# A SECONDARY DITHIZONE COMPLEX CONTAINING BOTH SILVER AND MERCURY

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The analytical reagent dithizone  $(1,5\text{-diphenyl-3-mercaptoformazan}; (I), H_2Dz)$  is known to form a series of primary dithizonates,  $M(HDz)_n$  (where M is a cation of charge  $n+)^1$ . X-Ray structural determinations for M = Hg(II), Cu(II) and Ni(II) show clearly that a proton has been removed from the thiol form of each dithizone ligand and that coordination is completed through a nitrogen atom<sup>2-4</sup>. This is illustrated by the structure (II) of the mercury(II) complex.



In the presence of excess of metal and/or at higher pH values, several metals will form secondary dithizonates to which formulae such as  $Ag_2Dz$ , HgDz, PdDz and CuDz have been ascribed<sup>1</sup> although the molecular complexity and structures remain to be determined. Their formation involves the replacement of the hydrogen from the imino group, :NH, of the ligand as well as from the thiol group. Freiser and Freiser have suggested recently<sup>5</sup> that the secondary copper complex is derived from copper(1) but a similar explanation can scarcely be extended to the silver complex.

The tendency of the imino-hydrogen to ionise is considerably increased if the sulphur atom of dithizone is bound to an alkyl group or to a metal<sup>6</sup> and the interesting possibility arises that in a primary complex  $M(HDz)_n$  the imino-hydrogens might be partly or wholly replaced by a different metal, M', to give mixed secondary complexes such as  $M(M'Dz)_j (HDz)_{n-j}$  for the case where M' is univalent. In fact when a yellow solution of primary mercury dithizonate ( $\lambda_{max}$ , 490 nm) is shaken with a concentrated neutral aqueous solution of silver nitrate, a magenta colour develops and the organic phase now has  $\lambda_{max}$  512 nm (Fig. 1). This observation originally made in these laboratories by Sahota<sup>7</sup> in 1963 is further studied in the present paper.

The possibility that silver ions had merely displaced mercury(II) ions to give a solution containing some primary silver dithizonate (for which  $\lambda_{max} = 470$  nm)

$$2 \operatorname{Ag}^{+} + \overline{\operatorname{Hg}(\operatorname{HDz})}_{2} \rightleftharpoons 2 \overline{\operatorname{Ag}(\operatorname{HDz})} + \operatorname{Hg}^{2+}$$
(1)

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is inconsistent with the observed bathochromic shift, for mixtures of primary mercury and silver dithizonates ought to absorb with a maximum between 470 and 490 nm. (Here and subsequently a horizontal superscript line is used to distinguish species in the organic phase.) However, the possibility of some interaction between these



Fig. 1. Absorption spectra of dithizonates: (1)  $2.5 \cdot 10^{-5}$  M primary silver dithizonate, AgHDz; (2)  $1.25 \cdot 10^{-5}$  M primary mercury dithizonate, Hg(HDz)<sub>2</sub>; (3)  $1.25 \cdot 10^{-5}$  M solution of magenta complex, Hg(AgDz)<sub>2</sub>. The open circles are values of absorbances calculated from the data in Table IV, Series 2.

individual complexes to give a different, magenta-coloured species demanded investigation. Although successful analytical determinations of mercury in the presence of silver (and vice versa) have been reported<sup>1</sup>, these cannot be taken as conclusive proofs of the absence of any interaction in view of the very small shift in absorption maxima which could well have been overlooked.

