

MERENTUTKIMUSLAITOKSEN JULKAISU N:o 145
HAVSFORSKNINGSINSTITUTETS SKRIFT

DETERMINATION OF TRACES OF HEAVY
METALS IN SEA WATER BY MEANS
OF DITHIZONE

I. METAL — DITHIZONE EQUILIBRIA

BY
FOLKE KOROLEFF



HELSINKI 1950 HELSINGFORS

MERENTUTKIMUSLAITOKSEN JULKAISU N:o 145
HAVSFORSKNINGSINSTITUTETS SKRIFT

DETERMINATION OF TRACES OF HEAVY
METALS IN SEA WATER BY MEANS
OF DITHIZONE

I. METAL — DITHIZONE EQUILIBRIA

BY
FOLKE KOROLEFF



HELSINKI 1950 HELSINGFORS

CONTENTS

	Page
PREFACE	5
I. INTRODUCTION OF DITHIZONE	7
1. The Metal Dithizonates	7
2. Quantitative Determination of Metals by Dithizone	9
3. Characteristics of Dithizone Reactions	11
II. APPARATUS AND REAGENTS	13
III. DETERMINATION OF AMOUNT OF DITHIZONE IN STANDARD SOLUTION	17
IV. EQUILIBRIUM OF DITHIZONE IN ALKALINE SOLUTIONS ..	20
V. METAL — DITHIZONE EQUILIBRIA	23
1. Bismuth	23
2. Cadmium	29
3. Cobalt	32
4. Copper	37
5. Lead	43
6. Mercury	46
7. Nickel	52
8. Silver	55
9. Thallium	57
10. Zinc	61
VI. SUMMARY AND CONCLUSIONS	64
LITERATURE CITED	68

PREFACE

The amount of heavy metals in sea water is generally very small, varying from 0 to about 20 micrograms per liter. These small amounts, however, play an important rôle for animal and vegetable life in sea water, just as for the rest of nature. At the present time of writing, however, only a few determinations of these metals have been made, as too many toilsome and wearisome analytical procedures have been involved.

Since the earliest days of analytical chemistry, organic reagents have been employed in facilitating the detection and determination of chemical substances. The importance of these reagents has been proved to be greater and greater as time goes on, especially for the determination of infinitesimal amounts.

Among the organic analytical reagents hitherto known, diphenylthiocarbazono or dithizone is the general heavy metal reagent *par excellence*. This reagent yields precipitates with no less than 17 metals, and its reaction with 10 of them can be used with advantage analytically. This offers the possibility for determining many metals systematically by means of the same reagent and by the same procedure. Although a large number of procedures have been worked out for detection and determination of traces of heavy metals with dithizone — at the time of writing there are about 240 original works published on the subject — the knowledge acquired is defective in the sense that there is very little information on the chemical behavior of the metallic salts of the reagent.

To eliminate this deficiency, I began in 1946 a theoretical and experimental investigation of dithizone and its salts on the suggestion of Prof. Buch, so that, on the basis of the results obtained, this reagent could be used with advantage for determination of traces of heavy metals in sea water.

Although the investigation in its entirety is not yet completed, the first part is in effect a unit in itself and is hereby presented.

I am greatly indebted to Professor Risto Jurva, Director of The Institute of Marine Research, and to Doctor Gunnar Granqvist, Chief of

the Hydrographic-Chemical Laboratory, that this investigation could be carried out. Further, to Professor Kurt Buch for constant interest in my work and readiness to facilitate it in every way.

I also wish to express my thanks to the institution »Svenska Vetenskapliga Centralrådet» in Finland and »The Shipping Foundation» for the financial help.

Finally I wish to convey my best thanks to Mr. Wilfred Hughes for kindly correcting the English manuscript, and to my Wife for helping me in calculations and preparing fair copies of the manuscript.

Helsingfors,
April 1950

Folke Koroleff

I. INTRODUCTION OF DITHIZONE

Diphenylthiocarbazone, or dithizone, $S = C \begin{cases} NH-NH-C_6H_5 \\ N=N-C_6H_5 \end{cases}$ was

first prepared by Emil Fischer (1) in 1878, while he was investigating the structure and reactions of phenylhydrazine. He also observed its acid character and prepared its zinc salt. It was not until 1925 before dithizone was used as an analytical reagent for heavy metals. During that year Hellmuth Fischer (2) began a series of investigations of the metallic dithizonates, and their possible applications in analytical chemistry.

Dithizone is a violet-black solid which dissolves in most organic solvents at least to some extent. In hydrocarbons it is only slightly soluble, but dissolves readily in chloroform and to a lesser extent in carbon tetrachloride. The latter two liquids are used almost exclusively in the preparation of solutions of dithizone for analytical purposes.

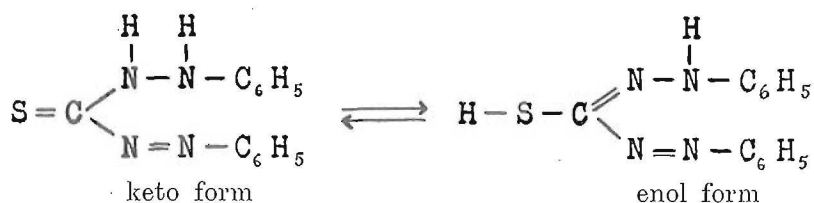
Dilute solutions of dithizone in chloroform and carbon tetrachloride are green, but more concentrated solutions are red in transmitted light and green in reflected light. In strongly polar solvents, such as nitrobenzene, dithizone is yellow.

When a solution of dithizone in chloroform or carbon tetrachloride is shaken with an aqueous solution of a reacting heavy metal, a complex salt is formed, which is usually soluble in the organic phase, to which it imparts a violet, red, orange or yellow color, depending on the metal involved.

Dithizone and its metallic salts, the so-called dithizonates, are virtually insoluble in neutral and acid aqueous solutions. In basic solutions, however, dithizone dissolves with a yellow color to give the ammonium or alkali metal dithizonate. Like dithizone itself, the dithizonates are more soluble in chloroform than in carbon tetrachloride.

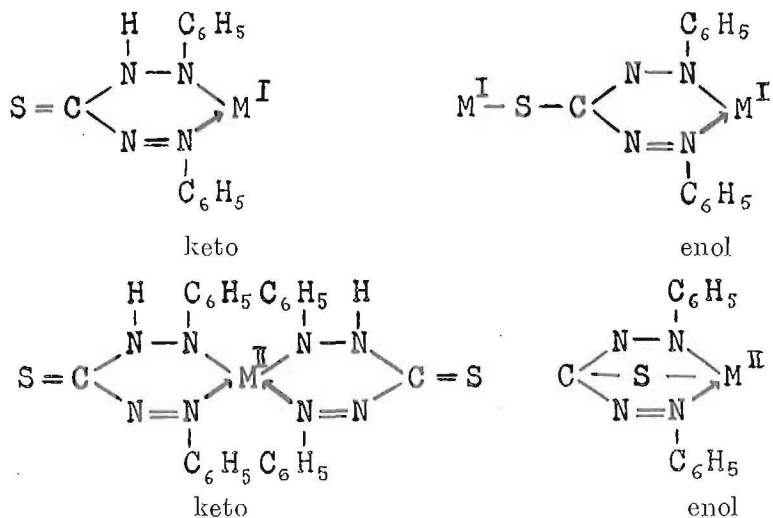
1. The Metal Dithizonates

According to H. Fischer, dithizone exists in two tautomeric forms, which he calls the keto form and the enol form.



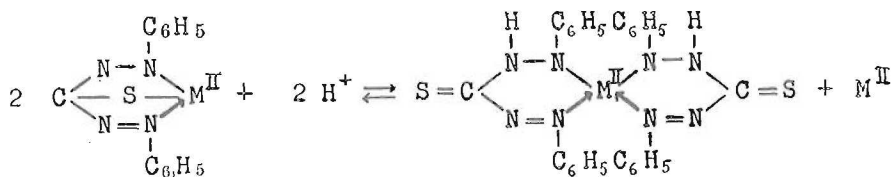
In the keto form, the hydrogen atom of the imide group of dithizone is replaced by metal, and in the enol form the hydrogen of the sulfhydryl group is also replaced. Consequently, the enol form contains twice as much metal as the corresponding keto form.

The formulae for the keto and enol forms of univalent and divalent metal dithizonates are as follows:

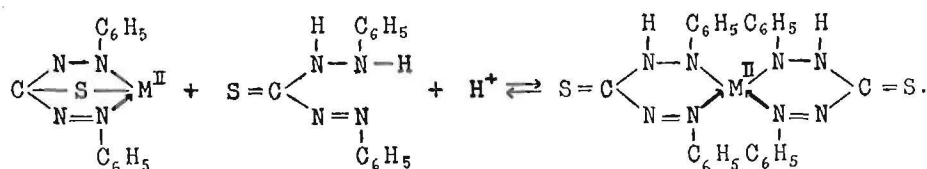


Again according to Fischer, the keto forms of all the metal dithizonates are known, but many of the enol forms have not yet been encountered.

The keto tautomer is preferably formed in acid or neutral solution, whereas the enol modification appears in alkaline solution or where an insufficient quantity of dithizone is present. The enol modification can be transformed into the keto tautomer by the action of an acid:



or by treating with an acid and dithizone:



The keto tautomer can be converted more or less readily into the enol form, if this exists, by treating with a base.

The elements in the enclosed section of the following Table (No. 1), taken from one of Sandell's works (3), form komplex salts with dithizone, but it should be noted that certain metals react only in one valence. For example Fe^{+2} , Sn^{+2} and Pt^{+2} react, but not Fe^{+3} , Sn^{+4} and Pt^{+4} .

TABLE I
METALS REACTING WITH DITHIZONE
(The enclosed elements yield dithizonates)

							B	C	N	O	F	
							Al	Si	P	S	Cl	
V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Cb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—
Pa	U											

2. Quantitative Determination of Metals by means of Dithizone

Three methods are generally available for quantitative determination of metals by dithizone, *viz.* (a) the gravimetric procedure, (b) the volumetric analysis, and (c) colorimetric determination, which all have in common that the metal is concentrated as dithizonate in chloroform or carbon tetrachloride. This takes place by shaking an aqueous solution of the metal in a separatory funnel with successive additions of a chloroform or carbon tetrachloride solution of dithizone until it can be seen from the unchanged green color of the last portion that all of the metal has been extracted. Practical results, however, have been obtained only with the second and third methods mentioned above.

The gravimetric procedure has so many practical difficulties compared with the other two that this method of determination is not recommended. The voluminous precipitate tenaciously holds water during the drying process and decomposes very readily at a temperature close to 100°C . The disadvantage is even more pronounced because of the tendency of the precipitate to explode. Further, it should be mentioned that the

oxide obtained by ignition is practically always contaminated with sulfide or sulfate formed from the dithizone.

The volumetric dithizone procedure is based on the principle of «extractive titration» introduced by Fischer, Leopoldi and von Uslar (4). By this method the metal is extracted from its aqueous solution at a pH where the reaction metal — dithizone is quantitative, and, if necessary, in the presence of complex-forming anions, with successive portions of standardized dithizone solution. The titration is carried out in a separatory funnel by shaking between additions to establish equilibrium between the metal and the reagent. The chloroform or carbon tetrachloride layer containing the dithizonate is drawn off from time to time until the green color of the dithizone solution is no longer changed through formation of colored dithizonates. The intense green color of the reagent serves, as its own indicator. Besides by Fischer, the titrimetric method has been used with good results by others, including Winkler (5, 6) and Horwitt/Cowgill (7).

The colorimetric methods have generally been regarded as giving the most satisfactory results for determination of small quantities of the metals. Two techniques have been used for colorimetric determinations: (1) the mono-color method; and (2) the di- or mixed-color method. By the mono-color method, originally developed by Fischer and Leopoldi (8), the metal is extracted as already described in the extractive titration method, and the combined extracts are then shaken with a dilute solution of a base in order to remove excess dithizone. This procedure can give, however, a source of error, *viz.* if the alkalinity of the wash solution is too high, some of the dithizonate may be partially decomposed; and if too low, an appreciable amount of free dithizone may be left in the organic solvent. It is easier to remove dithizone from a carbon tetrachloride solution than from a chloroform solution, as is shown in detail in chapter IV.

In the di- or mixed-color method the excess dithizone in the organic layer is not removed. In visual work the hue of the solution is compared with a series of standards, all prepared with the same amount of dithizone as the sample solution. These standards show a series of hues ranging from the unchanged green of the dithizone to the color of the metal dithizonate alone.

Fischer (9) has developed another method of mixed-color colorimetry, which is based on duplication rather than comparison with a standard series.

When a spectrophotometer is used to determine a metal by the mixed-color method, there are usually two possibilities in the choice of wave length: (1) to measure the absorption of light by the metal complex, and (2) to measure the absorption of light by the excess of dithizone after the reaction is completed.

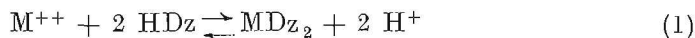
3. Characteristics of Dithizone Reactions

For detection or quantitative determination of individual metals in the possible presence of other ions which also react with dithizone, it is necessary to control conditions in the correct manner so that interference is eliminated. Among the factors affecting the dithizone reaction are: (a) the acidity of the aqueous solution; (b) the dithizone concentration; (c) the relative volume of the reagent solution and the volume of the aqueous solution; (d) the thoroughness with which the two immiscible liquids are shaken; (e) the presence in the solution of complex-forming substances and other cations and anions.

