2O_2
Fe^{3+}
Cl^-
Cu^{2+}
Pd^{2+}
Ni^{2+}
Increase in activity
80
70
60
50
40
30
20
10

FIG. 2/3

2.3. Interferences.

2.3.1. A survey of interferences.

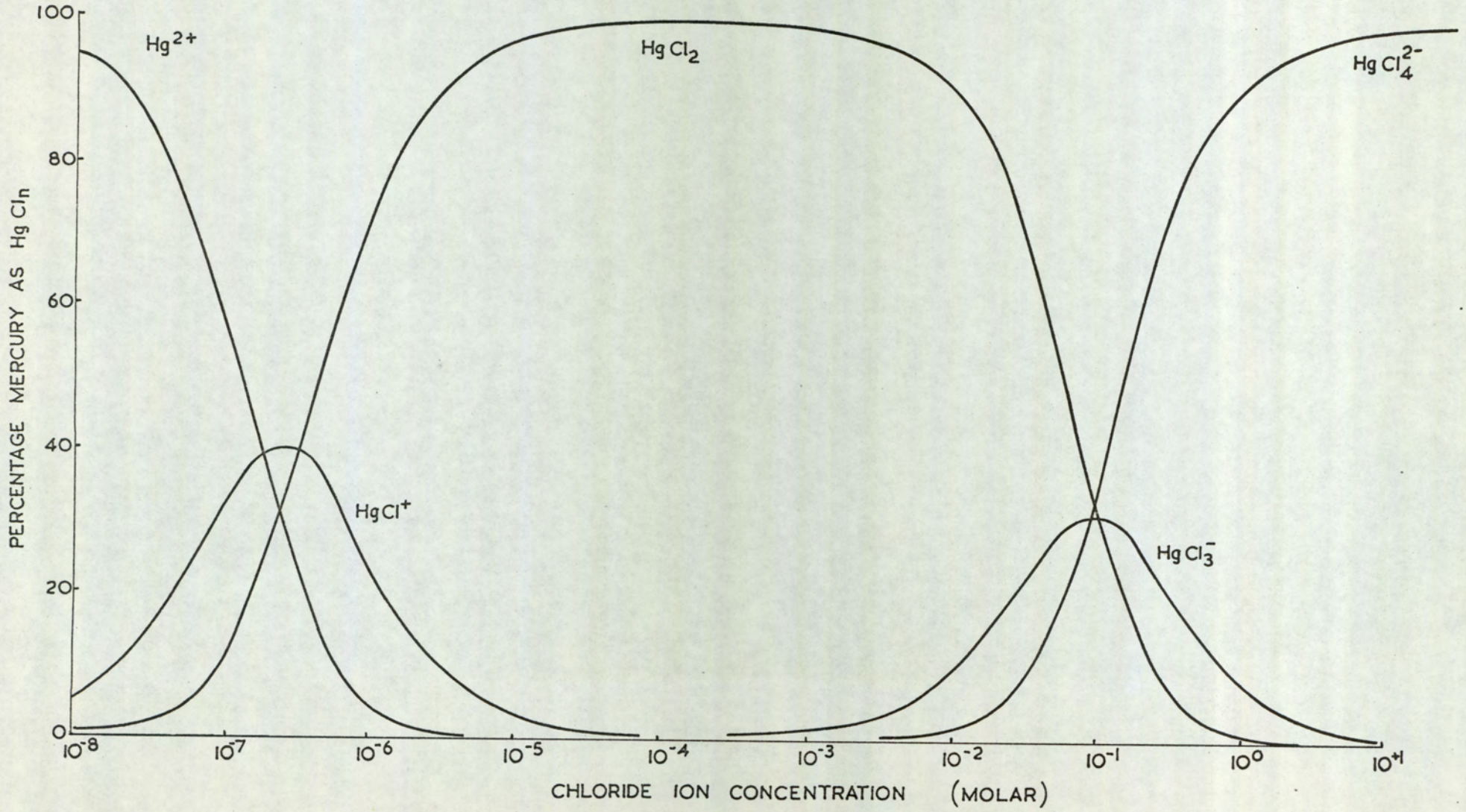
A theoretical treatment of interference has been given in chapter one (1.4.) and these conclusions have been confirmed with the Auto-Analyser. The investigation of interferences is very convenient with the Auto-Analyser and may easily be accomplished by using solutions of cations, anions, etc., in the sample cups. Fig.2/3 shows the recorder chart resulting from some of these studies. An interference is represented by any change in the otherwise constant activity extracted from the standard labelled mercury solution. In Fig. 2/3 palladium and chloride can be seen to interfere. Table 2/2 summarises the results for 58 ions and compounds.

The interference of the oxidising and reducing agents may be overcome by the addition of hydrogen peroxide which oxidizes Sn^{2+}, HPO_2^-, $S_2O_3^{2-}$ SO_3^{2-} and Pt^{2+} and reduces MnO_4^-, $Cr_2O_7^{2-}$, Ce^{4+} and if heated ClO_3^- . Nitrite is destroyed by the urea solution.

The interference of the remaining substances (Au^{3+}, Pd^{2+}, SCN^-, I^-, E.D.T.A., Cl^-, Br^-, HSO_4^- , NO_3^- are difficult to overcome. Chloride bromide, nitrate and bisulphate are dealt with in subsequent

sections. The metals must be removed by a prior solvent extraction procedure, e.g., a chloride/ether extraction for gold (.M5,L2) or a D.M.G./chloroform extraction for palladium (Y1). It has been pointed out in chapter one (Section 1.4.3.) that adding complexing agents to the aqueous phase has very little chance of improving the selectivity, because the complex with the interfering metal must be much stronger than that with mercury and mercury usually forms very strong complexes. Also the complexes of mercury react slowly with dithizone, so that complexing agents may interfere with the automatic method even though by the criterion of equations 1/60 and 1/61 they should not. E.D.T.A. for example, interferes with the automatic method but not with the manual method when much longer shaking times are used (30 mins).

FIG. 2/4


100
80
60
40
20
0
PERCENTAGE MERCURY AS Hg Cl$_n$
Hg^{2+}
$HgCl_2$
$HgCl_4^{2-}$
$HgCl^+$
$HgCl_3^-$
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{+1}
CHLORIDE ION CONCENTRATION (MOLAR)

2.3.2. The interference of chloride.

All the interfering substances mentioned in TABLE 2/2 prevent the extraction of mercury and so lower the activity in the organic phase except chloride bromide, nitrate and bisulphate. These exceptional anions increase the activity in the organic phase and so must increase the amount of mercury extracted. This is believed to be due to the extraction of ternary complexes.

In the absence of these anions, one mole of mercury reacts with two mole of Dithizone to form primary mercuric dithizonate :-

$$Hg^{2+} + 2\,H_2Dz \rightleftharpoons Hg(HDz)_2 + 2H^+$$

In the presence of one of these anions, one mole of mercury reacts with one mole of the anion and one mole of dithizone to form a ternary complex :-

$$Hg^{2+} + X^- + H_2Dz \rightleftharpoons Hg(HDz)X + H^+.$$

A given amount of dithizone can react with twice as much mercury when one of these anions is present .

In the case of chloride the situation is further complicated by the formation of mercuric chloro-complexes in the aqueous phase. Both the amount and nature of these complexes change with the chloride concentration. The situation is summarized in Fig. 2/4 which has been

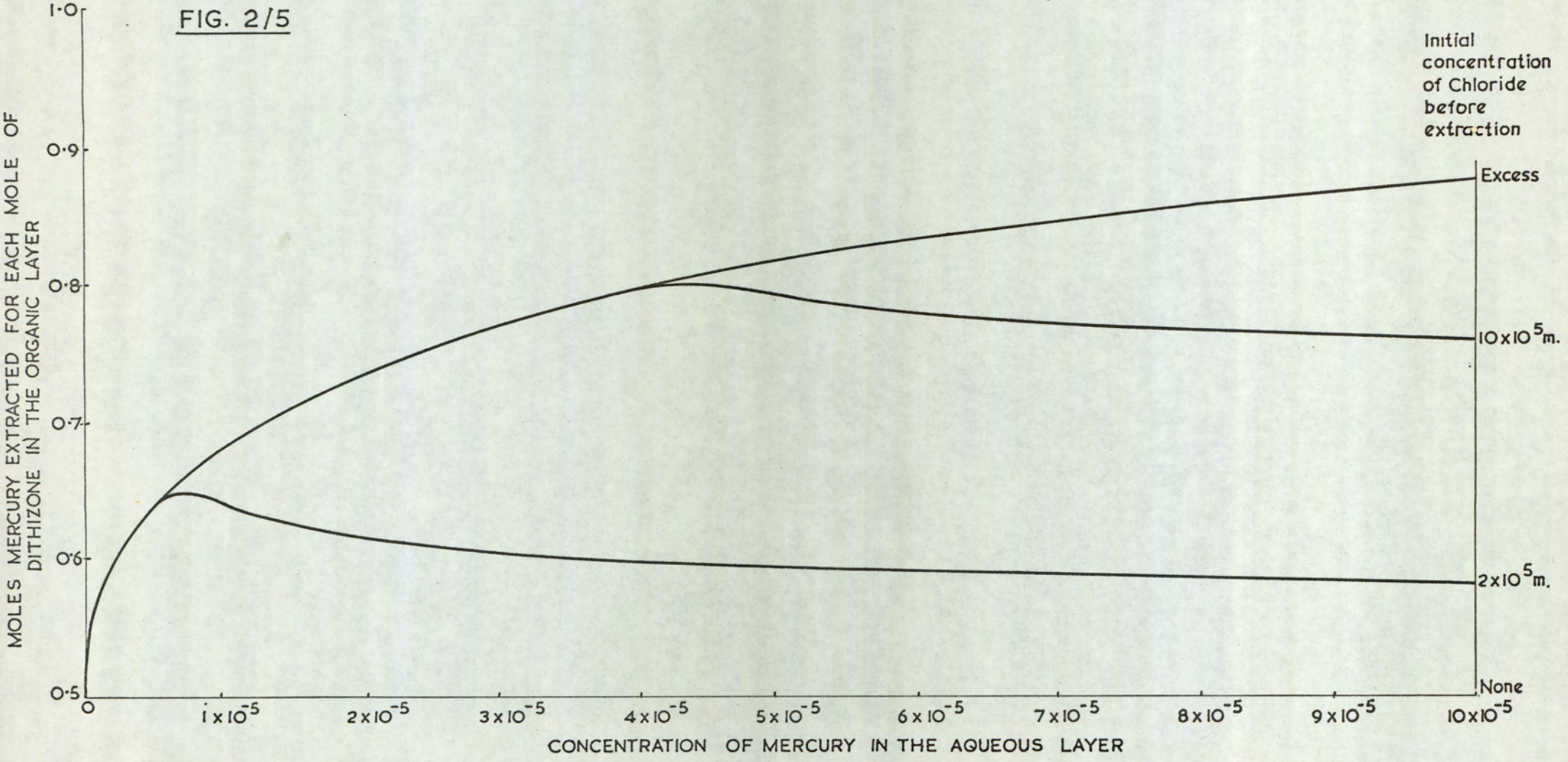
calculated from the stability products estimated by Marcus (M1). Below a chloride ion concentration of 10^{-8}M, mercury is present as free mercuric ions; between 10^{-6} and 10^{-2}M as mercuric chloride and above 10^{0}M as the tetrachloro-mercuric anion. Only within very narrow ranges of chloride ion concentration do appreciable amounts of $HgCl^{+}$($\simeq 10^{-7}$ M) and $HgCl_3^{-}$($\simeq 10^{-1}$M) exist.

In practice there is usually sufficient adventitious chloride to ensure that all the mercury in the aqueous phase is present as mercuric chloride. In the organic phase the mercury will then be present as a mixture of primary mercuric dithizonate and mercuric chloride dithizonate. In these circumstances the interference of mercury is represented by the reaction :-

$$HgCl_2 + Hg(HDz)_2 \rightleftharpoons 2\ HgClHDz.$$

This last equation will be used in all circumstances and any other complications will be treated as side reactions (e.g., the formation of other chloro-complexes or free dithizone). This is simply a matter of convenience. In chapter 3 it will be shown that it is possible to determine the extraction constant corresponding to this reaction without using intermediate constants which have been measured by another author at possibly some other ionic strength. With the aid of this extraction constant and the known stability products of the chloro-complexes of mercury it is

FIG. 2/5



NOTES. (1) Volumes of aqueous and organic layers equal

(2) Reagent – 2×10^{-5}m Dithizone

possible to predict the amount of mercuric chloride dithizonate which is formed under any conceivable circumstance. This has been done for a range of conditions and the results plotted as Fig.2/5.

An examination of Fig.2/5 reveals the intractable nature of the problem. If excess chloride is present, all the mercury in the aqueous phase will be present as mercuric chloride, and the amount of mercuric chloride dithizonate formed increases steadily with the amount of mercury in the aqueous phase, eventually converting all the primary dithizonate to chloride dithizonate. If chloride is present in smaller quantity the same curve is followed until all the chloride has been converted to mercuric chloride and any further increase in the concentration of mercury in the aqueous phase decreases the amount of chloride dithizonate formed, because mercuric chloride is converted to the monochloromercuric ion. If, on the other hand, a very large excess of chloride is added then anionic chlorocomplexes will be formed at the expense of the mercuric chloride and the amount of chloride dithizonate formed will decrease as the amount of chloride in the aqueous phase increases. At such high chloride concentrations free dithizone may be formed if the acidity is also high and the $\alpha_{Hg(Cl)}$ value exceeds that given by equation 1/60.

If there is no chloride in the sample and if there is excess mercury in the standard, then the same amount of mercuric chloride dithizonate will be formed in the organic phases of the standard and the sample; the amount of mercury extracted from the sample will be the same as that extracted from the standard and accurate results will be obtained. If, however, the standard contains excess chloride or if the sample contains chloride, more mercuric chloride dithizonate will be formed in the organic phase from the sample, because this will contain the highest concentration of mercury in the aqueous phase; more mercury will be extracted from the sample than from the standard and low results will be obtained.

The smallest amount of chloride which would just raise the amount of mercury extracted by 0.1% is about 10^{-3} p.p.m. This is such a low concentration that it is impossible to avoid contamination. Even distilled water contains more chloride than this. A vast majority of samples contain far more chloride than mercury so that chloride interference represents a very serious problem.

2.3.3. Overcoming chloride interference.

Five methods of overcoming chloride interference have been examined; only the last was successful.

Cadmium and ferric iron were added to complex the chloride and prevent the formation of mercuric chloride. Neither of these metals react with dithizone in acid solutions so that they would not interfere. The chloro-complexes of these metals were not sufficiently strong to break down the mercuric chloride complex. Those metals which do form strong enough chloro-complexes (Pd, Os) also extract with dithizone in acid solutions and so cannot be used.

Suppose sufficient metal ion (M^{2+}) is added to convert 99.9% of the mercuric chloride to mercuric ion, then :-

$$\frac{[HgCl_2]}{[Hg^{2+}]} = 10^{-3} = [Cl^-]^2 . 10^{13.2}.$$

(because for mercury and chloride

$\beta_2 = 10^{13.2}$ - ref: M.1.)

$\therefore \quad [Cl^-] = 10^{-8.1}$

If the amount of chloride contamination is such that in the aqueous phase there would be

$C_{Cl} = 2[HgCl_2] + [HgCl^+] + [MCl^+] + [Cl^-] = 10^{-4}M$

(a probable extent of contamination)

then $[MCl^+] \simeq 10^{-4}$

because all the other terms are negligably small, i.e., all the chloride is present as MCl^+.

$$\frac{[MCl^+]}{[M^{2+}]\,[Cl^-]} = \beta_1 = \frac{10^{-4}}{[M^{2+}]\;10^{-8.1}}$$

now suppose the maximum metal ion concentration that can be added is 1M.

$$[M^{2+}] = 10^{0.0}$$

$$\therefore \beta_1 = 10^{4.1}$$

This is the minimum value of the stability constant of the metal chlorocomplex which will suppress the formation of mercuric chloride. TABLE 2/3 gives some values for several metals. It can be seen that none are suitable. The theoretical results agree with the practical ones.

Another method tried was to add E.D.T.A. to complex the mercury and prevent the formation of mercuric chloride. Theoretically E.D.T.A. is a strong enough complexing agent to prevent the formation of the chloride dithizonate but not the primary dithizonate, as is required. Also E.D.T.A. does not form an extractable ternary complex with primary mercuric dithizonate because it is not a univalent ion. In chapter 4 this method of overcoming chloride interference will be dealt

with in detail and it will be shown to be perfectly satisfactory for manual analysis, where it is possible to allow a 30 min reaction time, but in the automatic method the reaction between dithizone and the E.D.T.A. complex of mercury is too slow, equilibrium is not reached and low analyses result.

A preliminary extraction of mercury as the diethyldithiocarbamate has been used, but this chelate also forms a ternary complex with mercuric chloride (Table 2/4) and this reagent offers no advantage over dithizone. Other reagents are possible, cupferron, thenoyl-triflouracetone and 8-hydroxy quinoline. These were not examined because they all form 1:2 complexes with mercury and are likely to form ternary complexes similar to those formed with dithizone and diethyldithiocarbamate.

Mercuric chloride dithizonate is destroyed by free dithizone by the reaction :-

$$HgClHDz + H_2Dz \rightleftharpoons HCl + Hg(HDz)_2.$$

so that in the presence of excess dithizone, chloride is not extracted. This explains why this ternary complex has not been encountered in spectrophotometric solvent extraction, because in this method of analysis excess dithizone must be used. This reaction can form the basis of a method for the separation of mercury and chloride. The separation has been

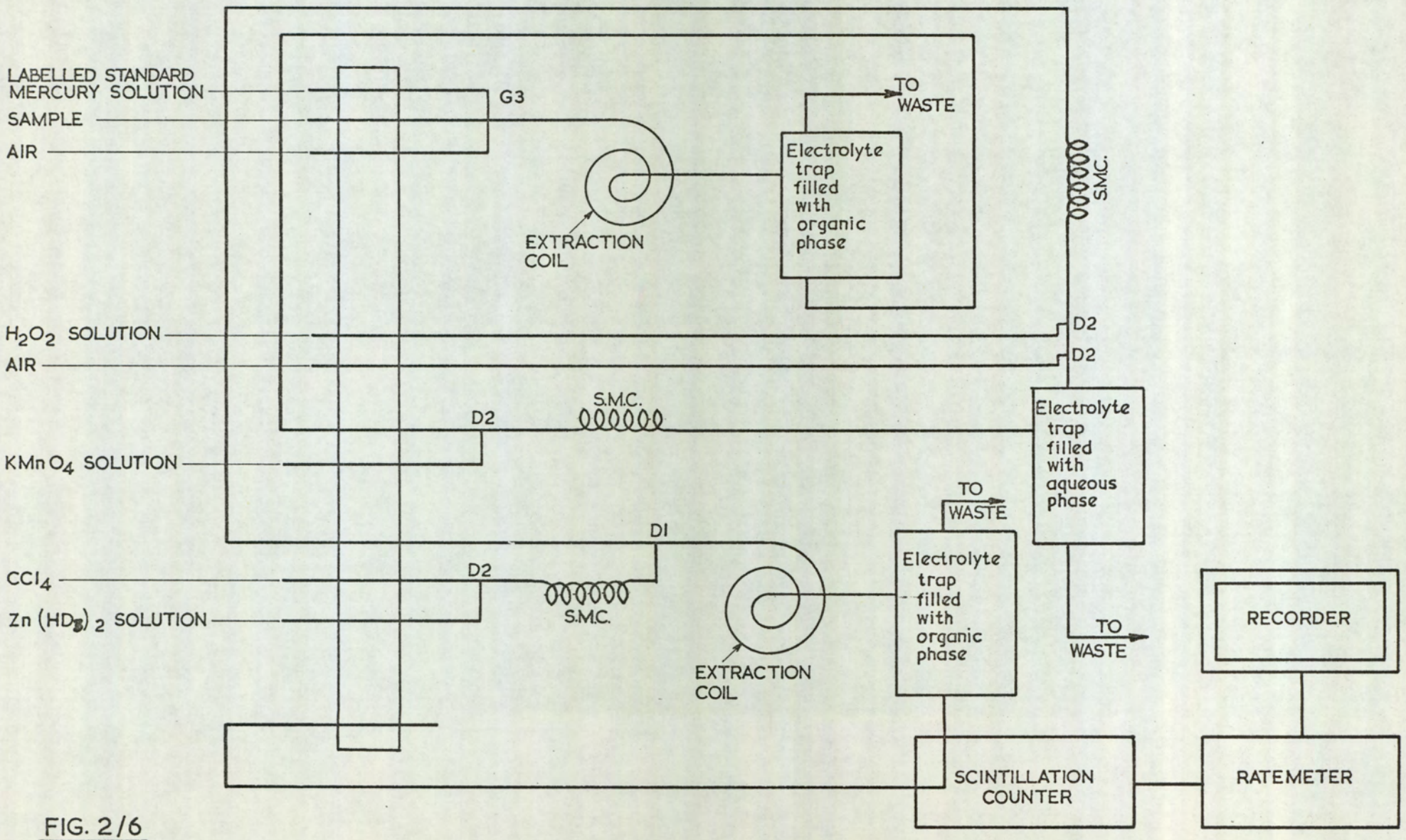

LABELLED STANDARD MERCURY SOLUTION
SAMPLE
AIR
G3
TO WASTE
Electrolyte trap filled with organic phase
EXTRACTION COIL
S.M.C.
H_2O_2 SOLUTION
AIR
D2
D2
S.M.C.
D2
Electrolyte trap filled with aqueous phase
$KMnO_4$ SOLUTION
TO WASTE
D1
CCl_4
D2
$Zn(HD_3)_2$ SOLUTION
S.M.C.
EXTRACTION COIL
Electrolyte trap filled with organic phase
TO WASTE
RECORDER
SCINTILLATION COUNTER
RATEMETER

FIG. 2/6

tested with ^{36}Cl as a tracer with the results reported in TABLE 2/4 - virtually complete separation is obtained.

After such a separation mercury is present in the organic phase and must be recovered as an aqueous solution for substoichiometric analysis. Two processes were examined to accomplish this.

(a) Destruction of the mercuric dithizonate and excess dithizone with nitrite and destruction of the excess nitrite with urea.

(b) Destruction of the mercuric dithizonate with permanganate and destruction of the excess permanganate with peroxide.

Both of these processes worked sufficiently well for the present purpose but isotope dilution analysis of the resulting solution gave high results (more activity extracted from a standard which had not been treated than from the same standard after the separation), see TABLE 2/5. At the time of this investigation no explanation of these results could be discovered and this separation was abandoned. Later, however, it was found that the isotope used contained a volatile mercury compound with a high partition coefficient. After this impurity had been removed good results were obtained. Nevertheless the arrangement required (Fig.2/6) is more complicated than that finally adopted (Fig. 2/2).

It was stated in section 2.3.2. that in the presence of excess chloride more mercury would be extracted from the sample than from the standard and that a low result would be obtained. This low result is obtained because in equation 1/3

$$W_{es} > W_{ea}$$

$$W_s = W_a \cdot \left(\frac{A_a}{W_{ea}} \cdot \frac{W_{es}}{A_s} - 1 \right) \text{--------1/3}$$

so that direct substitution of A_a and A_s into formulae 1/2 gives a lower result than the true result given by 1/3.

$$W_s = W_a \left(\frac{A_a}{A_s} - 1 \right)$$

Formulae 1/2 is the formulae that is used in substoichiometric analysis and must be used unless an empirical calibration graph is employed, because neither W_{es} nor W_{ea} is normally known.

The amount of mercuric chloride dithizonate formed depends upon three factors :-

(a) The concentration of mercuric chloride in the aqueous phase.

(b) The concentration of zinc dithizonate in the organic reagent.

(c) The value of the extraction constant $E_{HgClHDz}$ (see chapter 3).

If an excess of chloride is added to the aqueous phase (i.e., if $[Cl^-] > 10^{-6}$) the

concentration of mercuric chloride depends only upon the sum of the mercury concentrations in the sample and the standard.

$$[HgCl_2] \propto W_s + W_a.$$

Provided that a new calibration graph is prepared every time the organic reagent solution is replaced, the zinc dithizonate concentration will be constant. Finally the value of $E_{HgClHDz}$ will depend upon the temperature, ionic strength, presenceof other complexing agents in the aqueous phase, etc., but will usually be a constant.

If a new calibration graph is made every time a new labelled standard mercury solution is used W_a will be constant, for any one calibration graph. In these circumstances, the amount of chloride dithizonate formed and the amount of mercury extracted (W_{es}) are functions only of the amount of mercury in the sample (W_s). The activity extracted from the sample (A_s) is a function of the amount of mercury extracted (W_{es}) and the amount of mercury in the sample (W_s) (because A_a, W_a, and W_{ea} are now all constants). Finally, the conclusion is reached that, if all these conditions are satisfied, the activity extracted from the sample is a function solely of the amount of mercury in the sample. This is just the condition for a stable calibration graph. The conditions set out above are recapped below :-

(a) $E_{Hg.Cl.HDz}$ must not change.

(b) A new calibration graph must be prepared whenever any of the reagents are changed, particularly if the zinc dithizonate or standard labelled mercury solutions are changed.

(c) Sufficient excess chloride must be present that, whatever the amount of mercury in the sample, the mercury in aqueous phase is all converted to mercuric chloride.

If these conditions are satisfied and the amount of mercury in the sample is estimated from an empirical calibration graph, accurate results will be obtained provided that the amount of mercury in the sample is not so great that anionic chloro-mercuric complexes are formed.

For the manual method this procedure has several disadvantages :-

(a) It is time consuming.

(b) The shape of the calibration graph will vary with temperature, ionic strength, etc., (i.e., variation of $E_{HgClHDz}$).

(c) As the standards and samples are not extracted simultaneously it is no longer possible to work with reagent solutions which are rapidly decomposing. This limits the sensitivity.

Fortunately, these objections do not apply

to the automatic method. A calibration graph must always be prepared when using this method because the exact ratio of active standard to sample solutions, which depends upon the exact ratio of the diameters of the pump tubes, is not known, and in any case it does not take long to prepare one. The factors which affect the Extraction constant are much less likely to vary when a machine is used than in manual analysis (see section 2.1.2.). The use of the machine limits the sensitivity to reagent concentrations, which are quite stable for reasons in no way connected with chloride interference.

Before this method can be used in practice it is necessary to calculate how completely the mercuric ion must be converted to mercuric chloride and just how much chloride must be added to ensure this conversion.

Consider the extraction of a solution of mercuric chloride with a zinc dithixonate reagent (concentration D g . mole/litre). At equilibrium the mercuric chloride concentration is CD g.mole/litre, the mercuric chloride dithizonate concentration xD g.mole/litre, and the primary mercuric dithizonate concentration yD g.mole/litre. Then

$$E_{Hg.Cl.HDz} = \frac{x^2D^2}{CD \,.\, yD} = \frac{x^2}{C.y.} \qquad \text{-------2/4.}$$

$$D = yD + \frac{xD}{2.}$$

$$\therefore \quad y = 1 - x/2. \qquad \text{-------2/5.}$$

let

$$R = \frac{\text{Amount of Hg extracted when chloride is present.}}{\text{Amount of Hg extracted when chloride is absent.}}$$

$$R = \frac{yD + xD.}{D.} = y + x \quad \text{--------2/6.}$$

Substituting for x and y in equations 2/4 from equations 2/6 and 2/5 gives

$$E_{Hg.Cl.HDz} = \frac{4\ (R-1)^2}{(2-R).C.} \quad \text{---------2/7.}$$

This equation relates the amount of mercury extracted to the amount of mercuric chloride present in the aqueous phase. If R changes by 0.1% the activity of the organic phase will change by 0.1% which will not be measurable, so that it is possible to calculate the change in C necessary to bring about such a change in R.

Differentiating equation 2/7 gives

$$\frac{dC}{dR} = C \left\{ \frac{2}{R-1} + \frac{1}{2-R} \right\}$$

or

$$\frac{dC}{C} = \frac{dR.}{R} \left\{ \frac{2R}{R-1} + \frac{R}{2-R} \right\}$$

The expression in brackets has a minimum value at R = 1.5 and rises to infinity at the limiting values of R = 1 & R = 2 (i.e., all primary dithizonate or all chloride dithizonate). This means that at these limiting values R is independent of C, the smallest limits of chloride concentration will occur at R = 1.5 or when half

the primary dithizonate is converted to chlorodithizonate. At this value

$$\frac{dC}{C} = \frac{dR}{R} \cdot 9$$

and if $dR/R = 0.001 = 0.1\%$

$$\frac{dC}{C} = 0.009 = 0.9\%$$ --------2/8.

This last figure means that if the chloride concentration is adjusted so that not more than 0.9% of the mercuric chloride is converted to either the mono or tri chloro mercuric ions, changes in the chloride concentration will not change R by more than 0.1%. Chloride will not interfere provided it is between these two limits. These limits are :-

$$\frac{[HgCl_2]}{[Cl^-][HgCl^+]} = 10^{6.48}$$

(see ref M.1).

$$[Cl^-] = \frac{[HgCl_2]}{[HgCl^+]} \; 10^{-6.48}$$

$$= \frac{10^{-6.48}}{0.009} = \frac{10^{-6.48}}{10^{-2.05}} = 10^{-4.43} = \underline{3.7 \times 10^{-5} M}$$

This is the lowest permissible chloride concentration.

$$\frac{[HgCl_3]}{[HgCl_2][Cl^-]} = 10^{0.95}$$

(see ref M.1).

$$[Cl^-] = \frac{[HgCl_3^-]}{[HgCl_2]} \cdot 10^{-0.95}.$$

$$= 10^{-2.05} \cdot 10^{-0.95} = \underline{10^{-3.00}M.}$$

This is the maximum permissible chloride concentration.

In practice the chloride was added to the urea solution, this was diluted by both the sample and the labelled standard so that

$$[Cl]_{urea} = [Cl]_{aq.\ phase} \cdot \frac{(0.8 + 0.8 + 0.8)}{0.8}$$

$$= 3[Cl]_{aq.\ phase}$$

If the calibration graph is to run to 10^{-5}M mercury (i.e., 6 p.p.m. in the sample) 2×10^{-5}M of chloride must be added to convert all the mercury to mercuric chloride before any free chloride is present thus

$$[Cl] \text{ in aqueous phase} = 3.7 \times 10^{-5} + 2 \times 10^{-5}$$

$$= 5.7 \times 10^{-5}$$

$$[Cl]_{urea} = \underline{17 \times 10^{-5}M.}$$

The sample may cobtain enough chloride to reach the upper limit before interference begins, i.e.,

$$[Cl] \text{ aq. ph.} = 10^{-3}M.$$

$$[Cl] \text{ sample} = 3 \times 10^{-3}M.$$

$$= \underline{100 \text{ ppm.}}$$

This is a large enough tolerance for most purposes. In fact the tolerance is much larger than this because a variation in R of 1% can easily be lost in the experimental error and this is ten times that assumed above. When tested on the Auto-Analyser this method gave very satisfactory results. Standards with and without 20 ppm. of chloride gave the same peak heights and up to 1,000 ppm of chloride gave no interference.

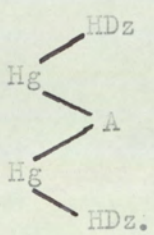
2.3.4. The interference of nitrate & bisulphate.

In section 2.3.2. it was mentioned that nitrate and bisulphate interfere in a similar way to chloride. In the case of these two ions, however, the nature of the complex in the aqueous phase is not known and must be determined experimentally. The general equation for the formation of ternary complexes is :-

$$HgA_n^{+(2-n)} + (2 - n)A^- + Hg(HDz)_2 \rightleftharpoons 2\ HgA.HDz. \quad (1)$$

In this equation the anion has been assumed univalent. If it were not univalent the ternary complex would be charged or a binuclear complex would be formed, i.e.,

$Hg.A.HDz^-$ or



If the complex were charged it would be soluble in the aqueous phase, would lower the activity extracted and would colour the aqueous phase organge or violet (as in the case of ethylenediamine). Neither of these happen so the complexes are not charged. In the case of sulphuric acid the binuclear complex with $A^{2-} = SO_4^{2-}$ is possible though unlikely. If this were the case the general reaction would be :-

$$Hg(SO_4)_n^{2(1-n)} + (1 - n)SO_4^{2-} + Hg(HDz)_2 \rightleftharpoons Hg_2SO_4(HDz)_2.$$

In TABLE 2/6 the results are given for the interference of nitrate. These give a conclusive result that n = 1. In TABLE 2/7 the results for sulphate are inconclusive. Either the interference is due to bisulphate with n = 1, or to sulphate with n = 0. This confusion is due to the way in which the tests were done. The increase in bisulphate concentration parallels that of sulphate because both are due to the partial ionisation of sulphuric acid. To clear this up, tests were carried out at very different acidities so that as the bisulphate concentration increased the sulphate decreased. These results in TABLE 2/8 clearly show that bisulphate is the interfering ion.

These interferences only occur at very high concentrations, and are very greatly reduced in magnitude when chloride is added to overcome chloride interference, as suggested in section 2.3.3. This is because mercuric chloride is a very strong complex and is formed at the expense of the mononitrato mercuric and monobisulphatomercuric ions, thus forcing reaction (1) to the left. If very high concentrations of nitrate or bisulphate ion are expected then it is necessary

to compensate for the small residual interference by preparing a calibration graph with inactive standards containing the same amount of interfering ion as is expected in the sample.