Starting from a solution of pure dithizone in chloroform of known concentration, solutions of primary mercury dithizonate, Hg(HDz)<sub>2</sub>, and of primary silver dithizonate, Ag(HDz), were prepared by equilibration with aqueous solutions of the appropriate salts at the optimum pH value<sup>1</sup>. The absorbance of each solution and that of 1:1 mixtures,  $A_m$ , was determined and compared with that calculated,  $A_c$ , on the assumption that Beer's law holds and that there is no molecular interaction. Results are shown in Tables I and II. These results show that the deviations from additivity as measured by  $(A_m - A_c)$  exceed the experimental error and they are not distributed randomly with wavelength, for there is a definite trend from negative to positive values. Such changes would be consistent with a small displacement of the equilibrium shown in eqn. (1) from right to left by excess of mercury ions, with the formation of some mercury dithizonate ( $\lambda_{max}$ , 490 nm;  $\varepsilon_{max}$ , 6.8 · 10<sup>4</sup>) from silver dithizonate ( $\lambda_{max}$ , 470 nm;  $\varepsilon_{max}$ , 3.1 · 10<sup>4</sup>). We believe that these small differences do arise from excess mercury retained in the organic phase, for the primary mercury dithizonate was prepared by equilibrating a fixed amount of dithizone with a 20%excess (Table I) and 250% excess (Table II) of mercury (II) chloride, whose solubility in chloroform is well established.

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# TABLE I

THE ABSORBANCES OF MIXTURES OF ca. 1.25 · 10<sup>-5</sup> M Hg (HDz)<sub>2</sub> with an equal volume of ca. 2.5 · 10<sup>-5</sup> M Ag (HDz) in chloroform

Wavelength (nm)	Measured absorbances			Calculated absorbance*	Difference $(A = A)$
	$A_{\rm Hg}$	$A_{A_B}$	A <sub>m</sub>	A,	Verm = viel
470	0.717	0.819	$0.751 \pm 0.006$	0.768	-0.017
475	0.768	0.810	$0.773 \pm 0.005$	0.789	-0.016
480	- 0.802	0.790	$0.787 \pm 0.004$	0.796	- 0.009
485	0.835	0.765	$0.789 \pm 0.004$	0.800	-0.011
490	0.850	0.725	$0.785 \pm 0.006$	0.783	+0.002
495	0.850	0.673	$0.763 \pm 0.005$	0.762	$\pm 0.001$
500	0.825	0.610	$0.723 \pm 0.004$	0.718	+0.005
505	0.784	0.537	$0.668 \pm 0.005$	0.661	+ 0.007
510	0.740	0.447	0.603 + 0.006	0.593	+0.010

 ${}^{\bullet}A_{c} = (A_{Hg} + A_{Ag})/2$ . The mean value and its standard deviation,  $\sigma$ , were calculated from independent determinations on four samples (see experimental section).

#### TABLE II

THE ABSORBANCES OF MINTURES OF ca, 7.5 · 10 ° <sup>6</sup> M Hg(HDz)<sub>2</sub> with an equal nolume of ca, 2.0 · 10 ° <sup>5</sup> M Ag(HDz)<sub>2</sub>

Wavelength (nm)	Measured absorbances			Calculated	Difference
	Aits	Ane	A <sub>m</sub>	A <sub>c</sub>	$(\Lambda_m - \Lambda_c)$
470	0.432	0.612	0.476 ± 0.021	0.522	- 0.046
475	0.455	0.606	$0.492 \pm 0.021$	0.531	- 0.039
480	0.472	0.594	$0.506 \pm 0.018$	0.533	- 0.027
485	0.487	0.578	$0.511 \pm 0.017$	0.533	- 0.022
490	0.490	0.551	$0.509 \pm 0.016$	0.521	-0.012
495	0.485	0.515	$0.500 \pm 0.012$	0.500	0
500	0.464	0.466	$0.475 \pm 0.009$	0.465	+ 0.010
505	0.436	0.408	$0.440 \pm 0.006$	0.422	+ 0.018
510	0.396	0.350	$0.397 \pm 0.005$	0.373	+ 0.024
515	0.347	0.283	$0.347 \pm 0.003$	0.315	+0.032
520	0.294	0.255	$0.292 \pm 0.002$	0.260	+ 0.032

\* See note to Table I.

In a third set of experiments (Table III) mercury(II) nitrate was used in place of the chloride and only a 10% excess was employed. The differences  $(A_m - A_c)$  now lie within experimental error although the consistent negative bias is unexplained.

It will be obvious that no errors are likely in normal analytical practice, for dithizone will usually be in excess. In substoicheiometric determinations<sup>4</sup>, errors can occur from the formation of the species Cl-Hg-HDz when the concentration of chloride ions is high; but this species will not occur under the conditions we have used.