(a) *Effect of pH on the selectivity of the dithizone reaction.* It has been well known for a long time that various metals which react with dithizone do so at different optimum pH values of the aqueous solution. Wichmann (10) constructed a series of tentative curves showing the relationship between pH of the aqueous solution and the completeness of extraction when dithizone is dissolved in chloroform, based on isolated data which have been reported, but these curves cannot be regarded as complete or correctly drawn. Fischer (11) and Fischer/Leopoldi (12) observed, of course, the importance of the pH, but they were content to divide the metals into groups depending on the character of the aqueous test solution. These groups are: 1) in dilute mineral acid, 2) in acetic acid solution, 3) in sodium hydroxide solution, 4) in slightly alkaline solutions containing cyanide, and 5) in strongly alkaline solutions containing tartrate.

The first step towards a more exact study of the reaction of dithizone with metal was taken by Kolthoff and Sandell (13). They have given an equation relating the extraction coefficient of a metal dithizonate, the pH of the aqueous solution being extracted, and the concentration of the chloroform solution of dithizone used to make the extraction.

The reaction of a divalent metallic ion with dithizone in water is written as:



in which HDz = dithizone. Dz as a symbol for the anion of dithizone in metal dithizonates has been suggested by Hibbard (14). The «equilibrium constant» for reaction (1) is:

$$k = \frac{[MDz_2]_w [H^+]_w^2}{[M^{++}]_w [HDz]_w^2} \quad (2)$$

The distribution coefficients for dithizone and complex between water and the organic solvent are as follows:

$$D_{\text{HDz}} = \frac{[\text{HDz}]_w}{[\text{HDz}]_o} \quad (3)$$

and

$$D_{\text{MDz}_2} = \frac{[\text{MDz}_2]_w}{[\text{MDz}_2]_o} \quad (4)$$

in which o and w indicate the organic solvent phase and aqueous solution respectively.

The quantities $[\text{HDz}]_w$ and $[\text{MDz}_2]_w$ appearing in the equilibrium constant (2) may be expressed in terms of appropriate quantities from (3) and (4); the equilibrium constant thus becomes:

$$\frac{[\text{MDz}_2]_o}{[\text{M}^{++}]_w} \frac{[\text{H}^+]_w^2}{[\text{HDz}]_o^2} = k \frac{D_{\text{HDz}}^2}{D_{\text{MDz}_2}} = K \quad (5)$$

Now $\frac{[\text{MDz}_2]_o}{[\text{M}^{++}]_w}$ is the experimentally observed distribution coefficient,

and it follows that:

$$\frac{[\text{MDz}_2]_o}{[\text{M}^{++}]_w} = K \frac{[\text{HDz}]_w^2}{[\text{H}^+]_o^2} \quad (6)$$

in which molar concentrations replace activities, for the solutions are generally very dilute.

This means that the extractability of the metallic ion M^{++} at a given pH increases as the square of the excess dithizone in the organic layer; also that, with a constant excess of dithizone, the extractability is inversely proportional to the square of the hydrogen ion concentration. The amount of metal extracted, then, is seen to be a sensitive function of both quantities.

If the pH of the aqueous solution is such that the metal ion is more or less completely hydrolyzed, another expression for the extractability must be derived.

The equation (6) was tested in a preliminary way by Kolthoff and Sandell for zinc with a chloroform solution of dithizone, and K was found to remain reasonably constant and equal to 3.2.

The equilibrium constants of the other metal dithizonates have not yet been determined. There is at present only a rough determination by Sandell (3) of the constant for copper- and silver-dithizonate in carbon tetrachloride, and also a preliminary determination by Buch (15) and Buch/Koroleff (16) for the zinc-, copper- and lead-dithizonates in carbon tetrachloride.

Dithizone is used as an analytical reagent for the determination or separation of the following of the metals in the enclosed part of Table 1,

page 9: bismuth, cadmium, cobalt, copper, lead, mercury, nickel, silver, thallium and zinc. In this work the equilibrium between these metals and their dithizone salts has been investigated both in carbon tetrachloride and chloroform.

The dithizonates of the various metals differ also among themselves in their stability towards alkalis, but an investigation of these facts and conditions is analytically not so important for this purpose. They have therefore been left out of consideration.

The influence on the extraction of metals with dithizone of the factors mentioned in points (b), (c) and (d) has been investigated in connection with the determination of the equilibrium constants.

(e). *Effect of complex-forming reagents on the selectivity of the dithizone reaction.* Proper control of pH alone is not always sufficient in effecting necessary separations in analytical practice. Separations may be accomplished in many cases by taking regard to the fact that various metallic complexes differ in their stability toward dithizone. Citrate and tartrate, for example, are used to prevent the precipitation of hydroxides or phosphates when the dithizone metals are extracted from alkaline solutions, but the presence of these complex-forming substances does not interfere with the dithizone extraction. Fischer and Leopoldi (8) originally proposed the use of cyanide as masking agent for certain metals; moreover, thiosulfate and halide may be used as complex-formers in acid solution.

In the present determination of the values of the equilibrium constants for the various metal dithizonates, K has also been determined in the presence of the usual complex-forming substances, to ascertain the eventual effect of various anions on the extraction of the metals.

As this investigation was made for determination of traces of metals in sea water by means of dithizone, the equilibrium constants have been determined in this medium and also in sodium chloride solution, on account of the high content of this salt in sea water. The influence of a possible cation effect on the dithizone reaction has not been investigated as sea water does not contain any amount of cations equal to that of sodium.

II. APPARATUS AND REAGENTS

In working with such a sensitive reagent as dithizone, the essential precaution is that there must be absolute purity both as regards reagent and glassware. Commercial chemicals, despite their A. R. quality, usually contain sufficient heavy metals to give reaction with dithizone and should therefore be purified by appropriate methods.

Another factor affecting the results is the sensitivity to light of the dilute solutions of dithizone and metal dithizonates. The work has been

carried out whenever possible in a dark room — never in direct sunlight — and all spectrophotometer readings have been made without delay at a room temperature of 20—22° C.

A. Apparatus

Spectrophotometer. A construction by König-Martens (17) was used. The original cuvettes could not be used as the bordering of their plane ends in brass; this had an immediate influence on the dilute solutions of dithizone. The cells used were cylindrical, made of Pyrex glass, with an internal diameter of 24 mm. and a thickness of 17.2 mm.

The measured absorption of light is expressed with the extinction coefficient ϵ defined by $I/I_0 = 10^{-\epsilon l}$, in which

I_0 = intensity of the incident light beam,

I = intensity of the transmitted light beam,

l = depth of solution traversed by the light.

The extinction coefficient of the solutions was calculated from $\epsilon = \frac{\log_{10} \text{tg}\alpha_1 - \log_{10} \text{tg}\alpha_2}{l}$ in which α_1 and α_2 are the nicol readings, with the test solutions to the left and right respectively.

pH meter. A Beckmann pH meter, laboratory model 1938, was used. The accuracy of the meter was 0.01 pH. pH-values over 10 were corrected by a special table. Clark and Lubs buffers were used in calibrating the instrument.

Shaker. A mechanical shaker, giving a horizontal end-over-end motion to the funnel and averaging 160 oscillations per minute, was used.

Stills. All stills throughout were made of Jena and Pyrex glass.

Glassware. Jena and Pyrex glassware was used throughout; containers were all glass-stoppered. They were first cleaned mechanically, then with concentrated sulfuric acid and potassium bichromate, and finally by shaking with neutral metal-free water and a carbon tetrachloride solution of dithizone.

B. Reagents

Dithizone. In the presence of a mild oxidizing agent or strong light,

the reagent is converted to diphenylthiocarbodiazone $S = C \begin{matrix} \diagup N = N - C_6H_5 \\ \diagdown N = N - C_6H_5 \end{matrix}$

Clifford (18) states that sunlight for example acts on chloroform to yield decomposition products such as phosgene, which then oxidize the dithizone. The oxidation compound is insoluble in acid and basic aqueous solutions, but dissolves readily in chloroform and carbon tetrachloride to form a yellow or brown solution. Due to the absence of acidic hydrogen atoms in the molecule, it does not react with metals. Some of the dithizone

products sold usually contain as impurities a few per cent sulfur, the carbazide and other oxidation products. These impurities are not soluble in dilute ammonium hydroxide, while dithizone dissolves readily. To purify the reagent, therefore, it is necessary only to shake the chloroform or carbon tetrachloride solution with ammonium hydroxide, separate the aqueous layer, and acidify to precipitate pure dithizone.

To prevent oxidation, solutions of dithizone are protected in a cool, dark place under a layer of an aqueous solution containing a mild reduction substance. Fischer and Leopoldi (8, 19) use sulfur dioxide or hydroxylamine hydrochloride, whereas Snyder (20) uses a solution of sodium sulfite.

In this investigation dithizone from Eastman Kodak was used and proved to be pure; the stock solution 0.013 per cent (weight by volume), therefore, was made by dissolving the dithizone in chloroform and carbon tetrachloride. The solutions were protected in a cool dark place under a layer of an aqueous solution of hydroxylamine hydrochloride. Despite these precautions the stock solutions were oxidized slowly. The portion, therefore, taken on each occasion to working solutions, containing 6 and 30 micrograms per ml., was purified in the usual manner. The standard solutions were used for a week only and showed no change in strength during this time.

Chloroform and carbon tetrachloride. To prepare a stable dithizone solution, it is necessary to use chloroform and carbon tetrachloride free from oxidation products. Clifford (18) recommends Biddle's (21) procedure for the purification of the organic solvents, and this procedure was used both for recovery of chloroform and carbon tetrachloride from used dithizone solutions and for improving the quality of the products, especially chloroform, as sold. This is carried out as follows: The organic solvent, separated from any aqueous phase, is washed until colorless with commercial sulfuric acid equal to 5 or 10 per cent of its volume, and is then treated with lime to remove any excess acid. The distillation is carried out slowly on a water bath, and alcohol is added to the chloroform distillate to the extent of 1.0—1.5 per cent of its volume. According to Biefeld and Patrick (22), alcohol should be added at the first distillation only.

Water. Ordinary waterworks water was distilled in an all-glass apparatus, and proved to be sufficiently metal-free after one distillation.

Hydrochloric acid. A metal-free (about 3 N) acid was procured as follows: The bottom of a desiccator was filled with concentrated C. P. acid and allowed to distill into a vial with metal-free water placed over the acid.

Sulfuric acid. Judex A. R. concentrated acid, diluted to required strength, was used. This acid contains as impurities 0.0001 per cent lead, but this metal reacts with dithizone first at a pH higher than 4.

Nitric acid. The acid was redistilled in an all-glass apparatus.

Acetic acid. Redistilled as for nitric acid.

Ammonium hydroxide. Prepared as for hydrochloric acid.

Ammonium thiocyanate. Saturated solution, purified by shaking with dithizone in carbon tetrachloride.

Sodium acetate, saturated and 0.1 M solution. The solutions were purified by shaking with dithizone in chloroform to remove reacting heavy metals.

Sodium chloride. 4 M solution, purified by shaking with dithizone in carbon tetrachloride.

Potassium chloride. 4 M solution, purified as for sodium chloride.

Potassium bromide. 0.2 M solution, do.

Potassium iodide. 0.2 M solution, do.

Potassium cyanide. »Baker's Analyzed« was used. The salt was added to the test solutions in solid form, as it does not contain metals reacting with dithizone.

Magnesium sulfate. 2 M solution, purified as for sodium chloride.

Citric acid, 0.2 M solution. Heavy metals reacting with dithizone at a pH less than 3 were removed by shaking with dithizone in carbon tetrachloride. When the acid was used at higher pH, reacting metals were removed in the final purification.

Sodium citrate. 0.4 M solution, purified as for sodium acetate.

Tartaric acid. 0.2 M solution, purified as for citric acid.

Sodium potassium tartrate. 0.4 M solution, purified as for sodium acetate.

Buffer solutions:

pH 1.0—2.2. 0.2 N hydrochloric acid and 0.2 N potassium chloride according to Clark and Lubs (23).

pH 3.0—7.0. 0.1 M acetic acid and 0.1 M sodium acetate, according to Cohn, Heyroth and Menkin (24).

pH 7.0—9.2. Boric acid in 0.05 N sodium chloride solution and 0.1 N borax, according to Palitzsch (25). Every single solution was purified with a chloroform solution of dithizone, and then with pure chloroform to remove water-soluble alkali dithizonate.

pH 9.2—12.0. 0.1 M alkaline soda and 0.1 M borax, according to Kolthoff and Vleeschhouwer (26). Purification as for the last-mentioned.

Sea water. Water collected from the North Sea was used, and purified by extraction with dithizone in chloroform.

The values of the equilibrium constants for the various metal dithizonates have in the main been determined as follows: A measured volume of water containing a definite amount of a metal was shaken in a separatory funnel with a measured volume of chloroform or carbon tetrachloride containing a known amount of dithizone. After reaching equilibrium, the amount of the metal in the organic layer was determined by the mixed-color method with the spectrophotometer.

All extractions have been made in 100 ml. separatory funnels, with the metal in buffer and salt solutions. When the pH was determined with the pH meter after the extraction, the buffer solutions could be diluted to $\frac{3}{4}$ parts with water, to prevent as far as possible the influence of anions present on the metal extraction. Before the real extraction, the aqueous phase was shaken with a few ml. of dithizone solution in the same funnel where the final determination was made, so that it should be definitely free from reacting metals. The organic layer was separated and the aqueous solution shaken with pure chloroform or carbon tetrachloride to remove any possible water-soluble alkali dithizonate. Finally the aqueous layer was freed from the last traces of organic solvent by blowing air through the funnel, which was kept in a horizontal position.