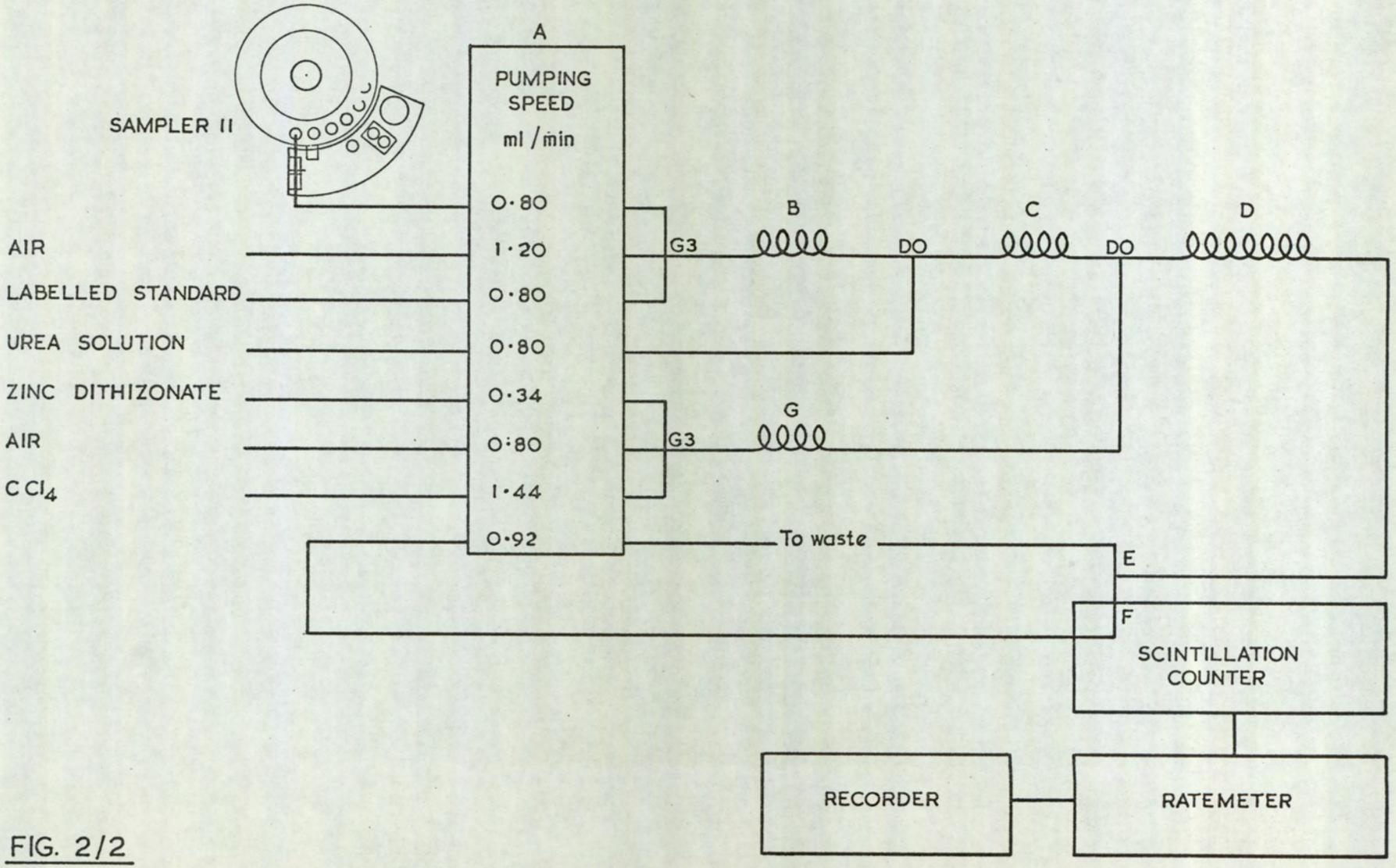

SAMPLER II
A
PUMPING SPEED ml / min
0·80
1·20
0·80
0·80
0·34
0·80
1·44
0·92
AIR
LABELLED STANDARD
UREA SOLUTION
ZINC DITHIZONATE
AIR
C Cl4
G3
G3
B
C
D
G
DO
DO
To waste
E
F
SCINTILLATION COUNTER
RECORDER
RATEMETER

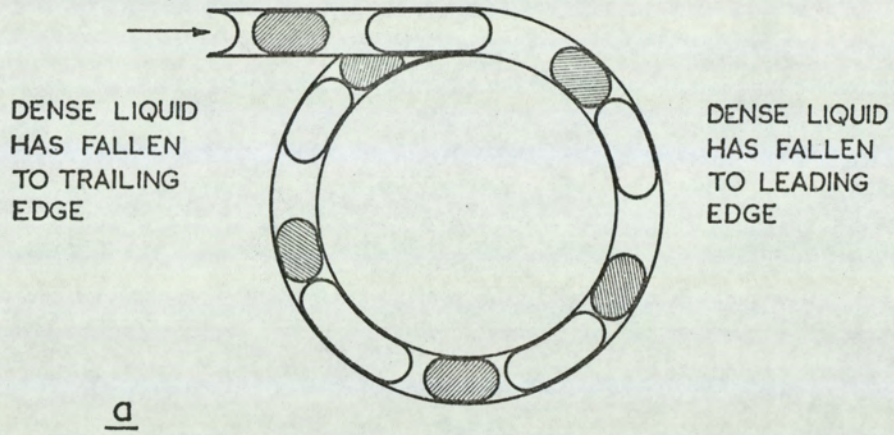
FIG. 2/2

2.4.1. Description of the method.

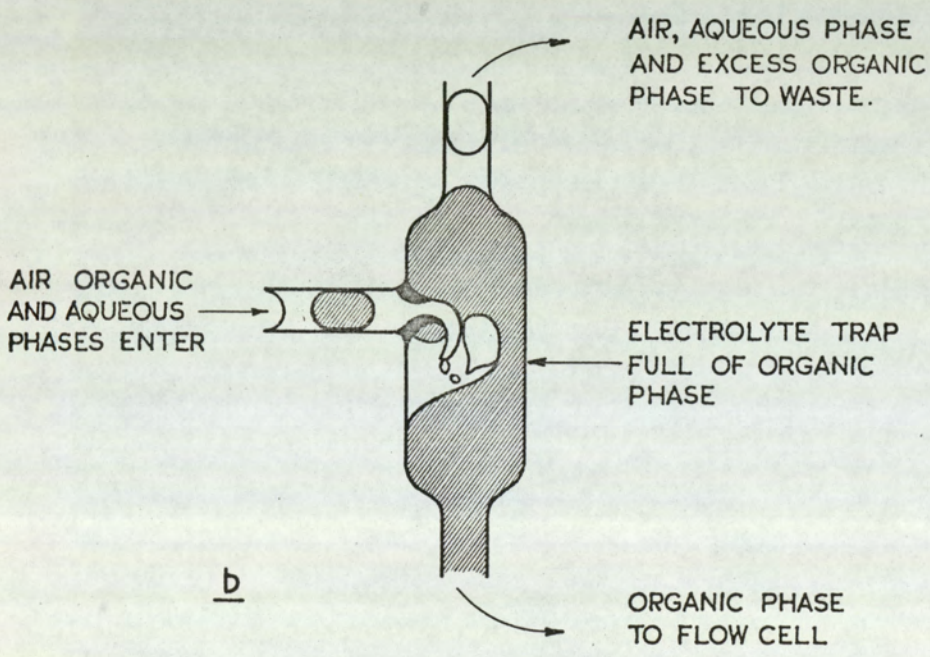
2.4.1.1. The operation of the apparatus.

The arrangement of the apparatus is shown in the flow diagram (FIG.2/2). Sampler II is programmed to deliver alternately samples (for 5 min) and wash solution (for 1 min). The samples and the standard labelled mercury solution are mixed in the first single mixing coil (B) where isotopic equilibrium occurs. This mixing is accomplished mechanically by the denser liquid falling from the leading edge to the trailing edge (see FIG.2.7a.). Urea solution, added to prevent the oxidation of the organic reagent by the nitrous fumes, is mixed with the solution from B in the second single mixing coil (C). The zinc dithizonate which has been diluted with carbon tetrachloride in the coil (G) is now added and the final mixture passed through the special extraction coil (D) (see ref. B2), where solvent extraction takes place. The two phases are separated in the electrolyte trap (E). At the beginning of the run this is filled with organic phase by closing the lower outlet and breaking the connection between this and the pump. During use the organic phase is pumped in faster than it is pumped out, so that the trap remains full. The excess organic phase and the aqueous phase

FIG. 2/7


DENSE LIQUID HAS FALLEN TO TRAILING EDGE
DENSE LIQUID HAS FALLEN TO LEADING EDGE

a

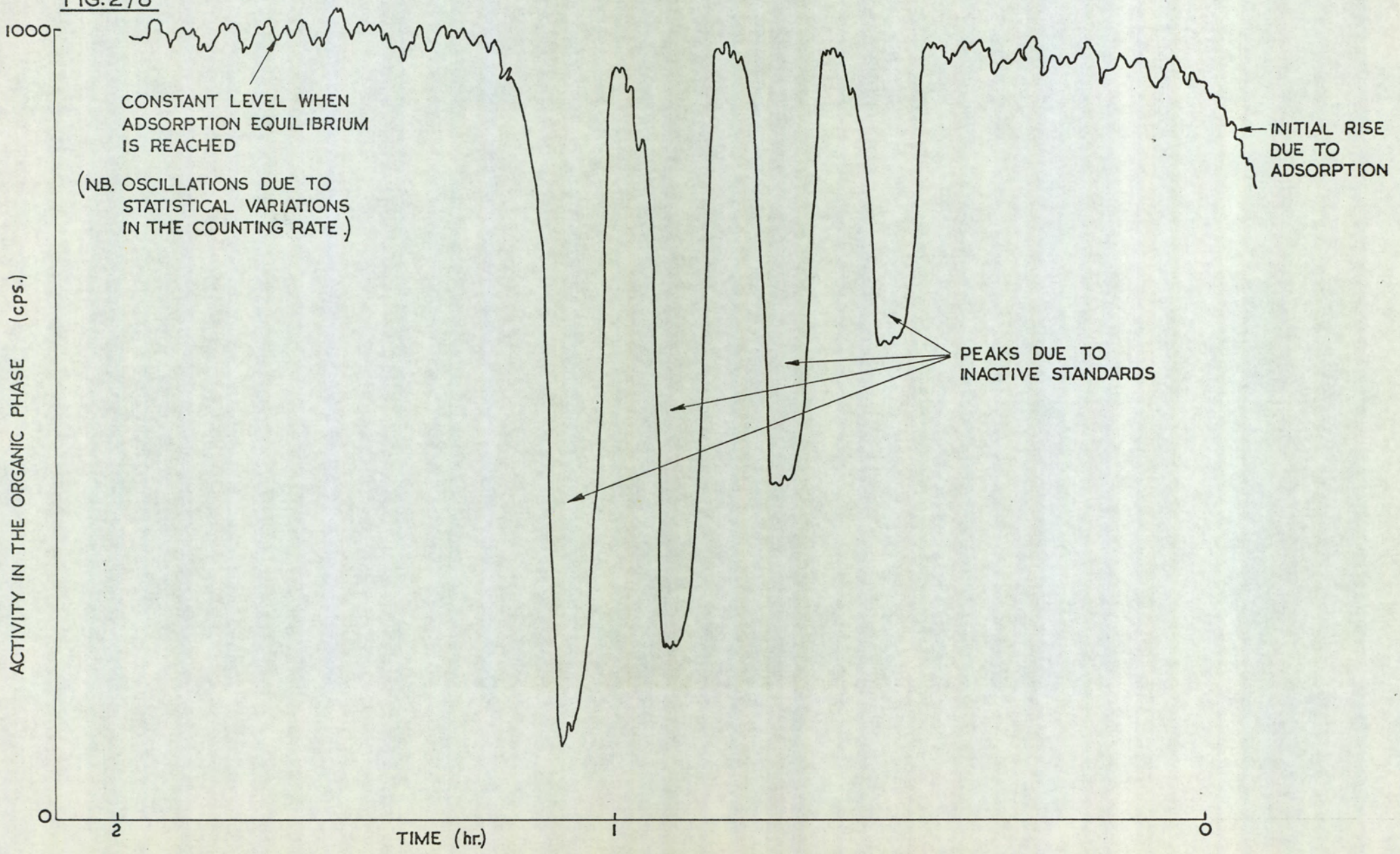

AIR, AQUEOUS PHASE AND EXCESS ORGANIC PHASE TO WASTE.
AIR ORGANIC AND AQUEOUS PHASES ENTER
ELECTROLYTE TRAP FULL OF ORGANIC PHASE
ORGANIC PHASE TO FLOW CELL

b

are run to waste and the heavier organic phase is pumped off from the lower outlet to the flow cell (F) in the scintillation counter (see Fig.2/7b). Here the activity of the organic phase is continuously measured and recorded by the strip chart recorder.

The sample solutions and the reagents are driven through the apparatus by the proportioning pump (A) at speeds governed by the diameter of the pump tubes. Speeds suitable for each solution are recorded on the flow diagram.

FIG. 2/8


1000
0
ACTIVITY IN THE ORGANIC PHASE (cps.)
CONSTANT LEVEL WHEN ADSORPTION EQUILIBRIUM IS REACHED
(N.B. OSCILLATIONS DUE TO STATISTICAL VARIATIONS IN THE COUNTING RATE.)
INITIAL RISE DUE TO ADSORPTION
PEAKS DUE TO INACTIVE STANDARDS
2
1
0
TIME (hr.)

2.4.1.2 The calibration graph.

The calibration graph is prepared by using standard inactive mercury solutions in the cups of sampler II. When chloride is added to overcome chloride interference (section 2.3.3.) a fresh calibration graph should be prepared whenever new reagents are made. If very large amounts of nitrate or bisulphate are expected in the sample, similar amounts should be added to the standard inactive mercury solution and to the wash solution (section 2.3.4.).

A typical calibration graph is shown in Fig.2/8. It was shown in chapter 1 (section 1.1.2.) that this is a rectangular hyperbola, however a plot of W_s versus A_a/A_s is a straight line. In Fig.2/9 some experimental results are plotted in this way. When chloride is added to overcome chloride interference the slope of the line is reduced and the line becomes slightly curved, Fig.2/10 illustrates this.

The range of the calibration graph depends upon concentration of the standard labelled mercury solution. It extends from

$$M_s = 0.3\, M_a \cdot \frac{r_a}{r_s} \quad \text{to} \quad M_s = 3\, M_a \cdot \frac{r_a}{r_s}$$

The concentration of zinc dithizonate suitable for such a range is given by the

FIG. 2/9

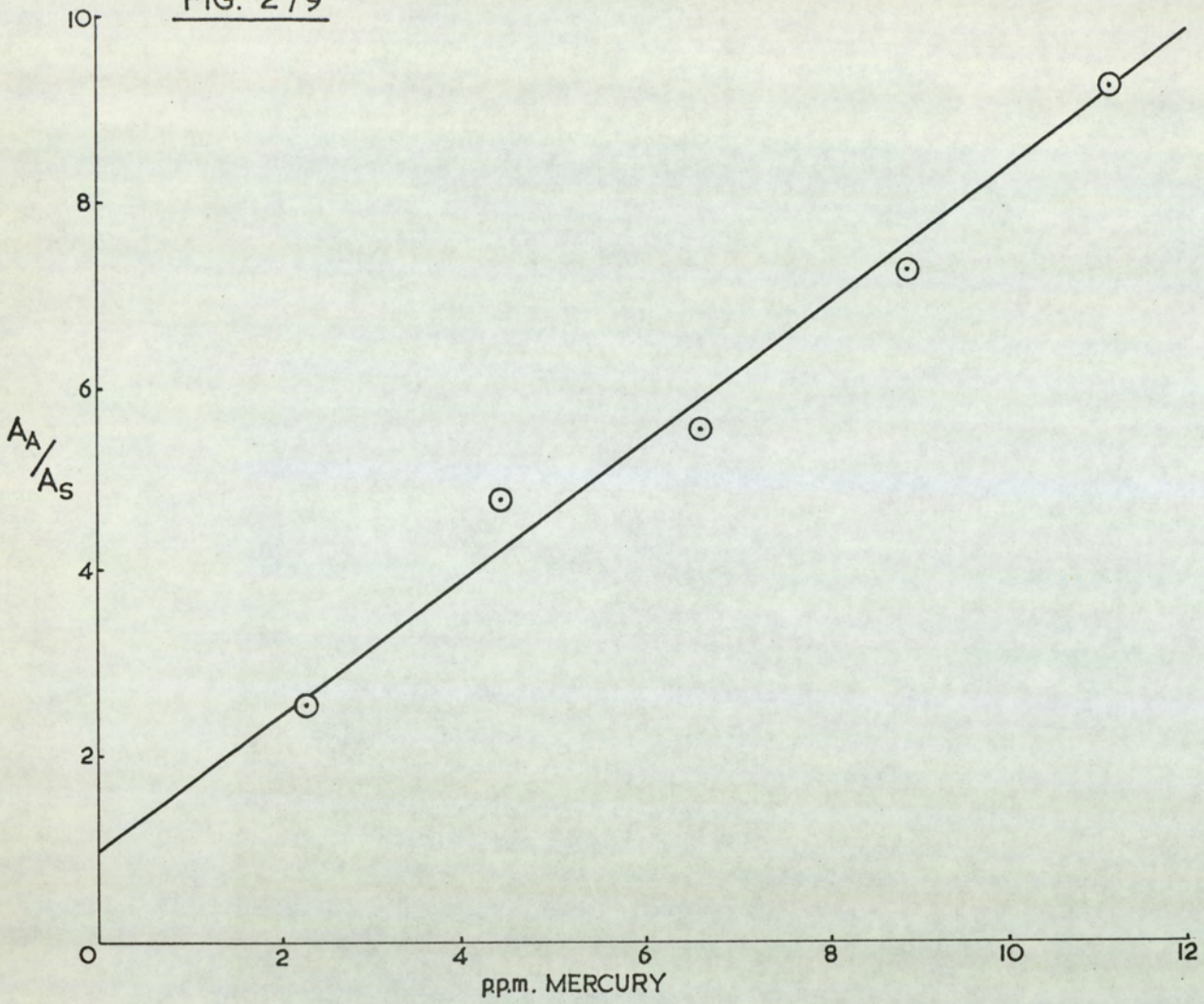
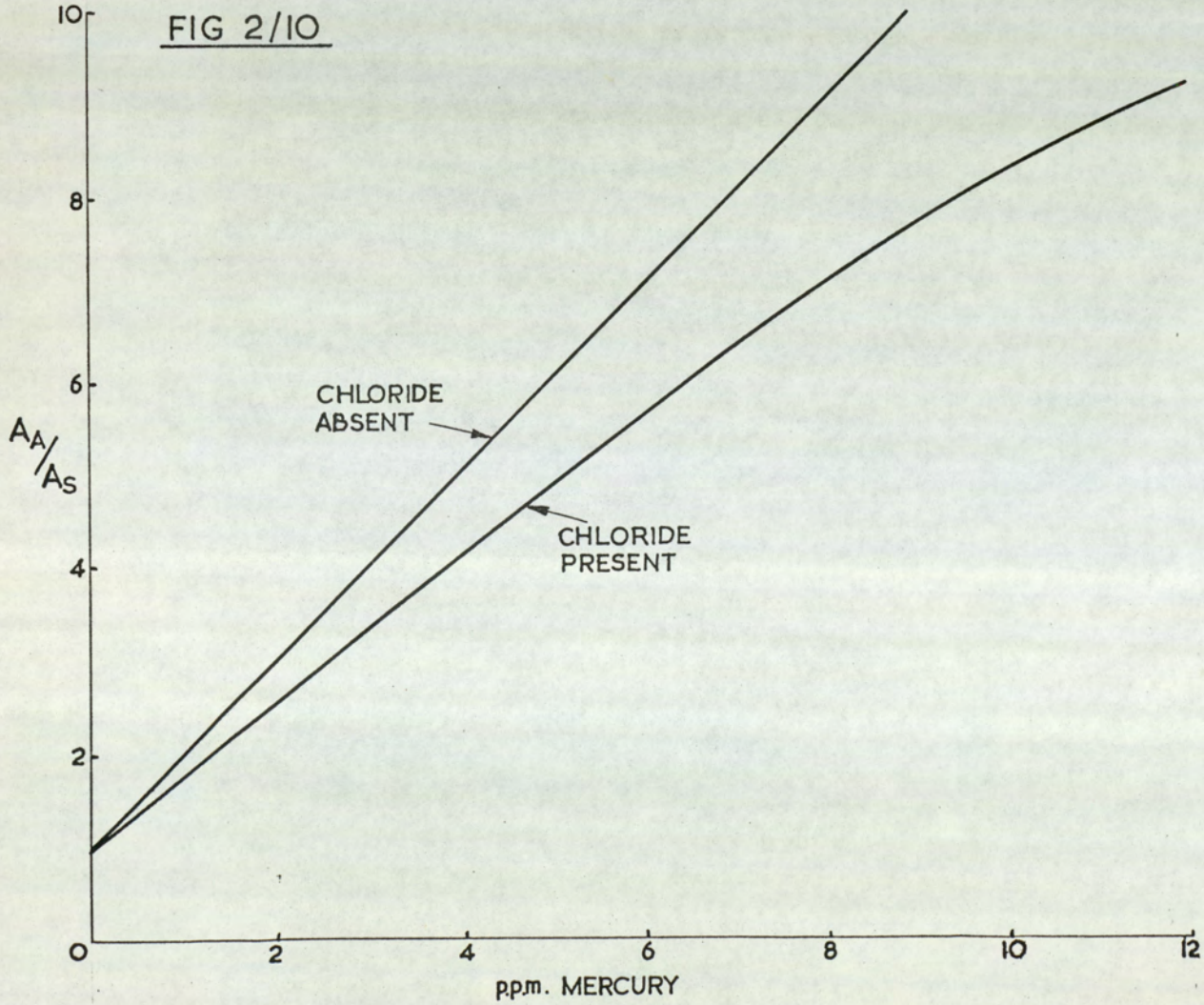


FIG 2/10



formulae

$$M_{Dz} = \frac{r_a M_a}{2r_{Dz}} \qquad \text{--------2/9.}$$

The suitability of the proposed reagent should be checked by ensuring that it extracts less activity from the standard labelled mercury solution than a solution of zinc dithizonate which is twice as concentrated.

In these formulae

M_s = The concentration of mercury in the sample.

M_a = The concentration of mercury in the standard labelled mercury solution.

M_{Dz} = The concentration of the zinc dithizonate solution.

r_s = The speed at which the sample solution is pumped.

r_a = The speed at which the standard labelled mercury solution is pumped.

r_{Dz} = The speed at which the zinc dithizonate solution is pumped.

2.4.2. Analysis of samples.

In order to demonstrate the usefulness of the method it has been used to analyse four samples of low grade cinnabar ore which had been previously analysed spectrophotometrically at the Warren Spring Laboratory and were generously provided by Dr. P. G. Jeffery*. The results are given in TABLE 2/10.

*Warren Spring Laboratory, Ministry of Technology, Stevenage, Herts., England.

2.4.3. Sensitivity and accuracy.

Unlike the manual method, the sensitivity and accuracy of the automatic method depends upon the specific activity of the radioactive isotope available. This is because the flow cell used is of small volume and the time constant of the ratemeter is much shorter than the counting times usually used manually.

Consider a flow cell of volume Vml in a scintillation counter of efficiency η through which an organic phase, activity A c/s/ml, is pumped. The total rate at which the organic phase is pumped is r_o ml/min. The sample is pumped for T min. The ratemeter has a time constant of τ sec. and the specific activity of the mercury is C curies/gm.

Then the coefficient of variation of the activity of the standard is given by

$$v^2(PA) = 10^4/\tau AV. \qquad \text{--------2/10}$$

The amount of mercury in the organic phase during the time the sample is pumped is

$$W_e = \frac{A.T.r_o.}{3.7\ C\ \eta}\ 10^{-10} \text{ gm.}$$

In the labelled standard

$$W_a = \frac{2}{3.7}\ \frac{A.T.r_o.}{C\ \eta}\ 10^{-10} \text{ gm.}$$

and in the sample

$$W_s = \frac{2}{3.7} \frac{q.A.\ T.r_o}{C\ \eta} . 10^{-10} gm. \quad \text{-------2/11.}$$

where $q = W_s/W_a$.

Now

$$v^2(W_s) = \frac{(1+q)^2}{q^2} . (v^2(PS) + v^2(PA))$$

$$v^2(PS) = v^2(PA)\ (1+q)$$

substituting from equation 2/10 gives

$$v^2(W_s) = \frac{(1+q)^2}{q^2} . \frac{10^4}{\tau\ AV.} .(2+q)$$

Using the limit $v(W_s) = 2.5\%$ developed in chapter one (section 1.3.5.) gives

$$A = \frac{(1+q)^2}{q^2} . \frac{10^4}{\tau\ V} . \frac{(2+q).}{6.25}$$

substituting for A in equation 2/11

$$W_s = \frac{0.54 \times 10^{-6}.}{6.25} \frac{T\ r_o}{C\ \eta} . \frac{(1+q)^2.\ (2+q)}{V \tau\ q}$$

This equation has a minimum when $q = 0.62$. Thus

$$W_s(min) = 0.95 \times 10^{-6}. \frac{T.\ r_o}{C\ \eta\ V \tau}$$

substituting the values

$T = 5$ min, $r_o = 1.8$ ml/min, $C = 0.5$ Ci/gm,

$= 0.50$, $V = 1.0$ ml $\tau = 25$ sec

which are figures for the apparatus and isotope usually used gives

$$W_s(\text{min}) = 1.4\ \mu g$$

In the calibration graph with the weakest labelled standard mercury solution that has been used, at $q = 0.6$ $W_s = 1.6\ \mu g$ and $v(W_s) = 5\%$. Smaller amounts of mercury can be determined if a lower precision can be tolerated. As little as $0.04\ \mu g$ gave a discernable peak.

2.4.4. The advantages of automatic substoichiometry.

In addition to the usual advantages of automatic methods (section 2.1.2.) there is one advantage peculiar to substoichiometry. It has been repeatedly emphasised in Chapter one that the same amount of mercury must be extracted from the sample and standard. If this condition is not satisfied the substoichiometric equation (1/2) cannot be used. This limitation does not apply to the automatic method. The method used to overcome chloride interference relies upon this advantage. In this method (section 2.3.3.) a reproducible calibration graph is obtained but this graph is not a rectangular hyperbola; it does not conform with equation 1/2. This advantage is very important, because the method used to overcome chloride in the manual method - addition of E.D.T.A. see chapter four - cannot be used in the automatic method.

2.4.5. Disadvantages of automatic substoichiometry.

(a) The stability of the reagent must be greater than in the manual method where the reagent must remain stable only for the few minutes between the extraction of the standard and the sample. In the automatic method the reagent must be stable for the whole time one calibration graph is used, at least one day. In the automatic method dithizone cannot be used below 10^{-5}M. Zinc dithizonate must be used in its place.

(b) The automatic method is less sensitive than the manual one because of the small size of the flow cell and the short counting time (see 2.4.4.).

(c) Compared with most automatic methods the solvent extraction procedure is slow. (section 2.2.4.). The substoichiometric method is slower still because of isotopic exchange with adsorbed mercury. (section 2.2.3.).

2.5. Experimental.

2.5.1. Reagents.

These were prepared from analytical reagent grade chemicals.

Radioisotopes. The isotope used was mercury - 203 as the acetate with a specific activity of 0.5Ci/gm. (Radiochemical Centra, Amersham, England). The material received from Amersham was diluted to 500 µg./ml.

For the experiments with chlorine-36, sodium chloride with a specific activity of 8.50 µ Ci/gm Cl was used (also from the Radiochemical Centre).

Standard labelled mercury solutions. These were prepared by diluting the mercury isotope solutions with 1M nitric acid. Various concentrations were used according to the range of the calibration graph required, (e.g., a 1 ppm standard gave a graph covering the range 0.3-3 ppm).

Standard inactive mercury solutions. An approximately 0.05M solution of mercuric nitrate was prepared and standardised by Volhards method (H1). This stock solution was diluted appropriately with 1M nitric acid.

Urea solutions. Either 1% in water or 1% in 10^{-4}M sodium chloride.

Zinc dithizonate stock reagent. Prepared by discolving 0.05 gm. of dithizone in 10 ml of ammonia solution (S.G.0.880) and diluting to 100 ml, then extracting with carbon tetrachloride until the colour of the organic phase changed from brown to pale green. This purified aqueous solution (free from carbodiazone) was mixed with a solution of 0.05g of zinc sulphate heptahydrate in 90 ml of water and 10 ml of glacial acetic acid, then extracted with 100 ml of carbon tetrachloride. The organic phase was filtered through a dry No. 41 Whatman paper and the zinc dithizonate concentration (c.a. 5×10^{-4}M) determined (after 100 fold dilution) from its absorbance at 538 nm. ($\varepsilon = 9.2 \times 10^{4}$(I.1.)). The working solution was prepared by the appropriate dilution of this stock reagent. A 2×10^{-5}M solution is suitable for the determination of mercury in the range 0.3 to 3 ppm.

2.5.2. Apparatus.

Technicon Auto-Analyser (Technicon Instruments Company Ltd., Hanworth Lane, Chertsey, Surrey, England). The system used comprised, as its main items, a two speed proportioning pump, a sampler Model II, and

a strip chart recorder (Bristol Dynamaster, Model 570, as supplied by Technicon).

Scintillation Counter. The detecter used was a 2" x 2". NaI(Tl) well type crystal; well diameter 1 in., volume 20 ml. This was associated with a single channel gamma-ray spectrometer (9000 series, Research Electronics Ltd., Cleckheaton, Yorkshire, England). In all experiments a setting of the discriminator voltage corresponding to 50 kev. was used. This gave a background counting rate of 10 cps. The output of the ratemeter (Model 9030) was fed to the strip chart recorder.

Flow-cell. Made from 32 cm. of 3.5 mm outside diameter soda-glass tubing wound into a coil 2.2 cm in diameter and 2 cm high, which fitted into the well of the scintillation counter.

Extraction coil, made from 3 m of 2.7 mm internal diameter soda-glass tubing, wound into a flat spiral of ten complete turns.(B2).

Pump tubing. Tygon tubes may be used for the aqueous solutions but acidaflex must be used for the zinc dithizonate reagent because Solvaflex, which is usually recommended

by Technicon (for organic solvents) causes very severe adsorption problems. (All types of tubing available from Technicon).

2.5.3. Calibration graphs.

The apparatus was set up as in FIG.2/2. The concentrations of the zinc dithizonate reagent, the standard labelled mercury solution and the standard inactive mercury solutions (which are placed in the cups) were chosen in accordance with the equations presented in section 2.4.1.2. The pump was started and the electrolyte trap was filled with organic phase. (see 2.4.1.1.). During this time the sampler was switched off with the cam in such a position that only wash solution was sampled. At first the activity in the organic phase rose because zinc dithizonate was being adsorbed on to the walls of the pump tubing. When equilibrium was reached this activity became constant (FIG.2/8). The sampler was now started and the inactive standards each produced a reduction in the activity of the organic phase. From the heights of these peaks a calibration graph was plotted. If chloride was absent this was a straight line (Fig.2/9) but if chloride was present, a curve.

2.5.4. Dissolution of samples.

One g. of ore (received as a fine powder and used directly) was refluxed for 30 min. with 25 ml of sulphuric acid (S.G.1.84) and 1g of potassium nitrate. After cooling and dilution, 1g of urea was added, the mixture filtered through a No. 42 Whatman paper, and the filtrate diluted to 250 ml in a calibrated flask. (A2).

The solution was analysed by the procedure described above (2.5.3.), using the following solutions. Standard labelled mercury solution 5×10^{-6}M, urea solution 1% in. 10^{-4}M. sodium chloride, zinc dithizonate reagent 5×10^{-6}M. The wash solution and the inactive standard mercury solutions were 1.8 M with respect to sulphuric acid to compensate for bisulphate interference.

2.5.5. Tracer experiments with chlorine - 36.

Five ml of an aqueous phase, containing various amounts of mercuric nitrate and labelled sodium chloride and 1 M in nitric acid was extracted with 5 ml of 6×10^{-5}M zinc dithizonate (or zinc diethyldithiocarbamate , or pure carbon tetrachloride) solution. The organic phase was

filtered through a dry No.41 Whatman paper and an aliquot of the organic phase evaporated to dryness on a planchet and the activity measured with an end window Geiger Müller counter.

2.5.6. Determination of carry over time.

For this experiment the Auto-Analyser was set up for normal colorimetric analysis (i.e., as FIG. 2, but with a colorimeter in place of the scintillation counter and ratemeter). The reagent used was 3×10^{-5}M dithizone and the standards contained 1, 4, 8, 10,16 and 100 ppm. mercury. The sampler was switched off and the samples changed manually, each being sampled for 10 min. The optical density of the organic phase at 505 nm. was monitored continuously, and the time required for the pen to traverse 95% of its maximum deflection was observed for each standard.

TABLE 2/1. Carry over and pumping rate.

Mercury conc. ppm.	r = 0.92 ml/min.		r = 2.76 ml/min.	
	rising edge	falling edge.	rising edge.	falling edge.
1	2.7	2.5	1.0	0.9
4	2.3	2.4	0.9	0.7
8	1.4	2.4	-	-
10	1.4	2.3	0.7	0.7
16	-	2.3	-	-
100	-	2.4	-	-
Calcd. V = 0.74 ml	2.4	min	0.81	min
Calcd. V = 0.5 ml	1.6	min.	0.55	min.

TABLE 2/3. Stability constants of some monochlorometal ions.

Ion.	$\log K_1$	Ref.	Comments
Cd^{2+}	2.00	V1	Too weak
Cu^{2+}	0.11	M4	Too weak
Fe^{3+}	0.62	R6	Too weak
Bi^{3+}	2.43	N3	Too weak
In^{3+}	2.36	- C3	Too weak
Pb^{2+}	1.60	N2	Too weak
Pd^{2+}	6.2	D3	Replaces Hg in $Hg(HDz)_2$
Rh^{3+}	2.45	C2	Replaces Hg in $Hg(HDz)_2$

TABLE 2/2. Interference study.

Substances which do not interfere			Metals which interfere by competing with mercury for the dithizone	Ions which interfere by oxidising dithizone	Substances which interfere by complexing mercury	Substances which interfere by reducing mercury to the metal	Anions which interfere by forming ternary complexes
Acetate	NH_4^+	Se^{4+}	Au^{3+}	MnO_4^-	SCN^-	$N_2H_3^+$ (b)	HPO_2^-
Citrate	K^+	Te^{4+}	Pd^{2+}	$Cr_2O_7^{2-}$	I^-		Cl^-
Tartate	Na^+	Tl^+	Pt^{2+}	NO_2^-	SO_4^{2-}	Sn^{2+} (a)	Br^-
Oxalate	Mg^{2+}	Cr^{3+}					HSO_4^- (e)
Borate	Ca^{2+}	Mn^{2+}		ClO_3^- (c)	EDTA (b)		NO_3^- (d)
Molybdate	Ba^{2+}	Fe^{2+}	Pt^{4+} (b)				
$S_2O_8^{2-}$	Al^{3+}	Fe^{3+}	Ag^+ (b)	Ce^{4+} (a)	$S_2O_3^{2-}$ (a)		
H_3PO_4	Ga^{3+}	Co^{2+}	Bi^{3+} (b)		F^- (a)		
H_2O_2	In^{3+}	Ni^{2+}					
ClO_4^-	Ce^{3+}	Cu^{2+}					
SO_4^{2}	Th^{4+}	Zn^{2+}					
	Sb^{3+}	Pb^{2+}					
	As^{3+}	Be^{2+}					

TABLE 2/2 (Continued)

Notes: (1) Standard labelled mercury solution 2.5×10^{-6}M, zinc dithizonate working solution 5×10^{-7}M. Acidity IN in HNO_3 except during the examination of H_2SO_4 and HNO_3 when the acidity was varied from 0.01N to 10N.

(2) Any substance changing the activity extracted by more than 1% is assumed to interfere in concentrations down to 0.1 ppm unless stated otherwise.

a = investigated at 1000 ppm only

b = inteferes if present in excess of 100 ppm.

c = interferes if present in excess of 10 ppm.

d = interferes if present in excess of 0.5 M.

e = interferes if present in excess of 0.05 M.

TABLE 2/4 Tracer experiments with ^{36}CL.

Mercury added µg.	Chloride added µg.	Chloride in the organic phase µg.	Conditions.
156	24.3	3.5	excess $HgCl_2$ - 50% Hg extracted
156	24.3	3.1	excess $HgCl_2$ - 50% Hg extracted
78	24.3	<0.04'	No H_2Dz - CCl_4 only
78	12.2	<0.2'	excess H_2Dz - 50% H_2Dz used
31.2	486	<0.1'	excess H_2Dz - 25% H_2Dz used
4.46	486	<0.01'	excess H_2Dz - 5% H_2Dz used
62.4	19.4	1.1	excess Diethyldithiocarbamate.