TABLE III

THE ABSORBANCE OF MIXTURES OF *ca*.  $0.9 \cdot 10^{-5} M \text{ Hg}(\text{HDz})_2$  with an equal volume of *ca*.  $1.8 \cdot 10^{-5} M \text{ Ag}(\text{HDz})_2$ 

Wavelength (nm)	Measured absorbances			Calculated	Difference
	A <sub>11µ</sub>	1	Λ <sub>m</sub>	$\Lambda_{c}$	$(r_{in} - r_c)$
470	0.520	0.569	$0.522 \pm 0.014$	0.545	-0.023
475	0.549	0.564	$0.538 \pm 0.013$	0.557	- 0.019
480	0.575	0.548	$0.544 \pm 0.016$	0.562	-0.018
485	0.596	0.530	$0.547 \pm 0.012$	0.563	-0.016
490	0.606	0.508	$0.544 \pm 0.015$	0.557	-0.013
495	0.606	0.465	$0.525 \pm 0.012$	0.536	-0.011
500	0.583	0.420	$0.494 \pm 0.008$	0.502	- 0.008
505	0.556	0.367	$0.455 \pm 0.009$	0.462	- 0.007
510	0.509	0.308	$0.406 \pm 0.009$	0.409	-0.003
515	0.453	0.252	$0.352 \pm 0.006$	0.353	- 0.001
520	0.387	0.196	0.297 + 0.005	0.292	+ 0.005

<sup>a</sup> Sec note to Table 1.

Since molecular interaction between primary dithizonates of silver and mercury cannot account for the formation of a magenta colour, we next consider the hypothesis that silver ions react according to eqn. (2):

$$\overline{Hg(HDz)}_2 + Ag^+ \rightleftharpoons \overline{HgDz} + \overline{Ag(HDz)} + H^+$$
(2)

for the absorption maximum of secondary mercury dithizonate, HgDz, has been reported as 515 nm in carbon tetrachloride<sup>1</sup>, so that its formation could account for the magenta colour. An even higher value, *viz.* 530 nm, has been found for a pure specimen dissolved in chloroform<sup>9</sup>. We do not believe this to be the sole reaction or even the main reaction for the following reasons.

1. The magenta-coloured solution, though sensitive to light, requires several minutes exposure to bright sunlight for the change to yellow : under the same illumination, solutions of secondary mercury dithizonate turn yellow within 30 sec.

2. In neutral or acid solution, solutions of primary mercury dithizonate are very slow to react with mercury(II) ions to give the secondary dithizonate. There seems no good reason why silver ions should react so much faster.

In the presence of excess of silver ions, primary silver dithizonate is readily converted to the secondary dithizonate, AgDz, which is only sparingly soluble, and its formation is evident from the formation of a violet precipitate. This would effectively drive eqn. (2) to the right and may give rise to some HgDz; but it is considered that the magenta colour is due mainly to the formation of a mixed complex according to eqn. (3).

$$\overline{Hg(HDz)}_2 + 2Ag^+ \Longrightarrow \overline{Hg(AgDz)}_2 + 2H^+$$
(3)

Unfortunately, it has not proved possible to devise conditions under which the magenta complex is the sole reaction product. In preliminary experiments, it was

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found that the extent of conversion of yellow primary mercury dithizonate to the magenta complex increases with the (excess) concentration of silver ions in the aqueous phase. However, there is a concomitant increase in the formation of insoluble secondary silver dithizonate, so that the effective concentration of the magenta species passes through a maximum. The presence of silver in the organic phase was an unambiguous proof of the presence of dissolved complexes containing this element and their nature followed from the following determinations.