III. DETERMINATION OF AMOUNT OF DITHIZONE IN STANDARD SOLUTION

An exact standard solution of dithizone in chloroform or carbon tetrachloride cannot be made by weighing, due to the fact that the dithizone is more or less converted to oxidation products. Fischer and his colleagues (4) — and others after them — have used the volumetric method as already described for standardization of dithizone solutions. The reagent solution is thereby usually titrated with a standard silver nitrate solution. In this investigation a modification of the volumetric method has been used, convenient for the use of a spectrophotometer.

This method is absolutely reliable only when the composition of two metal dithizonates is known for certain. Emil Fischer (1) already determined that of the zinc dithizonate to ZnDz_2 , and Buch/Koroleff (16) have found gravimetrically the composition AgDz for the yellow, and Ag_2Dz for the red silver dithizonate. Standard solutions of these two metals have been used in the following determination of dithizone content.

The pH was first experimentally fixed at which zinc and silver quantitatively combine with dithizone. The values for zinc are equal to or higher than 6.0 and 7.8, if dithizone is dissolved in carbon tetrachloride and chloroform respectively. Silver gives complete reaction even in 0.1 N sulfuric acid.

Special Solutions

Dithizone. A diluted solution containing about 6.0 micrograms of dithizone per ml. organic solvent was used.

Standard zinc solution. 0.02 per cent in approx. 0.1 N hydrochloric acid. Reagent-grade zinc was dissolved in a slight excess of HCl and diluted to volume. A 0.001 per cent zinc solution was prepared from this solution by dilution with metal-free water.

Standard silver solution. Stock solution 0.02 per cent in 0.1 N nitric acid, made of AgNO_3 dried at 110°C . The standard solution, 20 micrograms of silver per ml., was prepared by diluting the stock solution with metal-free water.

Procedure for zinc. Various quantities of metal in a 20 ml. buffer solution of pH 6.0 (CCl_4) and 7.8 (CHCl_3) were shaken with 10 ml. dithizone solution in a 100 ml. separatory funnel for 5 minutes in the dark. The organic layer was run into the 17.2 mm. cell, and the absorption of light of the solution determined at 535 and 620 $m\mu$, the wave lengths of maximum absorption by zinc dithizonate and dithizone respectively.

For silver, the various quantities of metal were extracted from 20 ml. 0.1 N sulfuric acid. The absorption of light of the organic solvents was measured at 620 $m\mu$ only, due to the rather uncertain readings at 460 $m\mu$, the wave length of maximum absorption by silver dithizonate.

The extinction coefficients corresponding to the various amounts of metal are given in Tables 2 and 3.

TABLE 2
EXTINCTION COEFFICIENTS CORRESPONDING TO VARIOUS AMOUNTS
OF ZINC

Zn taken γ	Carbon Tetrachloride		Chloroform	
	ϵ 620 $m\mu$	ϵ 535 $m\mu$	ϵ 620 $m\mu$	ϵ 535 $m\mu$
0	0.643	0.158	0.707	0.275
1.5	.491	.328	.546	.416
3.0	.330	.510	.428	.561
5.0	.132	.743	.250	.753
Zn Dz ₂	.000	.887	.000	1.010

TABLE 3
EXTINCTION COEFFICIENTS CORRESPONDING TO VARIOUS AMOUNTS
OF SILVER

Ag taken γ	Carbon Tetrachloride	Chloroform
	ϵ 620 $m\mu$	ϵ 620 $m\mu$
0	0.643	0.707
6	.455	.544
12	.267	.368
18	.080	.205
Ag Dz	.000	.000

The extinction coefficient ϵ was plotted on a diagram against the corresponding amount of metal; two straight lines were obtained for zinc, (one for each wave length), and one for silver as only one wave length was used. By adding a certain amount of metal the straight lines are broken and then continue parallel with the x-axis. The points where

the lines are broken give the amount of metal required to transform all dithizone present into dithizonate. The breaking points are obtained by recording on the graph certain lines parallel with the abscissa, at a distance therefrom equal to the ϵ -value of the pure metal dithizonate at the respective wave length. The values of the extinction coefficients mentioned are those shown at the end of Tables 2 and 3 and these are obtained by measuring the absorption of light of the dithizone solution shaken with an excess of metal. As the value of the coefficient is equal to 0 for ZnDz_2 and AgDz at 620 m μ , one of these parallel lines coincides with the x-axis. As the amount of metal obtained in the manner described was known, the corresponding amount of dithizone was calculated.

The determination for the carbon tetrachloride solution of dithizone gave with zinc 49.0, and with silver 48.8 micrograms of dithizone in 10 ml. of the solvent. Thus, a solution of dithizone in carbon tetrachloride, with an extinction coefficient of 0.643 at wave length 620 m μ , contains 48.9 micrograms of dithizone in 10 ml.

The determination for the chloroform solution of dithizone gave with zinc 60.0 and with silver also 60.0 micrograms of dithizone in 10 ml. The corresponding ϵ -value at 620 m μ was 0.707.

It has been experimentally stated that solutions of dithizone in carbon tetrachloride and chloroform obey the law of Beer. In this way, the following graph (Fig. 1) for the dithizone content in 10 ml. of organic solvent was obtained.

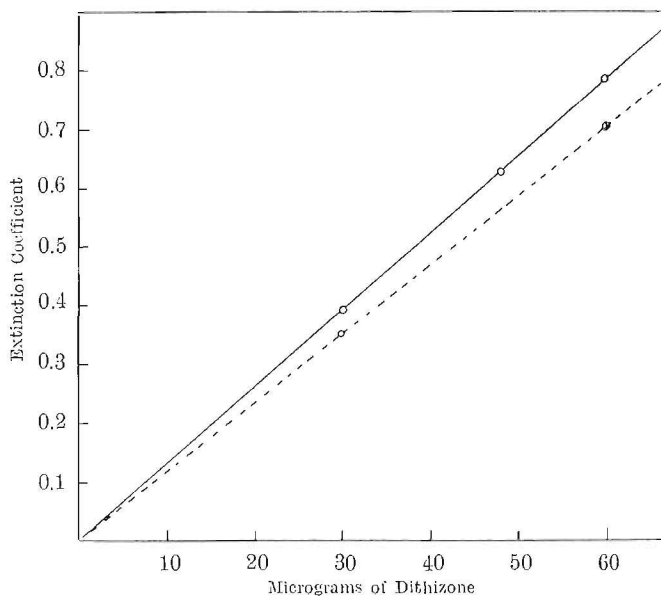


Fig. 1. — Extinction coefficients corresponding to amount of dithizone in 10 ml. carbon tetrachloride (—) and chloroform (-----). Absorption of light measured at 620 m μ .

IV. THE EQUILIBRIUM OF DITHIZONE IN ALKALINE SOLUTIONS

The equilibrium investigation is based on the fact that when a green solution of dithizone in chloroform or carbon tetrachloride is shaken with increased amounts of alkali, the yellow color of the aqueous layer becomes stronger the more alkali is present, whereas the green color of the organic solvent is proportionately reduced.

Where the mono-color method is used, it should be stressed, as already mentioned, that any excess of free dithizone should be removed. One must therefore know the partition coefficient of dithizone between the organic and the aqueous phase. Clifford and Wichmann (27) found for 1 : 200 ammonium hydroxide the following values:

$$\frac{[\text{HDz}]_{\text{NH}_4\text{OH}}}{[\text{HDz}]_{\text{CCl}_4}} = 41 \text{ (31}^\circ\text{)} \text{ and } \frac{[\text{HDz}]_{\text{NH}_4\text{OH}}}{[\text{HDz}]_{\text{CHCl}_3}} = 1.6 \text{ (30}^\circ\text{)}.$$

At pH 10 the respective coefficients are 19.4 and 0.76. Further, Biefeld and Patrick (22) state in their determination of lead with dithizone that when the reagent is dissolved in chloroform alkali dithizonate begins to form at pH 8.

A closer examination from the theoretical point of view was first made by Buch and Koroleff (16). They compared the conversion, which evidently is a function of the pH, with a neutralization reaction like that shown by color indicators with acid character. The keto tautomer by Fischer is hereby compared with the undissociated acid. It was also shown that the conversion from the keto form into the enol tautomer takes place with the splitting of the primary proton. The splitting of the secondary hydrogen atom is without optical effect. The investigation by Buch and Koroleff, however, was made only in nearly pure aqueous solutions, and when various impurities had been later eliminated a more exact determination could be made.

The equilibrium between dithizone and alkali dithizonate has also been studied in aqueous solutions containing various anions of analytical importance, and also in sea water.

The distribution constants of dithizone between water and organic solvent are:

$$k_1 = \frac{[\text{HDz}]_w}{[\text{HDz}]_o} \quad (1)$$

and

$$k_2 = \frac{[\text{H}^+]_w [\text{Dz}]_w}{[\text{HDz}]_w} \quad (2)$$

(1) multiplied by (2) gives the equation for the reaction:



$$\text{Thus } K = \frac{[\text{Dz}]_w [\text{H}^+]_w}{[\text{HDz}]_o} \quad (4)$$

Procedure: For the determination of K in equation (4) a definite volume of a dilute buffer solution was shaken in the dark in a 100 ml. separatory funnel with 10 ml. working solution of dithizone, containing 60 micrograms of the reagent. pH was measured with the pH meter after the shaking. The amount of dithizone in the organic layer was determined by obtaining the absorption of light with the spectrophotometer in 17.2 mm. cuvettes at 620 m μ wave length. The corresponding amount of dithizone was obtained from the curve in Fig. 1, page 19. By acidifying the aqueous layer, and by extracting with a portion of 10 ml.

TABLE 4

DITHIZONE — ALKALI DITHIZONATE EQUILIBRIUM

20 ml. aqueous solution (unless otherwise stated) and 10 ml. organic solvent containing 60 γ of dithizone.

Anions present in aqueous phase	Carbon tetrachloride				Chloroform			
	pH	ϵ 620 m μ	Dz in org. phase γ	$K \times 10^{-9}$	pH	ϵ 620 m μ	Dz in org. phase γ	$K \times 10^{-11}$
Dilute buffer	7.87	.0785	60.0			0.707	60.0	
» »	8.38	.515	39.2	1.2	9.70	.566	48.0	2.5
» »	8.71	.350	26.7	1.1	9.99	.490	41.5	2.3
» »	8.71	.350	26.7	1.2	10.46	.296	25.2	2.4
» »	9.07	.208	15.8	1.2	10.91	.150	12.7	2.3
» »	9.73	.062	4.7	1.1	11.36	.061	5.2	2.3
» » 40 ml.	8.40	.357	27.2	1.2	10.00	.351	29.8	2.5
» » 60 »	8.79	.155	11.8	1.1	10.54	.122	10.4	2.3
1 M NaCl	8.64	.450	34.3	0.85	10.06	.479	40.5	2.1
» »	9.17	.223	17.1	0.84	10.57	.285	24.2	2.0
2 M NaCl	8.75	.501	38.5	0.50	10.51	.427	36.3	1.0
» »	9.37	.243	18.4	0.48	11.37	.115	9.8	1.1
3 M NaCl	8.91	.548	42.0	0.26	10.67	.595	50.5	0.20
» »	9.36	.350	26.7	0.27	11.27	.389	33.0	0.22
Sea water, Cl = 12 ‰	8.46	.501	38.5	0.97	10.28	.402	34.1	2.1
» »	9.04	.255	19.2	0.97	10.97	.145	12.3	2.1
1 M KCl	8.89	.344	25.9	0.84				
» »	8.99	.293	22.5	0.84				
1 M MgSO ₄	8.68	.450	34.5	0.78				
» »	9.22	.215	16.5	0.79				
0.1 M KCN	9.32	.155	12.0	0.96	10.39	0.338	28.7	2.2
» »	9.49	.316	8.8	0.94	10.68	.214	18.2	2.4
0.5 M Na citrate	8.32	.621	47.5	0.63	10.14	.530	45.0	1.2
» »	8.70	.483	37.0	0.62	11.07	.188	15.6	1.2
0.5 M K Na tartrate	9.15	.278	21.2	0.64	10.19	.516	43.7	1.2
» »	9.36	.204	15.6	0.63	10.78	.324	27.4	1.0
0.1 M KCN +	9.59	.200	15.2	0.38	10.86	.460	38.2	0.40
0.5 M Na citrate	9.86	.128	9.7	0.36	11.45	.223	19.0	0.38

organic solvent, followed by a spectrophotometer reading, the amount of dithizone transformed into aqueous soluble form was obtained. The sum of these two amounts should be equal to the original amount of dithizone; the difference was never greater than one microgram.

After various attempts the time needed to attain equilibrium was determined. It was ascertained that the longer the shaking took place the greater amount of dithizone was transformed into the aqueous phase. This, however, depends on the fact that the yellow alkali dithizonate, in spite of shaking in the dark, gradually was decomposed; in this way, the sum of the two amounts of dithizone after shaking for one hour was 4 micrograms less than the original amount. It can be established accordingly that equilibrium is attained almost immediately, but to be perfectly sure for this purpose it was shaken mechanically for 5 minutes. The results are given in Table 4.

A clearer picture of the equilibrium between dithizone and alkali dithizonate is given by drawing the corresponding equilibrium curves shown in Fig. 2. These curves are calculated from the value of K with twice as much aqueous phase as organic solvent.