' limit of detection.

TABLE 2/5. The recovery of mercury after a chloride separation with dithizone.

Step		Oxidant	
		$KMnO_4$	$NaNO_2$
1. Separation of mercury from chloride with dithizone.	% mercury in aqueous layer	0	0
	% mercury in organic layer	100	105
2. Destruction of dithizone with the oxidant.	% mercury in aqueous layer	99	63
	% mercury in organic layer	5	2
	% mercury adsorbed on the separating funnel	0	35
3. Reaction of mercury with X.S. dithizone	% mercury in aqueous layer	0	3
	% mercury in organic layer	100	97
4. Isotope dilution analysis after steps 1 & 2	% mercury recovered	130	110

TABLE 2/6 Nitrate interference.

$[NO_3^-]$ Molar	$C_{Hg.}$ Molar	P %	$[Hg(HDz)_2$ Molar	$[HgNO_3HDz]$ Molar	K		
					n = 2	n = 1	n = 0
0.43	0.79×10^{-6}	1.3	1.09×10^{-6}	2.9×10^{-8}	0.0010	0.0022	0.0051
1.03	0.78×10^{-6}	2.0	1.08×10^{-6}	4.4×10^{-8}	0.0023	0.0022	0.0021
2.03	0.76×10^{-6}	4.0	1.06×10^{-6}	8.8×10^{-8}	0.0097	0.0048	0.0024
0.43	4.4×10^{-6}	3.3	1.06×10^{-6}	6.7×10^{-8}	0.0011	0.0026	0.0062
1.03	4.3×10^{-6}	5.0	1.05×10^{-6}	1.1×10^{-7}	0.0027	0.0026	0.0025
2.03	4.3×10^{-6}	7.5	1.02×10^{-6}	1.65×10^{-7}	0.0060	0.0030	0.0015

$$K = [HgNO_3HDz]^2 \Big/ [Hg(NO_3)_n]\,[Hg(HDz)_2]\,[NO_3]^{(2-n)}.$$

$$C_{Hg} = [Hg(NO_3)_n] = b - a\left(1 + \frac{P}{100}\right) V_o / V_a$$

now b = conc. Hg added to the aqueous phase before extraction (either 1.67×10^{-6} M or 5.3×10^{-6}M)

P = Percentage increase in the amount of mercury extracted.

$V_o/V_a = 0.77$

a = conc. of $Zn(HDz)_2$ reagent used = 1.1×10^{-6}M.

$$[Hg(HDz)_2] = a(1 - 10^{-2}P).$$

TABLE 2/7. The interference of sulphate.

C_{Hg} M	$[SO_4^{2-}]$ M	$[HSO_4^-]$ M	$[Hg(HD_z)_2]$ M	$[Hg_2SO_4(HDz)_2]$ M	$[HgHSO_4HDz]$ M	P %	Bisulphate Complex.			Sulphate Complex.	
							n=o	n=1	n=2	n=o	n=1
7.6×10^{-7}	0.03	0.05	1.04×10^{-6}	5.7×10^{-8}	1.2×10^{-7}	5.3	7.3	0.34	0.02	2.45	0.07
7.3×10^{-7}	0.12	0.28	1.01×10^{-6}	8.8×10^{-8}	1.8×10^{-7}	8.0	0.59	0.15	0.04	0.99	0.12
6.9×10^{-7}	0.29	0.71	0.95×10^{-6}	1.5×10^{-7}	2.9×10^{-7}	13.3	0.25	0.18	0.13	0.76	0.22
6.4×10^{-7}	0.59	1.41	9.0×10^{-7}	2.1×10^{-7}	4.1×10^{-7}	18.7	0.14	0.20	0.30	0.61	0.36
4.4×10^{-6}	0.12	0.28	1.04×10^{-6}	6.4×10^{-8}	1.3×10^{-7}	5.8	0.047	0.013	0.004	0.12	0.01
4.3×10^{-6}	0.29	0.71	8.8×10^{-7}	2.2×10^{-7}	4.4×10^{-7}	20.0	0.10	0.072	0.05	0.20	0.06
4.2×10^{-6}	0.59	1.41	7.9×10^{-7}	3.1×10^{-7}	6.3×10^{-7}	28.4	0.025	0.084	0.12	0.16	0.10

TABLE 2/7. (Continued).

(a) Both complexes

a = conc. of zinc dithizonate = 1.1×10^{-6}M.

b = conc. of mercury added to the aqueous phase before extraction (either 1.67×10^{-6}M or 5.3×10^{-6}M.).

$$C_{Hg} = [Hg(HSO_4^-)_n] \text{ or } [Hg(SO_4)_n].$$

$$= b - \frac{V_o}{V_a} \cdot a(1 - 10^{-2}P)$$

$$\frac{V_o}{V_a} = 0.77.$$

$$[Hg(HDz)_2] = a(1 - 10^{-2}P).$$

(b) Bisulphate complex.

$$[HgHSO_4.HDz] = 2.a.(10^{-2}P).$$

$$K = [Hg.HSO_4.HDz]^2 / [Hg(HSO_4)_n][Hg(HDz)_2][HSO_4^-]^{(2-n)}.$$

(c) Sulphate complex.

$$[Hg_2SO_4(HDz)_2] = a(10^{-2}P).$$

$$K = [Hg_2SO_4(HDz)_2] / [Hg(SO_4)_n][Hg(HDz)_2][SO_4]^{(1-n.)}.$$

TABLE 2/8. Distinction between a bisulphate and a sulphate complex.

$[H^+]$	$[HSO_4^-]$	$[SO_4^{2-}]$	P	Constant corresponding to 'a'	
				Bisulphate complex.**	Sulphate* complex
0.96	0.57	0.03	0.16	0.045	5.3
0.02	0.31	0.69	0.12	0.046	0.17

Notes:

** $K = [Hg\ HSO_4\ \ HDz]^2 \Big/ [Hg(HDz)_2]\ [HgHSO_4^+]\ [HSO_4^-]$

but $[Hg(HDz)_2]$ and $[Hg(HSO_4)^+]$ are constant and $[Hg.\ HSO_4.\ HDz]$ is proportional to P.

$\therefore\ K' = P^2 / [HSO_4^-]$ is constant

* $K = [Hg_2SO_4(HDz)_2] / [Hg^{2+}][SO_4^{2-}]\ [Hg(HDz)_2]$

but $[Hg(HDz)_2]$ and $[Hg^{2+}]$ are constant and $[Hg_2SO_4(HDz)_2]$ is proportional to P.

$\therefore\ K' = P / [SO_4^{2-}]$ is constant.

The values, recorded in the table are values of K'.

TABLE 2/10. Analysis of cinnibar ore.

Method of Analysis	Sample 1.	Sample 2.	Sample 3.	Sample 4.
Continuous Substoichiometry.	0.017	0.064	0.069	0.030
Spectrophotometry in this laboratory.	0.021	0.071	0.066	0.036
Spectrophotometry at Warren Spring Laboratory.	0.020	0.068	0.045	0.033

Figures in the table are % mercury.

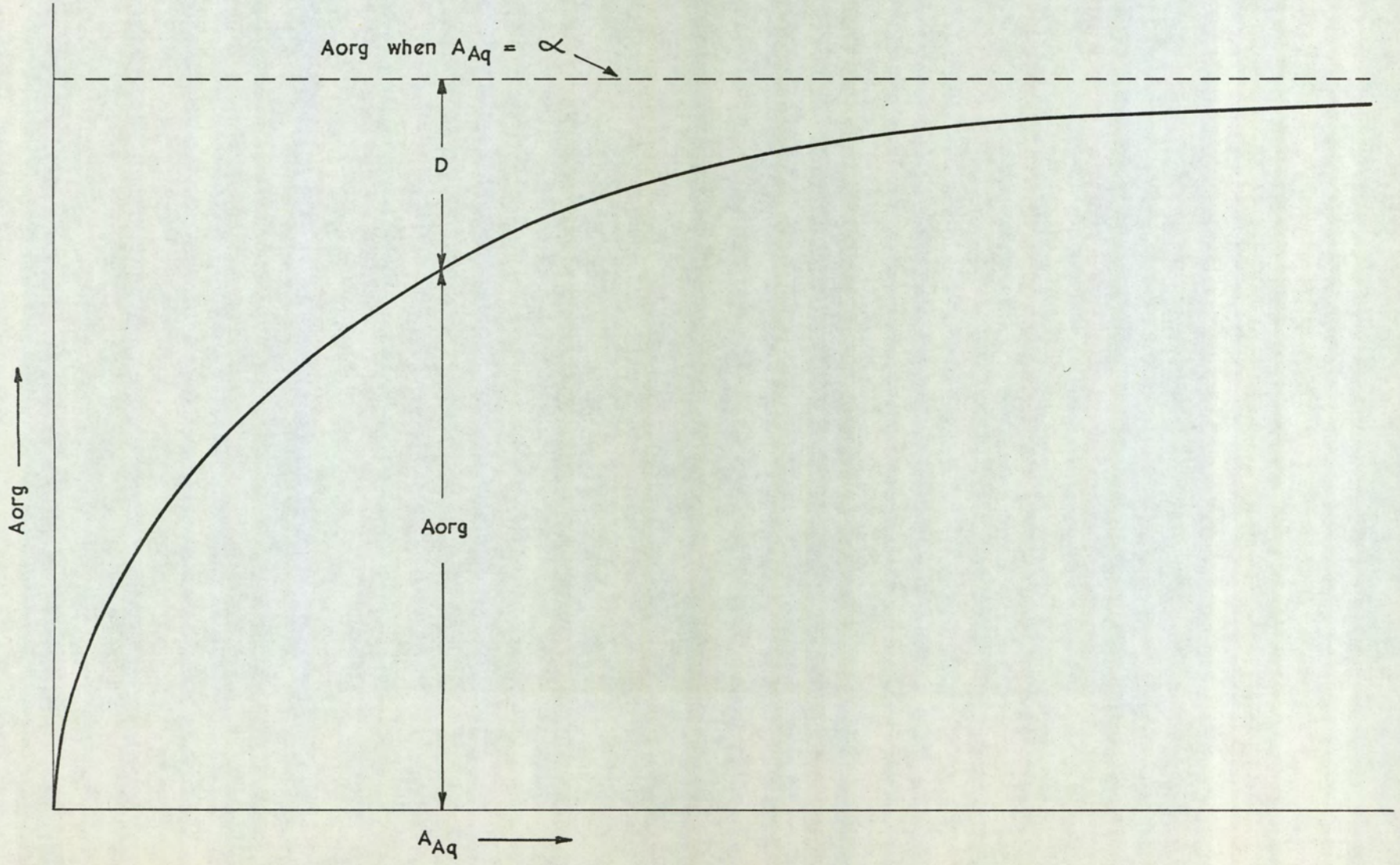
C H A P T E R T H R E E.

MERCURIC CHLORIDE DITHIZONATE.

Summary.

In chapter two the interference of chloride was attributed to the formation of mercuric chloride dithizonate. In this chapter the existence of this substance is proven and its reactions and properties are described.

FIG. 3/1



3.1. The existence of mercuric chloride dithizonate.

3.1.1. The reproducability graph.

If dithizone is reacted with an excess of labelled mercury, the reaction which occurs may be represented as :-

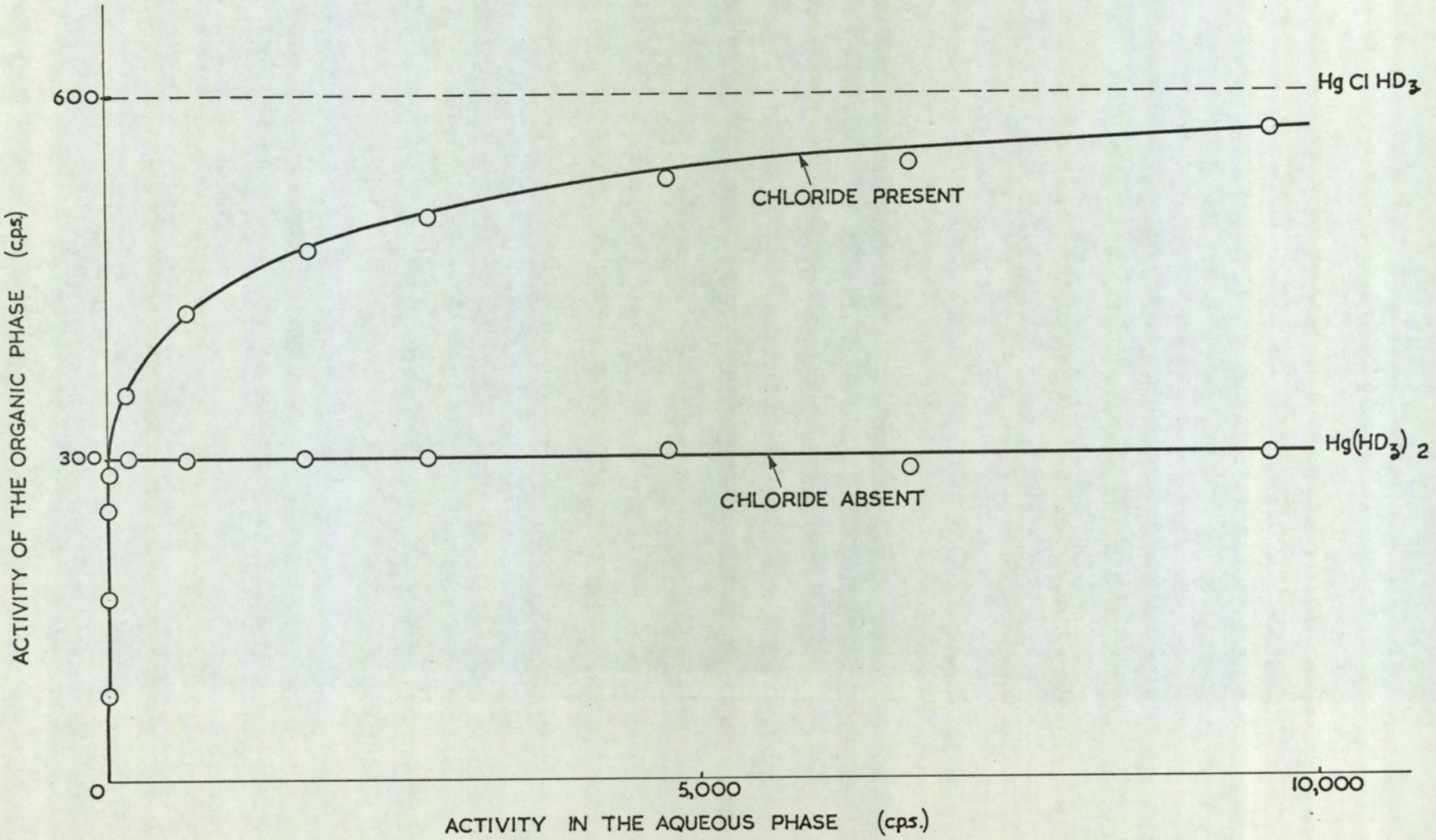
$$Hg(Aq) + n.\ H_2Dz \rightleftharpoons Hg(org)$$

Where Hg(Aq) represents any complex of mercury in the aqueous phase and Hg(org) similarly represents the complex present in the organic phase. The activity of the aqueous phase (A_{aq}) is proportional to the concentration of Hg(Aq), and the activity of the organic phase (A_{org}), is proportional to the concentration of Hg(org). This reaction will have an extraction constant (E).

$$E = E_{org} / A_{Aq.}\ [H_2DZ]^{n.}$$

A graph of A_{org} versus A_{aq} will be similar to FIG.3/1. An infinitely large excess of mercury in the aqueous phase will ensure that the reagent will be completely consumed. Any difference between this level and the actual activity of the organic phase extracted at any

FIG. 3/2


600
300
0
Hg Cl HD3
Hg(HD3) 2
CHLORIDE PRESENT
CHLORIDE ABSENT
ACTIVITY OF THE ORGANIC PHASE (c.p.s.)
5,000
10,000
ACTIVITY IN THE AQUEOUS PHASE (c.p.s.)

particular concentration of mercury in the aqueous phase (D in FIG.3/1) represents unconsumed reagent.

$$D = [H_2Dz] / n.$$

When E is large the smallest amount of mercury in the aqueous phase will reduce D virtually to zero, any further increase cannot change A_{org} and the graph will be a horizontal straight line. When E is small A_{Aq} must change significantly to affect a change in A_{org} and the graph will be a curve.

The extraction constant for primary mercuric dithizonate, the expected complex, is very large (10^{27} see B.1) and indeed when this experiment is conducted in the absence of chloride, (i.e., with mercuric nitrate, perchlorate or acetate), the resulting graph is a horizontal straight line, but in the presence of chloride, (i.e., with mercuric chloride), the graph is a curve (FIG.3/2).

This difference of behaviour could be due to the formation of undissociated mercuric chloride. Chloride will act as a competing ligand. As explained in section 1.4.2. this would lower the conditional extraction constant and could possibly result in a curve. The stability constants of the chloro-complexes of mercury are known (M1) and it is possible to calculate the magnitude of this effect.

$\beta_1 = 10^{6.74}, \beta_2 = 10^{13.22}, \beta_3 = 10^{14.17}, \beta_4 = 10^{15.22}$

In the experiment recorded in FIG.3/2 the free chloride ion concentration was 5×10^{-5}M.

$$\alpha_{Hg(Cl)} = 10^{-4.70}\, 10^{6.74} + 10^{-9.40}.10^{13.22} + 10^{-14.10}.\, 10^{14.17} + 10^{-18.80}.\, 10^{15.52}.$$

$$= 10^{2.04} + 10^{3.82} + 10^{0.07} + 10^{-3.28}$$

$$= 10^{3.83}.$$

$$E'_{Hg(HDz)_2} = 10^{26.66}.\, 10^{-3.82}$$

$$= 10^{22.84}$$

This value is still far too high to explain the results recorded in FIG.3/2. There are other reasons for believing this is not the correct explanation :-

(a) There is no free dithizone present in the organic phase. The organic phase is not green and shows no absorption at 620 nm. the wavelength of maximum adsorption of dithizone.

(b) Increasing the chloride concentration does not decrease the amount of mercury extracted until very high chloride ion concentrations are reached (see FIG.4/2).

(c) The amount of mercury extracted from mercuric chloride solutions is greater, not less, than that extracted from other mercuric salts,

and in fact tends to twice this amount when the concentration of mercuric chloride in the aqueous phase is large.

Plainly, mercuric chloride does not react with dithizone to form primary mercuric dithizonate, some other complex is formed. There are three complexes of mercury and dithizone which have the correct ratio of mercury to dithizone :-

(a) Secondary mercuric dithizonate

HgDz.

(b) Primary mercurous dithizonate

Hg(HDz)

(c) Mercuric chloride dithizonate (W2)

Hg.Cl.HDz.

The spectrum of the organic phase (FIG.3/3 - section 3.3.1.), proves the absence of secondary mercuric dithizonate but the spectra of the other two complexes are similar and it is not possible to distinguish them ex hypothesi. Mercurous dithizonate is unlikely to be formed because dithizone is not a strong enough reducing agent to accomplish this and there is no other reducing agent present. Also if this were the case, why is mercurous dithizonate not formed from solutions of mercuric perchlorate and acetate ? The mercuric ion concentration is higher in both these solutions

than in solutions of mercuric chloride. This should favour the reduction. This can be seen by examining the reaction for the formation of the mercurous complex.

$$Hg^{2+} + Hg(HDz)_2 + 2e \rightleftharpoons 2HgHDz$$

Mercuric chloride dithizonate has been prepared by Webb (W2) by mixing, in the correct proportions, solutions of dithizone and mercuric chloride in diethyl ether. This complex adequately explains all the features discussed above.

3.1.2. The transfer of chlorine from the aqueous to the organic phase.

If mercuric chloride dithizonate is formed when dithizone reacts with mercuric chloride, then chlorine must be transferred to the organic phase and if chlorine - 36 is used the organic phase will become radioactive. TABLE 2/4 of chapter 2 shows the results of such an experiment. These results conclusively demonstrate the presence of chloro-complexes in the organic phase.

There are other possible explanations of these results; there could be droplets of the

aqueous phase suspended in the organic phase; there could be partition of mercuric chloride between the two phases or there could be isotopic exchange between chloride in the aqueous phase and carbontetrachloride in the organic phase. These are not the true explanation however because in the absence of dithizone no chlorine-36 is extracted.

In these early experiments less chloride was extracted than was anticipated on the basis of the mercury - 203 experiments. This was due to the method used to measure the radioactivity. During the source preparation the organic phase was evaporated to dryness and some of the chloride dithizonate was decomposed, chlorine being lost as the volatile hydrogen chloride.

$$HgClHDz \xrightarrow{heat} HgDz + HCl$$

An improved method will be described in section 3.3.6.

3.1.3. The reaction between mercuric chloride and dithizone.

When strong (c.a.10^{-3}M) solutions of dithizone react with mercuric chloride a precipitate is formed, this does not happen with mercuric nitrate or perchlorate. This precipitate is mercuric chloride dithizonate

whose solubility in carbon tetrachloride is only 2×10^{-5}M (section 3.3.), whereas primary mercuric dithizonate, formed from the nitrate or perchlorate, has a solubility of 1×10^{-2}M. (section 3.5.).

When such strong solutions are used the reaction

$$HgCl_2 + H_2Dz \rightleftharpoons HgClHDz + HCl$$

is forced to the right by the nearly complete precipitation of mercuric chloride dithizonate. In these circumstances it is possible to study the reaction quantitatively. In three separate experiments one mole of mercuric chloride reacted with 1.05, 0.98 and 1.05 mole of dithizone. This result confirms the reaction and proves that the composition of the precipitate corresponds to the formula Hg.Cl.HDz.

3.1.4. Summary.

The discovery that chloride interfered in the substoichiometric determination of mercury in an unexpected way prompted an investigation into the nature of the complex formed when dithizone reacts with mercuric chloride. In the three previous sections it has been shown :-

(a) that this complex is neither primary nor secondary mercuric dithizonate.

(b) that the complex contains chlorine.

(c) that the complex has the composition Hg.Cl.HDz.

3.2. The reactions of mercuric chloride dithizonate.

3.2.1. The reaction between dithizone and mercuric chloride dithizonate.

If the experiment described in section 2.1.3. is repeated with less concentrated solutions of dithizone (1×10^{-5}M) no precipitate will be formed but, the organic layer still contains mercuric chloride dithizonate. This may be proven by adding a little dithizone. The organic layer containing mercuric chloride dithizonate (i.e., prepared from mercuric chloride) will react with the dithizone and destroy it. The organic layer containing no mercuric chloride dithizonate will not react with the dithizone which will impart a green colour to the solution.

Mercuric chloride dithizonate reacts with dithizone to form primary mercuric dithizonate :-

$$Hg.Cl.HDz + H_2Dz \rightleftharpoons Hg(HDz)_2 + H^+ + Cl^-$$

The reaction is rapid and quantitative. In five experiments it was found that 1 mole of mercuric chloride dithizonate reacted with 0.95, 0.93, 0.95, 0.92, 0.95 mole of dithizone respectively. This reaction explains why mercuric chloride dithizonate is not encountered when

determining traces of mercury by the spectrophotometric dithizone method. In this method an excess of dithizone is used and the chloride dithizonate is destroyed; in the substoichiometric method excess mercury is used and special precautions must be taken to prevent the interference of chloride (section 2.3.3.).

3.2.2. The reaction between hydroxyl ions and mercuric chloride dithizonate.

When solutions of mercuric chloride dithizonate in carbon tetrachloride are shaken with aqueous alkali, the chloride dithizonate is converted rapidly and completely to secon ary mercuric dithizonate:-

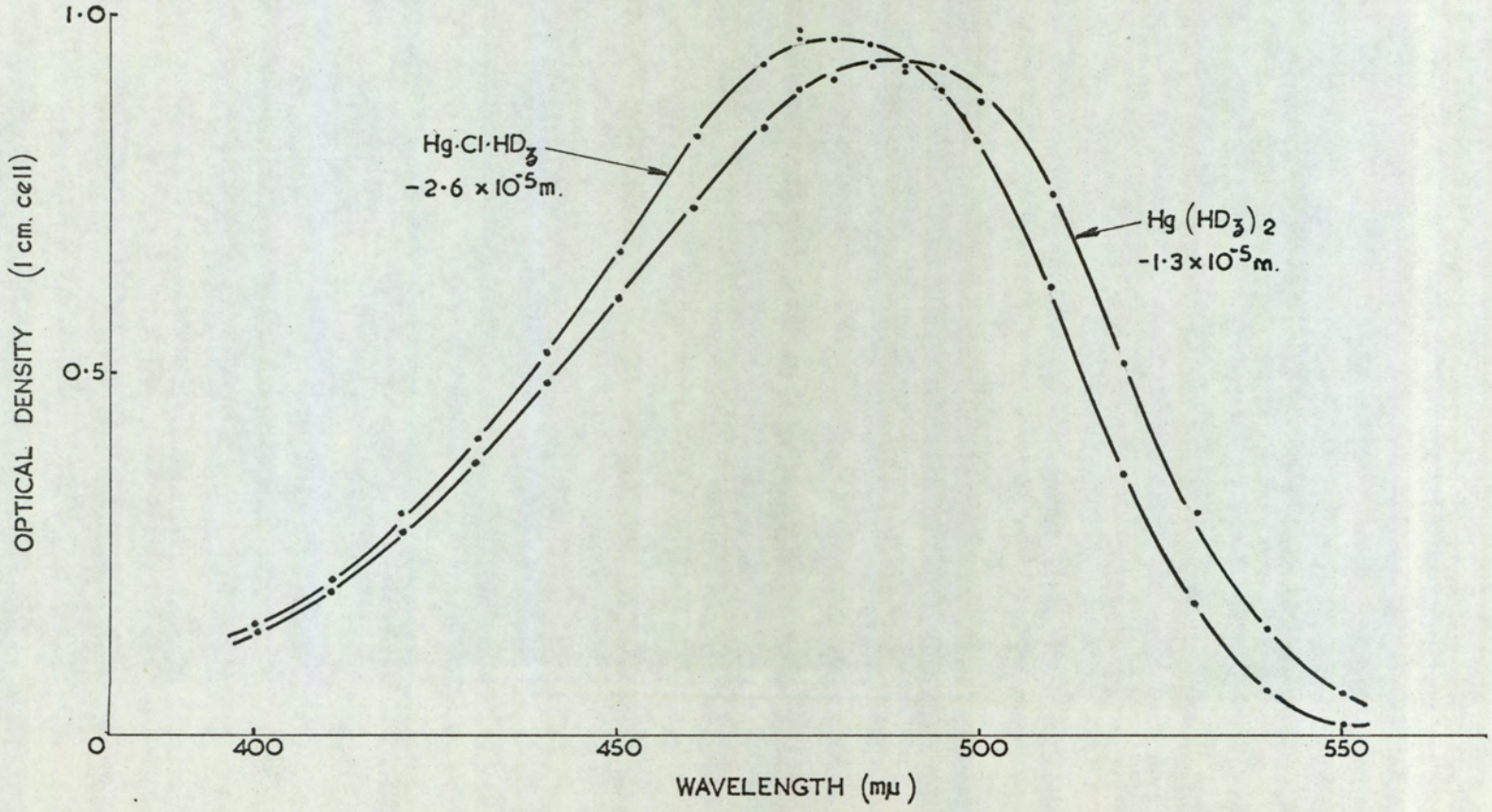
$$HgClHDz + OH^- \rightleftharpoons HgDz + H_2O + Cl^-$$

Even distilled water is sufficiently alkaline to accomplish this conversion. This is in complete contrast to the primary dithizonate which once formed reacts only slowly and incompletely with 1M sodium hydroxide. (I1, p.106).

3.2.3. The reaction of complexing agents in the aqueous phase with mercuric chloride dithizonate.

Mercuric chloride dithizonate can be reverted to dithizone in the same manner as primary mercuric dithizonate (I3) by using a reagent (e.g. Iodide or thiocyanate) which forms a very strong complex with mercuric ions. On the other hand, a reagent

FIG. 3/3


1·0
0·5
0
OPTICAL DENSITY (1 cm. cell)
Hg·Cl·HD3
-2·6 x 10⁻⁵m.
Hg (HD3)2
-1·3 x 10⁻⁵m.
400
450
500
550
WAVELENGTH (mμ)

can be selected (thiosulphate or ethylene-diamine-tetraacetate) which will decompose the chloride dithizonate but not the primary dithizonate. This is the basis of one method of overcoming chloride interference in substoichiometry (see chapter 4).

3.3. The properties of mercuric chloride dithizonate.

3.3.1. The spectrum of mercuric chloride dithizonate.

The spectrum of mercuric chloride dithizonate is compared with that of primary mercuric dithizonate in FIG.3/3. The extinction coefficient is 37,000 at the absorption maximum of 480 nm. The two spectra show an isobestic point at 490 nm.

3.3.2. The solubility of mercuric chloride dithizonate in carbon tetrachloride.

Two methods have been used to determine this solubility. In the first carbontetrachloride was saturated with solid mercuric chloride dithizonate and the absorbance of the resulting solution measured. In the second a strong solution of dithizone was shaken with a large excess of labelled mercuric chloride and the activity of the organic phase measured.

The solubility as determined radiochemically was 2.1×10^{-5}; spectrophotometrically 2.0×10^{-5}, both at 23°c.

3.3.3. The extraction constant of mercuric chloride dithizonate.

In section 3.1.1. it was suggested that the extraction constant is small for the reaction :-

$$HgCl_2 + H_2Dz \rightleftharpoons HgCl.HDz + H^+ + Cl^-.$$

This is wrong. An examination of FIG.3/2 shows that so long as there is excess dithizone in the organic phase all the added mercury forms primary mercuric dithizonate in the organic phase. Only when all the free dithizone has been consumed does mercury appear in the aqueous phase. The sloping curve is produced after all the dithizone has been converted to the primary dithizonate which is then converted to the chloride dithizonate in a further reaction. The small extraction constant is associated with this second reaction :-

$$HgCl_2 + Hg(HDz)_2 \rightleftharpoons 2\ HgClHDz.$$

for which

$$E_{HgClHDz} = [HgClHDz]^2_{org} \Big/ [HgCl_2][Hg(HDz)_2]_{org.}$$

This constant was measured by an experiment similar to that used to obtain the results presented in FIG. 3/2.

The activity (A_3, cps) extracted by a fixed amount of dithizone solution (concentration D g. mole/l) from an excess of a solution of labelled mercuric

perchlorate, which had a specific activity S cps/g.mole/l , was measured. This measurement was repeated with the addition of enough chloride to convert all the mercury to mercuric chloride. In this second case both the activity (A_2 cps) of the organic phase and the activity (A_1 cps) of aqueous phase were recorded.

now

$$2A_3 = SD = S[HgClHDz] + 2S[Hg(HDz)_2] \quad \text{-------3/2}$$

$$A_2 = S[HgClHDz] + S[Hg(HDz)_2] \quad \text{-------3/3}$$

$$A_1 = S[HgCl_2] \quad \text{-------3/4}$$

subtracting equation 3/3 from equation 3/2

$$2A_3 - A_2 = S[Hg(HDz)_2] \quad \text{-------3/5}$$

subtracting equation 3/5 from equation 3/3

$$2(A_2 - A_3) = S[HgClHDz] \quad \text{-------3/6}$$

substituting in equation 3/1 with the aid of equations 3/4, 5, and 6 gives

$$E_{HgHDz} = 4(A_2 - A_3)^2 \Big/ A_1(2A_3 - A_2) \quad \text{-------3/7}$$

so that neither the specific activity (S) nor the reagent concentration (D) need be measured.

The results of several experiments such as these are shown in TABLE 3/1. It can be seen that

the extraction constant is independent of concentration and acidity. The results have a mean value 0.83 and a standard deviation of 0.19. (N.B. In calculating the mean and standard deviation the two lowest results have been discarded because they are low due to the presence of adventitious chloride in the mercuric perchlorate solution).

At first sight these results may appear rather variable. These variations are mainly due to variations in A_2 and A_3 because A_1 is perfectly reproducible. The variation in A_3 is precisely the same as the variation in A_a in the absence of EDTA, discussed in chapter 1. (section 1.2.5.), whereas the variations in A_2 are the same as the variations in A_a in the presence of E.D.T.A., because if excess chloride is present variations in the amount of adventitious chloride can hardly affect the results (i.e., v(Cl) = 0.00%). Referring to TABLE 1.2/5A we find

$$v(A_3) = 2.28\%.$$

$$v(A_2) = 1.00\%.$$

Applying the general equation 1/5 to equation 3/7 gives

$$V(E) = V(A_2)\left(\frac{\partial E}{\partial A_2}\right)^2 + V(A_3)\left(\frac{\partial E}{\partial A_3}\right)^2$$

$$\frac{\partial E}{\partial A_2} = \frac{E}{A_2} \cdot \left(\frac{2R}{R-1} + \frac{R}{2-R}\right)$$

$$\frac{\partial E}{\partial A_3} = \frac{-E}{A_3} \cdot \left(\frac{2}{R-1} + \frac{2}{2-R}\right) \text{-------3/8}$$

where $R = A_2/A_3$

whence

$$v^2(E) = v^2(A_2) \cdot \left(\frac{2R}{R-1} + \frac{R}{2-R}\right)^2 + v^2(A_3)\left(\frac{2}{R-1} + \frac{2}{2-R}\right)^2$$

The mean value of R for TABLE 3/1 is 1.47 and the maximum and minimum values are 1.23 and 1.72 (neglecting the two very low values. TABLE 3/2 shows the calculated values of the standard deviation which are in satisfactory agreement with the experimental value (0.19).

3.3.4. The effect of adventitious chloride on the extraction constant.

The most serious difficulty in these experiments was due to the impossibility of preparing solutions and reagents entirely free from chloride. Chloride contamination causes low results for the stability constant because mercuric chloride dithizonate is formed even in the tests in which chloride should be absent. The activity A_3 is then too high. Several experiments suggest that chloride

contamination is occurring, but it is almost impossible to estimate the amount of this adventitious chloride.

(a) When chloride contamination is present, shaking the reagent with a slight excess of mercury gives an organic phase containing both primary mercuric dithizonate and mercuric chloride dithizonate. If measured at the isosbestic wavelength the absorbance of this solution is independent of the proportions in which the two components are present. An accurate measure of the reagent concentration can be obtained by constructing a calibration graph using standard mercury solutions and an excess of dithizone.

In TABLE 3/3 the molarities of some reagent solutions as measured by this method are compared with those obtained by measuring the activity A_3. The results by the spectrophotometric method are lower by about 10% as would be expected if at least 0.2 ppm. of chloride were present in the aqueous phase. Correcting the results of table 3/1 for this error would raise $E_{HgClHDz}$ to 1.3. Calculations showed that all the mercury in the aqueous phase without added chloride must be present as mercuric chloride and indeed TABLE 3/3 shows that the addition of further chloride did not raise the activity extracted.

(b) When the extraction constant was measured in 1.0M perchloric acid the results were low; zero with the smallest excess of mercury

(TABLE 3/4). When the experiment was repeated using 0.1M perchloric acid to measure A_3 the results were normal (TABLE 3/1). These results correspond to about 0.8 ppm of chloride, the additional chloride presumably coming from the additional perchloric acid.