Solutions of primary mercury dithizonate in chloroform were equilibrated with excess of silver ions in an aqueous phase and the magenta-coloured organic phase was separated and centrifuged to remove any suspended secondary silver dithizonate or other insoluble material. Three aliquot portions were then analysed. In one portion, total mercury  $[Hg]_T$ , and total silver,  $[Ag]_T$ , were determined after the solvent had been removed and the organic ligand destroyed by wet oxidation. In a second portion, total dithizone,  $[H_2Dz]_T$ , was determined by reversion. The third portion was equilibrated with 0.1 M sulphuric acid and the concentrations of extractable mercury,  $[Hg]_{ext}$ , and silver  $[Ag]_{ext}$ , were determined. Under these conditions it was shown that primary silver dithizonate and primary mercury dithizonate were unaffected whereas the secondary complexes react as follows:

$$\overline{Ag_2Dz} + H^+ \rightarrow \overline{Ag(HDz)} + Ag^+$$
(4)

$$2HgDz + 2 H^+ \rightarrow Hg(HDz)_2 + Hg^{2+}$$
(5)

and

$$\overline{\text{Hg}(\text{AgDz})}_2 + 2 \text{ H}^+ \rightarrow \overline{\text{Hg}(\text{HDz})}_2 + 2 \text{ Ag}^+$$
(6)

We can therefore write:

$$[\overline{Ag}]_{ext} = [\overline{Ag_2Dz}] + 2[\overline{Hg}(\overline{AgDz})_2]$$
(7)

$$[\overline{Hg}]_{ext} = 0.5 [\overline{HgDz}]$$
(8)

We also have the following mass balances:

$$[\overline{Ag}]_{T} = [\overline{Ag(HDz)}] + 2[\overline{Ag_{2}Dz}] + 2[\overline{Hg(AgDz)}_{2}]$$
(9)

$$[\overline{Hg}]_{T} = [\overline{Hg(HDz)}_{2}] + [\overline{HgDz}] + [\overline{Hg(AgDz)}_{2}]$$
(10)

$$[\overline{H_2Dz}]_T = [\overline{Ag(HDz)}] + [\overline{Ag_2Dz}] + 2[\overline{Hg(HDz)}_2] + [\overline{HgDz}] + 2[\overline{Hg(AgDz)}_2]$$
(11)

As pointed out above, little primary silver dithizonate can survive in the presence of a large excess of silver(I) and the term [Ag(HDz)] in eqns. (9) and (11) can be neglected.

• From eqns. (7) and (9) we obtain:

$$\left[\overline{\mathrm{Hg}(\mathrm{AgDz})}_{2}\right] = \left[\overline{\mathrm{Ag}}\right]_{\mathrm{ext}} - 0.5\left[\overline{\mathrm{Ag}}\right]_{\mathrm{T}}$$
(12)

$$\left[\overline{Ag_2Dz}\right] = \left[\overline{Ag}\right]_{T} - \left[\overline{Ag}\right]_{ext}$$
(13)

and from eqns. (10), (11), (12) and (13):

$$\left[\overline{Hg(HDz)}_{2}\right] = \left[\overline{H_{2}Dz}\right]_{T} - \left[\overline{Hg}\right]_{T} - 0.5\left[\overline{Ag}\right]_{T}$$
(14)

and

$$[\overline{HgDz}] = 2[\overline{Hg}]_{T} + [\overline{Ag}]_{T} - [\overline{H_2Dz}]_{T} - [\overline{Ag}]_{ext}$$
(15)

Calculations of the values of the concentrations of the species  $Hg(HDz)_{2}$ ,  $Hg(AgDz)_2$ , HgDz and  $Ag_2Dz$  were carried out by using eqns. (12), (13), (14) and (15) with the results shown in Table IV. The experimental value [Hg]<sub>ext</sub> was not used in these calculations, for separate measurements showed that reaction (5) was difficult to effect quantitatively with acidities as low as 0.1 M suppluric acid and over the time of shaking adopted. This was confirmed by values of [HgDz] calculated from eqn. (15) being greater than the experimental value (eqn. (8)). This discrepancy does not, of course, affect the validity of the calculation with regard to the complexes containing silver.