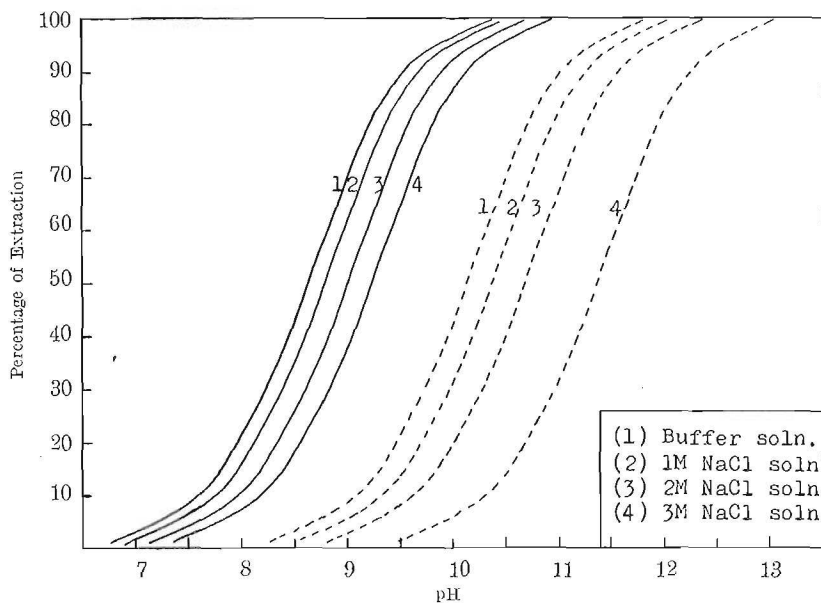


Fig. 2. — Effect of pH and amount of sodium chloride on the retention of dithizone by the carbon tetrachloride (—) and the chloroform (-----) layer.

Conclusions. From the results obtained it will be seen that the formation of the enol tautomer of dithizone begins at pH 7.0 and 8.5 when the reagent is dissolved in carbon tetrachloride and chloroform respectively. The conversion from keto form into the enol modification

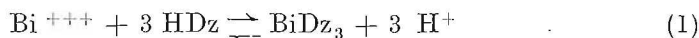
takes place with the splitting of the primary proton, and principles of chemical equilibrium can be applied on the reaction.

Where greater quantities of various salts are present, the formation of water-soluble dithizone is replaced in favor of the organic phase.

V. METAL — DITHIZONE EQUILIBRIA

1. Bismuth

Bismuth reacts with dithizone in weak acid solution to form a complex salt, which with an orange-yellow color is soluble in carbon tetrachloride and chloroform. Bismuth, as a trivalent metal, can be assumed to react according to the equation:



To obtain an experimental confirmation of the composition of this dithizonate and standard curves, the same procedure was used as in the determination of the dithizone content; in this case, however, the amount of dithizone is known.

Standard dithizone solution. 6 micrograms of dithizone per ml. organic solvent.

Standard bismuth solution. Stock solution 0.02 per cent was made by dissolving $\text{Bi}(\text{NO}_3)_3$ in 1 : 100 nitric acid. The working solution contained 20 γ Bi per ml. also in 1 : 100 nitric acid, and was prepared fresh every day.

Procedure: After various attempts it was established that the reaction between bismuth and dithizone is quantitative in neutral solution. In a 100 ml. separatory funnel various quantities of metal were shaken for 3 minutes in 20 ml. of a dilute acetate buffer pH 6.0 with 10 ml. standard dithizone solution. The organic layer was run into the 17.2 mm. cuvette and the absorption of light measured at 505 and 620 m μ wave lengths. The maximum absorption of light by bismuth dithizonate is 490 m μ , but at this wave length dithizone itself has a rather strong absorption, so for this reason 505 m μ was used. The extinction coefficient was calculated and plotted on a graph against the amount of metal. The result is given in Fig. 3.

From the graph it will be seen that bismuth dithizonate obeys Beer's law, and that 60 γ of dithizone is transferred to dithizonate with 16.4 γ of bismuth. The composition BiDz_3 is thereby confirmed.

The equilibrium constant of reaction (1) is expressed by

$$K = \frac{[\text{BiDz}_3]_o [\text{H}^+]_w^3}{[\text{Bi}^{+++}]_w [\text{HDz}]_o^3} \quad (2)$$

K has not yet been determined, but Greenleaf (28) has studied the effect of pH and concentration of dithizone on extraction of bismuth.

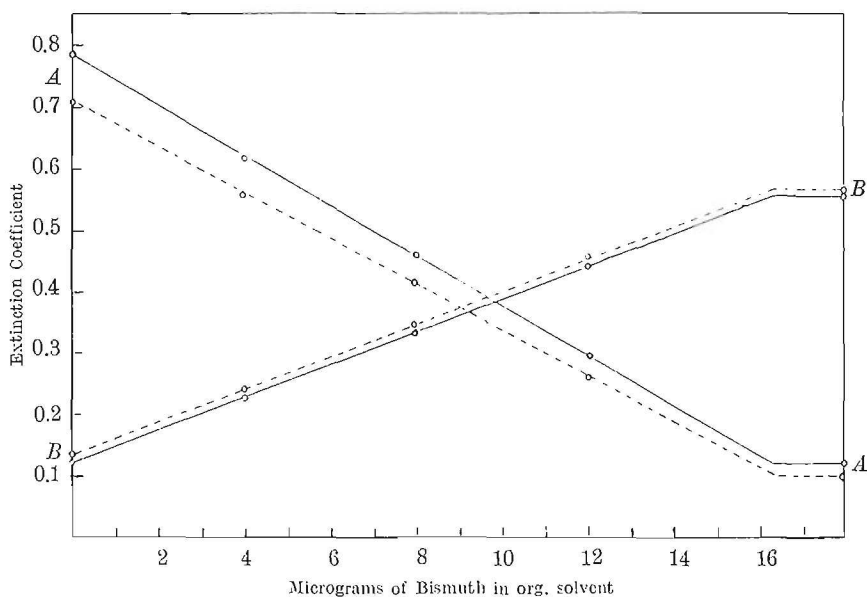


Fig. 3. — Determination of bismuth with dithizone by the mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, ——— CCl₄, - - - - - CHCl₃. A. Absorption of light measured at 620 m μ . B. Absorption determined at 505 m μ .

The procedure for determination of K was in the manner already described in outline, but as the same procedure is carried out also for other metals in this investigation it is given here more in detail:

Firstly, the time required to attain equilibrium between the metal and the reagent was established, and after this the real determination of the equilibrium constant followed. For practical reasons the volume of the standard dithizone solution was kept constant at 10 ml. The weaker standard solution contained 6, and the stronger 30 micrograms of dithizone per ml. The volume of the aqueous solution ranged from 10 to 50 ml.

It has already been mentioned that not all metal-dithizone reactions are simply reversible. To establish this fact, 10 ml. of the weaker standard solution of dithizone was transferred into metal dithizonate, and this solution was shaken the required time at a pH at which a part of the dithizonate is decomposed and the amount of metal left in the organic phase was determined as usual by the mixed-color method.

In tests where the equilibrium constant was determined with a great excess of dithizone (300 γ), the amount of metal combined with dithizone was obtained as follows: After the extraction the organic layer was separated and discarded; the pH of the aqueous phase was adjusted to a value at which the equilibrium is displaced entirely in favor of the

metal dithizonate, and extracted with 10 ml. of the weaker dithizone standard solution. The amount of metal thus obtained was subtracted from the original amount.

Various experiments proved that the reaction bismuth-dithizone is almost immediate, and for this reason the time of shaking was fixed at 5 minutes; the equilibrium constant was then determined in the manner described above. The result is given in Table 5. In this table the amount of metal in the organic layer is the mean of the quantities obtained at the two wave lengths. The difference was never greater than 0.2 micrograms. The various concentrations were calculated in mol per liter. From the above it can be seen that the value of K is reasonably constant, as it will be observed that the expression for K contains two factors raised to the third power. For example, it can be

TABLE 5
BISMUTH — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Bi added γ	ϵ 620 m μ	ϵ 505 m μ	Bi in org. phase γ	K
Carbon tetrachloride			0	0.785	0.122		
			BiDz ₃	.121	.556	16.4	
	1.67	10	10	.531	.288	6.2	5.7 $\times 10^9$
	2.43	10	20	.199	.504	14.3	5.3
	1.71	20	10	.596	.272	5.8	6.0
	2.06	20	20	.310	.432	11.6	5.8
	1.88	20	100	.258	.469	12.8	5.3
	1) 0.94	20	20			12.9	5.7
	2.20	50	10	.437	.351	8.6	5.8
	2.05	50	20	.372	.393	10.1	5.1
	2) 2.17	10	BiDz ₃	.287	.450	12.3	5.0
	2) 1.63	50	"	.589	.249	4.8	5.9
							M. 5.6 $\times 10^9$
	Chloroform			0	0.707	0.132	
			BiDz ₃	.101	.558	16.4	
2.82		10	10	.592	.214	3.1	2.3 $\times 10^6$
3.14		10	20	.387	.351	8.5	2.0
3.29		20	10	.450	.310	6.7	2.1
3.60		20	20	.253	.451	12.2	2.4
3.69		20	100	.216	.472	13.1	2.7
1) 2.43		20	20			12.6	2.0
3.23		50	10	.523	.259	4.9	2.2
3.46		50	20	.342	.337	9.8	2.5
2) 3.18		10	BiDz ₃	.398	.347	8.2	2.0
2) 3.04		50	"	.551	.238	4.1	2.4
							M. 2.3 $\times 10^6$

1) The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described on page 24.

2) Decomposing of bismuth dithizonate. Procedure on page 24.

mentioned that a value of the equilibrium constant equal to 5.8×10^9 is changed to 5.0×10^9 if pH is increased 0.02 units, and to 7.0×10^9 if the amount of bismuth in the organic layer is increased with 0.2 micrograms.

The dithizone method is used in determining bismuth in other metals and in biological material. The extraction is usually carried out in alkaline solution in the presence of complex-forming substances, to prevent the co-extracting of other metals which react with dithizone. There are reports by Hubbard (29) and Reith/van Dijk (30) which state that bismuth cannot be completely extracted under these conditions, whereas Haddock (31) found a quantitative extraction.

To investigate these facts, the equilibrium constant was determined in solutions containing the usual complex-formers and also in sea water and in sodium chloride solution. In these cases, however, the extraction of the metal is carried out partially in alkaline medium; it can be therefore supposed that the bismuth salt present is probably more or less hydrolyzed. The expression of K should then be another, which Sandell (3) points out also. With such small quantities of dithizone and metal present, however, an equation with both metal and metal hydroxide cannot be confirmed experimentally. In the results given in Table 6, therefore, the equilibrium constant was calculated in the same manner as for the values in Table 5.

TABLE 6
BISMUTH — DITHIZONE EQUILIBRIUM IN THE PRESENCE OF VARIOUS ANIONS
10 ml. organic solvent containing 60 γ of dithizone.

	Anions present in aqueous phase	pH	aq. phase ml.	Bi added γ	ϵ 620 $m\mu$	ϵ 505 $m\mu$	Bi in org. phase γ	K
Carbon tetrachloride	Sea water, Cl = 12 ‰	1.78	10	10	0.621	0.229	4.0	5.6×10^8
	» »	2.35	50	20	.388	.382	9.7	4.9 »
	1 M NaCl	3.56	10	10	.438	.350	8.5	8.5×10^4
	» »	3.91	50	20	.281	.452	12.3	8.0 »
	0.1 M KCN	1.42	10	10	.657	.204	3.1	3.7×10^9
	» »	1.92	50	20	.461	.334	7.9	3.2 »
	0.1 M Na citrate	6.60	10	10	.575	.261	5.1	3.9×10^{-6}
	» »	7.57	50	20	.224	.486	13.7	3.9 »
	0.1 M K Na tartrate ..	6.94	10	10	.469	.331	7.7	2.7 »
	» » ..	7.20	50	20	.356	.402	10.5	2.3 »
Chloroform	Sea water, Cl = 12 ‰	3.94	10	10	0.377	0.363	8.8	8.8×10^3
	» »	4.03	50	20	.308	.412	10.6	8.3 »
	1 M NaCl	3.81	10	10	.566	.228	3.7	3.7×10^2
	» »	4.84	50	20	.214	.479	13.2	3.2 »
	0.1 M KCN	3.19	10	10	.464	.300	6.5	1.8×10^5
	» »	3.88	50	20	.231	.466	12.7	1.4 »
	0.1 M Na citrate	8.31	10	10	.523	.263	4.9	2.6×10^{-11}
	» »	8.55	50	20	.437	.321	7.2	2.8 »
	0.1 M K Na tartrate ..	8.25	10	10	.610	.201	2.6	8.3×10^{-12}
	» » ..	8.58	50	20	.507	.269	5.3	8.3

The value of the equilibrium constant for bismuth dithizonate remained unchanged in the presence of the same anions, but certain substances had a great preventive effect on the extraction. A clearer picture of the results obtained is given by drawing the corresponding equilibrium curves, shown in Fig. 4. The curves are calculated from the value of K with no excess of dithizone and for twice as much aqueous phase as organic solvent.