(c) In TABLE 3/1 there are two results which are very much lower than the rest (0.21, 0.24). In these two experiments an exceptionally small excess of mercuric chloride was used. These results could be explained if as little as 0.02 ppm of chloride were present. This amount of chloride would have a very much smaller effect at higher mercuric chloride concentrations. This can be appreciated if equation 3/8 is used to predict the error in the stability constant caused by a 1% increase in A_3.

(1) for the average excess of mercury used,

$R = 1.47$

$$\Delta E = - E_o \left(\frac{2}{R - 1} + \frac{2}{2 - R} \right) \frac{A_3}{A_3}$$

$$= - 0.83 \left(\frac{2}{0.47} + \frac{2}{0.53} \right) 0.01.$$

$$= \underline{- 0.066.}$$

(2) For the two results which are low

$R = 1.08.$

$$\Delta E = - 0.83 \left(\frac{2}{0.08} + \frac{2}{0.92} \right) 0.01$$

$$= \underline{- 0.23.}$$

The experimental results can be used to correct the error in the value of the average result.

$$0.83 + 6.6 \times \frac{\Delta A_3}{A_3} = 0.23 + 23 \times \frac{\Delta A_3}{A_3}.$$

$$\frac{\Delta A_3}{A_3} = 0.60/16 = 0.037$$

$$\therefore \quad E_{HgClHDz} = 0.83 + 6.6 \times 0.037$$

$$= \underline{1.08}$$

(d) Yet other estimates of chloride contamination will be given in the next section. These range from 0.27 ppm to 0.98 ppm confirming the estimates made above.

None of these estimates is accurate and it is only possible to conclude that $E_{HgClHDz} \backsimeq 1$.

3.3.5. Other errors in the extraction constant.

(a) The formation of secondary mercuric dithizonate would seriously interfere with the determination of the extraction constant because of the very unstable nature of this substance. Calculations based on Breants value of the extraction constant of secondary mercuric dithizonate suggests that this complex should seriously interfere in 0.1M acid. This did not happen although the spectra of the organic phase

revealed some secondary dithizonate in the organic phase from the tests containing no chloride at pH2. This error was eliminated by adding 0.1M $HClO_4$ to this aqueous phase. When this precaution had been taken no further difficulty of this nature was encountered.

(b) The formation of mercuric nitrate dithizonate at high nitric acid concentrations would also result in an erroneous value of the extraction constant. This has been avoided by using only perchloric acid in these experiments. High concentrations of perchlorate do not increase the activity extracted so that mercuric perchlorate dithizonate is not formed.

(c) Another error occurs because mercuric chloride is slightly soluble in the organic phase - carbon tetrachloride. The partition coefficient :-

$$P_{HgCl_2} = [HgCl_2]\ (CCl_4) \Big/ [Hg(Cl_2]\ (H_2O) = 0.001$$

has been determined. The observed value (1×10^{-3}, mean of 24 results with a standard deviation of 0.4×10^{-3}) is too low to affect the results recorded in TABLE 3/1.

3.3.6. The determination of the extraction constant with chlorine - 36.

In section 3.1.2. it has been demonstrated that chlorocomplexes were formed in the organic phase but the experiments used were not sufficiently accurate to show that the amount of chloride extracted was that to be expected if mercuric chloride dithizonate with an extraction constant of 0.83, was formed. Further experiments were carried out in which the organic phase containing the chlorine - 36 was treated with dilute alkali and the alkaline aqueous phase counted by liquid scintillation spectrometry. This procedure converted mercuric chloride dithizonate in carbon tetrachloride, which would quench the scintillator, to sodium chloride in water, which does not and also avoids the loss of hydrogen chloride mentioned in section 3.1.2.

When chlorine - 36 is used to measure the extraction constant it is necessary to determine the amount of inactive chloride in the aqueous phase originating from the reagent. This blank was measured by varying the amount of active chloride added and measuring the change in activity of the chloride extracted.

If x μg of active chloride of specific activity S cps/μg are added to a test containing

y µg of inactive chloride and z µg are extracted into the organic phase which then has an activity of A cps.

$$A = z.S.\ x/(y + x) \qquad \text{-------3/9}$$

A, S and x are known or can be measured. y and z are to be determined.

A series of tests were conducted in which x was varied and A measured. A graph was plotted of 1/A versus 1/x. This is a straight line of intercept 1/zS. From this intercept z was calculated and from z the extraction constant $E_{Hg.Cl.HDz}$. The slope of this graph is y/zS and unfortunately y varied considerably from one extraction to the next. Because of this variation the points on the graph were widely scattered and the estimates of $E_{HgClHDz}$ very unreliable.

To illustrate this point more clearly and also to obtain an estimate of the amount of chloride contamination for section 3.3.4, the value of y for some of the extractions has been calculated by another procedure. If it is assumed that y is the same for two tests with x_1 and x_2 µg of active chloride and A_1 and A_2 cps in the organic phase, z and S may be eliminated from equation 3/9.

$$y = (A_2 - A_1) \ / \left(\frac{A_1}{x_1} - \frac{A_2}{x_2} \right)$$

The results of these experiments are given in TABLE 3/5. In calculating y; x and A from one extraction was combined successively with the results from the remaining extractions in the experiment (i.e., 3 extractions were carried out in experiment A and B, and 4 in experiment C). These results confirm those obtained with mercury - 203 and support the hypothesis that mercuric chloride dithizonate is present in the organic phase.

3.3.7. The partition coefficient of primary mercuric dithizonate and mercuric chloride dithizonate.

The partition coefficients of primary mercuric dithizonate ($P_{Hg(HDz)_2}$) and mercuric chloride dithizonate ($P_{Hg.Cl.HD_3}$) have been measured by Sandells method (S1). In this method a strong solution of the dithizonate dissolved in the organic solvent is equilibriated with the aqueous phase, the two phases are separated and the aqueous phase is extracted with pure organic solvent. The partition coefficient is calculated from measurements of the absorbancies of the two organic phases.

Let V_o = the volume of the second organic phase.

V_a = the volume of the aqueous phase used for the extraction.

C_{1O}= the concentration of the dithizonate in the first organic phase.

C_{2O}= the concentration of the dithizonate in the second organic phase.

C_{1A}= the concentration of the dithizonate in the first aqueous phase.

C_{2A}= the concentration of the dithizonate in the second aqueous phase.

A_{1O}= the absorbance of the first organic phase.

A_{2O}= the absorbance of the second organic phase.

P = the partition coefficient of the dithizonate.

$$P = \frac{C_{1O}}{C_{1A}} = \frac{C_{2O}}{C_{2A}}$$

$$C_{2O} \cdot V_o + C_{2A} V_a = C_{1A} \cdot V_a \cdot$$

dividing by C_{2A} gives

$$P \cdot V_o + V_a = \frac{C_{1A}}{C_{2A}} \cdot V_a \cdot$$

but $$\frac{C_{1A}}{C_{2A}} = \frac{C_{1O}}{C_{2O}} = \frac{A_{1O}}{A_{2O}}$$

$$P = \frac{V_a}{V_o} \left(\frac{A_{1O}}{A_{2O}} - 1 \right)$$

The results are given in TABLE 3/6; those for the chloride dithizonate are consistent and reliable but those for the primary dithizonate are low because the amount of dithizonate dissolved in the aqueous phase was very much less than the amount present in suspended droplets of the organic phase which had not been removed by filtration. There is a considerable amount of evidence to support this suggestion.

(a) The results for the primary dithizonate are inversely proportional to the rate of filtration (TABLE 3/6) because the finer, thicker, and slower papers retain the organic phase more completely and give higher results.

(b) The variation in the results is greater when the aqueous phases are filtered through several different papers than when all are filtered through one paper, because the time of filtration for one grade of paper varies from one paper to another. (TABLE 3/7).

(c) This relationship to the rate of filtration is not a coincidence due to a concommitant change in the efficiency of equilibration or reagent concentration. When one aqueous phase is divided into two, and each half filtered through a different grade of filter paper, different results are still obtained. (TABLE 3/8).

(d) The results for mercuric chloride dithizonate are independent of the speed of filtration. The smaller partition coefficient of mercuric chloride dithizonate results in a larger concentration of dithizonate in the aqueous phase, the amount of dissolved dithizonate being in this case much greater than the amount present as suspended organic phase, i.e., the reverse of the case with the primary dithizonate. (TABLE 3/6).

(e) If the organic phase is saturated with mercuric chloride dithizonate and contains a large amount of suspended solid, the droplets of

organic phase will contain proportionately more chloride dithizonate than in the previous case and a low result will be obtained. This result can be estimated by using the efficiency of filtration measured with the primary dithizonate.

$$P'_{HgClHDz} = \frac{P_{HgClHDz} \times P'_{Hg(HDz)_2}}{P'_{Hg(HDz)_2} + \frac{C_{TOT}}{C_{SOL}} \cdot P_{HgClHDz}.}$$

Where C_{TOT} is the total concentration of mercuric chloride dithizonate including suspended solid and C_{SOL} is the concentration of the saturated solution - both in the organic phase $P'_{HgClHDz}$ is the result for mercuric chloride dithizonate when the organic phase contains suspended solid and $P'_{Hg(HDz)_2}$ is the result with primary mercuric dithizonate with the same grade of filter paper as used in experiment with the chloride dithizonate.

TABLE 3/9 illustrates the good agreement obtained by these calculations.

Despite this evidence there are other possible explanations involving adsorption It is possible that all the results with primary mercuric dithizonate are high because most of the dithizonate originally present in the aqueous phase has been removed by adsorption on to the filter paper, the thicker, slower papers adsorbing more

dithizonate than the thinner faster ones. If this was the true explanation, then successive filtrates from the same aqueous phase through the same filter should contain increasing amounts of dithizonate because a filter paper which has already adsorbed some mercuric dithizonate from the first filtrate will adsorb less from the second. This does not happen with primary mercuric dithizonate with any grade of paper, but with mercuric chloride dithizonate it does happen with the thickest and slowest of them (TABLE 3/10). This is the reverse of what was expected because if mercuric chloride dithizonate is adsorbed more strongly than primary mercuric dithizonate the results for this substance should also vary with the grade of filter paper. It is still possible that the adsorption process is very slow and that the thicker slower papers having a longer time in contact with the solution, adsorb more dithizonate from it giving higher results. If this were true it is also possible that the adsorption sites were not appreciably taken up by the first and second filtrates so that no change in the results having been observed it would have been concluded that no adsorption had taken place. It still seems unlikely, however, that the most

strongly adsorbed substance, - the primary dithizonate, shows no evidence of adsorption, whereas the least strongly adsorbed does show such evidence. Also adsorption cannot explain the good agreement with experiment obtained when solid mercuric chloride dithizonate was suspended in the organic phase. It must not be concluded from this discussion that the primary dithizonate is not adsorbed, only that any such adsorption is completely obscured by the effects of incomplete filtration.

From these results it has been concluded that

$$P_{HgClHDz} = \frac{[HgClHDz]\,(CCl_4)}{[HgClHDz]\,(H_2O)} = 1.4 \times 10^4$$

and

$$P_{Hg(HDz)_2} = \frac{[Hg(HDz)_2]\,(CCl_4)}{[Hg(HDz)_2]\,(H_2O)} > 10^6$$

This last constant has also been determined by Duncan (D4) who obtained the value 3.4×10^3. Duncan separated the two phases with a centrifuge. A centrifuge has been used in this work also but did not give complete separation of the phases. Repeated centrifuging of the aqueous phase gave higher and higher results viz., once 1.7×10^4, twice 4.7×10^4, thrice 1.0×10^5.

3.3.8. The extraction constant of primary mercuric dithizonate.

In order to calculate the stability constant of mercuric chloride dithizonate an accurate value for the extraction constant of primary mercuric dithizonate is required. Many authors (D4, B1, K3, P1), have reported values of this constant, but the results have been calculated in different ways using different values of the stability products of the mercuric halides. These values have been recalculated (TABLE 3/11) by substituting the experimental results obtained by these authors into the equation :-

$$E_{Hg(HDz)_2} = \frac{[Hg(HDz)_2]_{org} \cdot [H^+]^2 \left\{1 + \sum_{n=1}^{n=4} \beta_n [X]^n\right\}}{[H_2Dz]^2_{org} \cdot C_{Hg}}$$

where C_{Hg} = the total concentration of all forms of mercury in the aqueous phase

$$= [Hg^{2+}] + [HgX^+] + [HgX_2] + [HgX_3^-] + [HgX_4^{2-}]$$

X = Cl or Br^- or I^-

$$\beta_n = [HgX_n] \Big/ [Hg^{2+}] [X]^n$$

The values of β_n used in these calculations were those of Marcus (M1). The values of $E_{Hg(HDz)_2}$ obtained by Pilipenko(P1) have also been corrected for the partial ionisation of sulphuric acid (Y2).

The results Pilipenko obtained using chloride are low due to a severe ionic strength effect from the high concentration of sulphuric acid (3M). These results have not been included in the calculations for the best value of $E_{Hg(HDz)_2}$. The mean of all the other values is $10^{26.66}$.

3.3.9. The stability constant of mercuric chloride dithizonate.

The stability constant of mercuric chloride dithizonate is given by :-

$$K_{Hg.Cl.HDz} = [HgClHDz] \Big/ [Hg^{2+}]\,[Cl^-]\,[HDz^-]$$

corresponding to the reaction

$$Hg^{2+} + Cl^- + HD_z^- \rightleftharpoons HgClHDz$$

where the reactants and products are in the aqueous phase.

This can be calculated from the equation

$$K^2_{HgClHDz} = \frac{E_{HgClHDz} \cdot \beta_{2(Cl)} \cdot E_{Hg(HDz)_2}}{P^2_{HgClHDz} \cdot E^2_{H_2Dz}}$$

$E_{HgClHDz} = 0.83$

$\beta_{2\ (Cl)} = 10^{13.22}$ (see M1)

$E_{Hg(HDz)_2} = 10^{26.66}$

$P_{HgClHDz} = 1.4 \times 10^4$

$$E_{H_2Dz} = \frac{[H^+][HDz^-]}{[H_2Dz]_{org}} = 1.6 \times 10^{-9} \qquad (I\ 2)$$

These values give

$$K_{HgClHDz} = 10^{24.55}$$

3.4. The importance of mercuric chloride dithizonate.

3.4.1. Ternary complexes in substoichiometric analysis.

In section 1.1.3. it has been shown that the important advantages of substoichiometric analysis are the improved selectivity and sensitivity. When ternary complexes, such as mercuric chloride dithizonate, are formed the selectivity is always reduced, the sensitivity may be reduced if it depends upon the completeness with which the metal complex is formed. This is not the case with mercury but may be so with other metals. This is true whatever method is used to overcome the interference of the ternary anion (chloride in this case) because the additional metal complexes formed in the aqueous phase (mercuric chloride, or mercuric ethylene-diamine-tetraacetate), necessarily raise the alpha coefficient and so lower the conditional extraction constant.

An example will illustrate this. In chapter 2 (section 2.3.3.) it was shown that to overcome chloride interference in the automatic method, 3.7×10^{-5} M chloride must be added to the aqueous phase. Consider the interference of copper. It is desired that very little copper shall be extracted, say :-

$$[Cu(HDz)_2] = 10^{-3}[Hg(HDz)_2]$$

For this to be true in the absence of chloride

$$E_{Cu/Hg} = \frac{10^{20.96}}{10^{53.32}} = 10^{-32.36}$$

by equation 1/53, but by equation 1/52

$$\frac{[Cu^{2+}]}{[Hg^{2+}]} = 10^{-3} \cdot 10^{6.18} = 10^{13.18}$$

when chloride is added to the extent of 3.7×10^{-5}M

$\log \alpha_{Hg(Cl)} = 3.58$

and by TABLE 2/3 $\alpha_{Cu(Cl)} = 10^{0.6} \times 10^{-4.57} + 1 = 1$

so that by equation 1/63

$$E'_{Cu/Hg} = 10^{-32.36} \times \frac{10^{7.16}}{10^{0}} = 10^{-25.20}$$

$$\therefore \frac{[Cu^{2+}]}{[Hg^{2+}]} = 10^{9.60}$$

thus the addition of chloride has lowered the amount of copper that can be tolerated by a factor of over a thousand. At a fixed pH; if the sensitivity is limited by equation 1/7 very similar considerations would apply. In the case of mercury however other factors limit the sensitivity (sections 1.3.8. and 2.4.3.).

This is no isolated case. There is evidence for other similar complexes; mercuric nitrate dithizonate, mercuric bisulphate dithizonate,

mercuric bromide dithizonate (section 2.3.4.), mercuric chloride diethyldithio-carbamate (section 2.3.3.), gold chloride dithizonate, gold chloride diethyldithiocarbamate (B3) and palladium chloride diethyldithiocarbamate (B4); No doubt many others exist. Compounds such as these present difficulties to the analyst, and if it is intended to estimate a metal by substoichiometric solvent extraction, a check should be carried out to ensure that the addition of common anions do not increase the amount of metal extracted.

3.4.2. The possibility of determining chloride radiochemically.

The properties of mercuric chloride dithizonate, as described in this chapter, suggest the possibility of determining chloride by substoichiometric neutron activation analysis. The method would be sensitive and specific but other halides would interfere.

The method would consist of adding 10 ml of a 10^{-2}M solution of mercuric chloride to solutions of the irradiated samples and standards and extracting these mixtures with 10 ml of 5×10^{-6}M primary mercuric dithizonate dissolved in carbon tetrachloride. The activities of the organic phases would be proportional to the amount of chloride in the samples or standards. The isotope of chlorine would be Cl - 38, a γ -ray emitter with a half life of 37 min, so that precautions against the short half life are necessary. Because a large excess of mercuric chloride has been used in

the aqueous phase 99.5% of the reagent will have been consumed but only a small proportion of the activity in the sample will be extracted. In spite of this, the sensitivity is adequate (2 µg Cl if a neutron flux of 10^{12} n/sec/cm^2 is used). This sensitivity can be increased by reducing the amount of mercuric chloride added but if this is done variations in temperature, the volume of the squeous phase, etc., could cause variations in the amount of chlorine extracted because the reagent would be incompletely consumed.

3.5. Experimental.

3.5.1. Apparatus and reagents.

The reagents were prepared from analytical reagent grade chemicals.

Mercuric perchlorate solutions. Prepared by dissolving mercuric oxide in perchloric acid. These were standardised by titration with E.D.T.A. using a urotropine buffer (pH 4) and xylenol orange indicator.

Dithizone and zinc dithizonate. see section 2.5.1.

When dithizone was required the zinc dithizonate solution was shaken with 0.1M perchloric acid and the organic layer filtered through a dry No.41 Whatman paper.

Mercuric dithizonate. A solution of 0.5g of dithizone in 50 ml of 0.1M sodium hydroxide was added dropwise to a solution of 0.3g of mercuric oxide dissolved in 100 ml of 1M perchloric acid. The precipitate was filtered and dried in a vacuum desiccator.

This product is the monohydrate $Hg(HDz)_2.H_2O$, having a solubility in carbon tetrachloride of 2×10^{-3}M. Refluxing the monohydrate with carbon tetrachloride in a Dean and Stark apparatus gave the anhydrous salt $Hg(HDz)_2$, having a

solubility in carbon tetrachloride of 1×10^{-2}M. Analysis of the monohydrate by the Dean & Stark method gave 0.19% H_2O; theoretical value for $Hg(HDz)_2 . H_2O$ is 0.25%.

Radioisotopes. (see section 2.5.1.)

Nucleonic equipment. The scintillation counter used for the measurement of mercury -203 activity was a 3 x 3 in. NaI(Tl) well type crystal associated with a single channel gamma ray spectrometer. In all experiments a setting of the discriminator voltage corresponding to 50 kev. was used.

The chlorine -36 activity was measured either by the evaporation on to planchets and counting with an end window Geiger-Müller detector (window thickness 2 mg/cm^2 or by a liquid scintillation spectrometer using NE220 scintillator.

Spectrophotometer. The spectra and absorbancies were measured with a Unicorn S.P.600 Spectrophotometer.

3.5.2. The reaction between mercuric chloride and dithizone.

A solution of dithizone in carbon tetrachloride (ca 2 x 10^{-3}M) was standardised by taking 8.00 ml of a 2.5 x 10^{-3}M solution of mercuric perchlorate in 0.1M perchloric acid and titrating it with the dithizone solution. The end point was determined spectrophotometrically. Accurate results can only be obtained when the organic phase used for spectrophotometry is returned to the separating funnel in which the reaction is conducted. This is due to the formation of mercuric chloridedithizonate in the initial stages of the titration owing to contamination by traces of chloride. During the titration this substance is destroyed and at the end point primary mercuric dithizonate alone is present.(see section 3.2.1.).

An excess of mercuric perchlorate solution (15 ml of 2.5 x 10^{-3}M) and potassium chloride solution (1 ml of 2 x 10^{-1}M) were shaken for 15 min. with 9.0 ml of the standardized dithizone solution. This causes the complete precipitation of mercuric chloride dithizonate. The organic phase was discarded and the aqueous phase centrifuged to remove the precipitate. The amount of mercury remaining in the aqueous phase was determined by a spectrophotometric titration exactly as in the standardisation of the dithizone solution.

3.5.3. The reaction between dithizone and mercuric chloride dithizonate.

A solution of mercuric chloride dithizonate was prepared by shaking a 2×10^{-5}M solution of dithizone in carbon tetrachloride with an excess of a 5×10^{-2}M mercuric chloride solution. This solution was washed with 0.1M perchloric acid and filtered through a dry No. 41 Whatman paper to remove any mercuric chloride present as droplets of the aqueous phase. A measured excess of the dithizone solution (2×10^{-5}M) was added to the purified solution and the excess remaining estimated from the absorbance at 620 nm.

3.5.4. The reversion of mercuric chloride dithizonate to dithizone.

A purified mercuric chloride dithizonate solution was prepared as in the previous experiment. This was shaken with 5 ml of 0.1M perchloric acid in which 1 g of either sodium iodide or sodium thiocyanate was dissolved. The dithizone liberated was estimated from the absorbance at 620 n.m. When iodide was used 92% of the dithizone was reovered; with thiocyanate 98%.

3.5.5. The suppression of chloride interference by a third ligand.

Five ml of a mercuric perchlorate solution (1.00×10^{-4}M) dissolved in any one of :- (a) 0.1M perchloric acid (b) 0.25M sodium ethylenediamine tetraacetate (c) 1.00×10^{-2}M sodium thiosulphate in 1.0M ammonium acetate or (d) 0.5M sodium acetate in 0.5M acetic acid, were added to 20 ml of labelled sodium chloride solution (2.75×10^{-4}M). The mixture was extracted with 25 ml of a 3.1×10^{-5}M solution of primary mercuric dithizonate in carbon tetrachloride. The organic phase was filtered through a dry No. 41 Whatman paper, and 20 ml shaken with 5 ml of 0.01M borax solution. Any mercuric chloride dithizonate was converted to sodium chloride which does not quench the liquid scintillator used to measure the activity of 2 ml of the aqueous phase.

3.5.6. The extraction constant of mercuric chloride dithizonate - mercury - 203.

Excess chloride was added to labelled mercuric perchlorate solution to give 1×10^{-4}M solutions of mercuric perchlorate and mercuric chloride having the same specific activities. From 1.0 to 25.0 ml of the mercury solution was diluted to 25.0 ml with perchloric acid solutions to make a final acidity of 0.01M, 0.10M or 1.00M. Each of these solutions was shaken for 15 min. with 10 ml of a 1×10^{-5}M solution of zinc dithizonate in carbon tetrachloride. The organic phase was filtered through a dry No. 41 Whatman filter paper and the activity of a 5 ml aliquot measured.

3.5.7. The partition coefficient of mercuric chloride at 25°c.

The organic phase produced by shaking 10 ml of a 1.35×10^{-3}M mercuric chloride solution (labelled with mercury - 203) with 200 ml of carbon tetrachloride was filtered through a No. 41 Whatman paper which had been impregnated with carbon tetrachloride by soaking the paper successively with mixtures of alcohol and carbon tetrachloride containing 10%, 20% etc., to 100% of carbon tetrachloride. These impregnated papers were used to prevent the extraction of mercuric chloride

by water absorbed by normal "dry" papers. A measured volume (V_o) of the filtered organic phase was shaken with 10 ml (V_A) of water and the activities of 5 ml aliquots of the first (A_1) and last(A_2) aqueous phase measured. The partition coefficient (P) was calculated from

$$\frac{1}{P} = \frac{V_o}{V_A}\left(\frac{A_1}{A_2} - 1\right)$$

3.5.8. The extraction constant of mercuric chloride dithizonate - chlorine -36.

Ten ml of 0.1M perchloric acid and 1.0 ml of 1 x 10^{-4}M mercuric perchlorate solution were mixed with 1, 2 or 5 ml of 1.31 x 10^{-4}M labelled chloride solution and diluted to 16 ml. The mixture was shaken for 15 min. with 10 ml of 8 x 10^{-5}M mercuric dithizonate solution. The organic phase was filtered and 5 ml shaken with 5 ml of 0.01M borax solution. 2 ml of the filtered borax solution were mixed with 10 ml of N.E.220 scintillator and the activity measured with a liquid scintillation spectrometer.

3.5.9. The partition coefficients of mercuric chloride dithizonate and primary mercuric dithizonate.

A large volume (1.8 litre) of a solution, 0.1M in perchloric acid, 0.4M in sodium perchlorate and 0.1M in mercuric chloride was shaken for 10 min. at 23°c with 10 ml of a 2×10^{-5}M primary mercuric dithizonate solution in carbon tetrachloride. This first organic phase was filtered and its absorbance measured at 480 n.m. The aqueous phase was filtered and extracted with 5 ml of pure carbon tetrachloride. This second organic phase was also filtered and the absorbance measured at 480 nm.

The above experiment gave the partition coefficient of mercuric chloride dithizonate. For the primary dithizonate, 2×10^{-3}M primary mercuric dithizonate was substituted for the first organic phase and the mercuric chloride was omitted from the aqueous phase.

3.5.10. The measurement of the reagent concentration by the Isosbestic method.

Three absorbancies were measured at the isosbestic wavelength 490 nm in 1 cm. cells. The reagent 5 ml of 1×10^{-5}M zinc dithizonate solution in carbon tetrachloride, was shaken 5 mins with (a) 15 ml of 0.1M perchloric acid (absorbance A_1) (b) 10 ml of 0.1 M perchloric acid and 5 ml of 1.0×10^{-5}M mercuric perchlorate in 0.1M perchloric acid (absorbance A_2) (c) 15 ml of 1.0×10^{-5}M mercuric perchlorate in 0.1M perchloric acid (absorbance A_3). The phases were separated, the organic phases filtered through dry filter papers and their absorbancies measured.

$$\text{M reag.} = 1 \times 10^{-5} \; (A_3 - A_1) \,/\, (A_2 - A_1).$$

TABLE 3/1. The extraction constant of mercuric chloride dithizonate at 23°c.

Acidity of the aqueous phase $[H^+]$ Molar	Reagent concentration in the organic phase $[H_2Dz]$ Molar = D.	Equilibrium concentration of mercuric chloride in the aqueous phase $[HgCl_2]$ Molar	Activity of the aqueous phase A_1 c/s.	Activity of the organic phase containing chloride A_2 c/s.	Activity of the organic phase not containing chloride A_3 c/s	Extraction constant
			Corrected for background activity = 10 c/s.			
1.0	2.56×10^{-4}	4.1×10^{-5}	89.7	344.1	280.0	0.82
1.0	2.80×10^{-5}	1.7×10^{-6}	47.6	421.6	392.1	0.21
1.0	2.80×10^{-5}	1.2×10^{-5}	331.2	521.0	392.1	0.74
1.0	2.80×10^{-5}	3.1×10^{-5}	874.6	588.7	392.1	0.88
1.0	2.80×10^{-5}	8.9×10^{-5}	2476.0	640.8	392.1	0.63
0.1	2.52×10^{-5}	3.6×10^{-5}	648.4	350.0	224.0	1.00
0.1	2.54×10^{-5}	4.8×10^{-6}	91.4	295.2	239.3	0.75
0.1	2.54×10^{-5}	1.6×10^{-5}	307.6	342.3	239.3	1.03
0.1	2.54×10^{-5}	3.6×10^{-5}	676.5	378.5	239.3	1.16
0.1	2.54×10^{-5}	9.5×10^{-5}	1798.1	412.8	239.3	1.01
0.01	2.68×10^{-5}	2.0×10^{-6}	52.8	393.7	362.5	0.24
0.01	2.68×10^{-5}	1.3×10^{-5}	348.3	472.2	362.5	0.55
0.01	2.68×10^{-5}	3.1×10^{-5}	844.9	527.5	362.5	0.68
0.01	2.68×10^{-5}	9.0×10^{-5}	2397.0	595.7	362.5	0.70

TABLE 3/2. Expected magnitude of the standard deviation of the results for the extraction constant of mercuric chloride dithizonate.

$R = A_2/A_3$	Calculated standard deviation.
1.23	0.16
1.47	0.12
1.72	0.14

TABLE 3/3. Comparison of reagent concentration determined radiochemically and spectrochemically.

Reagent solution	Molarity of reagent as determined		
	Spectrophotometrically	Radiochemically with no added chloride	Radiochemically with 0.5 ppm added chloride
1.	1.21×10^{-5}	1.38×10^{-5}	
	1.18×10^{-5}	1.36×10^{-5}	
2.	1.17×10^{-5}	1.31×10^{-5}	1.31×10^{-5}
	1.17×10^{-5}	1.28×10^{-5}	
3.	1.31×10^{-5}	1.31×10^{-5}	1.31×10^{-5}
	1.20×10^{-5}	1.31×10^{-5}	

TABLE 3/4. Effect of chloride contamination on the results in 1.0M perchloric acid.

Mercuric chloride concentration in the aqueous phase.	Results for $E_{HgClHDz}$ in 0.1M $HClO_4$.	Results for $E_{HgClHDz}$ in 1.0M $HClO_4$	Result for $E_{HgClHDz}$ in 1.0M $HClO_4$. (0.1M $HClO_4$ in tests with no chloride).
3×10^{-6}M	0.75	0.00	0.21
1×10^{-5}M	1.03	0.16	0.74
3×10^{-5}M	1.16	0.22	0.88
9×10^{-5}M	1.01	0.36	0.63

TABLE 3/5. The extraction constant mercuric chloride dithizonate ^{36}Cl method.

Experiment	Inactive chloride		$E_{HgClHDz}$
	µg	p.p.m.	
A	4.2	0.35	2.0
	6.9	0.46	
B	11.8	0.98	0.8
	7.4	0.49	
C	9.7	0.49	0.2
	8.3	0.41	
	5.3	0.27	

TABLE 3/6. The partition coefficients of primary mercuric dithizonate and mercuric chloride dithizonate.

Grade of filter	rate of filtration	$P_{HgClHDz.}$	$P_{Hg(HDz)_2.}$
No. 41	53 ml/min	1.3×10^4	6.0×10^4
No. 1	10 ml/min	-	1.05×10^5
No.542	7 ml/min	-	1.26×10^5
No. 42	5.5 ml/min	1.4×10^4	2.4×10^5
Thick pad	0.43ml/min	2.1×10^4	1.2×10^6

TABLE 3/7. Comparison of variation between filter papers with that within one grade of filter.

Grade of filter	Conditions	Results. (all with $Hg(HDz)_2$)
No.41 papers	(a) many different papers used.	Standard deviation of $\log_{10}P$ = 0.25.
	(b) Same filter paper used throughout.	Standard deviation of $\log_{10}P$ = 0.032.
No.542 papers	(a) First paper, rate = 7.5 ml/min.	P = 65,000
	(b) Second paper, rate = 1.3 ml/min.	P = 250,000

TABLE 3/8.

Equilibrium	$P_{Hg(HDz)_2}$ with No.41 papers.	$P_{Hg(HDz)_2}$ with No.42 papers.
A	155,000	196,000
B	84,000	250,000
C	110,000	255,000
D	100,000	200,000

TABLE 3/9 The error in $P_{HgClHDz}$ caused by incomplete filtration when solid dithizonate is present.

Type of paper	Experimental value of $P_{HgClHDz}$	Experimental value of $P_{Hg(HDz)_2}$	Calculated * value of $P_{HgClHDz}$ ($P_{HgClHDz} = 1.6 \times 10^4$)
No. 41	4,400	60,000	4,400
No. 42	12,000	240,000	10,000
Thick pad	30,000 ‡	1,200,000	14,000

‡ adsorbtion see table 3/10 if corrected for this adsorbtion 19,000 is obtained.

* $C_{TOT}/C_{SOL} = 10$

TABLE 3/10. Test for adsorption.

Filtrate	Grade of Filter					
	No. 41 paper		No. 42 paper		thick pad	
	HgClHDz	$Hg(HDz)_2$	HgClHDz	$Hg(HDz)_2$	HgClHDz	$Hg(HDz)_2$
1st	13,000	29,000	14,000	67,000	29,000	1,200,000
2nd	12,000	27,000	14,000	60,000	22,000	1,000,000
3rd	11,000	27,000	14,000	62,000	19,000	1,100,000
4th	12,000	28,000		67,000		1,000,000
5th	12,000	27,000				
6th		27,000				

C H A P T E R F O U R.

THE CHLORIDE ETHYLENE-DIAMINE-TETRA-ACETATE COMPLEXES OF MERCURY.

Summary.

Methods for overcoming the interference of chloride in automatic analysis are given in Chapter two. A method for overcoming the interference of chloride in manual analysis, based upon the addition of E.D.T.A., is described in this chapter. An account is also given of the discovery, whilst studying this E.D.T.A. method, of the mercuric chloride E.D.T.A. complexes and of the measurement of their stability constants.

4.1. Introduction.

In chapter two the interference of chloride in the continuous substoichiometric determination of mercury was described; in overcoming this interference an empirical approach was used. It was suggested in chapter two that adding Ethylene-diamine-tetraacetate to the aqueous phase might prevent this chloride interference in the manual substoichiometric method. This ligand forms a complex with mercury, strong enough to prevent the formation of mercuric chloride dithizonate, which causes the interference, but not so strong that it prevents the formation of primary mercuric dithizonate upon which the analysis depends. This method is unsatisfactory for the continuous method. The reaction of mercuric ethylenediamine-tetraacetate with dithizone is so slow that it did not occur during the time allowed by the autoanalyser (in TABLE 2/2 E.D.T.A. is listed as an interference). However the reaction is virtually complete when 10^{-5}M solutions are shaken for 30 min, as can be done in the manual method.

In this chapter the investigation of this method of overcoming chloride interference will be described. It has been found that the complexes of mercury formed in the presence of E.D.T.A. and

chloride are stronger than either mercuric chloride or mercuric ethylenediaminetetraacetate. These complexes are mercuric chloride ethylenediamine-tetraacetate's analogous to mercuric hydroxy ethylenediaminetetraacetate and mercuric ammine ethylenediaminetetraacetate (R3) and palladium chloride ethylenediaminetetraacetate (B7). These complexes have not been isolated but their stability constants have been estimated.

4.2. The theoretical selection of ligands suitable for overcoming chloride interference.

4.2.1. The conditions which must be fulfilled by the ligand.

In order to use the substoichiometric equation (1/2), the whole of the dithizone must be converted to a mercury complex in the organic phase, no other dithizone complex may be formed in either phase and no other mercury complex may be present in the organic phase. If these conditions are satisfied the amount of mercury extracted from the sample and standard will be identical and will depend exclusively upon the amount of reagent used. (section 1/2). In the case under consideration, there are three ligands present; dithizone, the reagent; chloride, the interfering anion and the third ligand (L) added to prevent chloride interference. A large number of simple and mixed complexes could be formed some of which would prevent satisfactory substoichiometry by breaking these conditions.