From Table IV it is clear that, as the excess of silver is increased, the ratio

ANALYSES OF MAGENTA-COLOURED SOLUTIONS AND CALCULATIONS OF THEIR COMPOSITIONS

1*		24		3°	
1.52 0.0066		1.95 0.02		1.49 0.02	
0.74		1.01		0.27	
0.58		0.69		0.85	
1.31		1.52		0.69	
0.47		0.68		0.70	
0.05		0.15		≤0.04	
0.28	(0.10)	0.165	(-0.17)	0.00	(-0.28)
0.18	(0)	0.335	(0)	0.275	(0)
0.28	(0.28)	0.51	(0.51)	0.00	(0.0)
0.11	(0.11)	0.01	(0.01)	0.15	(0.15)
0	(0.36)	0	(0.67)	0	(0.55)
	<ul> <li><i>I</i>"</li> <li>1.52</li> <li>0.0066</li> <li>0.74</li> <li>0.58</li> <li>1.31</li> <li>0.47</li> <li>0.05</li> <li>0.28</li> <li>0.18</li> <li>0.28</li> <li>0.11</li> <li>0</li> </ul>	/*         1.52         0.0066         0.74         0.58         1.31         0.47         0.05         0.28       (0.10)         0.18       (0)         0.28       (0.28)         0.11       (0.11)         0       (0.36)	I*       2 <sup>h</sup> 1.52       1.95         0.0066       0.02         0.74       1.01         0.58       0.69         1.31       1.52         0.47       0.68         0.05       0.15         0.28       (0.10)       0.165         0.18       (0)       0.335         0.28       (0.28)       0.51         0.11       (0.11)       0.01         0       (0.36)       0	$l^{*}$ $2^{*}$ $1.52$ $1.95$ $0.0066$ $0.02$ $0.74$ $1.01$ $0.58$ $0.69$ $1.31$ $1.52$ $0.47$ $0.68$ $0.05$ $0.15$ $0.28$ $(0.10)$ $0.165$ $(-0.17)$ $0.18$ $(0)$ $0.335$ $(0)$ $0.28$ $(0.28)$ $0.51$ $(0.51)$ $0.11$ $(0.11)$ $0.01$ $(0.01)$ $0$ $(0.36)$ $0$ $(0.67)$	$l^{*}$ $2^{h}$ $3^{\circ}$ $1.52$ $1.95$ $1.49$ $0.0066$ $0.02$ $0.02$ $0.74$ $1.01$ $0.27$ $0.58$ $0.69$ $0.85$ $1.31$ $1.52$ $0.69$ $0.47$ $0.68$ $0.70$ $0.55$ $0.15$ $\leq 0.04$ $0.28$ $(0.10)$ $0.165$ $(-0.17)$ $0.00$ $0.18$ $(0)$ $0.335$ $(0)$ $0.275$ $0.28$ $(0.28)$ $0.51$ $(0.51)$ $0.00$ $0.11$ $(0.11)$ $0.01$ $(0.01)$ $0.15$

\* 400-fold excess of  $Ag^+$  on equilibrating equal phase volumes. \* 1000-fold excess of  $Ag^+$  on equilibrating equal phase volumes.

<sup>6</sup> The primary mercury dithizonate was shaken with half its volume of 0.02 M AgNO<sub>3</sub> (pH=6.2) and the separated organic phase was again equilibrated with half its volume of 0.02 M AgNO<sub>3</sub> (pH = 6.2). This corresponds to 1330-fold excess of Ag<sup>+</sup> overall.

<sup>d</sup> Figures in parentheses are concentrations calculated on the assumption that the species Hg(AgDz)(HDz)exists but not  $Hg(AgDz)_2$ .

TABLE IV

 $[Hg(AgDz)_2]:[Hg(HDz)_2]$  increases as predicted. However, while there was no net loss of mercury when the magenta compound was formed in series 1 ( $[Hg]_T$  calc. = 1.52/2=0.76; found 0.74) or in series 2 (calc. 0.98; found 1.01) there is an increasingly heavy loss of dithizone (14% and 22%) owing to the precipitation of insoluble Ag<sub>2</sub>Dz. In the third series the loss of dithizone was still greater (53%) and there was also a loss of mercury suggesting that HgDz had been co-precipitated with Ag<sub>2</sub>Dz before the magenta organic phase was collected and analysed. Other results (not reproduced in detail) support the general conclusion that a mixed secondary complex Hg(AgDz)<sub>2</sub> is being formed according to eqn. (3).