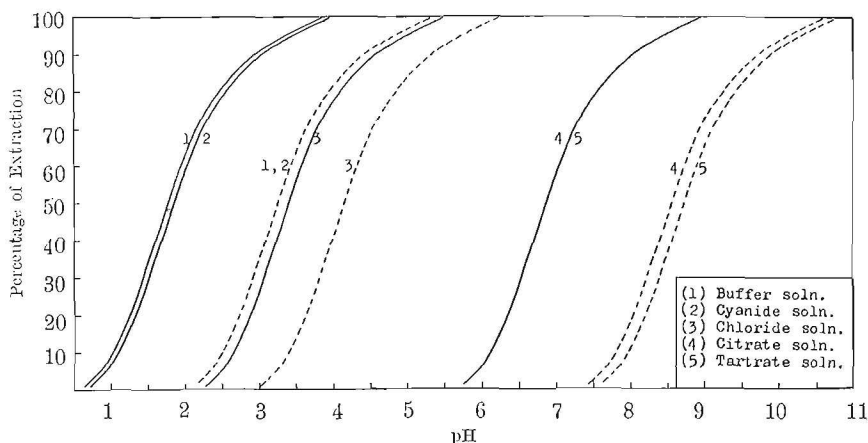


Fig. 4. — Equilibrium curves for bismuth dithizonate in carbon tetrachloride (—) and chloroform (-----). No excess of dithizone.

In the above experiments the usual concentrations of cyanide and citrate were used. If bismuth is to be determined in various metals, however, the quantities should be considerably increased. Haddock (31) accordingly uses solutions of 0.5 M in ammonium citrate and 2 M in potassium cyanide.

A closer examination of the completeness of the extraction of bismuth in the presence of the salts in the concentrations mentioned above gave the following result: The extraction should be carried out in alkaline medium but pH must not have such a high value that all dithizone present is converted to alkali dithizonate. An excess of the reagent is necessary and the extraction should be repeated at least twice. Following this practice, an additional amount of metal was obtained at pH 9—9.5 and 10.5—11 with the reagent dissolved in carbon tetrachloride and chloroform respectively. When a carbon tetrachloride solution of dithizone was used at pH 11, no metal was extracted, as at this pH all of the dithizone is converted to the enol modification.

According to Reith and van Dijk (30), bismuth forms possibly also another complex salt with dithizonate. By titrating the metal at pH 7.5, they found that only about half of the amount of dithizone required at pH 4.0 was required at the higher pH value to obtain dithizonate

The usual bismuth dithizonate is orange in color; this new salt, however, imparts to the organic solvents a deep red color.

A further investigation of this bismuth dithizonate with dithizone in carbon tetrachloride confirmed partly the observations made by Reith and van Dijk, *viz.* that the salt is formed in weak alkaline solution at pH 7—8 and with a deficiency of dithizone. Whether this dithizonate is obtained by treating BiDz_3 with alkali has not been observed. The composition was found to be Bi_2Dz_3 , by shaking a fixed amount of dithizone in carbon tetrachloride at pH 8 with an excess of metal, discarding the organic phase, making the aqueous solution weak in acid, and then determining the amount of bismuth left according to the mixed-color method.

In this investigation the color of the so-called enol form Bi_2Dz_3 was found to be red-orange and not deep red as stated by Reith and van Dijk. The difference in color between the two dithizonates is rather small, but it can be observed by comparing one with the other. Both show maximum absorption of light at 490 $\text{m}\mu$ wave length, and their absorption curves are also practically identical.

Discussion and observations: The value of the equilibrium constant for bismuth dithizonate in carbon tetrachloride and chloroform has been determined, and from this it appears that the metal should be extracted at a pH value which is 1.5 units higher if the reagent is dissolved in chloroform.

The results show also that the reaction of bismuth with dithizone is simply reversible; accordingly BiDz_3 can be decomposed quantitatively with 0.15 N (CCl_4) and 0.05 N (CHCl_3) acid.

In the absence of citrate, tartrate and greater amounts of halide, bismuth can be titrated quantitatively with dithizone at pH 3.8 (CCl_4) and 5.2 (CHCl_3). Both of these pH values are higher than those reported in literature. Accordingly, Yu-Lin-Yao (32) titrates at pH 3.0 (CCl_4) and Reith/van Dijk at 4.0 (CHCl_3). Further, Sandell (3) separates bismuth from thallium and lead by extracting at pH 2.5—3 with dithizone dissolved in chloroform. The reaction between bismuth and dithizone is not quantitative at these pH values, but a complete extraction can of course be made by shaking with a greater excess of dithizone, and with repeated portions.

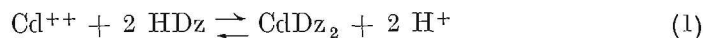
In the presence of complex-forming substances such as citrate and tartrate, bismuth should be extracted from an alkaline solution with a pH of about 9.5 (CCl_4) or 10.5 (CHCl_3). If bismuth is to be determined in various metals, an excess of dithizone is necessary and the extraction should be repeated at least twice.

In the presence of an excess of metal in alkaline solution, bismuth forms another complex salt with dithizone, which is red-orange in color

and has the composition Bi_2Dz_3 . As an excess of dithizone is always used in determining traces of bismuth, the formation of the second dithizonate need not be taken into account, if only the final determination of the metal is made at a pH of 5—6.

2. Cadmium

When a neutral or basic solution of a cadmium salt is shaken with dithizone in chloroform or carbon tetrachloride, a red cadmium dithizonate is obtained, which, if the concentration is not too high, is soluble in the organic solvents mentioned. The solubility in chloroform is greater than in carbon tetrachloride. The reaction takes place in accordance with the equation:



and the equilibrium constant is as follows:

$$K = \frac{[\text{CdDz}_2]_o [\text{H}^+]_w^2}{[\text{Cd}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

Before determining the constant, it was necessary to verify the composition of the dithizonate; this was accomplished by making calibration curves in the manner already described for bismuth.

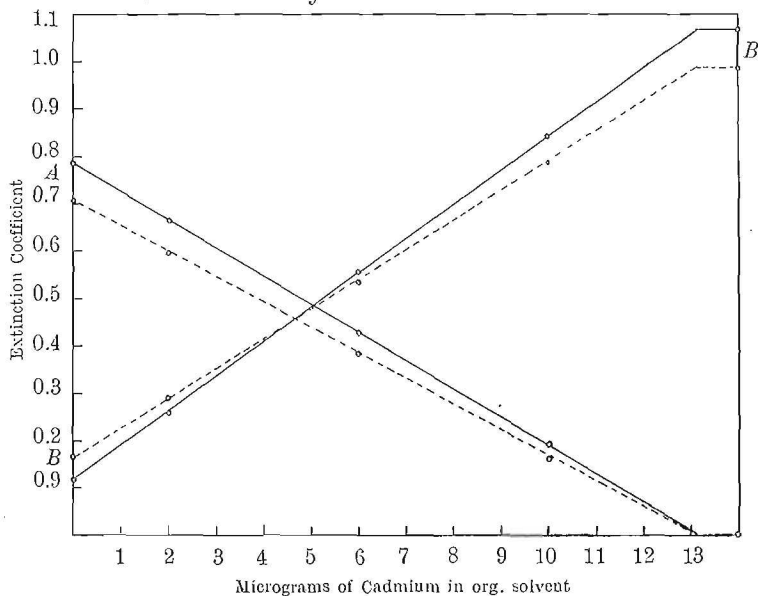


Fig. 5. — Determination of cadmium with dithizone by the mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . A. Absorption of light measured at 620 $m\mu$. B. Absorption determined at 515 $m\mu$.

Standard cadmium solution, 0.002 per cent. This solution was prepared fresh every day, by diluting a 0.02 per cent solution obtained by dissolving cadmium sulfate, $3 \text{ CdSO}_4 \times 8 \text{ H}_2\text{O}$, in 0.1 N sulfuric acid.

After various attempts it was ascertained that cadmium combines quantitatively with dithizone in neutral solution. The extractions were made with 20 ml. acetate buffer pH 7.0 and 10 ml. of the dithizone working solution containing 60 γ of the reagent. The absorption of light was measured at 515 and 620 $m\mu$ wave length, the maximum by cadmium dithizonate and dithizone respectively. The calibration curves are given in Fig. 5, from which it can be seen that the composition of the dithizonate is CdDz_2 .

The value of the equilibrium constant was determined in the same manner as the constant for bismuth dithizonate, and a 5 minutes shaking-out proved in this case also to be sufficient. The results are given in Table 7.

TABLE 7
CADMIUM — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Cd added γ	ϵ 620 $m\mu$	ϵ 515 $m\mu$	Cd in org. phase γ	K
Carbon tetrachloride			0	0.785	0.120		
			CdDz_2	.000	1.065	13.2	
	3.93	10	8	.571	0.384	3.6	39
	4.50	10	20	.173	.848	10.2	37
	4.27	20	8	.498	.460	4.8	40
	4.54	20	20	.206	.817	9.7	42
	4.36	20	100	.118	.922	11.1	35
	¹⁾ 3.30	20	20			8.7	38
	4.06	50	8	.650	.275	2.2	38
	4.45	50	20	.325	.661	7.6	39
	²⁾ 3.72	10	CdDz_2	.590	.343	3.2	37
	²⁾ 5.63	50	»	.077	.976	11.8	40
Chloroform			0	0.707	0.166		
			CdDz_2	.000	.990	13.2	
	4.50	10	8	.501	.404	3.8	3.3
	5.50	10	20	.062	.916	12.0	3.4
	5.12	20	8	.357	.571	6.5	3.6
	5.06	20	20	.185	.768	9.6	3.4
	4.79	20	100	.130	.838	10.8	3.6
	¹⁾ 3.75	20	20			7.5	3.5
	5.47	50	8	.331	.600	7.0	3.4
	5.58	50	20	.111	.860	11.1	3.3
	²⁾ 4.07	10	CdDz_2	.589	.302	2.1	3.6
	²⁾ 5.52	50	»	.185	.774	9.7	3.3

¹⁾ The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

²⁾ Decomposing of cadmium dithizonate. Procedure on p. 24.

In the methods used to date for determination of traces of cadmium, the extraction has taken place in alkaline solution in the presence of complex-forming substances such as seignette salt, used by Fischer and

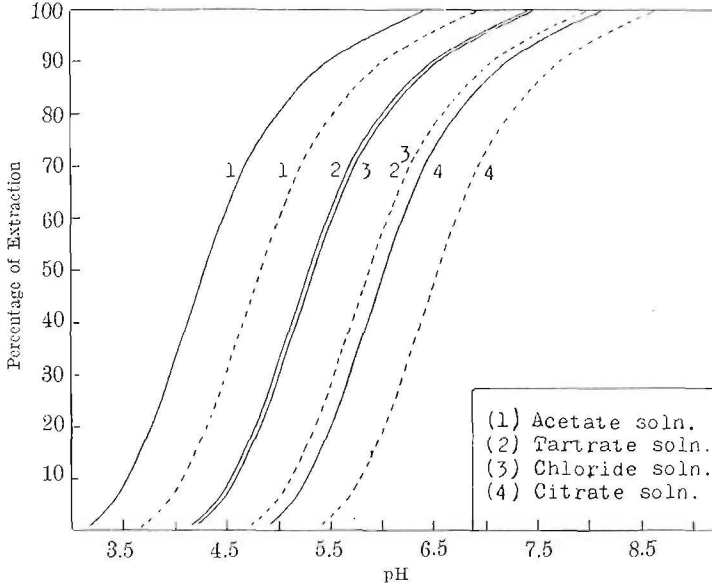


Fig. 6. — Equilibrium curves for cadmium dithizonate in carbon tetrachloride (—) and chloroform (-----). No excess of dithizone.

Leopoldi (33), and sodium citrate, used by Sandell (34). To ascertain any possible influence of anions on the extraction, the value of the equi-

TABLE 8
CADMIUM — DITHIZONE EQUILIBRIUM IN THE PRESENCE OF VARIOUS ANIONS
10 ml. organic solvent containing 60 γ of dithizone.

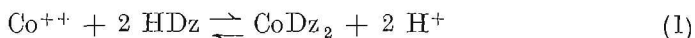
	Anions present in aqueous phase	pH	aq. phase ml.	Cd added γ	ϵ		Cd in org. phase γ	K
					620 $m\mu$	515 $m\mu$		
CCl ₄	Sea water, Cl = 12 ‰ ..	3.98	10	8	0.631	0.300	2.6	15
	» »	4.75	50	20	.291	.716	8.3	15
	1M NaCl	5.19	10	8	.501	.456	4.7	0.26
	» »	6.16	50	20	.100	.930	11.3	0.28
	0.2M Na citrate	6.59	10	8	.326	.660	7.6	1.3×10^{-2}
	» »	6.56	50	20	.200	.821	9.8	1.0 »
	0.2M K Na tartrate	4.69	10	8	.667	.268	2.1	0.39
	» »	5.37	50	20	.369	.618	6.9	0.38
CHCl ₃	Sea water, Cl = 12 ‰ ..	4.98	10	8	0.409	0.512	5.5	1.3
	» »	5.66	50	20	.140	.822	10.5	1.2
	1M NaCl	6.11	10	8	.340	.588	6.8	2.7×10^{-2}
	» »	6.68	50	20	.106	.866	11.2	2.4 »
	0.2M Na citrate	7.84	10	8	.325	.608	7.1	1.4×10^{-5}
	» »	7.85	50	20	.238	.714	8.8	1.3 »
	0.2M K Na tartrate	5.92	10	8	.381	.550	6.1	2.8×10^{-2}
	» »	6.16	50	20	.228	.721	8.9	3.3 »

librium constant was determined in solutions containing the salts mentioned above, and also in sea water and sodium chloride solution. The results can be seen from Table 8 and from Fig. 6, in which the equilibrium curves for cadmium dithizonate in carbon tetrachloride and chloroform are drawn. The curves are calculated as for bismuth, from the values of K .