(a) Complexes of the type Hg.L.HDz must not be formed. If the ligand is a monovalent anion this complex would be uncharged and soluble in the organic phase. Many such ligands are

known (section 3.4.1.) and ligands which are monovalent will probably be unsatisfactory. However very hydrophilic anions (such as acetate or glycollate) may be suitable because the anion would be unfavourable to its formation in the organic phase and the hydrophobic dithizone would be unfavourable to its formation in the aqueous phase. Similarly, charged complexes, which would be formed if the ligand were not a monovalent anion, are unlikely to be stable because they are necessarily soluble in the squeous phase. (N.B. I have observed such water soluble complexes with ethylenediamine, they are easily detected by the colour they impart to the aqueous phase). Ion association complexes are also unlikely because the solvent (carbon tetrachloride) has a low polarity.

(b) Mixed complexes with chloride (Hg.Cl.L) will only interfere if they are soluble in the organic phase. Once again this is probable only if the ligand is a monovalent anion.

(c) The uncharged complex between the ligand and mercury (Hg_mL_2, where m is the charge on the ligand) may also be extracted into the organic phase and must be avoided.

(d) In addition to the complexes formed with the third ligand, the analyst must ensure the absence of a significant amount of any of: mercuric chloride dithizonate; secondary mercuric dithizone, or free dithizone.

Very little is known about metal complexes with mixed ligands. It is not possible to state with certainty whether a particular ligand would form such complexes nor are their equilibrium constants known. Until these constants have been measured, it is necessary to decide every case by experiment. The field can be narrowed by examining only those complexes which satisfy condition (d). The constants for all these complexes are known and it is possible to develop a set of equations representing these conditions and to decide which ligands satisfy them.

4.2.2. The graph of α_{Hg} versus pH.

For every suitable ligand there must be a range of mercury concentrations, chloride ion concentration and pH over which negligibly small amounts of dithizone, secondary mercuric dithizonate and mercuric chloride dithizonate are formed.

The formation of these three substances are governed by the three equations

$$E_{Hg(HDz)_2} = \frac{[Hg(HDz)_2]_{org.} \; [H^+]^2}{[H_2Dz]^2_{org.} \; [Hg^{2+}]} \qquad \text{-------4/1}$$

$$E_{HgDz} = \frac{[HgDz]^2_{org} \; [H^+]^2}{[Hg(HDz)_2]_{org.} [Hg^{2+}]} \qquad \text{-------4/2}$$

$$E_{Hg.Cl.HDz} = \frac{[Hg.Cl.HDz]^2_{org.}}{[HgCl_2] \; [Hg(HDz)_2]_{org.}} \qquad \text{-------4/3}$$

Introducing

$$\beta_{HgCl_2} = \frac{[HgCl_2]}{[Hg^{2+}] \; [Cl^-]^2}$$

into equations 4/3 gives

$$E_{HgClHDz} \cdot \beta_{HgCl_2} = \frac{[HgClHDz]^2_{org.}}{[Hg^{2+}][Cl^-]^2 \; [Hg(HDz)]_{org.}} \qquad \text{-------4/4}$$

From equations 4/1, 4/2 and 4/4, the amount of dithizone, secondary mercuric dithizonate and

and mercuric chloride dithizonate, formed for any possible combincation of mercuric ion concentration, chloride ion concentration and pH. can be calculated.

In an aqueous solution of mercuric ions containing chloride and a third ligand (L), there will be three kinds of complexes, the chlorocomplexes of mercury, ($HgCl_n$), mercury complexes with the ligand (HgL_m) and free mercuric ions.

Let

$$\alpha_{Hg} = \frac{[Hg^{2+}] + \sum[HgCl_n] + \sum[HgL_m]}{[Hg^{2+}]} \qquad \text{------4/5}$$

$$= C_{Hg} \Big/ [Hg^{2+}] \qquad \text{------4/6}$$

where C_{Hg} is the total concentration of mercury in the aqueous phase whatever its form.

The value of α_{Hg} depends upon which particular complex predominates in the aqueous phase because this will provide the largest term in the numerator of equation 6.

For example, if mercuric chloride predominates:-

$$\alpha_{Hg} \simeq \beta_{HgCl_2} \cdot [Cl^-]^2$$

or if HgL predominates

$$\alpha_{Hg} \simeq K_{HgL} \cdot [L]$$

where K_{HgL} is the stability constant of the complex HgL.

If the ligand, pH, etc., have been successfully chosen and chloride interference suppressed, the predominant complex in the aqueous phase must be one of the complexes between mercury and the ligand. This follows from the absence of mercuric chloride dithizonate in the organic phase and hence the absence of mercuric chloride in the aqueous phase. If the stability constants of the complexes of the ligand with mercuric and hydrogen ions are known it is always possible to calculate α_{Hg}. Usually this will be a function of pH because most ligands are weak acids. (N.B. For further details of such calculations see R3).

Combining equation 6 with equations 2, 3 and 4 and taking logarithms give :-

$$\log \alpha_{Hg} = 2pH + \log E_{Hg(HDz)_2} + \log C_{Hg} - \log[Hg(HDz)_2]_{org.} + 2 \log [H_2Dz]_{org.} \qquad \text{-------4/7}$$

$$\log \alpha_{Hg} = 2pH + \log E_{HgDz} + \log C_{Hg} + \log [Hg(HDz)_2]_{org.} - 2 \log [HgDz]_{org.}$$

$$\log \alpha_{Hg} = \log E_{HgClHDz} + \log \beta_{HgCl_2} + \log C_{Hg} + \log [Hg(HDz)_2]_{org.} + 2 \log [Cl^-] - 2 \log [HgClHDz]_{org.} \qquad \text{-------4/8.}$$

In alkaline solutions equation 8 must be modified because of the formation of the dithizonate ion in the aqueous phase.

Let

$$\alpha_{H_2Dz} = \frac{[H_2Dz]_{org.} + \frac{V_a}{V_o}[HD\bar{z}]}{[H_2Dz]_{org.}}$$

$$= C_{H_2Dz} \Big/ [H_2Dz]_{org} \qquad \text{-------4/9}$$

where the volumes of the aqueous phase is V_a and the organic phase V_o.

Now

$$E_{H_2Dz} = \frac{[H^+]\ [HD\bar{z}]}{[H_2Dz]_{org.}}$$

$$\therefore \alpha_{H_2Dz} = 1 + \frac{V_a}{V_o} \cdot \frac{E_{H_2Dz}}{[H^+]}$$

substituting for $[H_2Dz]_{org}$ in equation 4/7 from equation 4/9 gives

$$\log \alpha_{Hg} = 2pH + \log E_{Hg(HDz)_2} + \log C_{Hg} - \log [Hg(HDz)_2]_{org.} + 2 \log C_{H_2Dz} - 2 \log C_{H_2Dz} - 2 \log \frac{V_a}{V_o} - 2 \log E_{H_2Dz}$$

-------4/10

From these equations, the amounts of free dithizone, secondary mercuric dithizonate and mercuric chloride dithizonate can be calculated if the other concentrations and constants are known.

For the purpose of selecting suitable ligands it is necessary to select maximum permissible values for the concentrations of free dithizone (D_{max}), secondary mercuric dithizonate (S_{max}) and mercuric chloride dithizonate (C_{max}) and to calculate the maximum permissible alpha value (α_D) and the minimum permissible alpha coefficient (either α_S or α_C) from the equations.

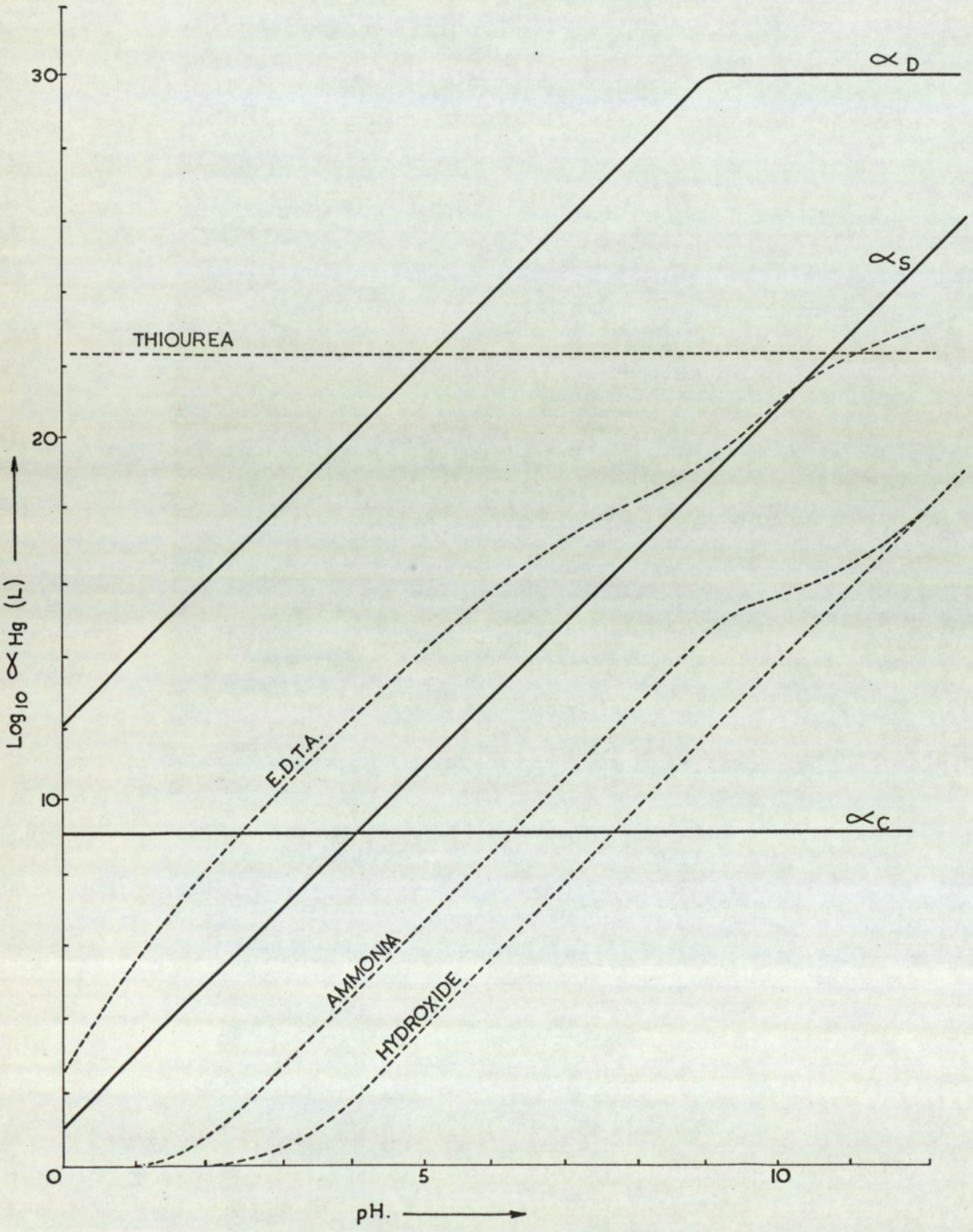
$$\log \alpha_D = 2\,pH + 2 \log D_{max} + \log E_{Hg(HDz)_2} + \log C_{Hg} - \log [Hg(HDz)_2]_{org} - 2 \log \alpha_{H_2Dz} \qquad \text{-------4/11}$$

$$\log \alpha_S = 2\,pH - 2 \log S_{max} + \log E_{HgDz} + \log C_{Hg.} + \log [Hg(HDz)_2]_{org} \qquad \text{-------4/12}$$

$$\log \alpha_C = -2 \log C_{max} + \log E_{HgClDz} + \log \beta_{HgCl_2} + \log C_{Hg} + \log [Hg(HDz)_2]_{org} + 2 \log [Cl^-] \qquad \text{-------4/13}$$

In order to select a suitable ligand, graphs are constructed of $\log \alpha$ versus pH for α_D, α_S, α_C, α_{Hg}: If α_{Hg} lies between α_D and either α_C or α_S (whichever is the greater), the ligand will

FIG. 4/1


30
20
10
0
5
10
pH. ⟶
Log10 ∝Hg (L) ⟶
∝D
∝S
∝C
THIOUREA
E.D.T.A.
AMMONIA
HYDROXIDE

prevent chloride interference. One such graph is shown in FIG. 4/1.

4.2.3. The screening test for suitable ligands.

It may be that the most convenient ligand is also one which barely prevents the formation of mercuric chloride dithizonate. The variables in equations 18, 19 and 20 have been chosen so that such ligands are not rejected unnecessarily; a low chloride concentration, a high mercury concentration, a high reagent concentration and concentrations of free dithizone, secondary mercuric dithizonate, and mercuric chloride dithizonate which would alter the amount of mercury extracted by 0.5%.

$[Hg(HDz)_2] = C_{Hg} = 1.0 \times 10^{-5}$ M

$D_{max} = S_{max} = C_{max} = 1.0 \times 10^{-7}$ M

$[Cl^-] = 1.0 \times 10^{-4}$ M,

The constants required are

$\log \beta_{HgCl_2} = 13.22$ (see M1).

$\log E_{HgClHDz} = -0.08$ (see sections 3.3.3. and 3.3.6.).

$\log E_{Hg(HDz)_2} = 26.66$ (see section 3.3.8.).

$\log E_{H_2Dz} = -8.80$ (see I2).

Substituting these values give the equations

$$\log \alpha_D = 12.66 + 2\,pH - 2 \log \alpha_{H_2Dz} \qquad \text{-------4/14}$$

where

$$\alpha_{H_2Dz} = 1 + 10^{-8.80}/[H^+]$$

(assuming $V_a = V_o$.)

below pH 7 $\alpha_{H_2Dz} = 1$

above pH 10 $\log \alpha_{H_2Dz} = 8.80 + pH.$

below pH 7

$$\log \alpha_D = 12.66 + 2\,pH \qquad \text{-------4/15}$$

and above pH 10

$$\log \alpha_D = 30.26$$

$$\log \alpha_S = 1.0 + 2\,pH \qquad \text{-------4/16}$$

$$\log \alpha_C = 9.22 \qquad \text{-------4/17}$$

These lines are plotted in FIG. 4/1 together with the $\alpha_{Hg(L)}$ values for the ligands; hydroxide ammonia, E.D.T.A., and thiourea. Ammonia and hydroxide are unsatisfactory, E.D.T.A. can be used between pH 2.5 and 10.0, thiourea between pH 5.1 and 10.7. The ligand concentration used in these calculations was 0.1M, except for hydroxide.

This procedure has been carried out for the 24 ligands shown in TABLE 4/1. In some cases the alpha-values have been taken directly from reference R3, in other cases the constants have been obtained from other references as given in the table.

These conclusions have been confirmed experimentally, using chlorine-36 as a tracer. It was shown that acetate partially suppresses the extraction of chloride, and that thiosulphate and E.D.T.A. do so completely (TABLE 4/2). These experiments do not prove the absence of other dithizone complexes nor do they prove the validity of the equations used, this will be done in the following sections.

4.3. Confirmation of equation 4/7.

To confirm this equation experimentally, thiosulphate in the presence of a large excess of cadmium was chosen as the competing ligand. In order to use the same ligand to confirm both equation 4/7 and equation 4/8, a lower alpha coefficient was required than could be obtained with thiosulphate alone. The addition of cadmium ions allowed the use of solutions so acid that the lower limit of $\alpha_{Hg(L)}$ was set by the formation of mercuric chloride dithizonate (α_C) rather than the formation of secondary

mercuric dithizonate (α_s).

To appreciate this conclusion equations 4/16 and 4/17 must be examined (see also FIG. 4/1). At pH 4.07 $\alpha_c = \alpha_s = 10^{9.22}$. Below pH 4.07 mercuric chloride dithizonate is the most important interference ($\alpha_c > \alpha_s$), above pH 4.07 secondary mercuric dithizonate is the dominant impurity. These conclusions only apply to solutions in which α_{Hg} is near the lower limit, if α_{Hg} is near the higher limit free dithizone will be the most important interference. Another limitation is that equations 4/16 and 4/17 only apply to the conditions set out in section 4.2.3. The more general equation obtained by combining equations 4/12 and 4/13 is :-

$$pH = 8.07 + \log [Cl^-]$$

$$\text{if } S_{max} = C_{max}$$

The concentration of thiosulphate which gives an alpha coefficient of $10^{9.22}$ is :-

$$\alpha_{Hg(S_2O_3^=)} = [S_2O_3^=]^2 \cdot 10^{29.3}$$

(N.B. $\beta_2 = 10^{29.3}$ for thiosulphate and the predominant complex is $Hg(S_2O_3)_2^{2-}$ if $[S_2O_3^=] < 10^{-2}$, see reference D5).

$\therefore$ if $\alpha_{Hg(S_2O_3^=)} = 10^{9.22}$.

$[S_2O_3^=] = 10^{-10.0}$ molar.

This concentration is very much smaller than the mercury concentration (10^{-5}M) and it would be impossible to adjust the total amount of thiosulphate added to the required accuracy. For example, if by mistake 0.001% more mercury were added than that calculated all the excess thiosulphate would be consumed. However, if a large concentration of cadmium ions (1M say) is added the thiosulphate ions are removed as the cadmium complex ($Cd\ S_2O_3$) and larger quantities of thiosulphate are required.

$$\alpha_{S_2O_3\,(Cd)} = 1 + [Cd^{2+}]\,10^{3.9}$$
$$= 10^{3.9}$$

(β_1 for cadmium and thiosulphate is $10^{3.9}$ and in 1M cadmium solution CdS_2O_3 is the predominant complex: see reference N4).

$$[S_2O_3^{2-}] = C_{S_2O_3} \Big/ \alpha_{S_2O_3(Cd)}.$$

where

$$C_{S_2O_3} = [S_2O_3^{2-}] + [Cd\ S_2O_3]$$

$$\alpha_{Hg(S_2O_3)} = C^2_{S_2O_3} \cdot 10^{-7.8} \times 10^{29.3}$$
$$= C^2_{S_2O_3} \cdot 10^{21.5}$$

if $\alpha_{Hg} = 10^{9.22}$

$C_{S_2O_3} = 10^{-6.1}$

which is satisfactory.

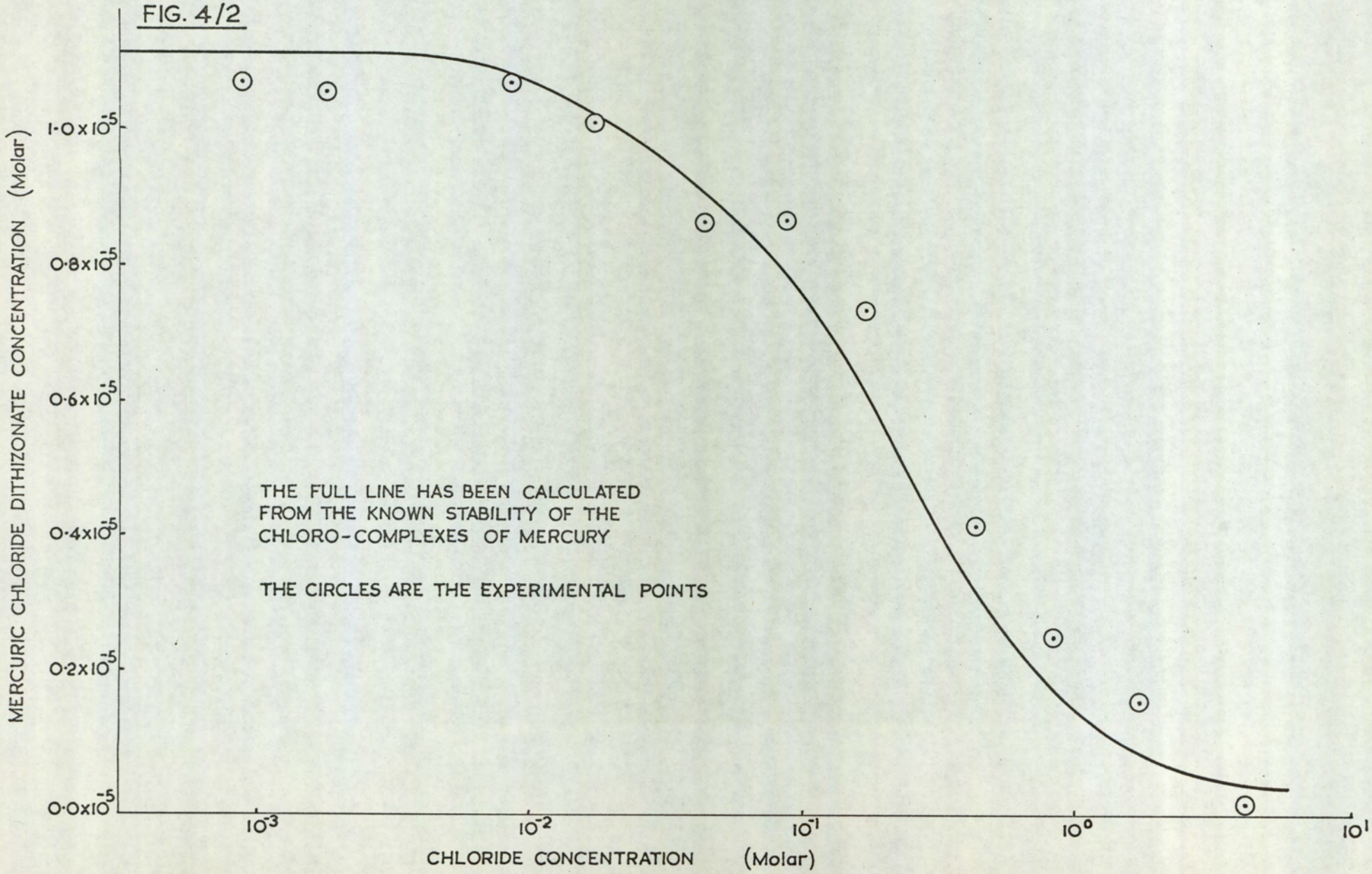
Using these conditions (thiosulphate in the presence of 1M cadmium ions) equation 4/7 has been confirmed experimentally with the results given in TABLE 4/3. There is a constant difference between the experimental and calculated values of $\log \alpha_{Hg}$ of 0.42. This is probably due to the accumulation of small errors in the constants used in the calculations. To illustrate this the experimental results could be used to calculate $E_{Hg(HDz)_2}$ via equation 4/7 using $\alpha_{Hg(S_2O_3)}$ calculated from equation 4/18. This procedure gives a value $10^{26.08}$ which is not statistically different from the values considered in section 3.3.8. of chapter 3 ($E = 10^{26.66}$).

4.4. Verification of equation 4/8.

In the previous section (4.3.), thiosulphate was chosen as the competing ligand because it could be used to verify both the equation 4/7 relating to the upper limit (the production of free dithizone) and the equation 4/8 relating to the lower limit (the production of mercuric chloride dithizonate). The experiments with free dithizone were perfectly satisfactory but whilst investigating the formation of mercuric chloride dithizonate, solid mercuric thiosulphate (HgS_2O_3) was formed, this dissolved in the organic phase and gave erroneous results. This substance was not precipitated in the earlier experiments because at the higher concentrations of thiosulphate used complexes of a different composition ($Hg(S_2O_3)_2^{2-}$), soluble in the aqueous phase, were formed instead.

In place of thiosulphate, chloride has been used as a competing ligand. The experimental results were used to calculate an experimental alpha coefficient withbthe aid of equation 4/8. The concentration of mercuric chloride dithizonate being estimated by comparing the activity extracted in the presence of chloride with the activity extracted when chloride is absent. The alpha coefficient expected on theoretical

FIG. 4/2


MERCURIC CHLORIDE DITHIZONATE CONCENTRATION (Molar)
1·0x10⁻⁵
0·8x10⁻⁵
0·6x10⁻⁵
0·4x10⁻⁵
0·2x10⁻⁵
0·0x10⁻⁵
10⁻³
10⁻²
10⁻¹
10⁰
10¹
CHLORIDE CONCENTRATION (Molar)
THE FULL LINE HAS BEEN CALCULATED FROM THE KNOWN STABILITY OF THE CHLORO-COMPLEXES OF MERCURY
THE CIRCLES ARE THE EXPERIMENTAL POINTS

grounds was calculated from the equation :-

$$\alpha_{Hg(Cl)} = 1 + \sum_{n=1}^{n=4} [HgCl_n] / [Hg^{++}] \quad \text{-------4/19}$$

$$= 1 + \sum_{n=1}^{n=4} {}_n[Cl^-]^n \quad \text{-------4/20}$$

where $\beta_1 = 10^{6.74}$, $\beta_2 = 10^{13.22}$, $\beta_3 = 10^{14.17}$, $\beta_4 = 10^{15.22}$

(see ref. M1).

The results are in good agreement. (TABLE 4/4). The maximum difference is 0.34 in $\log \alpha_{Hg}$, and the largest errors only occur at a high chloride concentration where small errors in the activities cause large errors in the alpha coefficients. A better impression of the accuracy is given by FIG. 4/2 where the experimental estimates of the mercuric chloride dithizonate concentration are compared with those calculated from equations 4/20 and 4/8.

These results show that the concentration of chloride required to reduce the mercuric chloride dithizonate concentration to negligible proportions is too great for this ligand to be used in substoichiometric analysis. To find a ligand suitable for this purpose E.D.T.A. was investigated.

4.5. The mercuric chloride ethylene-diamine-tetra-acetate complexes.

4.5.1. The anamalous experimental results obtained when both chloride and E.D.T.A. are present in the aqueous phase.

The experimental alpha coefficient was calculated from equation 4/8 as in section 4.4. The theoretical alpha value was calculated from the equations :-

$$\alpha_{Hg} = \alpha_{Hg(Cl)} + \alpha_{Hg(y)} - 1. \qquad \text{-------4/21}$$

$$\alpha_{Hg(y)} = 1 + K_y [Y] + K_{Hy} [Y][H^+] \qquad \text{-------4/22}$$

$K_y = 10^{21.80}$ is the stability constant of the mercuric ethylenediamine tetraacetate anion. (ref: S3).

$K_{Hy} = 10^{24.90}$ is the stability constant of the complex anion, $H\,HgY^-$

$[Y]$ = the concentration of the free ion of E.D.T.A.

$$\alpha_{y(H)} = C_y / [Y]. \qquad \text{-------4/23}$$

$\therefore$ from equations 4/22 and 4/23

$$\alpha_{Hg(Y)} = 1 + K_y C_y / \alpha_{y(H)} + K_{Hy} . C_y . [H^+] / \alpha_{y(H)} \qquad \text{-------4/24}$$

Where C_y is the analytical concentration of E.D.T.A., excluding that present as mercury complexes.

$$C_y = [Y] + [YH] + [H_2Y] + [H_3Y] + [H_4Y]$$

$$y(H) = 1 + [H^+] . 10^{10.34} + [H^+]^2 \; 10^{16.58} + [H^+]^3 . 10^{19.33}$$

(see ref. S4).

The results are recorded in TABLE 4/5. The experimental alpha coefficients are always higher than those calculated from the known complexes of chloride and E.D.T.A. This suggests that there is some new complex formed which is stronger than the known complexes, (i.e., has a higher alpha coefficient).

4.5.2. The identification of the new complexes.

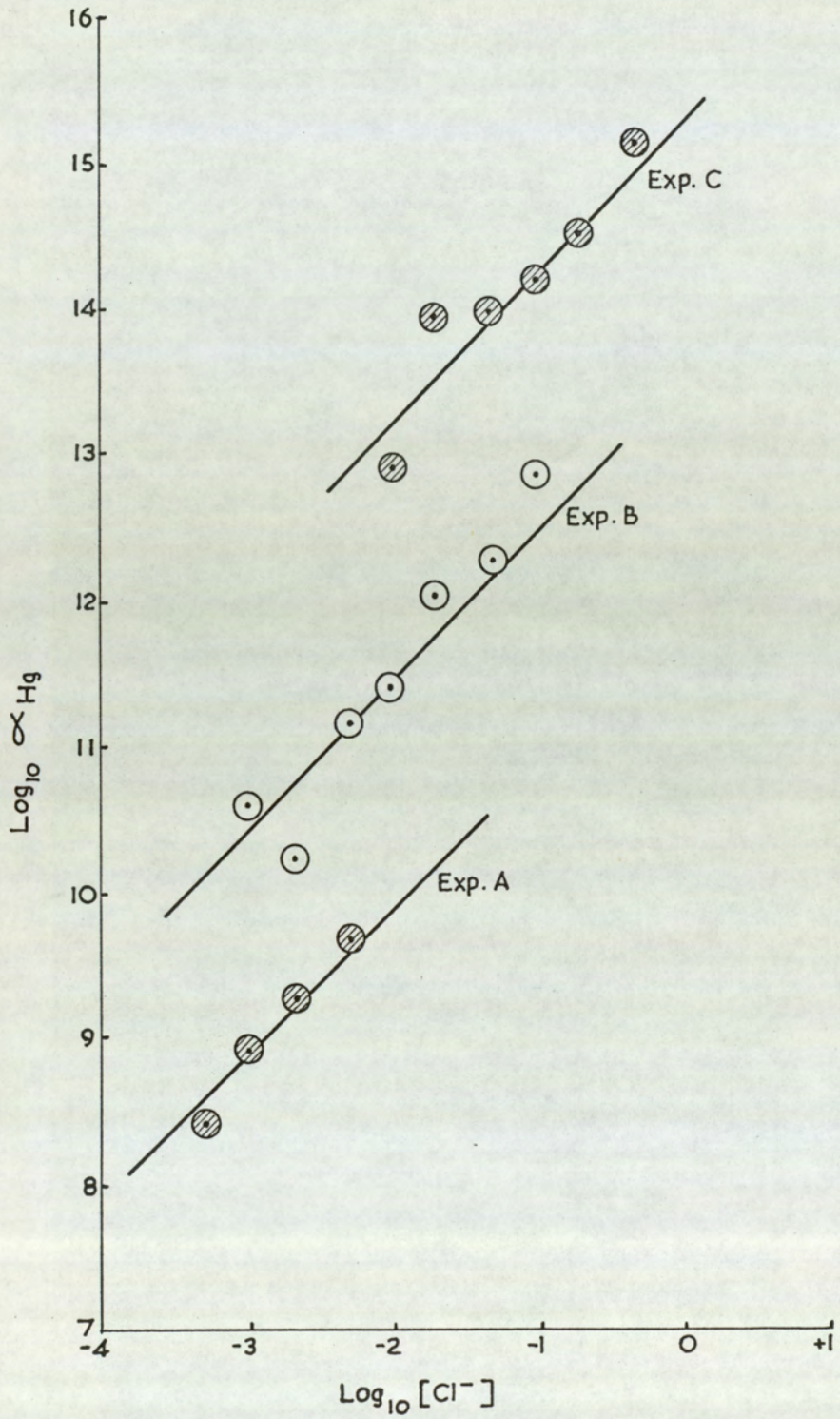
This new complex was presumed to be formed from hydrogen, chloride, mercury and E.D.T.A. ions by some reaction such as :-

$$Hg^{2+} + h\,H^+ + c\,Cl^- + y\,Y^{4-} \rightleftharpoons HgH_hCl_cY_y^{(2 + h - c - 4y)}.$$

for which the equilibrium constant would be

$$K = [Hg\,H_h\,Cl_c\,Y_y] / [H_g^{2+}] [H^+]^h [Cl^-]^c [Y^{4-}]^y$$

FIG. 4/3


16
15
14
13
12
11
10
9
8
7
-4
-3
-2
-1
0
+1
Exp. C
Exp. B
Exp. A
$Log_{10} \propto_{Hg}$
$Log_{10} [Cl^-]$

If such a complex were formed

$$\alpha_{Hg} = \alpha_{Hg(Cl)} + \alpha_{Hg(Y)} + \alpha_{Hg(Cl,Y)} - 2 \qquad \text{-------4/25}$$

where

$$\alpha_{Hg(Cl,Y)} = 1 + [HgH_hCL_cY_y] / [Hg^{2+}]$$

If $\alpha_{Hg(Cl,Y)}$ were very much larger than any other term in equation 2, which is true for the experimental results which are being discussed:-

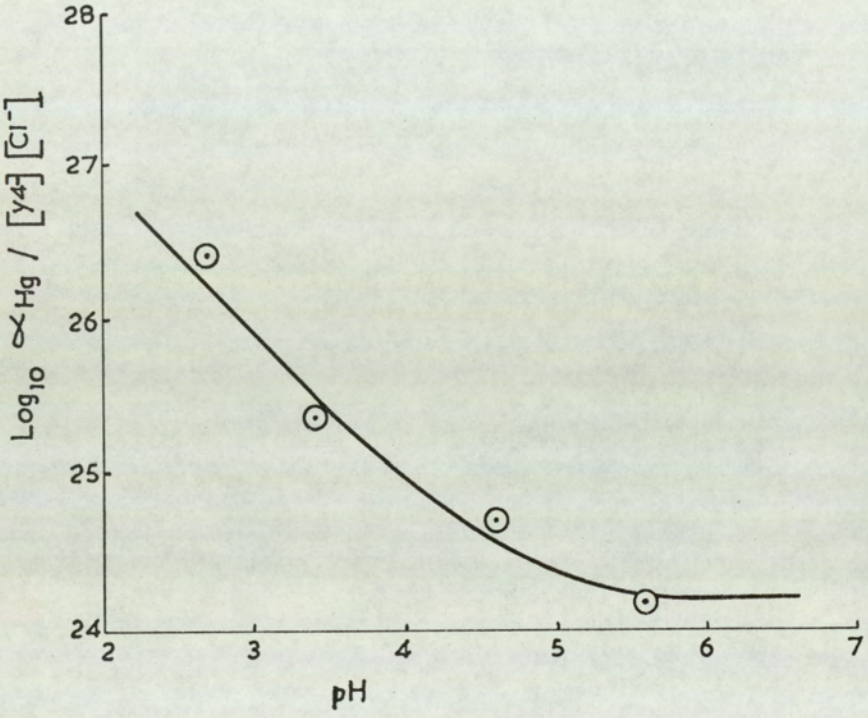
$$\alpha_{Hg} = K.[H^+]^h [Y]^y [Cl^-]^c$$

so that a plot of $\log \alpha_{Hg}$ (experimental value) versus $\log [Cl^-]$ would be a straight line of slope 'c' if both $[H^+]$ and $[Y^{4-}]$ are kept constant. FIG. 4/3 shows such a graph for some of the experimental results. In every case the graph had a slope of one. A further assumption was made that y was also one. This is justified by the almost universal formation of 1 : 1 complexes between metals and E.D.T.A. and by the absence of any other kind of complex amongst the known E.D.T.A./mercury complexes. Thus

$$K.[H^+]^h = \alpha_{Hg} / [Y^{4-}] [Cl^-] \qquad \text{-------4/26}$$

and a plot of $\log [H^+]$ versus the logarithm of the function on the right of equation 5 should be

FIG. 4/4



a straight line of slope 'h'. The experimental results gave a curve (FIG. 4/4) which approached a slope of one in acid solution and a slope of zero in alkaline solution.