Although with such a large excess of silver(I) there seems little probability of only partial replacement of imino-hydrogens by silver leading to Hg(AgDz)(HDz) this hypothesis was examined quantitatively. From the appropriate equations it can be deduced that

$$[Hg(AgDz)(HDz)] = 2[Ag]_{ext} - [Ag]_T$$
(12a)

$$[Ag_2Dz] = [Ag]_T - [Ag]_{cxt}$$
<sup>(13)</sup>

$$[Hg(HDz)_2] = [H_2Dz]_T - [Hg]_T - [Ag]_{ext}$$
(14a)

$$[\overline{HgDz}] = 2[\overline{Hg}]_{T} + [\overline{Ag}]_{T} - [\overline{H_2Dz}]_{T} - [\overline{Ag}]_{ext}$$
(15a)

and the calculation of the concentrations from the experimental data is shown in parentheses in Table IV. Since it predicts negative values for  $[Hg(HDz)_2]$ , this hypothesis is clearly untenable.

It is significant that the magenta complex is formed so readily merely by shaking primary mercury dithizonate with excess of silver ions in neutral solution, whereas there is no rapid colour change and formation of secondary mercury dithizonate on shaking with excess of mercury(II) ions in neutral solution or indeed in alkaline solutions below pH  $\sim 13$  (0.1 *M* KOH). If secondary mercury dithizonate is formulated as (III) it is clear that its formation from the primary complex (II) must involve breaking bonds from mercury to sulphur and mercury to nitrogen as one dithizone ligand is eliminated. On the other hand the formation of the mixed complex to give (IV)—a possible conformation of the magenta species—can take place mercly by replacing ionisable protons.



Although we have not succeeded in isolating a pure specimen of Hg(AgDz)<sub>2</sub>, calculations based on the mixture obtained in series 1 and 2 leads to the value  $v_{max}$  60,000-66,000 at  $\lambda_{max}$  510 nm.

### EXPERIMENTAL

The customary precautions were taken in cleansing glassware and in preparing pure solvents and reagents free from traces of metals<sup>10,11</sup>. AnalaR dithizone was purified until the peak ratio,  $A_{605}/A_{445}$ , reached 2.6. The stock solution (2·10<sup>-4</sup> M) was kept in the dark.

Aqueous solutions were prepared from AnalaR reagents in deionised water. Absorption spectra were recorded with a Unicam SP700 spectrophotometer, but definitive measurements of absorbance were made on matched 1-cm cells with a Unicam SP500.

# Preparation of primary dithizonates

Solutions of dithizone in chloroform  $(1.5-2.5\cdot10^{-5} M)$  were shaken in separatory funnels with aqueous solutions of mercury(II) chloride (or nitrate) or silver nitrate, the metal being in excess. The organic phase was then separated and washed once with 0.1 M sulphuric acid and three times with deionised water before being transferred to a dry stoppered flask which was kept in the dark. Fresh solutions were prepared daily as required.

# Studies of possible interaction between primary dithizonates of silver and mercury(II)

Solutions of primary dithizonates were prepared severally from a  $2.48 \cdot 10^{-5} M$  dithizone solution with a 20% excess of mercury(II) chloride or silver nitrate. Two samples were prepared by taking 5.00 ml of Ag(HDz) solution and making up to 10.00 ml in a volumetric flask with the solution of Hg(HDz)<sub>2</sub>. Two other samples were prepared from 5.00 ml of Hg(HDz)<sub>2</sub> solution made up to 10.00 ml with the chloroform solution of primary silver dithizonate. The same pipette was used throughout. Absorbances were measured about 1 h after preparation (Table I). In a second series the silver dithizonate was prepared from  $2 \cdot 10^{-5} M$  dithizone with a twofold excess of mercury(II) chloride or silver nitrate, respectively (Table II). In the third series, a  $1.8 \cdot 10^{-5} M$  solution of dithizone was used to prepare the primary dithizonates with only a 10% excess of mercury(II) nitrate or silver nitrate, respectively (Table II).