From the above, the conclusion can be drawn that a quantitative determination of traces of cadmium can be made in neutral solutions in the absence of foreign anions. In the presence of citrate and tartrate the metal should be extracted from an alkaline solution with a pH of 8 to 1 N sodium hydroxide, as, according to Fischer and Leopoldi (33), CdDz_2 is the most stable of all metal dithizonates and is not decomposed by the solution last mentioned.

3. C o b a l t

Cobalt combines with dithizone in neutral and alkaline solution, giving a red-violet dithizonate soluble in carbon tetrachloride and chloroform. As cobalt is a divalent metal, the reaction occurs according to the equation:



The composition of the dithizonate was confirmed by obtaining standard curves in the manner already described.

Standard cobalt solution. The stock solution was made by dissolving $\text{Co}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$ in 0.1 N nitric acid, and contained 0.2 mg. of Co per ml. The working solution, containing 10 γ of Co per ml., was obtained by diluting the stock solution with metal-free water.

Reaction (1) proceeds somewhat slowly, but a quantitative extraction was nevertheless obtained after vigorously shaking at pH 6.8 (CCl_4) and 7.9 (CHCl_3) for 5 minutes. The various quantities of metal were extracted from 20 ml. dilute borax-boric acid buffer with 10 ml. dithizone working solution. The absorption of light by the organic phase was measured in 17.2 mm. cells at 525 and 620 $m\mu$ wave lengths. Cobalt dithizonate gives maximum absorption at 535 $m\mu$, but the absorption of the green color by dithizone itself is rather great at this wave length, so for this reason the first-mentioned was used.

The curves are given in Fig. 7, and from these it appears that the composition of the dithizonate is CoDz_2 and that Beer's law holds.

The equilibrium constant for reaction (1) can be expressed as:

$$K = \frac{[\text{CoDz}_2]_o [\text{H}^+]_w^2}{[\text{Co}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

The value of K has not been determined before.

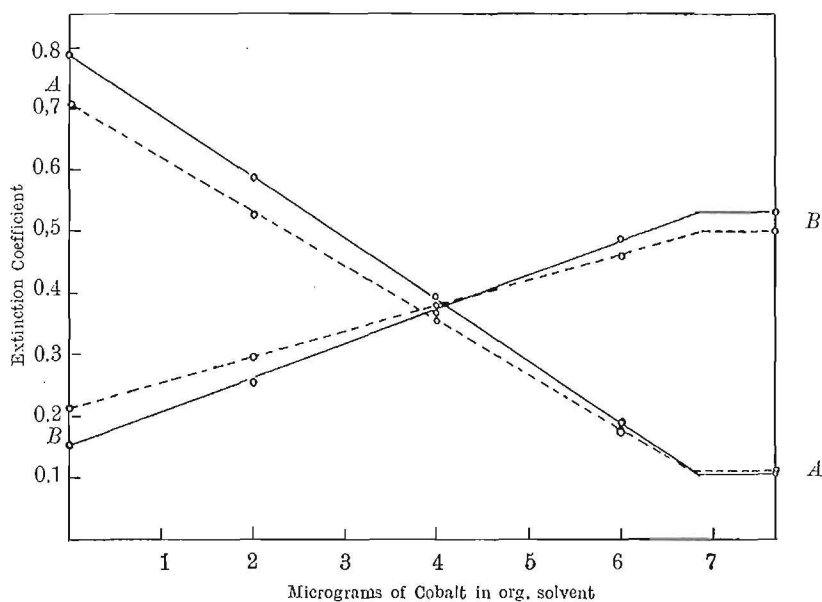


Fig. 7. — Determination of cobalt by the dithizone mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, ——— CCl_4 , - - - - CHCl_3 . A. Absorption of light measured at 620 $m\mu$. B. Absorption determined at 525 $m\mu$.

As already pointed out, the reaction between cobalt and dithizone is rather slow. In more acid solutions, therefore, quite a long time is required for extraction before equilibrium is attained. The effect of time on the extraction of cobalt was studied at pH 4.9 (CCl_4) and 6.0 (CHCl_3), with 10 ml. dithizone working solution and 20 ml. aqueous phase containing 8 γ of cobalt. The shakings were carried out in the dark and the results are given in Table 9.

TABLE 9

EFFECT OF TIME ON THE EXTRACTION OF COBALT
20 ml. aqueous solution pH 4.9 (CCl_4) and 6.0 (CHCl_3),
10 ml. dithizone standard solution. 8 γ Co taken.

Time of shaking in minutes	Micrograms of Cobalt found in organic phase	
	Carbon tetrachloride	Chloroform
5	0.9	0.15
15	3.5	0.6
30	4.3	3.3
60	5.0	4.0
90	5.6	4.4
120	5.5	4.4

The experiments show that equilibrium is attained after shaking for one and a half hours, so this time was used accordingly. A longer extraction then 2 hours cannot be used because of the instability of the dithizonate, which after this time begins already to decompose. This can be observed by the fact that a smaller quantity of cobalt is extracted after shaking 2 hours than after one and a half hours.

Apart from this, the determination of the equilibrium constant was made as already described for bismuth. The results are given in Table 10.

TABLE 10
COBALT — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Co added γ	ϵ 620 $m\mu$	ϵ 525 $m\mu$	Co in org. phase γ	K
Carbon tetrachloride			0	0.785	0.152		
			CoDz ₂	.102	.532	6.9	
	4.06	10	5	.527	.295	2.6	38
	4.32	10	10	.305	.414	4.8	42
	4.37	20	5	.474	.326	3.1	36
	4.33	20	10	.362	.388	4.2	38
	4.61	20	50	.162	.504	6.3	43
	¹⁾ 3.51	20	10			6.5	40
	5.08	50	5	.348	.391	4.4	36
	4.02	50	10	.592	.257	1.9	38
							M. 39
Chloroform			0	0.707	0.212		
			CoDz ₂	.106	.500	6.9	
	6.06	10	5	.354	.377	4.0	3.2 10^{-2}
	6.30	10	10	.184	.461	5.9	3.1
	5.35	20	5	.603	.259	1.2	3.4
	6.02	20	10	.288	.409	4.7	2.9
	6.01	20	50	.771	.466	6.1	3.6
	¹⁾ 5.03	20	10			6.3	3.2
	5.44	50	5	.642	.246	0.8	3.0
	5.92	50	10	.399	.354	3.5	2.9
							M. 3.2 10^{-2}

¹⁾ The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

According to Sandell (3) the reaction in equation (1) is not simply reversible; once formed in basic solution, the dithizonate is not readily decomposed by dilute acid. Hibbard (35) uses this fact for separating cobalt from zinc and lead. The dithizonates in chloroform of the metals mentioned are shaken three or more times in succession with 0.01 N hydrochloric acid. This process passes zinc and lead to the aqueous phase, while cobalt remains in the organic layer. The following series of experiments (Table 11) show, however, that CoDz₂ decomposes partly

at pH 2, especially if a longer period of extraction is resorted to. The experiments were made with 20 ml. dilute buffer solutions and 10 ml. cobalt dithizonate solution, obtained by reverting the standard solution of the reagent to dithizonate. The value of the equilibrium constant for the reaction (1), when it takes place from right to left, was not determined, as it is of no practical importance.

TABLE 11

EFFECT OF PH AND TIME OF SHAKING ON THE DECOMPOSING OF COBALT DITHIZONATE

20 ml. aqueous solution and 10 ml. organic solvent containing 6.9 γ Co combined with dithizone.

pH	Time of shaking in minutes	Micrograms of Cobalt found in organic phase	
		Carbon tetrachloride	Chloroform
2.20	5	4.1	2.7
2.20	30	1.3	0.0
1.88	5	2.7	1.4
1.88	30	0.4	0.0

The slow reaction between cobalt and dithizone is one of the reasons why the reagent is not commonly used in determining traces of this metal. Besides by Hibbard, the reagent is used by Sandell and Pehrlich (36) for the determination of cobalt in silicate rocks, and by Marston and Dewey (37) for the extraction of cobalt in plant and animal tissues. The determinations are based on the extraction of cobalt with a carbon

TABLE 12

COBALT — DITHIZONE EQUILIBRIUM IN THE PRESENCE OF VARIOUS ANIONS

10 ml. organic solvent containing 60 γ of dithizone.

	Anions present in aqueous phase	pH	aq. phase ml.	Co added γ	ϵ 620 $m\mu$	ϵ 525 $m\mu$	Co in org. phase γ	K
CCl ₄	Sea water, Cl=12 ‰	4.44	10	5	0.417	0.355	3.7	31
	» »	4.45	50	10	.401	.361	3.8	35
	1M NaCl	4.91	10	5	.356	.388	4.3	12
	» »	4.87	50	10	.325	.402	4.6	13
	0.2M Na citrate	6.26	10	5	.624	.242	1.6	4.4×10^{-4}
	» »	6.51	50	10	.576	.268	2.1	4.8
CHCl ₃	Sea water, Cl=12 ‰	6.00	10	5	0.382	0.361	3.7	2.4×10^{-2}
	» »	5.67	50	10	.516	.301	2.2	2.6
	1M NaCl	5.61	10	5	.575	.273	1.5	7.7×10^{-3}
	» »	7.14	50	10	.160	.468	6.2	8.1
	0.2M Na citrate	7.55	10	5	.648	.245	0.7	2.9
	» »	8.26	50	10	.459	.332	2.8	3.0×10^{-7}

tetrachloride solution of dithizone from an ammoniacal citrate solution of the sample. The equilibrium constant therefore was determined in this medium and also in sodium chloride solution and sea water, in order to isolate possibly with dithizone the cobalt content in natural waters. The time of shaking was in this case also one and a half hours. The results are given in Table 12 and Fig. 8.

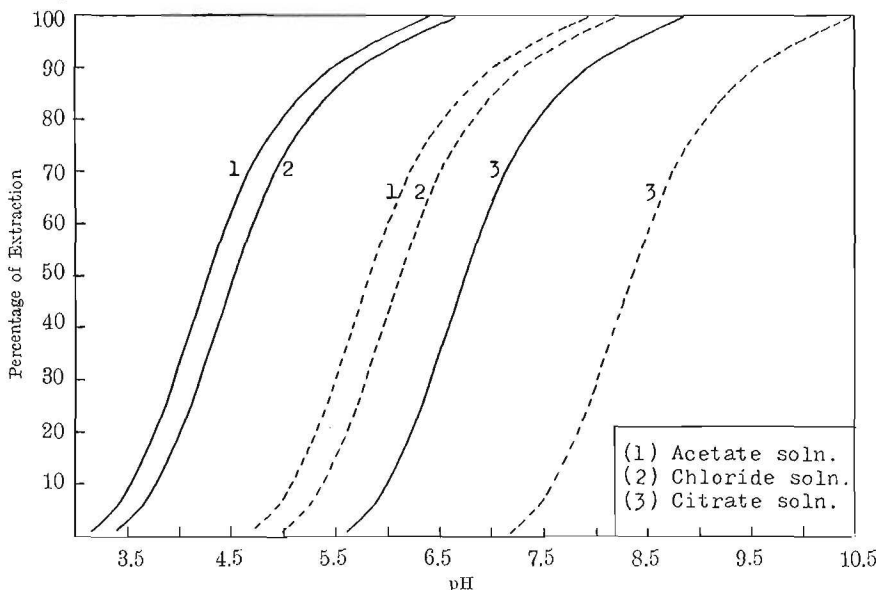


Fig. 8. — Equilibrium curves for cobalt dithizonate in carbon tetrachloride (—) and chloroform (-----). No excess of dithizone.

Discussion: The reaction between cobalt and dithizone proceeds very slowly in weak acid solution and under normal working conditions equilibrium will probably not be attained; this takes place first after vigorous shaking for about 90 minutes. The equilibrium constant is of little importance; in practice, one should take into account the so-called distribution constant after 5 minutes extraction, which can be calculated from Table 9.

From the values of K it can be observed that cobalt, like bismuth and cadmium, is extracted to the same extent at a pH value which is 1.5 units lower where dithizone is dissolved in carbon tetrachloride than where a chloroform solution of the reagent is used.

The metal should preferably be determined in alkaline solution pH 8.5—9, using the higher value if the sample solution contains citrates.

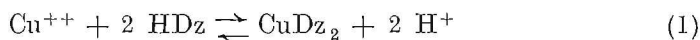
Further, it has been proved that the decomposing of the cobalt dithizonate begins at a higher pH value than usually stated in literature. By isolating cobalt from lead and zinc, the combined dithizonates should be shaken with 0.005 N acid for 10—20 seconds only. During this time CoDz_2 remains unchanged.

4. Copper

A. Cupric copper

Divalent copper gives two complex salts with dithizone. The one used for analytical purposes is formed in dilute acid solution and is of violet color; the other is formed when the metal reacts with the reagent in basic solution and has a green-yellow color. Both are soluble in chloroform and carbon tetrachloride.

The violet salt is Fischer's keto form and is formed according to the equation:



which can also be seen from the standard curves in Fig. 9. The curves were constructed in the usual manner, with 20 ml. of acetate buffer pH 6.0 and 10 ml. dithizone standard solution. The absorption of light by the copper dithizonate-dithizone solution was measured in 17.2 mm. cells at 535 and 620 $m\mu$ wave length. CuDz_2 shows maximum absorption at 545 $m\mu$, but the difference in the values of the extinction coefficient of pure dithizone and copper dithizonate is greater at 535 $m\mu$.