These calculations suggest that there are two complexes formed under these experimental conditions :-

$$Hg.Cl.Y.^{3-} \quad \text{and} \quad H.Hg.Cl.Y^{2-}$$

Fitting two constants

$$K_{HgClY} = [HgCl.Y^{3-}] / [Hg^{2+}] [Cl^{-}] [Y^{4-}]$$

and

$$K_{H\ HgClY} = [H.Hg.Cl.Y^{2-}] / [H^{+}] [Hg^{2+}] [Cl^{-}] [Y^{4-}]$$

to the experimental values of $\alpha_{Hg(Cl,Y)}$ (calculated from equation 4/25 using the values of $\alpha_{Hg(Y)}$ calculated from equation 4/24, and of $\alpha_{Hg(Cl)}$ calculated from equation 4/20) by the method of least squares gave the values

$$K_{HgClY} = 10^{24.2} \quad \text{and} \quad K_{H\ HgClY} = 10^{28.9}$$

The 95% confidence limits of these results are :-

$$10^{23.76} < K_{HgClY} < 10^{24.56} \quad \text{if } K_{H.HgClY} = 10^{28.90}$$

and

$$10^{28.73} < K_{Hg.H.Cl.Y.} < 10^{29.17} \quad \text{if } K_{HgClY} = 10^{24.20}$$

These figures only represent the precision with which the amount of mercuric chloride dithizonate formed could be measured and the constants would be in error if the assumed formulae of the complexes ($HgClY^{3-}$ and $H\,HgClY^{2-}$) were wrong or if any of the constants used in the calculations were inaccurate.

If these fitted values of K_{HgClY} and $K_{H\,HgClY}$ are assumed correct and are used to calculate a value of $\alpha_{Hg(Cl,Y)}$ from the equation :-

$$\alpha_{Hg(Cl,Y)} = 1 + 10^{24.2}[Cl^-]\,C_Y/\alpha_{Y(H)} + 10^{28.9}\,[Cl^-]\,[H^+]\,C_Y/\alpha_{Y(H)} \qquad \text{-------4/28}$$

then this value of $\alpha_{Hg(Cl,Y)}$ may be used to calculate a theoretical alpha coefficient via equation 4/25. This calculated value is compared with the experimental result in TABLE 4/6. An analysis of variance of the differences between these two series of alpha coefficients (TABLE 4/7) shows that there is no significant variation with either chloride concentration or pH. The residual variations can be entirely assigned to experimental error.

4.5.3. The extraction of mercuric chloride dithizonate from solutions of mercury containing both chloride and E.D.T.A.

When E.D.T.A. is used as the competing ligand the alpha coefficient is never so high that free dithizone is formed. Only the formation of mercuric chloride dithizonate need be considered. The amount of mercuric chloride dithizonate extracted from an aqueous phase containing both chloride and E.D.T.A. depends upon the alpha coefficient in a manner described by equation 4/8. This equation may be modified slightly to :-

$$2 \log X_c = 2 \log \frac{[HgClHDz]}{[Hg(HDz)_2]} = \log \beta_{HgCl_2} \cdot E_{HgClHDz}$$

$$+ \log C_{Hg} - \log [Hg(HDz)_2] + 2 \log [Cl^-] - \log X_{Hg}$$

The alpha coefficient depends upon the nature of the complex which is predominant in the aqueous phase. At very low chloride concentrations this will be HgY^{2-}, at slightly higher chloride concentrations either $HgClY^{3-}$ or $H.HgClY^{2-}$, at moderate chloride concentrations $HgCl_2$, and at very high chloride concentrations $HgCl_4^{2-}$. The relationship between chloride ion concentration and the proportion of primary mercuric dithizonate converted to mercuric

FIG. 4/6 Experimental

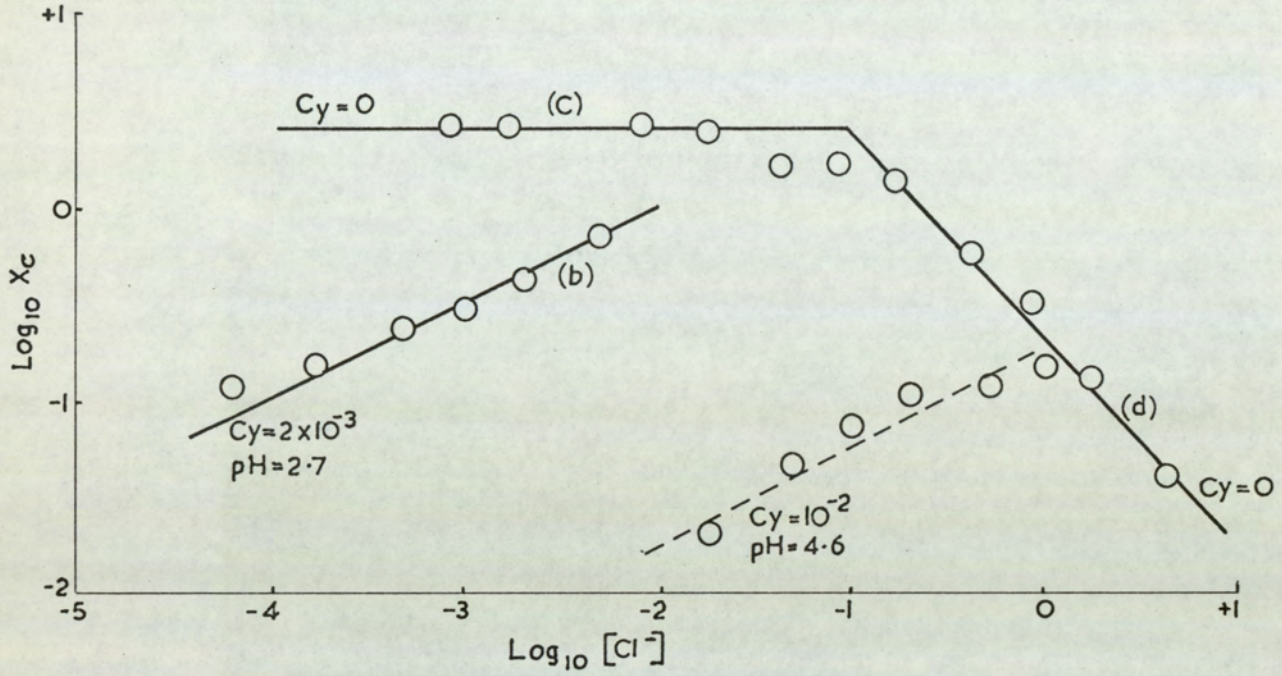
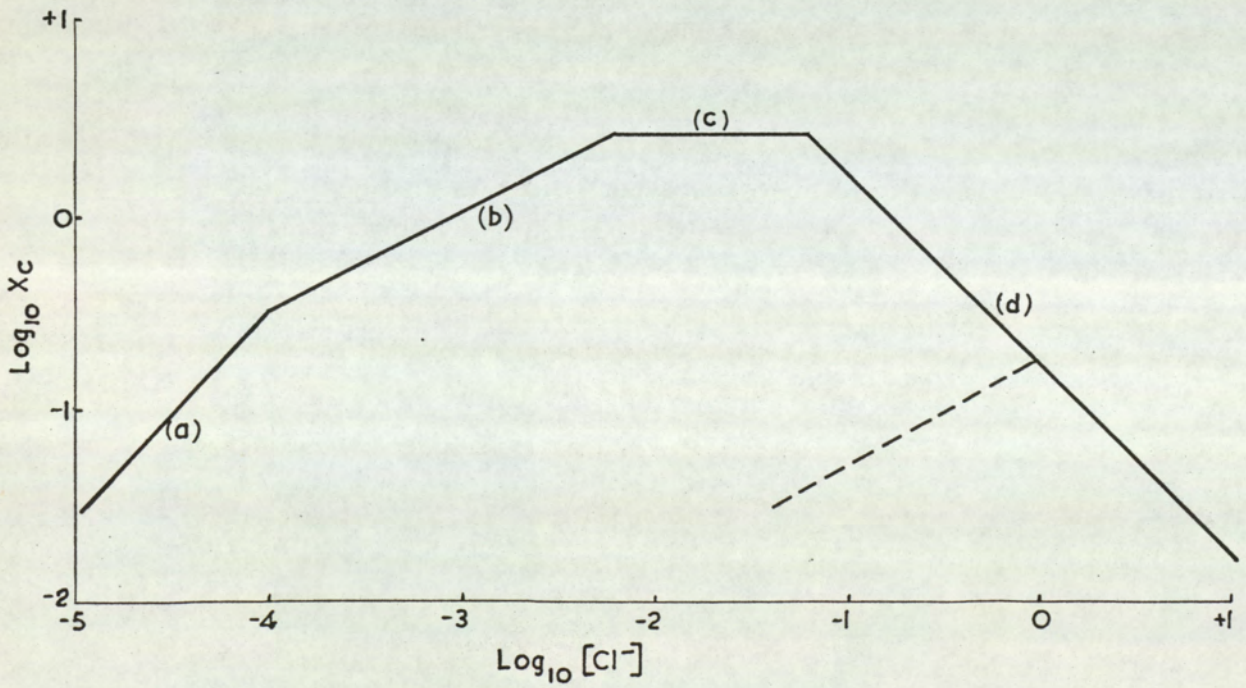


FIG 4/5 Idealized



chloride dithizonate (X_c) will be different for each of these four regions. A graph of log X_c versus log $[Cl^-]$ will consist of four straight lines each with its own individual slope.

(a) if HgY^{2-} predominates

$$\log \alpha_{Hg} = \log K_{HgY} + \log C_Y - \log X_{Y(H)}$$

slope = + 1

(b) if $HgClY^{3-}$ predominates

$$\log \alpha_{Hg} = \log K_{HgClY} + \log C_Y - \log \alpha_{Y(H)} + \log [Cl^-]$$

or if $H.Hg.Cl.Y^{2-}$ predominates

$$\log \alpha_{Hg} = \log K_{H\,HgClY} + \log C_Y + \log [Cl^-] + \log [H^+] - \log \alpha_{Y(H)}$$

For both of which; slope = + 1/2.

(c) if $HgCl_2$ predominates

$$\log \alpha_{Hg} = \log \beta_{HgCl_2} + 2 \log [Cl^-]$$

slope = 0

(d) if $HgCl_4^{2-}$ predominates

$$\log \alpha_{Hg} = \log \beta_{HgCl_4} + 4 \log [Cl^-]$$

slope = - 1.

These conclusions are illustrated in FIG.4/5 and in FIG. 4/6 the experimental data is plotted in the same way.

The positions of the lines (a) and (b) depend on the concentration of E.D.T.A. (C_Y) and the pH (because $\alpha_{Y(H)}$ depends upon pH). FIG. 4/5 is drawn for a low concentration of E.D.T.A. or for a low pH. At higher E.D.T.A. concentrations or more alkaline solutions, line (c) may disappear because $\alpha_{Hg(Cl)}$ does not exceed $\alpha_{Hg(Y)}$ until the chloride concentration is so high that $HgCl_4^=$ is the predominant complex. This is shown by the dotted line in FIGS. 4/5 and 4/6. In acid solutions line (b) will extend to lower chloride concentrations because the acid complex has the higher stability constant (i.e., $K_{H.HgClY} > K_{HgClY}$).

4.6. The use of E.D.T.A. to prevent the formation of mercuric chloride dithizonate during the substoichiometric determination of mercury.

It was shown in the previous section that E.D.T.A. forms a number of complexes with mercury. The particular complex which predominates depends upon the pH and the chloride ion concentration. The amount of E.D.T.A. required to obtain a certain alpha coefficient will depend upon the nature of the predominant complex and can be calculated from equations 4/25, 4/28, 4/22 or 4/20. The alpha coefficient required to prevent the formation of the undesirable mercuric chloride dithizonate can be calculated from equation 4/13. If alternatively the pH and chloride concentration are such that during the substoichiometric extraction more secondary mercuric dithizonate is formed than mercuric chloride dithizonate equation 4/12 should be used to choose an alpha coefficient which will prevent sufficient secondary dithizonate forming to interfere. Also it must be recalled that the alpha coefficient must not exceed that given by equation 4/11 or else free dithizone will be formed. Because of the rather complex nature of this situation these equations have been solved for a range of conditions normally encountered

in substoichiometric analysis and the results are presented in TABLE 4/8.

The effectiveness of this procedure can be judged in the neutron activation analyses carried out in co-operation with the International Atomic Energy Agency. When the extraction is carried out in the absence of E.D.T.A. mercuric chloride dithizonate is precipitated during the first extraction removing all the adventitious chloride from the aqueous phase. In neutron activation analysis strong dithizone solutions are used (c.a.10^{-3}M). In isotope dilution analyses the solutions are much weaker (c.a.10^{-7}M) and mercuric chloride dithizonate does not precipitate. See chapter 3, section 3.1.3.).
In the second extraction no mercuric chloride dithizonate is formed because no chloride is present. The second extraction will give accurate results but the activity of the first extraction will be too high. When E.D.T.A. is added no mercuric chloride dithizonate is formed, both extractions will have the same activity and both will give accurate results. This is illustrated in TABLE 4/9 and in TABLE 4/10 the results calculated from any of the extractions containing no mercuric chloride dithizonate are compared with the average results from many laboratories quoted by the Atomic Energy Agency (I4). Clearly the addition of E.D.T.A. overcomes the interference of chloride in manual substoichiometric analysis.

4.7. Experimental.

All reagents were prepared from analytical reagent grade chemicals.

In carrying out the experiments in this section difficulties were met when it was attempted to thermostat the solutions at 25°c. During the period of shaking (one hour in some cases) the solutions cooled to very nearly room temperature. To eliminate this error the solutions were allowed to equilibrate in a thermostated bath at 23°c - the room temperature, no temperature change then occurred during the shaking time.

For a description of the apparatus and reagents see section 3.5.1. of chapter 3.

4.7.1. Tracer experiments with chlorine - 36 to demonstrate that a third ligand will prevent the formation of mercuric chloride dithizonate.

Five ml. of a 1×10^{-4} M mercuric perchlorate solution dissolved in any one of (a) 0.1 M perchloric acid, (b) 0.5 M sodium acetate and 0.5 M acetic acid, (c) 0.25 M sodium ethylene-diamine-tetra-acetate, or (d) 1×10^{-2} M sodium thiosulphate and 1.0 M ammonium acetate, were added to 20 ml of 2.75×10^{-4} M labelled sodium chloride solution. The mixture was shaken for 15 min. with 25 ml of a 3.1×10^{-5} M solution

of primary mercuric dithizonate in carbon tetrachloride. The organic phase was filtered through a dry No. 41 Whatman filter paper and 20 ml shaken with 5 ml of an 0.01 M borax solution. Any mercuric chloride dithizonate was converted to sodium chloride which does not quench the liquid scintillator used to measure the activity of 2 ml of the filtered aqueous phase.

The results are presented in TABLE 4/2.

4.7.2. The experimental verification of equation 4/7.

To 10 ml of an 0.1 M perchloric acid solution and 3 ml of a 2×10^{-5} M mercuric perchlorate solution labelled with mercury - 203, were added x ml (x = 0.25, 0.50, 1.0 and 3.0) of an 0.607 M sodium thiosulphate solution. Each of the above solutions also contained enough cadmium sulphate so that the final molarity of this salt in the aqueous phase was 1.0M. The mixture was shaken for 2 mins. with 10 ml of 0.845×10^{-5} M zinc dithizonate solution in carbon tetrachloride. The two phases were filtered through dry No. 41 Whatman filter papers and 5 ml of each counted in a gamma-ray spectrometer. The optical density of

the organic layer was measured at 620 nm. in a 1 cm. cell, using an S.P.600 unicam spectrophotometer.

The pH was calculated from the equation

$$pH = \log_{10} \left\{ \frac{13.00 + x}{1.300} \right\}$$

The concentration of free dithizonate in the organic layer was calculated from the absorbance (A) at 620 nm.

$$[H_2Dz]_o = A / 32,800 \qquad \text{(ref:- I1).}$$

The quotient

$$[Hg(HDz)_2]_o \Big/ C_{Hg} = A_o \Big/ A_a = Q$$

was calculated from the measured activities of the organic (A_o) and aqueous (A_a) phases.

This gives sufficient information to calculate an experimental alpha coefficient via equation 4/7 - see TABLE 4/11. In TABLE 4/3 these experimental alpha coefficients are compared with the theoretical ones based upon the known equilibrium constants of mercuric and cadmium thiosulphate and the concentration of thiosulphate used.

4.7.3. The experimental verification of equation 4/8.

To 5 ml of a 1 x 10^{-4} M solution of labelled mercuric perchlorate in 1 x 10^{-2} M acetic acid, x ml of calcium chloride solution (either 4.276 M or 4.276 x 10^{-2} M) and (5 - x) ml of water were added. (N.B. x = 5, 2, 1, 0.5, 0.2 and 0.1). This mixture was shaken 15 mins. with 10 ml of 0.95 x 10^{-5} M zinc dithizonate solution in carbon tetrachloride. The two layers were separated and filtered through dry No. 41 Whatman filter papers and 5 ml of each counted.

To obtain the activity of the organic layer in the absence of mercuric chloride dithizonate, the mercuric perchlorate solution was diluted to 10 ml with a solution of 1 x 10^{-2} M E.D.T.A. dissolved in a buffer 0.1 M in acetic acid and 0.1 M in ammonium acetate. The chloride solution and the water were omitted.

The equilibrium concentrations of the various mercury species were calculated from the equations

$$[HgClHDz]_o = \left\{\frac{A_o - A_s}{A_s}\right\} \times 2 \times 0.95 \times 10^{-5}.$$

$$[Hg(HDz)_2]_o = \left\{\frac{2A_s - A_o}{A_s}\right\} \times 0.95 \times 10^{-5}.$$

$$C_{Hg} = \frac{A_a}{A_s} \times 0.95 \times 10^{-5}.$$

where A_a is the activity of the aqueous phase A_o is the activity of the organic phase, both obtained when x ml of chloride solution was added, and A_s is the activity of the organic layer when no chloride was added.

To calculate the alpha coefficient from equation 4/8, it is unnecessary to calculate the concentrations of the individual species. By substituting the above equations into equation 4/8 one obtains :-

$$\log_{10} \alpha_{Hg} = 13.14 + 2 \log_{10}[Cl^-] + \log_{10} \left\{ \frac{A_a(2A_s - A_o)}{4 (A_o - A_s)^2} \right\} \quad \text{-------4/27}$$

The experimental results are set out in TABLE 4/12 and the measured alpha-coefficients are compared with those calculated from the chloride concentration and the known stability constants of the chloro-mercuric complexes in TABLE 4/4.

4.7.4. The estimation of the alpha coefficient when both E.D.T.A. and chloride are present in the aqueous phase.

Four series of E.D.T.A. solutions were prepared. Within each series the E.D.T.A. concentration was fixed and the E.D.T.A. was dissolved in a buffer of one particular pH. The concentrations of E.D.T.A. and the composition of the buffer solutions used are given in TABLE 4/13. Each series consisted of four solutions, a 1×10^{-4}M labelled mercuric perchlorate solution, two chloride solutions, either 2 M or 1×10^{-2}M, and a solution only containing E.D.T.A. and the buffer.

Thus one litre of the mercuric perchlorate solution used in experiment A (pH 2.68, $Cy = 2 \times 10^{-3}$M) contained 2×10^{-3} mole of disodium ethylenediaminetetraacetate 4×10^{-3} mole of perchloric acid and 1×10^{-4} mole of mercuric perchlorate.

An aliquot of one of the chloride solutions and 5 ml of the mercuric perchlorate solutions were diluted to 10 ml with the pure E.D.T.A./buffer. This mixture was shaken for thirty minutes (if $[Cl^-] < 0.1M$) or one hour (if $[Cl^-] > 0.1M$) with 10 ml of zinc

dithizonate solution in carbon tetrachloride (c.a. 1×10^{-5}M). The two phases were separated and filtered through Whatman No. 41 filter papers. 5 ml of each phase was used to measure the activities.

To obtain the activity of the organic layer in the absence of mercuric chloride dithizonate, the mercuric perchlorate solution was diluted to 10 ml with a solution of E.D.T.A. (1×10^{-2}M) in a buffer containing 0.1M acetic acid and 0.1M ammonium acetate. No chloride solution was added.

The alpha coefficient was calculated from equation 4/27 as in the previous section. The experimental results are given in TABLE 4/14 and these results are interpreted in section 4/5.

4.7.5. The neutron activation and analysis of samples provided by the International Atomic Energy Agency.

(a) Neutron Activation.

Each sample (1g) and standard (9 mg HgO) was sealed into a silica tube which was then sealed into a larger silica tube. These were then all placed in a standard "A" can and irradiated under the Harwell radiation service (BEPO or DIDO) at 10^{12} neutrons / cm^2 / sec for one week. The samples were allowed to decay for a further week before analysis, so that the activity due to mercury was a result of the activation of mercury - 202 to mercury - 203, most of the mercury - 198 having decayed.

(b) Dissolution of the samples.

The sample tubes were cut open and placed in a 250 ml round bottomed flask together with 5 ml of concentrated nitric acid (specific gravity 1.42), 2.5 ml of concentrated sulphuric acid (specific gravity 1.84), and 1.00 ml of the carrier solution, 0.1M mercuric perchlorate. The flask was now attached to the S.A.C. apparatus (reference A2) and refluxed, adding nitric acid whenever charing was observed. After wet ashing the flask was cooled and the contents diluted with 50 ml of water (this water was used

to wash down the inside of the condensor and receiver), 1g of urea was added to destroy the nitrous fumes and the resulting solution was transferred to a volumetric flask and diluted to 100 ml.

The standard was treated in the same way as the samples except that the carrier was omitted.

(c) Substoichiometric extraction in the absence of E.D.T.A.

Fifty ml of the solution from each sample was successfully extracted with two 13 ml portions of 3×10^{-3} M dithizone in chloroform. The extracts were filtered and 10 ml of each counted.

In the case of the standard 5 ml of solution and 1.00 ml of 0.1 M mercuric perchlorate carrier were diluted to 50 ml with 0.1 M perchloric acid and then extracted and counted exactly as were the samples.

(d) Substoichiometric extraction in the presence of E.D.T.A.

Fifty ml of the sample solution was neutralized with sodium hydroxide (2M) to a pH of about 4. Ten ml of 1×10^{-1} M E.D.T.A. in 1.0 M ammonium acetate 1.0M acetic acid buffer were added and the extractions were carried out with two 13 ml portions of dithizone as described above.

For the standard 5 ml of the solution 1.0 ml of 0.1 M mercuric perchlorate carrier and 10 ml of E.D.T.A. buffer were used.

(e) Purity of the isotope extracted.

Decay curves and gamma ray spectra were prepared from all the extracts and were used to demonstrate the purity of the mercuric isotope isolated. No contamination was discovered.

TABLE 4/1. The selection of ligands suitable for the prevention of mercuric chloride dithizonate formation.

Suitable ligands		Possible ligands		Unsuitable ligands	
Ligand	Ref.	Ligand	Ref.	Ligand	Ref.
E.D.T.A.	R3	Acetate	M6	Ammonia	R3
D.C.T.A.	R3	Ethylenediamine	W1	Diethanolamine	B8
D.P.T.A.	R3	Glycine	F1	Ethanolamine	B8
E.G.T.A.	R3	Tren	R3	Methylamine	B8
Den	R3			Pyridine	B8
Trien	R3	Chloride *	M1	Triethanolamine	B8
Piccolinic acid	R3			Hydroxide	R3
O-phenan-throline	R3				
Sulphite	T2				
Thiosulphate	D5				
Thiourea	R3				
Thioglycollate	K4				

* this anion requires a modified treatment.

N.B. This table only refers to the suitability of the alpha-coefficient of mercury with the ligand. Other complexes may be formed which render the ligand unsuitable (see 4.2.1. a, b and c).

TABLE 4/2. The experimental demonstration that mercuric chloride dithizonate is not formed in the presence of a suitable ligand.

C_{Hg} = 2.0×10^{-5}M, $[Cl^-] = 1.07 \times 10^{-4}$M,

$[Hg(HDz)_2] = 6.1 \times 10^{-5}$M.

chloride labelled with 36-Cl.

ligand (V)	C_Y	pH	Activity of organic phase observed	Activity of organic phase calculated theoretically
None	-	1.7	65 c/s	-
Acetate	2×10^{-1}M	4.5	40 c/s	43 c/s
E.D.T.A.	5×10^{-2}M	5.0	0.7 c/s	0.0 c/s
Thiosulphate	2×10^{-3}M	7.0	0.4 c/s	0.0 c/s

TABLE 4/3. Experimental demonstration of the accuracy of equation 4/7 using dithiosulpato-cadmium as the competing ligand.

Concentration of thiosulphate (Molar)	Observed $\log_{10} \alpha_{Hg}$ (Equation 4/7).	Calculated $\log_{10} \alpha_{Hg}$ (Equation 4/18
$10^{-1.94}$	18.03	17.62 (0.41)*
$10^{-1.65}$	18.65	18.20 (0.45)*
$10^{-1.365}$	19.15	18.77 (0.38)*
$10^{-1.12}$	19.70	19.26 (0.44)*

* Difference $\log_{10} \alpha_{obz} - \log_{10} \alpha_{calc.}$ due to cumulative errors in the constants used (see section 4.3.).

TABLE 4/4. Experimental demonstration of the accuracy of equation 4/8, using chloride as the competing ligand.

Concentration of chloride (Molar)	Observed $\log_{10} \alpha_{Hg}$ Equation 4/8	Calculated $\log_{10} \alpha_{Hg}$ Equation 4/20
1.71×10^{0}	16.01	16.17
8.56×10^{-1}	14.66	15.00
4.28×10^{-1}	13.57	13.85
1.71×10^{-1}	12.16	12.42
8.56×10^{-2}	11.37	11.49
4.28×10^{-2}	10.76	10.68
1.71×10^{-2}	9.74	9.76
8.56×10^{-3}	9.08	9.12
4.28×10^{-3}	8.48	8.50
1.71×10^{-3}	7.68	7.69
8.56×10^{-4}	7.08	7.09

TABLE 4/5. The anomalous results observed when using both chloride and E.D.T.A. together, as competing ligands.

Experiment	Chloride ion concentration (Molar)	Observed $\log_{10} \alpha_{Hg}$ (Eqn 4/8)	Calculated $\log_{10} \alpha_{Hg}$ (Eqn 4/25)
A. pH 2.68, $C_Y = 2 \times 10^{-3}$ M.	5.0×10^{-3}	9.69	8.68
	2.0×10^{-3}	9.29	8.07
	1.0×10^{-3}	8.89	7.84
	5.0×10^{-4}	8.43	7.76
	1.6×10^{-4}	7.83	7.74
	0.6×10^{-4}	7.19	7.14
B. pH 3.42, $C_Y = 1 \times 10^{-2}$ M.	1.0×10^{-1}	12.86	11.68
	5.0×10^{-2}	12.28	10.92
	2.0×10^{-2}	12.06	10.34
	1.0×10^{-2}	11.41	10.22
	5.0×10^{-3}	11.14	10.15
	2.0×10^{-3}	10.29	10.17
	1.0×10^{-3}	10.62	10.19

TABLE 4/5 (Continued).

Experiment.	Chloride ion concentration (Molar)	Observed $\log_{10} \alpha$ (Eqn 4/8)	Calculated $\log_{10} \alpha_{Hg}$ (Eqn 4/25)
C.			
pH 4.60,	5.0×10^{-1}	15.16	14.11
$C_Y = 1 \times 10^{-2}$ M	2.0×10^{-1}	14.52	12.83
	1.0×10^{-1}	14.21	12.47
	5.0×10^{-2}	14.00	12.41
	2.0×10^{-2}	13.94	12.43
	1.0×10^{-2}	12.90	12.45
D.			
pH 5.58,	4.0×10^{-1}	14.70	13.75
$C_Y = 2.13 \times 10^{-4}$ M.	2.0×10^{-1}	14.67	12.91
	1.0×10^{-1}	13.82	12.72
	4.0×10^{-2}	13.35	12.71

TABLE 4/6. Comparison of experimental alpha-coefficients with those calculated upon the assumption that mercuric chloride ethelynediamine tetra-acetate was present.

Experiment	Chloride ion concentration	$\log \alpha_{Hg}$ observed (calculated from Eqn 4/8	$\log \alpha_{Hg}$ calculated (calculated from Eqn 4/25	Difference observed -calculated
A.				
pH 2.68	5.0×10^{-3}	9.69	9.36	+ 0.36
$C_Y = 2 \times 10^{-3}$	2.0×10^{-3}	9.29	8.92	+ 0.37
Molar	1.0×10^{-3}	8.89	8.61	+ 0.28
	5.0×10^{-4}	8.43	8.30	+ 0.13
	1.6×10^{-4}	7.83	7.83	0.00
	6.0×10^{-5}	7.19	7.40	- 0.21
B.				
pH 3.42,	1.0×10^{-1}	12.86	12.56	+ 0.30
$C_Y = 1.10^{-2}$	5.0×10^{-2}	12.28	12.35	- 0.07
Molar	2.0×10^{-2}	12.06	11.99	+ 0.07
	1.0×10^{-2}	11.41	11.71	- 0.30
	5.0×10^{-3}	11.14	11.40	- 0.26
	2.0×10^{-3}	10.29	11.01	- 0.72
	1.0×10^{-3}	10.62	10.72	-0.10

TABLE 4/6. (Continued).

Experiment	Chloride ion concentration	$\log \alpha_{Hg}$ observed (calculated from Eqn 4/8)	$\log \alpha_{Hg}$ calculated (calculated from Eqn 4/25).	Difference observed -calculated
C. pH 4.60, $C_Y = 1.\times 10^{-2}$ Molar	5.0×10^{-1}	15.16	14.83	+ 0.33
	2.0×10^{-1}	14.52	14.44	+ 0.08
	1.0×10^{-1}	14.21	14.16	+ 0.05
	5.0×10^{-2}	14.00	13.87	+ 0.13
	2.0×10^{-2}	13.94	13.48	+ 0.46
	1.0×10^{-2}	12.90	13.20	- 0.30
D. pH 5.58, $C_Y = 2.13 \times 10^{-4}$ Molar	4.0×10^{-1}	14.70	14.57	+ 0.13
	2.0×10^{-1}	14.67	14.33	+ 0.34
	1.0×10^{-1}	13.82	14.13	-0.31
	4.0×10^{-2}	13.35	13.86	-0.41

TABLE 4/7. Analysis of variance of residual errors.

Source of Variation	Total sum of Squares	Degrees of Freedom	Mean Square	F	P
pH (Note 1).	4,148.29	2	2,074	2.05	25%
$[Cl]^-$	6,937.74	10	694	0.68	50%
error(Note 2)	9,106.71	9	1,012	-	-
Total	20,192.74	21	-	-	-

Note 1. The effect of pH is confused with that of ligand concentration but there are good chemical reasons for supposing that there will be no effect due to ligand concentration (see section 4.5.2.).

Note 2. error - interaction pH x $[Cl^-]$.

Note 3. S.S. due to pH = Total S.S. - S.S. within pH.

S.S. due to $[Cl^-]$ = Total S.S. - S.S. within $[Cl^-]$.

S.S. due to error = Total S.S. - S.S. due to pH - S.S. due to $[Cl^-]$.

Note 4(a) 23 results, 2 constants have been extracted, 21 degrees of freedom remain.

TABLE 4/7 (Continued).

Note 4(b) 4 different pH used - 3 degrees of freedom - one constant estimated ($K_{H\ HgCl\ EDTA}$) - 2 degrees of freedom remain.

(c) 12 different [Cl^-] used - 11 degrees of freedom - one constant estimated ($K_{HgCl\ EDTA}$) - 10 degrees of freedom remain.

N.B. S.S. = Sum of Squares.

TABLE 4/8. The minimum concentration of E.D.T.A. necessary for accurate substoichiometric analysis.

pH / pCl	0	1	2	3	4	5	6	7
0	19.7	16.7	14.0	12.1	10.9	9.6	7.8	6.4
1	18.7	15.7	13.0	11.1	9.9	8.6	6.8	5.6
2	17.7	14.7	12.0	10.1	8.9	7.6	6.0	6.2
3	16.7	13.7	11.0	9.1	7.5	6.2	6.0	6.6
4	15.4	12.4	9.7	7.8	6.2	5.8	6.0	6.6
5	13.7	10.7	8.0	6.4	5.8	5.8	6.0	6.6

The table gives values of the constant 'A' for use in the equation

$$\log_{10} C_Y = A + \log_{10} C_{Hg} + \log_{10} [Hg(HDz)_2]_{org.}$$

For example chloride concentration 10^{-2}M, excess mercury left in the aqueous phase 10^{-5}M, reagent concentration 10^{-6}M, pH 5.

Then $A = 7.6$, and

$$\log_{10} C_Y = 7.6 - 5 - 6 = -3.6$$

i.e., at least 4×10^{-4}M E.D.T.A. must be used.

TABLE 4/9. The effect of chloride interference on the activities extracted during neutron activation analysis.

Sample	Experiment A. first irradiation. no E.D.T.A. added.		Experiment B. second irradiation. E.D.T.A. added.	
	Chloride Interference Present.		Chloride Interference Absent.	
	Activity extracted in the first extraction.	Activity extracted in the second extraction.	Activity extracted in the first extraction.	Activity extracted in the second extraction.
Treated	248 c/s	186 c/s	240 c/s	238 c/s
Untreated	2.4 c/s	1.6 c/s	2.2 c/s	2.2 c/s

N.B. These two experiments were carried out on samples which had been irradiated separately and the activity in Experiment A are not expected to agree with those in Experiment B.

TABLE 4/10. The analysis of cereals for mercury by neutron activation analysis.

Sample	Result by the Substoichiometric method.	Best Result (Note).
Treated	4.9 ppm.	**4.6 p.p.m.**
Untreated	0.044 ppm	**0.044 p.p.m.**

Note: The mean result obtained by all those who collaborated with the International Atomic Energy Agency.

TABLE 4/11. The experimental results used to confirm equation 4/7.

$[S_2O_3^{2-}]$ Molar	pH	Q	$[H_2Dz]$ Molar	$\log_{10}\alpha_{Hg}$
1.14×10^{-2}	1.01	1.50	7.0×10^{-6}	18.03
2.24×10^{-2}	1.02	0.808	1.03×10^{-5}	18.65
4.34×10^{-2}	1.03	0.423	1.28×10^{-5}	19.15
7.60×10^{-2}	1.09	0.218	1.52×10^{-5}	19.70

TABLE 4/12. The experimental results used to confirm equation 4/8. (N.B. A_s = 985 c/s).