# **Preparation of the magenta-coloured mixed complex**

A solution of primary mercury(II) dithizonate was shaken (5 min) with an equal volume of 0.02 M silver nitrate in deionised water: this solution had an initial pH of *ca*. 5.2 after adjustment with a few drops of diluted ammonia or potassium hydroxide solution. Equilibrations were carried out at dawn or in diffuse light with separatory funnels wrapped in aluminium foil. After standing for 15 min to allow the phases to separate, the organic phase was withdrawn and filtered or centrifuged to remove any suspended secondary silver dithizonate and protected from light and adventitious impurities before analysis.

# Analysis of the magenta-coloured extract

Determination of total mercury and silver. A 5-ml aliquot portion was heated gently on a hot-plate in a conical flask with 10 ml of 0.1 M sulphuric acid and a few drops of dilute potassium permanganate solution until the solvent had evaporated:

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it was then boiled for 5 min to destroy the dithizone. Oxalic acid was next added to reduce excess of permanganate and the volume made up to 25 ml. In one 10-ml aliquot portion the total concentration of silver and mercury was determined by the dithizone method<sup>1</sup>. In a secon<sup>4</sup> aliquot portion, mercury alone was determined after masking the silver with 2 M anymonium chloride<sup>12</sup>. At least two determinations were made on two different samples of the organic phase.

Determination of total dithizone. An aliquot portion of the magenta-coloured organic phase was shaken with an equal volume of a 6% (w/v) solution of potassium iodide in 0.125 M sulphuric acid. The concentration of dithizone obtained by this reversion procedure<sup>13</sup> was calculated from the absorbance at 605 nm.

Determination of extractable silver and mercury. A 5-ml aliquot portion of the magenta solution was shaken for 2 min with 0.1 M sulphuric acid (10 ml) when the colour changed to yellow. The aqueous phase was transferred quantitatively to a 25-ml volumetric flask and made up to volume with deionised water. Silver and mercury were determined in aliquot portions as described above.

### SUMMARY

The magenta colour  $(\lambda_{max} 512 \text{ nm})$  produced when a solution of primary mercury(11) dithizonate, Hg(HDz)<sub>2</sub>, in chloroform is shaken with aqueous silver nitrate in large excess is shown to be caused by the formation of a mixed secondary complex Hg(AgDz)<sub>2</sub> which is readily reverted by 0.1 *M* sulphuric acid. The absorbances of chloroform solutions of primary mercury and primary silver dithizonates are additive, showing the absence of any molecular interaction.

# RÉSUMÉ

La coloration magenta  $(\lambda_{max}512 \text{ nm})$  produite lorsqu'on mélange une solution de dithizonate de mercure  $(Hg(HDz)_2)$  dans le chloroforme, avec une solution aqueuse de nitrate d'argent en excès est due à la formation d'un complexe secondaire mixte  $Hg(AgDz)_2$ , réversible en milieu acide sulfurique 0.1 M. Les absorptions des solutions chloroforme de dithizonates primaires de mercure et d'argent d'additionnent, montrant l'absence d'interaction moléculaire.

# ZUSAMMENFASSUNG

Beim Schütteln einer Lösung von primärem Quecksilber(II)dithizonat, Hg(HDz)<sub>2</sub>, in Chloroform mit wässriger Silbernitratlösung in grossem Überschuss entsteht eine Magentafärbung ( $\lambda_{max}$  512 nm). Es wird gezeigt, dass diese Färbung durch die Bildung eines gemischten sekundären Komplexes Hg(AgDz)<sub>2</sub> hervorgerufen wird, der durch 0.1 *M* Schwefelsäure sofort zurückverwandelt wird. Die Extinktionen der Chloroformlösungen von primärem Quecksilber- und primärem Silberdithizonat sind additiv und zeigen dass keine molekulare Wechselwirkung vorliegt.

### REFERENCES

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