Standard copper solution, 0.02 per cent, was obtained by dissolving uneffloresced crystals of $\text{CuSO}_4 \times 5 \text{H}_2\text{O}$ in 0.1 N sulfuric acid. A weaker solution, containing 10 γ Cu per ml., was prepared from this, by diluting with metal-free water.

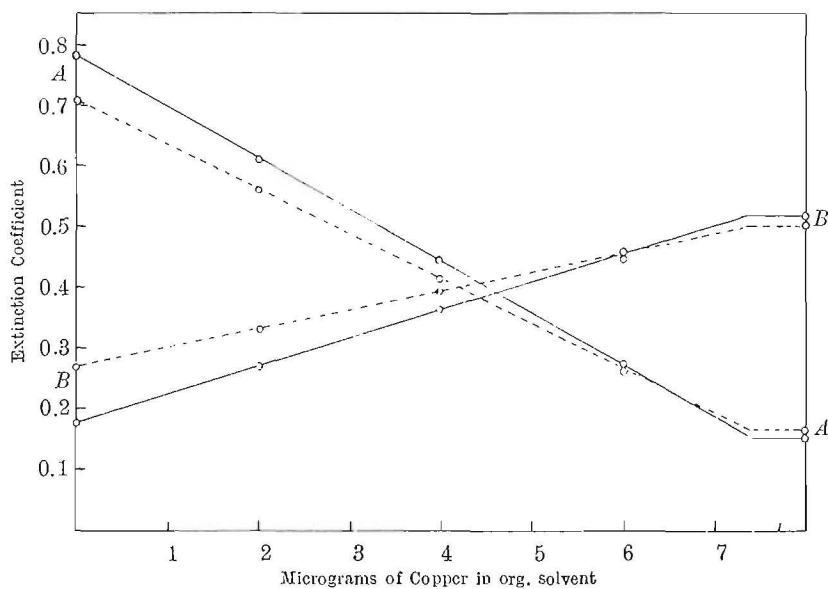


Fig. 9. — Determination of copper with dithizone by the mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . A. Absorption of light measured at 620 $m\mu$. B. Absorption determined at 535 $m\mu$.

Dithizone is one of the most important colorimetric reagents in the determination of traces of copper, and for this reason the value of the equilibrium constant for the reaction (1):

$$K = \frac{[\text{CuDz}_2]_o [\text{H}^+]_w^2}{[\text{Cu}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

has also been determined before. As already mentioned in this work, there is a rough determination by Sandell (3) for keto cupric dithizonate in carbon tetrachloride with $K = 1 \times 10^{10}$, and also one by Buch (15) based on the extractive titration method with $K = 1 \times 10^8$. Further, Greenleaf (28) has made an investigation similar to that for bismuth and studied the effect of pH and concentration of dithizone on the extraction of copper. The equilibrium constant, however, was not calculated.

Unlike bismuth and cadmium, but in the same manner as cobalt, copper combines very slowly with dithizone in acidic solution. It is therefore of great importance to know the shaking time required to attain equilibrium. The effect of time on the completeness of the extraction has also been observed by Barnes (38, 39, 40), who in part uses this in the determination of the rate of release of mercury from antifouling compositions into sea water. The time was established as being 2 hours, arrived at after the following experiment, Table 13, made with 10 ml. dithizone working solution and 20 ml. 0.6 N sulfuric acid and 20 ml. HCl—KCl buffer pH 1.9, when dithizone was dissolved in carbon tetrachloride and chloroform respectively. 10 micrograms of copper were present.

TABLE 13

EFFECT OF TIME ON THE EXTRACTION OF COPPER

20 ml. 0.6 N H_2SO_4 (CCl_4) and buffer solution pH 1.9 (CHCl_3),
10 ml. dithizone standard solution. 10 μ Cu taken.

Time of shaking in minutes	Micrograms of Copper found in organic phase	
	Carbon tetrachloride	Chloroform
5	4.2	0.8
15	5.2	1.3
30	5.5	1.7
60	5.6	3.6
120	5.8	4.6
150	5.8	4.6

According to Sandell (3), it is of great importance, especially in the determination of copper, that the organic solvent is absolutely pure; the above series of experiments, therefore, were made with A. R. carbon tetrachloride of various manufactures. The result, however, was the same.

With a carbon tetrachloride solution of dithizone, the reaction with copper occurs in such an acid solution that buffers cannot be used. The determination of the value of the equilibrium constant, therefore, had to be made with sulfuric acids of various strengths. After the extraction, the acids were titrated with 0.1 N NaOH and the H^+ -ion concentration was taken as equal to the normality of the acid. The determination gave the result shown in Table 14.

TABLE 14
COPPER — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	H^+	aq. phase ml.	Cu added γ	620 ϵ $m\mu$	535 ϵ $m\mu$	Cu in org. phase γ	K
Carbon tetrachloride			0	0.785	0.181		
			CuDz ₂	.156	.517	7.4	
	0.8	10	5	.425	.369	4.2	3.2 $\times 10^{10}$
	0.4	10	10	.230	.475	6.0	3.6
	0.7	20	5	.443	.362	4.0	3.3
	0.8	20	10	.336	.419	5.3	3.1
	1.5	20	50	.276	.448	6.0	3.6
	¹⁾ 4.0	20	10			8.9	3.3
	0.5	50	5	.461	.349	3.8	3.0
	1.5	50	10	.486	.340	3.5	3.9
							M. 3.4 $\times 10^{10}$
Chloroform	pH		0	0.707	0.275		
			CuDz ₂	.161	.500	7.4	
	1.22	10	5	.611	.314	1.3	3.4 $\times 10^6$
	1.87	10	10	.342	.424	5.0	3.2
	1.74	20	5	.520	.351	2.6	3.1
	1.95	20	10	.352	.419	4.8	3.1
	2.02	20	50	.231	.475	6.5	3.3
	¹⁾ 1.01	20	10			6.2	3.3
	2.06	50	5	.481	.368	3.1	3.2
	1.75	50	10	.495	.362	2.9	3.2
							M. 3.2 $\times 10^6$

¹⁾ The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

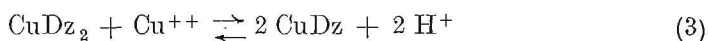
Because of such acid solutions, it could not be ascertained whether the reaction in equation (1) is simply reversible or not. Preliminary trials, however, showed that 7 N acid decomposes quantitatively CuDz₂ dissolved in carbon tetrachloride, and this is in accordance with a report by Vesterberg and Sjöholm (41). Further Greenleaf (28) states that the metal can be recovered quantitatively from the chloroform extract of copper dithizonate by shaking with 6 N hydrochloric acid.

In addition to copper, other metals which react with dithizone in acid solution are: bismuth, gold, mercury, palladium and silver. So far as silver, mercury, and bismuth are concerned, the use of alkali halides

or halogen acids as precipitants and complex formers permits the separation of copper from these metals. Laug and Nelson (42) determine copper in a bromide solution at pH 1, in consequence of the formation of slightly dissociated HgBr_4^- . Morrison and Paige (43) extract copper in acidified potassium iodide solution to convert silver, mercury and bismuth into their iodide complexes.

To find out the effect of the salts mentioned above — and also that of sodium chloride and sea water — on the extraction of copper, K was determined with the metal in the following solutions: sea water $\text{Cl} = 12 \text{ ‰}$, 1 M NaCl, 0.5 M KBr and 0.1 M KI. The value of the equilibrium constant remained unchanged.

Divalent copper gives, as already mentioned, also another salt with dithizone and this is formed in neutral and basic solution in the presence of an excess of copper, according to the equation:



The salt is soluble in the organic liquids and imparts to them a yellow-green color.

According to Fischer this so-called enol tautomer should be formed also if CuDz_2 is treated with alkali, but this dithizonate is unchanged after 30 minutes shaking at pH 10.5. At a higher pH than 11.5 the salt changes to another color, probably depending on its own decomposing.

If desired, the mono-color method can be used for determination of copper; excess dithizone is removed then, for example, with several portions of borax-sodium carbonate buffer pH 10.5. Mehurin (44) recommends in this case a mixture of sodium pyrophosphate and sodium carbonate, since he found that ammonia exercises a bleaching action on solutions containing minute quantities of copper dithizonate.

The composition of this dithizonate was determined with dithizone in carbon tetrachloride at pH 7.0, where the reaction is quantitative if copper is in excess. 10 ml. dithizone standard solution was shaken with 20 ml. acetate buffer containing 20 γ of copper. The organic layer was separated and the copper left in the aqueous phase was determined according to the mixed-color method at 5.2 micrograms. Thus, 60 γ of dithizone combines with 14.8 γ of copper, which corresponds to the composition CuDz .

Reaction (3), like reaction (1), is rather slow and the equilibrium constant was not determined in this case, but Table 15, with percentage of CuDz formed after a thorough shaking for 5 minutes, gives a view of the formation conditions. The percentage is calculated from the extinction coefficients. The absorption of light was measured at 545 $m\mu$, the maximum wave length of CuDz_2 , and also at 475 $m\mu$, which is near 455 $m\mu$, the maximum wave length of CuDz .

TABLE 15
EFFECT OF PH ON THE FORMATION OF CuDz IN THE PRESENCE OF AN
EXCESS OF COPPER
20 ml. aqueous solution containing 20 γ Cu, and 10 ml. dithizone standard
solution.

	pH	ϵ 545 $m\mu$	ϵ 475 $m\mu$	CuDz %
CCl_4	1.00	0.541	0.363	0
	3.80	.510	.375	8
	4.60	.404	.401	35
	5.30	.229	.446	78
	7.50	.152	.473	100
CHCl_3	5.00	0.510	0.363	0
	7.00	.469	.374	11
	7.70	.364	.407	42
	8.45	.220	.458	87
	10.00	.174	.470	100

Reaction (3) is not simply reversible; CuDz once formed is almost as stable towards acids as CuDz_2 .

B. Cuprous copper

According to Sandell (3), univalent copper reacts with dithizone in acid solutions to form a violet dithizonate. In alkaline solutions again, a yellow-brown salt is obtained which is only partially soluble in the organic solvents. Welcher (45), however, reports that the color of the first-mentioned dithizonate is red-brown to violet, and the other green-brown and probably a compound of divalent copper.

The univalent copper dithizonates are analytically of little importance, but they are of interest for giving uniform indications for the color and constitution of the metal dithizonates.

A stable standard solution of univalent copper cannot be made except under great difficulties, so other methods had to be applied. The following procedure gave results: 30 ml. 0.1 N hydrochloric acid containing 0.5 g. of hydroxylamine hydrochloride and 10 ml. (300 γ) dithizone standard solution were placed in a separatory funnel and shaken with about 20 mg. absolutely pure cuprous chloride in solid form. The organic layer was colored brown and several attempts showed no violet nuance.

To determine the amount of copper in this dithizonate, 5 ml. of the organic layer was separated and washed with $\text{NH}_2\text{OH} \times \text{HCl}$ -solution and decomposed by shaking in a separatory funnel with two portions of 15 ml. 1 N H_2SO_4 and 0.5 ml. 0.1 per cent KMnO_4 solution. The combined aqueous solutions were decolorized with hydroxylamine hydrochloride and thoroughly shaken to dissolve all manganese dioxide. A suitable

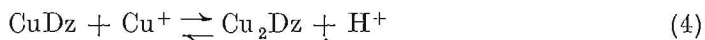
aliquot of the solution was adjusted to pH 4 with ammonia, and the copper was determined according to the mixed-color method.

The decomposing procedure mentioned above has been suggested by Sandell (3) as being suitable for mercury and copper dithizonate, but the method has not been investigated for copper. It was tested for this purpose in connection with the violet cupric dithizonate and gave correct results.

Five ml. of the dithizone solution used contained originally 150 γ of dithizone and after three attempts it was found that this amount combines with 37.0 γ of copper. One can therefore take it as proved that univalent copper in acid solution forms a dithizonate of brown color corresponding to the formula CuDz.

The other cuprous dithizonate turned out to be violet-colored and insoluble in carbon tetrachloride. The salt was obtained thus: immediately after the appearance of the brown dithizonate the aqueous layer was made alkaline with ammonia, followed by a vigorous shaking.

A determination of the composition of this salt was too complicated, but the formation takes place most probably in accordance with the reaction:



The similarity with corresponding silver salts is striking:

Cu Dz	brown,	soluble in carbon tetrachloride
Ag Dz	yellow,	» » » »
Cu ₂ Dz	violet,	insoluble in carbon tetrachloride
Ag ₂ Dz	red-violet,	» » » »

Conclusions: The results obtained point out that the reaction between divalent copper and dithizone appears very slowly in a more acid solution. Under normal working conditions the real equilibrium constant is not of much use, but eventual conclusions must be arrived at on the basis of the partition constant, obtained after 5 minutes shaking. The values of this constant can be calculated from Table 13. In other respects, in accordance with Sherman and McHargue (46), it has been proved that the extraction of copper proceeds more slowly than usually stated in literature.

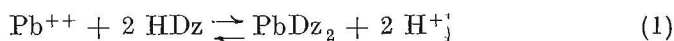
Copper should preferably be determined in about 0.001 N acid with a carbon tetrachloride solution of dithizone, but also at this acidity the extraction must be made with excess dithizone and repeated several times if the time of shaking should be reasonable. At a pH of 2, only mercury, silver and bismuth also combine with dithizone, but they could be eliminated by adding bromide and iodide, which have no influence on the extraction of copper.