$[Cl^-]$ Molar	A_o c/s	A_a c/s	$[HgClHDz]$ Molar	$[Hg(HDz)_2]$ Molar	C_{Hg} Molar	$\log_{10} \alpha_{Hg}$
4.28×10^{0}	987	3933	4×10^{-8}	9.25×10^{-6}	3.79×10^{-5}	19.18
1.71×10^{0}	1045	3874	1.16×10^{-6}	8.92×10^{-6}	3.74×10^{-5}	16.01
8.56×10^{-1}	1119	3860	2.58×10^{-6}	8.21×10^{-6}	3.72×10^{-5}	14.66
4.28×10^{-1}	1204	3704	4.23×10^{-6}	7.39×10^{-6}	3.57×10^{-5}	13.57
1.71×10^{-1}	1369	3574	7.41×10^{-6}	5.80×10^{-6}	3.45×10^{-5}	12.16
8.56×10^{-2}	1436	3549	8.70×10^{-6}	5.16×10^{-6}	3.42×10^{-5}	11.37
4.28×10^{-2}	1433	3415	8.65×10^{-6}	5.18×10^{-6}	3.30×10^{-5}	10.76
1.71×10^{-2}	1510	3338	10.13×10^{-6}	4.44×10^{-6}	3.22×10^{-5}	9.74
8.56×10^{-3}	1539	3376	10.70×10^{-6}	4.16×10^{-6}	3.26×10^{-5}	9.08
1.71×10^{-3}	1532	3286	10.54×10^{-6}	4.23×10^{-6}	3.17×10^{-5}	7.68
8.56×10^{-4}	1539	3309	10.70×10^{-6}	4.16×10^{-6}	3.19×10^{-5}	7.08

TABLE 4/13. The composition of the buffers used in the experiments with both E.D.T.A. and chloride.

Experiment	pH	Concentration of disodium ethylenediaminetetraacetate	Concentration of ammonium acetate	Concentration of acetic acid	Concentration of perchloric acid
A	2.68	2×10^{-3}M	Nil	Nil	4×10^{-3}M
B	3.42	1×10^{-2}M	1×10^{-2}M	2×10^{-1}M	Nil
C	4.60	1×10^{-2}M	2×10^{-1}M	Nil	1×10^{-1}M
D	5.58	2.5×10^{-4}M	1×10^{-1}M	1×10^{-2}M	Nil

TABLE 4/14. The experimental results obtained when the aqueous phase contained both chloride and E.D.T.A.

Experiment	Chloride concentration $[Cl^-]$ Molar	Activity of the aqueous phase A_a c/s	Activity of the organic phase A_o c/s	Activity of the standard A_s c/s	Alpha coefficient $\log_{10} \alpha$ Hg.
A.					
pH 2.68	4.96×10^{-3}	3146	879.4	702.8	9.69
$C_Y = 2 \times 10^{-3}$M	1.96×10^{-3}	3170	815.8	702.8	9.29
	9.6×10^{-4}	3206	791.8	702.8	8.89
	4.6×10^{-4}	3217	778.1	702.8	8.43
	1.6×10^{-4}	3249	754.8	702.8	7.83
	5.9×10^{-5}	3266	743.5	702.8	7.19

TABLE 4/14 (Continued).

Experiment	Chloride concentration $[Cl^-]$ Molar	Activity of the aqueous phase A_a c/s	Activity of the organic phase A_o c/s	Activity of the standard A_s c/s	Alpha co-efficient $\log_{10} \alpha$ Hg
B.					
pH 3.42	1.0×10^{0}	1814	274.6	236.1	14.92
$C_Y = 1 \times 10^{-2}$M	5.0×10^{-1}	1733	293.4	236.1	13.91
	2.0×10^{-1}	1790	301.5	236.1	12.99
	1.0×10^{-1}	1813	277.2	236.1	12.86
	5.0×10^{-2}	1802	276.0	236.1	12.28
	2.0×10^{-2}	1846	257.8	236.1	12.06
	1.0×10^{-2}	1829	258.9	236.1	11.41
	5.0×10^{-3}	1903	252.9	236.1	11.14
	2.0×10^{-3}	1893	253.2	236.1	10.29
	1.0×10^{-3}	1848	242.0	236.1	10.62
C.					
pH 4.60	1.0×10^{0}	1899	324	303.4	15.65
$C_Y = 1 \times 10^{-2}$M	5.0×10^{-1}	1892	321	303.4	15.16
	2.0×10^{-1}	1895	318	303.4	14.52
	1.0×10^{-1}	1917	314	303.4	14.21
	5.0×10^{-2}	1939	310	303.4	14.00
	2.0×10^{-2}	1921	306	303.4	13.94
	1.0×10^{-2}	1928	308	303.4	12.90

TABLE 4/14 (Continued).

Experiment	Chloride concentration $[Cl^-]$ Molar	Activity of the aqueous phase A c/s a	Activity of the organic phase A c/s o	Activity of the standard A c/s s	Alpha co-efficient $\log_{10} \alpha_{Hg}$
D.					
pH 5.58					
$C_Y = 2.13 \times 10^{-4}$M	1.0×10^{0}	4152	964.1	886.6	15.29
	4.0×10^{-1}	4167	941.0	883.4	14.70
	2.0×10^{-1}	4226	918.7	886.7	14.67
	1.0×10^{-1}	4196	911.4	870.5	13.82
	4.0×10^{-2}	4219	891.8	865.3	13.35
	2.0×10^{-2}	4665	881.1	856.3	12.94

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CONTINUOUS SUBSTOICHIOMETRIC DETERMINATION OF TRACES OF MERCURY BY RADIOACTIVE ISOTOPE-DILUTION ANALYSIS*

G. B. BRISCOE, B. G. COOKSEY, J. RŮŽIČKA† and M. WILLIAMS‡
Department of Chemistry, The University of Aston in Birmingham, Birmingham 4, England

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Summary—The possibility of automating substoichiometric analysis by isotope dilution has been proposed previously. Automation where the analysis is based on solvent extraction has now been carried out experimentally. Preliminary experiments are described by means of which optimum conditions for this type of automated determination can be chosen and its reproducibility and selectivity checked. As an example traces of mercury down to 5×10^{-8} g are determined and the method is applied to the analysis of low-grade cinnabar ores.

IN recent years the substoichiometric determination of a number of metals by radioactive isotope dilution has been developed.[1] This method has attracted interest because though its sensitivity can be comparable with that of neutron-activation analysis, it eliminates the use of a nuclear reactor and the need for special handling facilities. In a preliminary communication,[2] the possibility of carrying out continuous substoichiometric analysis by isotope dilution was recently discussed. This procedure would have several advantages.

1. Safety precautions in a radiochemical laboratory aim to restrict radioactive contamination to a minimum. This is more easily achieved when the radioactive solutions are processed automatically by a machine.

2. In many methods of trace metal analysis the accuracy is limited at low metal concentrations (below about $10^{-6}M$) by the reproducibility of the blanks. In an automatic process every sample is treated identically so that reproducibility of blanks and calibration is guaranteed.

3. Preparation of the radioactive samples for counting is time-consuming and may lead to errors, especially when β-active samples are measured after evaporation on planchets. These difficulties are avoided in continuous analysis where flow-counters can be used.

It was pointed out[2] that continuous substoichiometry might be based on precipitation, complexation followed by ion-exchange, or solvent extraction. The present paper describes the experimental verification of the last possibility. Trace amounts of mercury have been determined by continuous isotope dilution with mercury-203, a substoichiometric amount of zinc dithizonate in carbon tetrachloride being used as the extraction reagent.

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† On leave from Department of Nuclear Chemistry, Faculty of Technical and Nuclear Physics, Prague 1, Břehová 7, Czechoslovakia.

‡ Present address: Learned Journals Division, Pergamon Press Ltd., Headington Hill Hall, Oxford, England.

EXPERIMENTAL

Reagents

These were prepared from analytical reagent grade chemicals.

Radioisotope. The isotope used was mercury-203, as the acetate, with a specific activity of 500 mc/g (Radiochemical Centre, Amersham, England). The material received from Amersham was diluted to give a mercury isotope solution of 500 μg/ml.

Standard labelled mercury solutions. Prepared by dilution of the mercury isotope solution with 1*M* nitric acid. Various concentrations were used according to the range of calibration required (*e.g.*, a 1-ppm standard gave a calibration graph covering the range 0·2–4·0 ppm of mercury).

Urea solutions, 1%. In water or $10^{-4}M$ sodium chloride.

Standard inactive mercury solutions. An approximately 0·05*M* solution of mercury(II) nitrate was prepared and standardized by Volhard's method.[3] This stock solution was diluted appropriately with 1*M* nitric acid.

Zinc dithizonate stock reagent. Prepared by dissolving 0·05 g of dithizone in 10 ml of ammonia solution (s.g. 0·880) and diluting to 100 ml, then extracting with carbon tetrachloride until the colour of the organic phase changed from brown to pale green. This purified aqueous solution (free from carbodiazone) was mixed with a solution of 0·05 g of zinc sulphate (heptahydrate) in 90 ml of water and 10 ml of glacial acetic acid, then extracted with 100 ml of carbon tetrachloride. The organic layer was filtered through a dry No. 41 Whatman paper and the zinc dithizonate concentration (*ca.* $5 \times 10^{-4}M$) determined (after 100-fold dilution) from its absorbance[4] at 538 mμ ($\varepsilon = 9{\cdot}2 \times 10^4$). The working solution was prepared by appropriate dilution of this stock reagent. A $2 \times 10^{-5}M$ solution is suitable for determination of mercury in the range 0·4–4 ppm.

Apparatus

Technicon AutoAnalyzer (Technicon Instruments Company Ltd., Hanworth Lane, Chertsey, Surrey, England). The system used comprised, as its main items, a two-speed proportioning pump, a sampler (Model II) and a strip-chart recorder (Bristol Dynamaster Model 570 single point, as supplied by Technicon).

Scintillation counter. The detector used was a 2 × 2 in. NaI(Tl) well-type crystal: well-diameter 1 in., volume 20 ml. This was associated with a single channel gamma-ray spectrometer (9000 Series, Research Electronics Ltd., Cleckheaton, Yorkshire, England). In all experiments a setting of discriminator voltage corresponding to 50 keV was used. This gave a background counting rate of 10 cps. The output from the ratemeter (Model 9030) was fed into the strip-chart recorder. Satisfactory results were obtained with this combination only when no earth connection was used in the recorder; otherwise the recorder pen oscillated violently. If a matched ratemeter/recorder combination is used, this difficulty should not arise.

Flow-cell. Made from 32 cm of 3·5-mm outside diameter soda glass tubing, wound into a coil, 2·2 cm in diameter and 2 cm high, which fitted into the well of our scintillation counter.

The arrangement of apparatus shown in the flow diagram (Fig. 1) resulted from all our investigations on continuous substoichiometry and was that used for the final analytical procedure. During the development of the method there was no dilution, *in situ*, of a more stable concentrated zinc dithizonate working solution with carbon tetrachloride: zinc dithizonate reagents of appropriate strength (see Figs. 2–5) were used directly.

Sampler II is programmed to deliver alternately samples (for 5 min) and 1*M* nitric acid wash-solution (for 1 min). The samples (or nitric acid wash solution) and standard labelled mercury solutions were driven by the proportioning pump (A) into the first single mixing coil (B) where isotopic exchange occurred. Urea solution, added to prevent oxidation of the organic reagent by nitrous fumes, was mixed with the solution from B in the second single mixing coil (C). The zinc dithizonate reagent was now added and this final mixture passed through the special extraction coil (D),[5] where solvent extraction took place. The two phases were separated in the electrolyte trap (E), the activity of the organic phase being continuously measured in the flow-cell (F) and recorded by the strip-chart recorder.

Development of Method

The determination of mercury with dithizone was chosen for this work because a manual substoichiometric method by isotope dilution had previously been developed.[6] Otherwise it would have been necessary, with the aid of the theory of substoichiometry,[1] to select a suitable extraction reagent and to investigate the influence of pH and time of extraction. In either case the following routine tests must be carried out whenever a substoichiometric determination by solvent extraction is being automated.

Choice of reagent concentration

The apparatus is set up as in Fig. 1 but with 1*M* nitric acid replacing the samples. During this experiment the concentration of the zinc dithizonate reagent is increased in a series of steps, from pure solvent to excess of reagent relative to the concentration of mercury in the labelled standard solution (Fig. 2).

The pumping action is started and the first level of activity registered (Fig. 2, plateau *c*) represents the quantity of mercury extracted by pure solvent. For successful substoichiometry this level must not be different from that of plateau *b*. As the concentration of reagent is increased, increasing amounts of activity are extracted (plateaux *d*, *e*, *f*, *g*) from the labelled standard solution until an

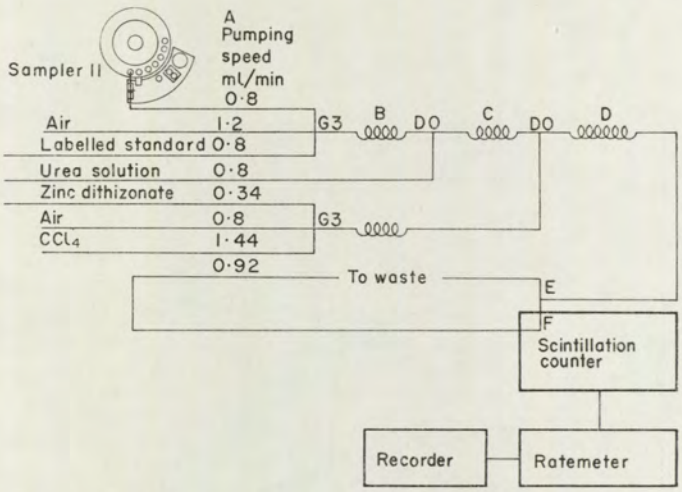

FIG. 1.—Flow diagram for continuous substoichiometric determination of mercury with the Technicon AutoAnalyzer.

excess of reagent extracts all the mercury and no further increase in activity is possible (*g*, *h*). For a substoichiometric separation any concentration of reagent could be used (*d*, *e*, *f*) which is below this limit. However, the concentration chosen (*f*) should be as high as possible so that the amount of mercury extracted minimizes statistical variations in the counting procedure. There is no need to repeat this experiment every time new reagents are prepared. The concentration of the proposed reagent should merely be checked by ensuring that it extracts less activity from the standard labelled mercury solution than is extracted by a solution of zinc dithizonate concentrated enough to give an excess of reagent with certainty.

Adsorption problems. The difference between plateaux *a* (background of the scintillation counter alone) and *b* (background of scintillation counter with flow-cell in the well), both recorded before any liquid is introduced into the apparatus, is caused by contamination of the flow cell from previous experiments. This is small for a glass flow-cell (negligible at first, but building up slowly over *ca.* 1 month, after which it is best to replace the cell and allow its activity to decay before reuse) but is important when plastic cells are used: most plastics strongly adsorb metal dithizonates (Tygon, Solvaflex, Acidflex and polythene were all useless in practice). Because of this adsorption it is necessary to use Acidflex tubing instead of the Solvaflex tubing normally recommended for pumping organic solvents (both tubings available from Technicon). Solvaflex tubing will remove all the zinc dithizonate from the reagent for several hours after pumping has started; even with Acidflex it is necessary to wait a short time (*ca.* 10 min) for adsorption losses to come to equilibrium and a constant activity to be registered. The time needed to register plateaux *a*, *b* and *c* is, however, very short (*ca.* 30 sec).

Stability of reagent

Very dilute (10^{-6} to $10^{-8}M$) solutions of organic reagents are often unstable. For automated substoichiometry the stability of such reagents is more critical than in the corresponding manual methods, because standards and samples are not processed simultaneously.

To test for reagent stability in the determination of mercury, the apparatus was arranged to deliver a substoichiometric reagent concentration. If the reagent is stable there should be no observable decrease, even after several hours, in the activity extracted. Figure 3 shows such a test with dithizone or zinc dithizonate as the extraction reagent. Clearly, zinc dithizonate is much more stable than dithizone and so it was used in all subsequent experiments.

In the present case the stability of the extraction reagent limits the sensitivity of the method and in order to determine 5×10^{-8} g of mercury it is necessary to dilute, *in situ*, a more stable concentrated zinc dithizonate working solution with carbon tetrachloride as shown in Fig. 1.

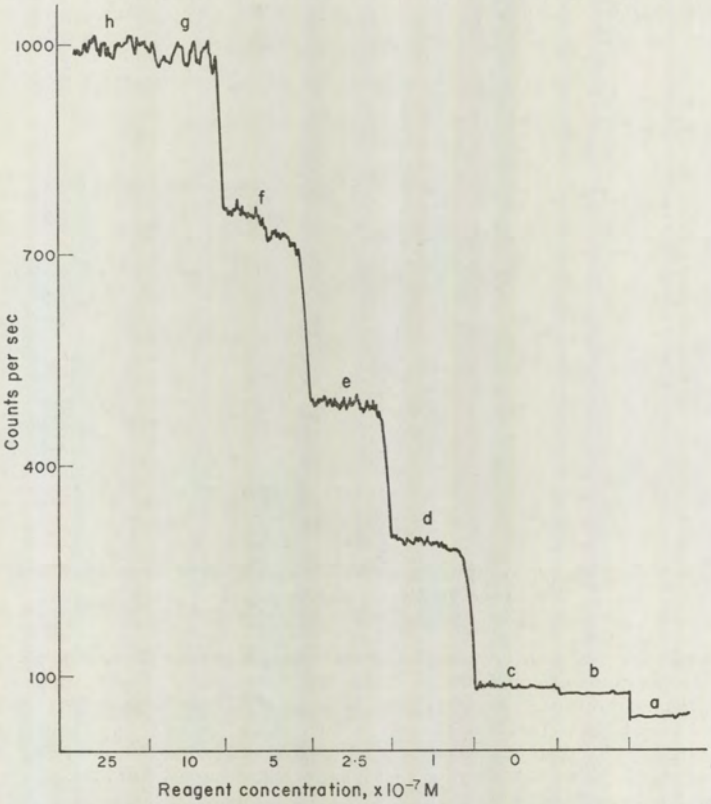

Fig. 2.—Extraction plateaux obtained with different concentrations of zinc dithizonate solution (standard labelled mercury solution: $3 \times 10^{-7}M$).

Time of extraction

It is important to check that extraction is complete in the time allowed by the AutoAnalyzer system. This is easily done by inserting a second extraction coil and seeing if there is any change in the activity extracted. It is particularly important to check this when a metal complex is used as the extraction reagent.

Choice of sampling rate

The maximum sampling rate depends primarily on the time required to replace with new solution all the old solution in the flow-cell and the electrolyte trap. This can be determined by measuring the time necessary (t_b min) for 95% of the maximum deflection to be registered on the strip-chart recorder. The maximum sampling rate is then $60/t_b$ samples/hr. For the arrangement shown in Fig. 1, t_b is 6 min, giving a maximum sampling rate of 10 samples/hr.

The sampling rate can be increased in two ways.

1. By increasing the rate at which the organic phase is pumped; however, if the sensitivity is to be maintained under such conditions, a more dilute extraction reagent would have to be used and this might be unstable. For a given sensitivity the stability of the extraction reagent limits the maximum sampling rate that can be used.

2. By reducing the size of the flow-cell, but this would reduce the counting efficiency and hence the sensitivity.

The compromise represented by Fig. 1 gives a high sensitivity but a low sampling rate.

Interferences

The effect of interferences on the extraction was investigated by using solutions of various cations (as their nitrates or sulphates), anions (as their potassium, sodium or ammonium salts) and other substances (*e.g.*, hydrogen peroxide) in the cups of Sampler II. Figure 4 shows the results of some of these studies. An interference is represented by any change in the otherwise constant activity extracted

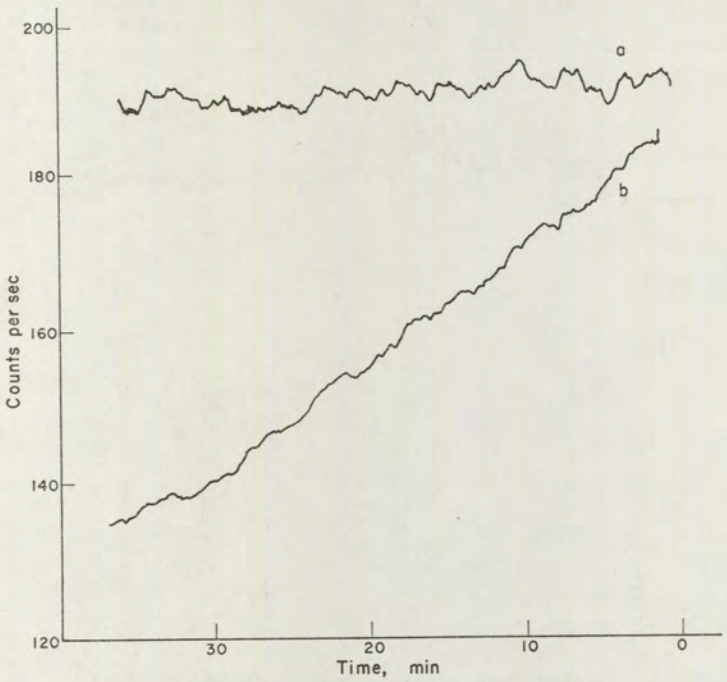

FIG. 3.—Stability of extraction reagent.
a—Zinc dithizonate ($1 \times 10^{-6}M$).
b—Dithizone (initially $2 \times 10^{-6}M$).
(Standard labelled mercury solution: $2 \times 10^{-5}M$).

from the standard labelled mercury solution (*e.g.*, palladium and chloride in Fig. 4). Table I summarizes the results for 58 ions and compounds.

It should be possible to overcome most interferences fairly easily and, for routine analysis, automatically. Cations can be masked with a suitable reagent; oxidizing and reducing agents can be destroyed with say hydrogen peroxide. Thus, silver and bismuth should be complexed with chloride and EDTA. Permanganate, dichromate and chlorate should be reduced with hydrogen peroxide or iron(II) sulphate. Tin(II), platinum(II), sulphite and hypophosphite should all be oxidized by hydrogen peroxide.

The anions in the last column of Table I present a more serious difficulty, particularly chloride, which is almost impossible to remove at the very low concentrations where interference is still encountered (calculated to be down to about 0·001 ppm). These anions appear to form ternary complexes of the type Cl·Hg·HDz[7] (H_2Dz = dithizone) so that a given amount of zinc dithizonate could extract twice as much mercury from solutions containing them as from solutions in which mercury is extracted as the primary dithizonate, $Hg(HDz)_2$. This will lead to an increase in the activity extracted, in contrast with other interferences (*e.g.*, palladium in Fig. 4) which cause a decrease.

It can be predicted theoretically that interference from chloride will be overcome if its concentration is between 6×10^{-5} and $6 \times 10^{-3}M$, under which condition all mercury is present as mercury(II) chloride. This has been confirmed experimentally and we recommend the use under all circumstances

of a 1% urea solution in $10^{-4}M$ sodium chloride. This method is, of course, only satisfactory if an empirical calibration graph is constructed. The chemistry of the reactions is being investigated more fully and will be reported at a later date.

Calibration graph

The calibration graph (Fig. 5) was prepared by using standard inactive mercury solutions in the cups of Sampler II. A fresh calibration graph should be prepared whenever new reagents are made up, particularly when the method given above to overcome interference from chloride is used. If a very large amount (*ca.* $1M$) of bisulphate or nitrate is present, a similar amount should be added to the standard inactive mercury solution to compensate for their small but noticeable interference.

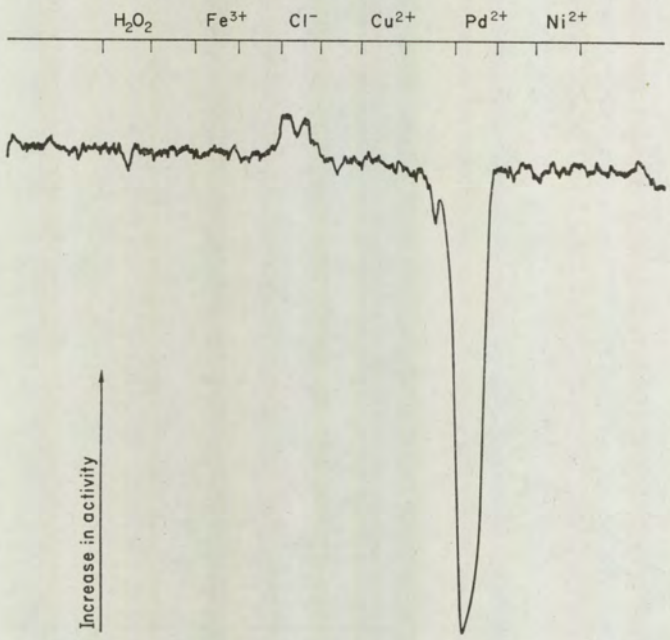

FIG. 4.—Effect of foreign ions (conditions as detailed in Table I).

As can be seen from Fig. 5, as little as $2{\cdot}5 \times 10^{-7}$ g of mercury in 5 ml of solution (0·05 ppm) can be determined (in a 6-min run 4·8 ml of sample solution are consumed). The lowest amount of mercury we have determined by this method is 5×10^{-8} g in 5 ml (0·01 ppm).

Analysis of Test Samples

In order to demonstrate the usefulness of the method, we analysed several samples of low-grade cinnabar ore which had previously been analysed spectrophotometrically for mercury at the Warren Spring Laboratory.

One g of ore (received as fine powder and used directly) was refluxed for 30 min with 25 ml of sulphuric acid (s.g. 1·84) and 1 g of potassium nitrate. After cooling and dilution, 1 g of urea was added, the mixture filtered through a No. 42 Whatman paper, and the filtrate diluted to 250 ml in a calibrated flask.

The solution was analysed with the apparatus as shown in Fig. 1, using the following solutions: standard labelled mercury solution—$5 \times 10^{-6}M$; urea solution—1% in $10^{-4}M$ sodium chloride; zinc dithizonate working solution—$5 \times 10^{-6}M$. The AutoAnalyzer was run at a rate of 5 samples/hr, and gave the results shown in Table II.

DISCUSSION

Our results for the determination of mercury in the low-grade cinnabar ores (Table II) by continuous substoichiometry are in good agreement with the spectrophotometric results, though for Sample 3 there was disagreement with the spectrophotometric values reported by Warren Spring Laboratory. For the determination

TABLE I.—STUDY OF INTERFERENCES*†

Substances which do not interfere at a concentration of 1000 ppm	Metals which interfere by competing with mercury for the zinc dithizonate	Ions which interfere by oxidizing zinc dithizonate	Substances which interfere by complexing mercury	Ions which interfere by reducing mercury to metal	Anions which interfere by forming ternary complexes
NH_4^+ Se^{4+} SO_4^{2-}	Au^{3+}	MnO_4^-	CN^-¶	Sn^{2+}¶	Cl^-
K^+ Te^{4+} ClO_4^{2-}	Pd^{2+}	$Cr_2O_7^{2-}$	SCN^-	$N_2H_5^+$‡	Br^-
Na^+ Tl^+ Acetate	Pt^{2+}	NO_2^-	I^-		HPO_2^-
Mg^{2+} Cr^{3+} Citrate	Pt^{4+}‡	ClO_3^-‡‡	SO_3^{2-}		HSO_4^-**
Ca^{2+} Mn^{2+} Tartrate	Ag^+‡	Ce^{4+}¶	$S_2O_3^{2-}$¶		NO_3^-††
Ba^{2+} Fe^{2+} Oxalate	Bi^{3+}‡		F^-¶		
Al^{3+} Fe^{3+} Borate			EDTA‡		
Ga^{3+} Co^{2+} Molybdate					
In^{3+} Ni^{2+} $S_2O_8^{2-}$					
Ce^{3+} Cu^{2+} H_3PO_4					
Th^{4+} Zn^{2+} H_2O_2					
Sb^{3+} Pb^{2+}					
As^{3+} Be^{2+}					

* Standard labelled mercury solution: $2{\cdot}5 \times 10^{-6}M$; zinc dithizonate working solution: $5 \times 10^{-7}M$; acidity $1N$ in HNO_3 (chosen so as to overcome the known interference from Bi^{3+} and Cu^{2+}) except during the examination of H_2SO_4 and HNO_3 when the total acidity varied from 0·01 to $10N$.

† Any ion or substance changing the activity extracted by more than 1% is assumed to interfere; concentrations down to 0·1 ppm or less interfere unless stated otherwise.

‡ Interferes if present in excess of 100 ppm.

¶ Investigated only at 1000 ppm.

** Interferes if present in excess of $0{\cdot}05M$.

†† Interferes if present in excess of $0{\cdot}5M$; interference from using $1M$ HNO_3 as a working medium can be compensated for by adding it to the standards used for calibration.

‡‡ Interferes if present in excess of 10 ppm.

of traces of mercury with dithizone, continuous substoichiometry is more sensitive by an order of magnitude than spectrophotometry as judged by comparing Fig. 5 with spectrophotometric data.[8]

The advantages of the automatic method mentioned earlier should be weighed against the disadvantages which are now evident. First, there is a slow contamination of parts of the instrument (tubing, nipples, glass coils, *etc.*) by adsorption of radiomercury. Secondly, the automatic method is less sensitive than manual substoichiometry (by about one order of magnitude in the case of mercury) because the flow-cell is small and the organic phase passes rapidly through it. Fortunately radioisotopes of other metals are available with higher specific activities than that of mercury-203, many of them as carrier-free isotopes. This should permit determination of these metals at even lower concentrations than in the case of mercury.

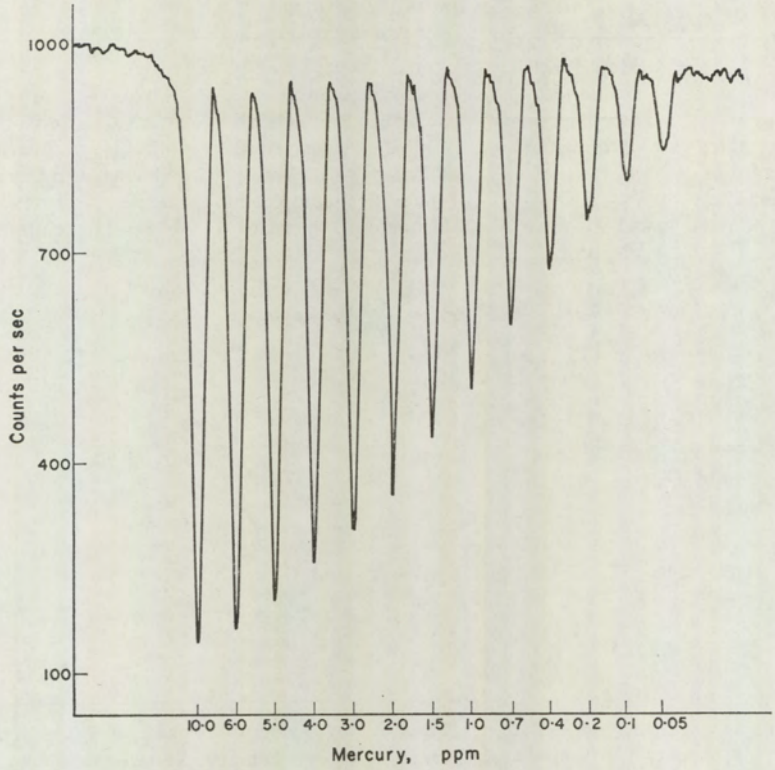

Fig. 5.—Calibration graph for determination of mercury (standard labelled mercury solution: $5 \times 10^{-6}M$; zinc dithizonate solution: $7 \times 10^{-7}M$).

Table II.—Analysis of low-grade cinnabar ores*

Method of analysis	Mercury, %			
	Sample 1	Sample 2	Sample 3	Sample 4
Continuous substoichiometry†	0·017	0·064	0·069	0·030
Spectrophotometry in this laboratory†‡	0·021	0·071	0·066	0·036
Spectrophotometry at Warren Spring Laboratory¶	0·020	0·068	0·045	0·033

* Provided by Dr. P. G. Jeffery, Warren Spring Laboratory, Ministry of Technology, Stevenage, Herts., England.
† Results are the average of duplicate analyses.
‡ Using the Unicam SP600 and dithizone; sample dissolution as for continuous substoichiometry.
¶ Using dithizone screened with EDTA and KSCN; sample dissolution as for continuous substoichiometry.

Because the volume which can be sampled by the AutoAnalyzer is small (maximum of 10 ml), an increase in sensitivity by increasing the sample volume would entail a preliminary extraction. However, this disadvantage could be outweighed by introduction of the radioisotope before the preliminary extraction. Because isotope-dilution analysis is being used, this preliminary separation need not then be quantitative. As the radioisotope is not being introduced into the AutoAnalyzer continuously, the strip-chart records and their evaluation would differ from those discussed above.

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Zusammenfassung—Vor kurzem wurde die Möglichkeit angegeben, die unterstochiometrische Analysenmethode durch Isotopenverdünnung zu automatisieren. Bei einer auf flüssig-flüssig-Extraktion beruhenden Analyse wurde die Automation jetzt experimentell verifiziert. Es werden Vorversuche angegeben, durch die die optimalen Bedingungen für diese Art automatischer Analyse ausgewählt und deren Reproduzierbarkeit und Selektivität geprüft werden können. Als Beispiel werden Quecksilbermengen bis herunter zu 5×10^{-8} g bestimmt und die Methode auf die Analyse geringwertiger Zinnober-Erze angewandt.

Résumé—On a proposé antérieurement la possibilité d'automatiser l'analyse substoechiométrique par dilution isotopique. On a maintenant réalisé expérimentalement l'automatisation pour les cas où l'analyse est basée sur une extraction par solvant. On décrit des expériences préliminaires au moyen desquelles on peut choisir les conditions optimales pour ce type de détermination automatisée et vérifier la reproductibilité et la sélectivité. A titre d'exemple, on dose des traces de mercure pouvant descendre jusqu'à 5×10^{-8} g et applique la méthode à l'analyse de minerais de cinabre pauvres.

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Mercuric Chloride Dithizonate: Its Reactions, Properties, and Stability Constant

By **G. B. Briscoe*** and **B. G. Cooksey**, Department of Chemistry, The University of Aston in Birmingham. Gosta Green, Birmingham 4

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Mercuric Chloride Dithizonate: Its Reactions, Properties, and Stability Constant

By G. B. Briscoe* and B. G. Cooksey, Department of Chemistry, The University of Aston in Birmingham. Gosta Green, Birmingham 4

Dithizone reacts with an excess of mercuric chloride to form mercuric chloride dithizonate, not primary mercuric dithizonate. The reactions of mercuric chloride dithizonate are studied and its solubility, extinction coefficient, partition coefficient, and stability constant are measured.

In a previous paper [1] we noted that chloride interferes in the substoicheiometric determination of mercury and attributed this interference to the formation of mercuric chloride dithizonate: ClHgSC(:N·NHPh)·N:NPh or HgClHDz.

This substance has been prepared by Webb and his co-workers [2] by mixing, in the correct proportions, solutions of mercuric chloride and dithizone in diethyl ether. The present paper describes the reactions and properties of this substance and the determination of its stability constant.

EXPERIMENTAL

Reagents.—These were prepared from analytical reagent grade chemicals.

Mercuric perchlorate solutions. These were prepared by dissolving mercuric oxide in perchloric acid. They were standardised by titration with EDTA using a urotropine buffer (pH 4) and Xylenol Orange indicator.

[1] G. B. Briscoe, B. G. Cooksey, J. Růžička, and M. Williams, *Talanta*, 1967, **14**, 1457.

[2] J. L. A. Webb, I. S. Bhatia, A. H. Corwin, A. G. Sharp, *J. Amer. Chem. Soc.*, 1950, **72**, 91.

Dithizone and Zinc dithizonate solutions. Prepared by dissolving dithizone (0·05 g.) in ammonia solution (10 ml.) (*d* 0·880) and diluting to 100 ml., then extracting with carbon tetrachloride until the colour of the organic phase changed from brown to pale green. When dithizone solutions were required this purified aqueous solution was acidified with 1M-hydrochloric acid and extracted with 100 ml. of carbon tetrachloride. The organic phase, filtered through a dry No. 41 Whatman paper, was about 1×10^{-3}M. When zinc dithizonate was required the purified aqueous solution was mixed with a solution of zinc sulphate (heptahydrate) (0·05 g.) in water (90 ml.) and glacial acetic acid (10 ml.), then extracted with carbon tetrachloride (100 ml.). The organic phase, filtered as above, was about 5×10^{-4}M.

Mercuric dithizonate. A solution of dithizone (0·5 g.) in 0·1M-sodium hydroxide (50 ml.) was added dropwise to a solution of mercuric oxide (0·3 g.) dissolved in 1M-perchloric acid (100 ml.). The precipitate was filtered off and dried in a vacuum-desiccator. This product is the monohydrate $Hg(HDz)_2,H_2O$, having a solubility in carbon tetrachloride of 2×10^{-3}M. Refluxing the monohydrate with carbon tetrachloride in a Dean and Stark apparatus gave the anhydrous salt $Hg(HDz)_2$ having a solubility in carbon tetrachloride of 1×10^{-2}M. Analysis of the monohydrate by the Dean and Stark method gave 0·19% H_2O; the theoretical value for $Hg(HDz)_2,H_2O$ is 0·25% H_2O.

Radioisotopes. The isotopes used were mercury-203, as the acetate, with a specific activity of 500 mc/g., and chlorine-36, as sodium chloride, with a specific activity of 850 μc/g. (Radiochemical Centre, Amersham).

The mercury-203 solution was used to label a 1×10^{-4}M-solution of mercuric perchlorate and a $1{\cdot}35 \times 10^{-3}$M-solution of mercuric chloride.

The labelled sodium chloride solution received from Amersham was evaporated to dryness, the residue weighed, redissolved and diluted to 50 ml. ($\equiv 1{\cdot}3 \times 10^{-2}$M). All experiments involving chlorine-36 used solutions of this specific activity.

Apparatus.—Nucleonic equipment. The scintillation counter used for the measurement of the mercury-203 activity was a 3 × 3 in. NaI(Tl) well type crystal. This was associated with a single channel γ-ray spectrometer. In all experiments a setting of discriminator voltage corresponding to 50 kev was used.

The chlorine-36 activity was measured either by evaporation on to planchets and counting with an end-window Geiger–Müller detector (window thickness 2 mg./cm.^{2}) or by means of a liquid scintillation spectrometer using NE 220 scintillator.

Spectrophotometer. The spectra and absorbancies were measured with a Unicam SP 600 spectrophotometer.

Filter paper. Whatman No 41, carefully dried, was used.

The Reaction between Mercuric Chloride and Dithizone.—A solution of dithizone in carbon tetrachloride (*ca.* 2×10^{-3}M) was standardised by taking 8·0 ml. of a $2{\cdot}5 \times 10^{-3}$M-solution of mercuric perchlorate in 0·1M-perchloric acid and titrating it with the dithizone solution. The end point was determined spectrophotometrically. Accurate results can be obtained only when the organic phase used for the spectrophotometry is returned to the separating funnel in which the reaction is conducted. This is due to the formation of mercuric chloride dithizonate in the initial stages of the titration owing to contamination by traces of chloride. During the titration this substance is destroyed and at the end point primary mercuric dithizonate alone is present (see ' The reaction between dithizone and mercuric chloride dithizonate ').

An excess of mercuric perchlorate solution (15 ml. of $2{\cdot}5 \times 10^{-3}$M) and potassium chloride solution (1 ml. of 2×10^{-1}M) were shaken for 15 min. with 9·0 ml. of the standardised dithizone solution. This causes the complete precipitation of mercuric chloride dithizonate. The organic phase was discarded and the aqueous phase centrifuged to remove the precipitate. The amount of mercury remaining in the aqueous phase was determined by a spectrophotometric titration exactly as in the standardisation of the dithizone solution. In three experiments it was found that 1 mole of dithizone reacted with 0·97, 1·02, and 0·95 mole of mercuric chloride to form mercuric chloride dithizonate.

The Solubility of Mercuric Chloride Dithizonate in Carbon Tetrachloride.—This solubility has been determined by two methods. In the first, carbon tetrachloride was saturated with solid mercuric chloride dithizonate and the absorbance at 480 mμ of the resulting solution measured. In the second a 2×10^{-4}M-solution of dithizone was shaken with an excess of labelled mercuric chloride and the activity of the filtered organic phase measured. Both experiments were conducted at 23°. The solubility as determined spectrophotometrically was $2{\cdot}0 \times 10^{-5}$M and radiochemically was $2{\cdot}1 \times 10^{-5}$M.

The Extraction of Chlorine into the Organic Phase.—An aqueous phase (5 ml.), 1M in nitric acid, and containing various amounts of mercuric nitrate and labelled sodium chloride solution, was extracted with 5 ml. of a 7×10^{-5}M-solution of zinc dithizonate in carbon tetrachloride or with 5 ml. of carbon tetrachloride. The organic phase was filtered, an aliquot portion evaporated to dryness on a planchet and the activity measured. The results are given in Table 1.

TABLE 1

The distribution of chlorine between the organic and aqueous layers

Mercury added (μg.)	Chloride added (μg.)	Chloride in organic layer (μg.)	Conditions
156	24·3	3·5	Excess $HgCl_2$; 50% Hg extracted
156	24·3	3·1	Excess $HgCl_2$; 50% Hg extracted
78	24·3	0·04 *	No H_2Dz; CCl_4 only
78	12·2	0·2 *	Excess H_2Dz; 50% H_2Dz used
31·2	486	0·1 *	Excess H_2Dz; 50% H_2Dz used
4·46	486	0·01 *	Excess H_2Dz; 5% H_2Dz used

* Limit of detection.

The Reaction between Dithizone and Mercuric Chloride Dithizonate. A solution of mercuric chloride dithizonate was prepared by shaking a 2×10^{-5}M-solution of dithizone in carbon tetrachloride with an excess of a 5×10^{-2}M-mercuric chloride solution. This solution was washed with 0·1M-perchloric acid and filtered to remove any mercuric chloride solution present as droplets of aqueous phase. A measured excess of the dithizone solution (as above) was added to the purified solution and the excess remaining estimated from the absorbance at 620 mμ. In five individual experiments, 1 mole of mercuric chloride dithizonate was found to react with 0·95, 0·93, 0·92, and 0·95 mole of dithizone.

The Reversion of Mercuric Chloride Dithizonate to Dithizone with Iodide or Thiocyanate.—A purified mercuric chloride

dithizonate solution was prepared as in the previous experiment. This was shaken with 5 ml. of 0·1M-perchloric acid in which 1 g. of either sodium iodide or sodium thiocyanate was dissolved. The dithizone liberated was estimated from the absorbance at 620 mμ. When iodide was used, 92% of the dithizone was recovered; with thiocyanate 98% was recovered.

The Suppression of Chloride Interference by Thiosulphate and EDTA.—A mercuric ion solution (5 ml.) ($1·0 \times 10^{-4}$M), dissolved in any one of: (*a*) 0·1M-perchloric acid, (*b*) 0·25M-sodium EDTA, (*c*) $1·0 \times 10^{-2}$M-sodium thiosulphate in 1·0M-ammonium acetate, was added to 20 ml. of a $2·75 \times 10^{-4}$M labelled sodium chloride solution. The mixture was extracted with 25 ml. of a $3·1 \times 10^{-5}$M-solution of primary mercuric dithizonate in carbon tetrachloride. The organic phase was filtered and 20 ml. shaken with 5 ml. of a 0·01M-borax solution. This solution was filtered and the activity of 2 ml. determined. Any mercuric chloride dithizonate was converted into sodium chloride which does not quench the liquid scintillator used. This counting method was preferred to planchet counting as it gave the most reproducible results.

The amount of chloride extracted in the presence of either thiosulphate or EDTA was not statistically significant when compared with the background.

The Extraction Constant for the Formation of Mercuric Chloride Dithizonate.—Excess of chloride was added to the labelled mercuric perchlorate solution to give 1×10^{-4}M-solutions of mercuric perchlorate and mercuric chloride having the same specific activities. From 1·0 ml. to 25·0 ml. of the murcury solution was diluted to 25 ml. with perchloric acid to give a final acidity of 0·01M, 0·1M, or 1·0M. Each of these solutions was shaken for 15 min. with 10 ml. of a 5×10^{-6}M-solution of zinc dithizonate in carbon tetrachloride. The organic phase was filtered and the activity of a 5 ml. aliquot determined.

The extraction constant was calculated by comparing the activities extracted in the presence and absence of chloride.

The Partition Coefficient of Mercuric Chloride, at 25°.—The organic phase produced by shaking 10 ml. of the $1·35 \times 10^{-3}$M labelled mercuric chloride solution with 200 ml. of carbon tetrachloride was filtered through a paper impregnated with carbon tetrachloride. This was carried out by soaking the paper successively with mixtures of alcohol and carbon tetrachloride containing 10%, 20% *etc.* to 100% carbon tetrachloride. These impregnated papers were used to prevent the extraction of mercuric chloride by water absorbed by the normal papers. The filtered organic phase was shaken with 10 ml. of water and the activities, A_1 and A_2, of 5 ml. of the aqueous phases from both extractions, measured. The partition coefficient $P(HgCl_2)$ was calculated from:

$$1/P(HgCl_2) = [(A_1/A_2) - 1](V_{org}/V_{aq})$$

where V_{org} = volume of the organic phase and V_{aq} = volume of the aqueous phase from the second extraction.

This is a modification of Sandells [5] method.

The Extraction Constant of Mercuric Chloride Dithizonate using Chlorine-36.—In two experiments 10 ml. of 0·1M-perchloric acid was mixed with 1, 2, or 5 ml. of the $1·31 \times 10^{-4}$M labelled chloride solution. In a third experiment 5 ml. of 0·1M-perchloric acid was mixed with 10 ml. of the same labelled chloride solution. Each mixture was made up to 16·0 ml. after the addition of 1·0 ml. of a $1·0 \times 10^{-4}$M-mercuric perchlorate solution, and shaken for 15 min. with 10 ml. of an 8×10^{-5}M-mercuric dithizonate solution in carbon tetrachloride. The organic phase was filtered and 2 ml. evaporated to dryness. The residue was dissolved in 2 ml. of dioxan, mixed with 10 ml. of NE 220 scintillator, and the activity measured.

The Partition Coefficient of Mercuric Chloride Dithizonate, at 23°.—To 10 ml. of a 2×10^{-5}M primary mercuric dithizonate solution in carbon tetrachloride was added 1·8 l. of an aqueous solution 0·1M in mercuric chloride, 0·4M in sodium perchlorate, and 0·1M in perchloric acid. The mixture was shaken for 10 min. and the two phases were separated and filtered. The aqueous phase was then shaken with 5·0 ml. of carbon tetrachloride, the two phases were separated, and this second organic phase was filtered. The absorbance of both organic phases was measured at 480 mμ and the partition coefficient calculated from the ratio of these absorbancies.

An attempt was made to determine the partition coefficient of primary mercuric dithizonate in a similar manner, substituting 2×10^{-3}M primary mercuric dithizonate solution in carbon tetrachloride for the first organic phase and omitting the mercuric chloride from the aqueous phase.

RESULTS AND DISCUSSION

The Evidence for the Formation of Mercuric Chloride Dithiozonate.—Several lines of evidence suggest that dithizone reacts with mercuric chloride to form mercuric chloride dithizonate and not primary mercuric dithizonate as is formed with mercuric nitrate and perchlorate.

(1) Reaction of dithizone with an increasing excess of labelled mercury, and plotting a graph of the activity of the organic phase *versus* the activity of the aqueous phase gives, in the absence of chloride, a horizontal straight line, characteristic of a high extraction constant. In the presence of chloride a curve is obtained, characteristic of a low extraction constant. At high mercuric chloride concentrations the amount of mercury extracted tends to twice the amount extracted in the absence of chloride because dithizone reacts with twice as much mercury when forming mercuric chloride dithizonate (I) as when forming primary mercuric dithizonate (II). From these curves (Figure 1) it was first implied the interference of chloride in the substoicheiometric determination of mercury was due to mercuric chloride dithizonate.

(I) ClHgSC(:N·NHPh)·N:NPh or HgClHDz

(II) PhN:N·(PhNH·N:)CSHgSC(:N·NHPh)·N:NPh or $Hg(HDz)_2$

(2) When concentrated (*ca.* 10^{-3}M) solutions of dithizone react with mercuric chloride a precipitate is formed; this does not happen with mercuric nitrate or perchlorate. This precipitate is mercuric chloride dithizonate whose solubility in carbon tetrachloride is only 2×10^{-5}M. When this precipitate is formed mercury reacts with dithizone in a molar ratio of 1 : 1 not 1 : 2 as when primary mercuric dithizonate is formed.

(3) When mercuric chloride is labelled with chlorine-36 and reacts with dithizone in carbon tetrachloride,

activity is found in the organic phase. This is not due to isotopic exchange between chloride and carbon tetrachloride, or to the partition of mercuric chloride because when the dithizone is omitted no activity is extracted, (Table 1).

The Reactions of Mercuric Chloride Dithizonate.—Mercuric chloride dithizonate reacts with dithizone to form primary mercuric dithizonate:

$$HgClHDz + H_2Dz \rightleftharpoons Hg(HDz)_2 + H^+ + Cl^-$$

This reaction explains why mercuric chloride dithizonate is not encountered when determining traces of mercury by the spectrophotometric dithizone method. In this method an excess of dithizone is used and the chloride dithizonate is destroyed; in the substoicheiometric method an excess of mercury is used and special precautions must be taken to prevent the interference of chloride.

Mercuric chloride dithizonate can be reverted to dithizone in the same manner as primary mercuric dithizonate[3] by using a reagent (*e.g.*, iodide or thiocyanate) which forms a very strong complex with the mercuric ion. On the other hand a reagent can be selected (*e.g.*, thiosulphate or EDTA) which will decompose the chloride dithizonate but not the primary dithizonate. This is the basis of one method of overcoming the interference of chloride in the substoicheiometric determination of mercury.

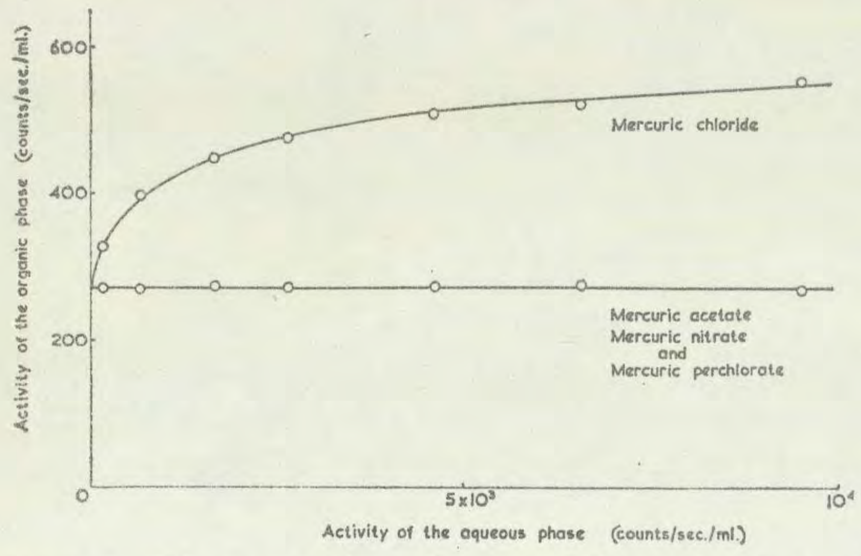

FIGURE 1 The extraction of mercury from mercuric salts by dithizone

When shaken with alkaline solutions the chloride dithizonate is converted rapidly and completely into secondary mercuric dithizonate:

$$HgClHDz + OH^- \rightleftharpoons HgDz + H_2O + Cl^-$$

Even distilled water is sufficiently alkaline to accomplish this conversion. This is in complete contrast to the primary dithizonate which once formed reacts only slowly and incompletely with 1M-alkali.[4]

The Spectra and Extinction Coefficient of Mercuric Chloride Dithizonate.—When primary mercuric dithizonate (orange) is converted into mercuric chloride dithizonate (yellow) there is only a slight change in colour. The two spectra are compared in Figure 2. The extinction coefficient of mercuric chloride dithizonate is 37,000 at the absorption maximum of 480 mμ.

The Extraction Constant of Mercuric Chloride Dithizonate.—The activity extracted by a fixed amount of dithizone, from a solution containing an excess of labelled mercuric perchlorate was measured. The

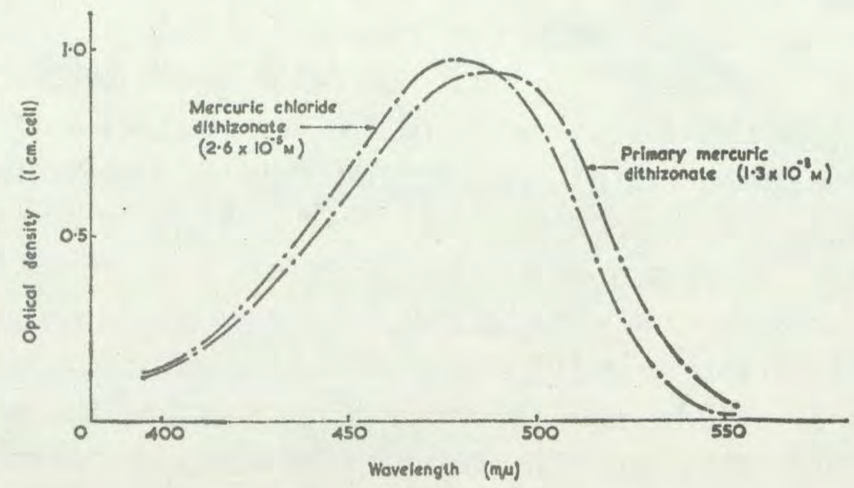

FIGURE 2 The spectra of mercuric chloride dithizonate and primary mercuric dithizonate

measurement was repeated with the addition of enough chloride to convert all the mercury into mercuric chloride. The extraction constant was calculated by comparing these activities. Let A_1 = the activity of 5 ml. of the aqueous phase which contained chloride, after extraction with dithizone; A_2 = the activity of 5 ml. of the organic phase in equilibrium with the aqueous phase containing chloride; and A_3 = the activity of 5 ml. of the organic phase in equilibrium with the aqueous phase not containing chloride. Then, $E(HgClHDz) = 4(A_2 - A_3)^2/A_1(2A_3 - A_2)$

where $E(HgClHDz) = [HgClHDz]_{org}^2/[HgCl_2][Hg(HDz)_2]_{org}$

the equilibrium constant for the reaction

$$HgCl_2 + Hg(HDz)_{2(org)} \rightleftharpoons 2HgClHDz_{(org)}$$

where 'org' denotes the organic phase, in this case carbon tetrachloride.

The mean of the experimental results is 0·83 and their standard deviation is 0·19. (Table 2). In calculating these values the results 0·21 and 0·24 have been discarded because the interference of chloride is greatly magnified when the concentration of mercury in the aqueous phase is very low.

Contamination of the reagents with chloride is the most serious source of error in these experiments. If the results are corrected for the small amount of chloride believed to be present, the constant is raised from 0·83 to 1·3. However, because of the arbitrary nature of this correction, the experimentally determined value of 0·83 has been used in subsequent calculations. Other possible sources of error are the partition of mercuric chloride and the formation of secondary mercuric dithizonate, (HgDz). The spectra of the organic phase did not show the presence of secondary mercuric dithizonate even in the experiments carried out at pH 2. The partition coefficient of mercuric chloride

$$P(HgCl_2) = [HgCl_2]_{org}/[HgCl_2]$$

[3] H. Irving and R. S. Ramakrishna, *Analyst*, 1960, **85**, 860.

[4] G. Iwantscheff, 'Das Dithizon und seine Anwendung in der Mikro-und Spurenanalyse,' p. 106, Verlag Chemie, Weinheim, 1958.

between water and carbon tetrachloride has been measured. The observed value, $1{\cdot}0 \times 10^{-3}$ (twenty four results with a standard deviation of $0{\cdot}4 \times 10^{-3}$) is too low to affect the results reported in Table 2.

This extraction constant has also been determined using chlorine-36 to measure the amount of mercuric chloride dithizonate in the organic phase. The measured activity will depend, in this case, on the amount of inactive chloride in the aqueous phase, originating from the reagents, *i.e.*, the blank. If y = the amount of inactive chloride in the tests; x = the amount of active chloride added; s = the specific activity of the active chloride used; z = the amount of chloride extracted into the organic phase as mercuric chloride dithizonate; and A = the measured activity corresponding to z, then the specific activity of the chloride in the test will be $sx/(y + x)$ so that $A = zsx/(y + x)$ or $1/A = (1/sz) + (y/szx)$.

A series of tests were carried out in which x varied (*i.e.*, $x_1, x_2, \cdots x_n$) giving a corresponding series of values of A ($A_1, A_2, \cdots A_n$). In these tests z was kept constant by using a fixed amount of mercury in the aqueous phase and a fixed concentration of primary mercuric dithizonate in the organic phase. From the intercept of a plot of $1/A_n$ *versus* $1/x_n$, z was determined and hence the extraction constant of mercuric chloride dithizonate calculated.

The experimental results lie on a very poor straight line, and so this estimate of z is subject to a large error. The deviation of the results from a straight line is due to a variation in the amount of inactive chloride in the aqueous phase and this blank can be determined by treating the results in a different manner. Consider two tests using different amounts of active chloride. Then

$$A_1 = zsx_1/(y + x_1) \text{ and } A_2 = zsx_2/(y + x_2)$$

Eliminating z and s gives

$$y = (A_2 - A_1)/[(A_1/x_1) - (A_2/x_2)]$$

The results (Table 3) show that there are variations in the amount of inactive chloride present in the tests, which account for the large variations in the estimates of E(HgClHDz). However, the results are consistent with those obtained with mercury-203.

The Partition Coefficient of Mercuric Chloride Dithizonate.—The partition coefficient of mercuric chloride dithizonate between water and carbon tetrachloride has been determined by Sandell's [5] method. The measured value (Table 4) is higher than Duncan's result [6] for primary mercuric dithizonate, 3×10^3 ($\log_{10} P = 3{\cdot}48$). This is the reverse of the order expected and an attempt was made to determine the partition coefficient of primary mercuric dithizonate also. Unfortunately the amount of primary dithizonate dissolved in the aqueous phase was very much smaller than the amount present as suspended droplets of the first organic phase which had not been removed by filtration. As the filtration was improved the apparent ' partition coefficient ' increased (Table 4). We can only conclude that the partition coefficient of primary mercuric dithizonate is greater than 10^6 ($\log_{10} P = 6$).

Another explanation for these results is the adsorption of the primary dithizonate on the filter paper. The thicker filters adsorbing the dithizonate more completely. If this were the true explanation, then suc-

TABLE 2

The extraction constant of mercuric chloride dithizonate using ^{203}Hg at 23°

Acidity of the aqueous phase $[H^+]$ (M)	Reagent concentration in CCl_4 $[H_2Dz]$ (M)	Equilibrium concentration of mercuric chloride, in the aqueous phase $[HgCl_2]$ (M)	Activity of aqueous phase (counts/sec.) A_1	Activity of organic phase containing HgClHDz (counts/sec.) A_2 (corrected for background = 10 counts/sec.)	Activity of organic phase not containing HgClHDz (counts/sec.) A_3	Extraction constant E(HgClHDz)
1·0	$2{\cdot}56 \times 10^{-4}$	$4{\cdot}1 \times 10^{-5}$	89·7	344·1	280·0	0·82
,,	$2{\cdot}80 \times 10^{-5}$	$1{\cdot}7 \times 10^{-6}$	47·6	421·6	392·1	0·21
,,	,,	$1{\cdot}2 \times 10^{-5}$	331·2	521·0	392·1	0·74
,,	,,	$3{\cdot}1 \times 10^{-5}$	874·6	588·7	392·1	0·88
,,	,,	$8{\cdot}9 \times 10^{-5}$	2476·0	640·8	392·1	0·63
0·1	$2{\cdot}52 \times 10^{-5}$	$3{\cdot}6 \times 10^{-5}$	648·4	350·0	224·0	1·00
,,	$2{\cdot}54 \times 10^{-5}$	$4{\cdot}8 \times 10^{-6}$	91·4	295·2	239·3	0·75
,,	,,	$1{\cdot}6 \times 10^{-5}$	307·6	342·3	239·3	1·03
,,	,,	$3{\cdot}6 \times 10^{-5}$	676·5	378·5	239·3	1·16
,,	,,	$9{\cdot}5 \times 10^{-5}$	1798·1	412·8	239·3	1·01
0·01	$2{\cdot}68 \times 10^{-5}$	$2{\cdot}0 \times 10^{-6}$	52·8	393·7	362·5	0·24
,,	,,	$1{\cdot}3 \times 10^{-5}$	348·3	472·2	362·5	0·55
,,	,,	$3{\cdot}1 \times 10^{-5}$	844·9	527·5	362·5	0·68
,,	,,	$9{\cdot}0 \times 10^{-5}$	2397·0	595·7	362·5	0·70

TABLE 3

The extraction constant of mercuric chloride dithizonate using ^{36}Cl; at 23°

Experiment	Inactive chloride (blank) (μg.)	Extraction constant
A (3 tests)	4·2	2·0
	6·9	
B (3 tests)	11·8	0·8
	7·4	
C (4 tests)	9·7	0·2
	8·3	
	5·3	

[5] R. W. Geiger and E. B. Sandell, *Analyt. Chim. Acta*, 1953, 8, 197.

[6] J. F. Duncan and F. G. Thomas, *J. Chem. Soc.*, 1960, 2814.

cessive filtrates, from the same aqueous phase through the same filter paper, should contain increasing amounts

TABLE 4

The partition coefficient of mercuric chloride dithizonate and primary mercury dithizonate (logarithmic values)

Type of filter	Mercuric chloride dithizonate	Primary mercuric dithizonate
No. 41 Whatman paper	4·15; 4·16; 4·16; 4·09; 4·08; 4·09; 4·13; 4·14; 4·09; 4·10; 3·98	4·13; 4·26; 4·43; 4·45; 4·68; 4·70; 4·74; 4·76; 4·80; 4·83; 4·86; 4·87; 4·91; 4·92; 4·92; 5·00; 5·04; 5·04; 5·19; 4·92; 4·92; 4·76
	Mean = 4·11	Mean = 4·78
	s = 0·05	s = 0·25
No. 42 Whatman paper	4·24; 4·23; 4·22; 4·27; 4·15; 4·15; 4·14; 4·15; 4·28; 4·05; 3·96; 4·10	5·29; 5·29; 5·30; 5·36; 5·40; 5·41; 5·42; 5·42; 5·52; 5·41
	Mean = 4·16	Mean = 5·38
	s = 0·09	s = 0·07
Thick pad	4·29; 4·50; 4·00; 4·19; 4·30; 4·32; 4·20; 4·48; 4·53; 4·46	6·04; 6·27; 6·04; 5·95
	Mean = 4·33	Mean = 6·08
	s = 0·17	s = 0·14

of dithizonate, because a filter paper which has already adsorbed some mercuric dithizonate from the first filtrate will adsorb less from the second. This is exactly the behaviour observed with mercuric chloride dithizonate and thick filter pads. The first filtrate giving $P = 30{,}000$, the second $P = 22{,}000$, and the third $P = 19{,}000$. This final result should be compared with that obtained with No. 41 and No. 42 papers when all the filtrates gave the result $P = 14{,}000$. With primary mercuric dithizonate however, no evidence of adsorption was obtained.

The Extraction Constant of Primary Mercuric Dithizonate.—In order to calculate the stability constant of mercuric chloride dithizonate an accurate value for the extraction constant of primary mercuric dithizonate is required.

$$E[\mathrm{Hg(HDz)_2}] = [\mathrm{Hg(HDz)_2}]_{org}[\mathrm{H^+}]^2/[\mathrm{H_2Dz}]_{org}{}^2[\mathrm{Hg^{2+}}]$$

which is the equilibrium constant for the reaction

$$\mathrm{Hg^{2+}} + 2\mathrm{H_2Dz_{(org)}} \rightleftharpoons 2\mathrm{H^+} + \mathrm{Hg(HDz)_{2\,org)}}$$

Many authors have reported values of this constants[6-9] but the results have been calculated in different ways using different values for the stability constants of the mercuric halides. We have recalculated these values (Table 5) by substituting the experimental results obtained by these authors into the equation:

$$E[\mathrm{Hg(HDz)_2}] = \frac{[\mathrm{Hg(HDz)_2}]_{org}[\mathrm{H^+}]^2\left(1 + \sum_{n=1}^{n=4}\beta_n[\mathrm{X}]^n\right)}{[\mathrm{H_2Dz}]_{org}{}^2 C_{\mathrm{Hg}}}$$

where C_{Hg} = the total concentration of all forms of mercury in the aqueous phase,

$$= [\mathrm{Hg^{2+}}] + [\mathrm{HgX}] + [\mathrm{HgX_2}] + [\mathrm{HgX_3}] + [\mathrm{HgX_4}];$$

$\mathrm{X} = \mathrm{Cl^-}$ or $\mathrm{Br^-}$ or $\mathrm{I^-}$;

$\beta_n = [\mathrm{HgX}_n]/[\mathrm{Hg^{2+}}][\mathrm{X}]^n$.

TABLE 5

Recalculated logarithmic values for the extraction constant of primary mercuric dithizonate

Author	Halide anion used: Chloride	Bromide	Iodide
Pilipenko	24·63	25·93	26·80
Kato	27·27	—	26·90
Breant	—	—	26·83
Duncan	26·23	—	—

The values of β_n we have used in our calculations are those of Marcus.[10] The values of $E[\mathrm{Hg(HDz)_2}]$ obtained by Pilipenko[7] have also been corrected for the partial ionization of sulphuric acid.[11] The results Pilipenko obtained using chloride are low owing to a gross ionic strength effect from the high concentration of sulphuric acid (3M). These results have not been included in the calculation for the best value of $\log_{10} E[\mathrm{Hg(HDz)_2}]$. The mean of all the other values is 26·66, the mean result by any one author using any one halide being treated as a single result. The 95% confidence limits of this value are 26·15—27·17, based on variance between these results.

The Stability Constant of Mercuric Chloride Dithizonate.—The stability constant of mercuric chloride dithizonate is given by:

$$K(\mathrm{HgClHDz}) = [\mathrm{HgClHDz}]/[\mathrm{Hg^{2+}}][\mathrm{Cl^-}][\mathrm{HDz^-}]$$

corresponding to the reaction

$$\mathrm{Hg^{2+}} + \mathrm{Cl^-} + \mathrm{HDz^-} \rightleftharpoons \mathrm{HgClHDz}$$

where the reactants and product are in the aqueous phase.

This can be calculated from the equation:

$$K(\mathrm{HgClHDz})^2 = \frac{E(\mathrm{HgClHDz})\beta_2(\mathrm{Cl^-})E[\mathrm{Hg(HDz)_2}]}{P(\mathrm{HgClHDz})^2 E(\mathrm{HDz})^2}$$

where $E(\mathrm{HgClHDz}) = 0{\cdot}83$, $\beta_2(\mathrm{Cl^-}) = 10^{13{\cdot}22}$ (ref. 10), $E[\mathrm{Hg(HDz)_2}] = 10^{26{\cdot}66}$, $P(\mathrm{HgClHDz}) = 1{\cdot}4 \times 10^4$, and $E(\mathrm{HDz}) = [\mathrm{H^+}][\mathrm{HDz^-}]/[\mathrm{H_2Dz}]_{org} = 1{\cdot}6 \times 10^{-9}$ (ref. 12); these values give $\log_{10} K(\mathrm{HgClHDz}) = 24{\cdot}55$.

Ternary Complexes in Substoicheiometric Solvent Extraction.—Substoicheiometry has two advantages over conventional analytical methods;[13] it is more sensitive and more selective. However, we have shown in this paper that chloride interferes in the

[7] A. T. Pilipenko, *Zhur. analit. Khim.*, 1953, **8**, 286.
[8] M. Breant, *Bull. Soc. chim. France*, 1956, 948.
[9] T. Kato, S. Takei, and A. Okagami, *Japan Analyst*, 1956, **5**, 689.
[10] Y. Marcus, *Acta Chem. Scand.*, 1957, **11**, 599.
[11] T. F. Young, L. F. Maranville, and H. M. Smith, in 'The Structure of Electrolyte Solutions,' ed. W. J. Hamer, Wiley, New York, 1959, p. 51.
[12] H. Irving and C. F. Bell, *J. Chem. Soc.*, 1952, 1216.
[13] J. Růžička and J. Starý, Atomic Energy Review, I.A.E.A., Vienna, 1964, **2**, 3.

substoicheiometric method but not in the conventional method. Even if the interference of chloride is overcome (by adding thiosulphate or EDTA) the conditional extraction constant [14] will be reduced, reducing the selectivity of the method, its sensitivity, and its advantages over conventional analysis.

This is no isolated case. We have evidence for other similar complexes, mercuric nitrate dithizonate, mercuric bromide dithizonate, mercuric chloride diethyldithiocarbamate, gold chloride dithizonate, gold chloride diethyldithiocarbamate, palladium chloride dithizonate, and palladium chloride diethyldithiocarbamate. Compounds such as these present difficulties to the analyst and if it is intended to estimate a metal by substoicheiometric solvent extraction a check should be carried out to ensure that the addition of common anions do not increase the amount of metal extracted.

Summary of the Constants Determined in this Paper.—(i). The extraction constant of mercuric chloride dithizonate at 23°

$$E(\mathrm{HgClHDz}) = [\mathrm{HgClHDz}]_{org}^{2}/[\mathrm{HgCl_2}][\mathrm{Hg(HDz)_2}]_{org} = 0{\cdot}83$$

[14] A. Ringbom, 'Complexation in Analytical Chemistry,' ch. VII, Interscience, New York, 1963.

(ii) The partition coefficient of mercuric chloride dithizonate between water and carbon tetrachloride at 23°

$$P(\mathrm{HgClHDz}) = [\mathrm{HgClHDz}]_{org}/[\mathrm{HgClHDz}] = 1{\cdot}4 \times 10^{4}$$

(iii) The stability constant of mercuric chloride dithizonate

$$K(\mathrm{HgClHDz}) = [\mathrm{HgClHDz}]/[\mathrm{Hg^{2+}}][\mathrm{Cl^-}][\mathrm{HDz^-}] = 3{\cdot}5 \times 10^{24}\ \mathrm{l.^2\ mole^{-2}}$$

(iv) The solubility of mercuric chloride dithizonate in carbon tetrachloride at 23° is 2×10^{-5}M.

(v) The extinction coefficient at $\lambda_{max.}$ 4800 Å of mercuric chloride dithizonate dissolved in carbon tetrachloride at 23°

$$\varepsilon(\mathrm{HgClHDz}) = 37{,}000$$

(vi) The partition coefficient of mercuric chloride between water and carbon tetrachloride at 25°

$$P(\mathrm{HgCl_2}) = [\mathrm{HgCl_2}]_{org}/[\mathrm{HgCl_2}]_{aq} = 1 \times 10^{-3}$$

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