The formation of green-yellow cupric dithizonate can be disregarded in this connection as the determinations are made with an excess of dithizone. The mono-color method can be used, as CuDz is not formed if CuDz_2 is treated with a dilute base.

It has also been established that the method for decomposing of copper dithizonate, suggested by Sandell, can be used with advantage.

5. Lead

Lead reacts with dithizone in neutral and weak alkaline solutions to form a complex salt which is soluble with a red color in carbon tetrachloride and chloroform. As lead in this case is divalent, the composition of its dithizonate is PbDz_2 , experimentally confirmed by Clifford (47). The reaction is as follows:



The standard curves, Fig. 10, were obtained as usual with 20 ml. acetate buffer of pH 6.5 (CCl_4) and 7.2 (CHCl_3), at which values lead quantitatively combines with the reagent, and 10 ml. dithizone standard solution. The absorption of light was measured at wave length $515 \text{ m}\mu$, the maximum absorption by PbDz_2 , and at $620 \text{ m}\mu$.

Standard lead solution, 0.02 per cent, was prepared by dissolving recrystallized and dried lead nitrate in 0.1 N nitric acid. The working solution containing 0.002 per cent lead was prepared fresh every day by diluting the stock solution with metal-free water.

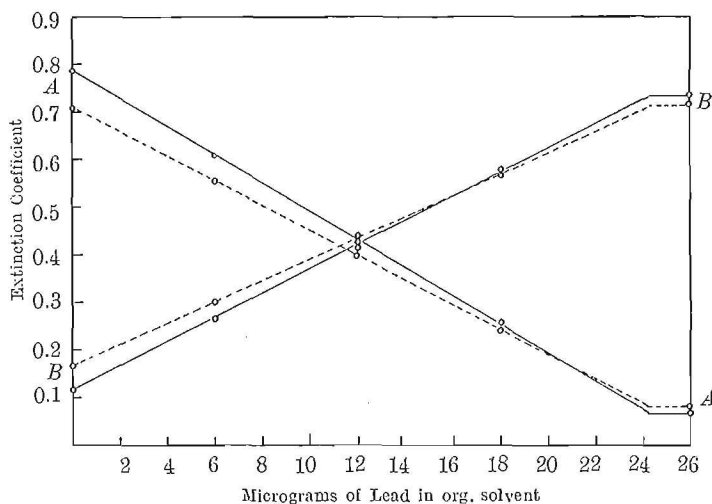


Fig. 10. — Determination of lead by the dithizone mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . A. Absorption of light measured at $620 \text{ m}\mu$. B. Absorption determined at $515 \text{ m}\mu$.

The equilibrium constant for reaction (1) is as follows:

$$K = \frac{[\text{PbDz}_2]_o [\text{H}^+]_w^2}{[\text{Pb}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

The value of K has at an earlier stage been preliminarily determined by Buch and Koroloff (16) at 1.48×10^{-3} for lead dithizonate in carbon tetrachloride. Further, Clifford/Wichmann (27) and Biefeld/Patrick (22) have studied the effect of pH and different quantities of dithizone on the extraction of lead, but they have not determined the value of the equilibrium constant. In this investigation the constant was determined in the manner already described.

The reaction between lead and dithizone is immediate; the time of extraction was thus fixed at 5 minutes. The result is given in Table 16.

TABLE 16
LEAD — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Pb added γ	ϵ 620 $m\mu$	ϵ 515 $m\mu$	Pb in org. phase γ	K
Carbon tetrachloride			0	0.785	0.120		
			PbDz ₂	.068	.734	24.3	
	4.84	10	15	.488	.373	10.2	2.4
	5.60	10	30	.155	.657	21.6	2.4
	4.34	20	15	.691	.198	3.1	2.6
	4.84	20	30	.410	.441	12.7	2.5
	5.15	20	100	.176	.641	20.9	2.4
	1) 4.07	20	30			18.6	2.4
	5.15	50	15	.656	.226	4.2	2.6
	4.80	50	30	.524	.339	8.8	2.4
	2) 4.13	10	PbDz ₂	.677	.206	3.5	2.3
	2) 4.79	20	»	.468	.391	10.7	2.4
							M. 2.4
Chloroform			0	0.707	0.166		
			PbDz ₂	.077	.710	24.3	
	4.81	10	15	.629	.236	3.1	0.15
	5.27	10	30	.398	.436	12.0	.14
	4.93	20	15	.640	.227	2.8	.15
	5.29	20	30	.458	.385	9.7	.13
	5.54	20	100	.232	.585	18.6	.13
	1) 4.71	20	30			19.2	.14
	5.45	50	15	.546	.308	6.3	.15
	5.79	50	30	.349	.476	14.0	.12
	2) 4.84	10	PbDz ₂	.610	.261	4.1	.11
	2) 4.90	50	»	.627	.234	3.2	.12
							M. 0.13

1) The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

2) Decomposing of lead dithizonate. Procedure on p. 24.

Determinations of traces of lead are almost exclusively made by the dithizone method, and many procedures have been worked out. The extraction of the metal is most often carried out with a chloroform solution of the reagent, and in alkaline medium. As all of the dithizone metals react with the reagent under these conditions, a complex-forming substance (preferably cyanide) is always added. The only other metals extracted in cyanide solution are bismuth, thallium and stannous tin. Further, citrate or tartrate is added to the test solution to prevent the precipitation of metals as hydroxides or phosphates. According to Biefeld and Patrick (22), various anions present have a preventive effect on the extraction of lead. Under apparently identical conditions, they found that lead was extracted up to 50 per cent by a chloroform solution of dithizone at pH 5.61 in cyanide solution, 5.86 in acetate solution, 6.35 in tartrate solution, and 7.75 in a solution containing cyanide and citrate.

The effect of the above-mentioned anions, and the influence of sea water and sodium chloride on the extraction of lead was studied; the results are shown in Table 17 and Fig. 11.

TABLE 17

LEAD — DITHIZONE EQUILIBRIUM IN THE PRESENCE OF VARIOUS ANIONS
10 ml. organic solvent containing 60 γ of dithizone.

	Anions present in aqueous phase	pH	aq. phase ml.	Pb added γ	620 ϵ m μ	515 ϵ m μ	Pb in org. phase γ	K
Carbon tetrachloride	Sea water, Cl = 12 ‰ ..	4.64	10	15	0.621	0.252	5.4	0.90
	» »	5.72	50	30	.250	.581	18.3	0.88
	1M NaCl	5.10	10	15	.603	.269	6.1	0.14
	» »	5.91	50	30	.337	.500	15.2	0.10
	0.1M KCN	4.77	10	15	.463	.392	10.9	4.7
	» »	4.82	50	30	.451	.403	11.2	4.3
	0.2M K Na tartrate	6.11	10	15	.568	.302	7.2	2.0×10^{-3}
	» »	6.51	50	30	.445	.410	11.6	2.0 »
	0.2M Na citrate	6.67	10	15	.648	.232	4.5	5.4×10^{-5}
	» »	7.56	50	30	.333	.507	15.4	5.4 »
	0.1M KCN +	6.80	10	15	.621	.254	5.6	4.6×10^{-5}
	0.2M Na citrate	7.23	50	30	.495	.366	9.8	4.3 »
Chloroform	Sea water, Cl = 12 ‰ ..	5.38	10	15	0.515	0.331	7.5	6.6×10^{-2}
	» »	6.06	50	30	.302	.523	15.8	6.2 »
	1M NaCl	5.58	10	15	.583	.274	4.9	9.6×10^{-3}
	» »	6.91	50	30	.191	.616	20.2	9.7 »
	0.1M KCN	4.87	10	15	.497	.351	8.2	0.90
	» »	5.73	50	30	.230	.575	18.4	0.85
	0.2M K Na tartrate	6.38	10	15	.585	.278	4.8	2.3×10^{-4}
	» »	6.92	50	30	.435	.404	10.6	2.3 »
	0.2M Na citrate	7.67	10	15	.432	.407	10.8	7.0×10^{-5}
	» »	7.83	50	30	.389	.452	12.6	6.3 »
	0.1M KCN +	7.25	10	15	.571	.286	5.3	5.1 »
	0.2M Na citrate	8.70	50	30	.461	.382	9.7	4.8 »

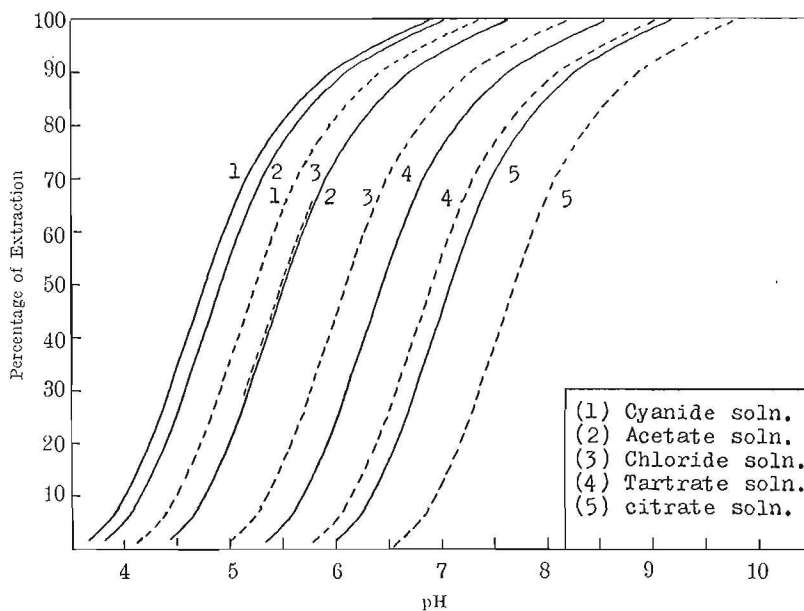


Fig. 11. — Equilibrium curves for lead dithizonate in carbon tetrachloride (—), and chloroform (-----). No excess of dithizone.

The results obtained confirm those given by Biefeld and Patrick. The metal is readily extracted from a cyanide solution acidified with hydrochloric acid, and shows the greatest pH range for complete extraction. The disadvantage in the use of this medium, however, depends upon the highly poisonous character of the hydrogen cyanide which is formed if the solution is overacidified. The difference in value of the equilibrium constant in cyanide and acetate solution is very little, and for this reason the extraction of the metal is best carried out in the latter solution. The use of acetate offers the further advantage that the pH is very easily regulated to the required value.

Precipitations of metals as hydroxides or phosphates are best prevented by adding tartrate to the test solution. Thus, in the presence of this salt the extraction can be made at a pH which is 0.7 units lower than is the case when citrate is used.

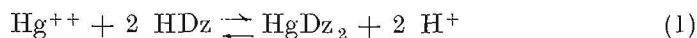
As the reaction between lead and dithizone is simply reversible, the dithizonate can be decomposed and the metal completely retransferred to the aqueous phase by treating with 0.001 N acid.

6. Mercury

Mercury, like copper, combines with dithizone to form four different dithizonates.

A. Mercuric mercury

For analytical purposes the mercuric salts are the most important, especially that formed in acid solution, which is soluble with an orange color in carbon tetrachloride and chloroform. The reaction takes place as follows:



That the composition is the one described can be seen from the standard curves in Fig. 12.

Standard mercury solution, 0.02 per cent, was made by dissolving sublimate in 0.1 N hydrochloric acid. A weaker solution containing 20 γ Hg per ml. was obtained by diluting with metal-free water. This solution was prepared fresh every day.

The various quantities of metal were extracted from 20 ml. 0.1 N sulfuric acid with 10 ml. standard dithizone solution. The spectrophotometer readings were made at 490 and 620 $m\mu$, the wave lengths of maximum absorption of light by mercuric dithizonate and dithizone respectively.

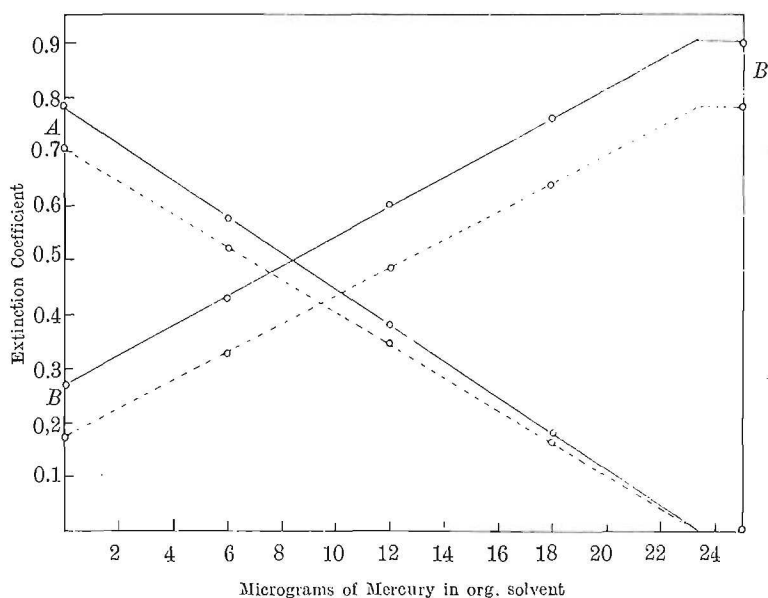


Fig. 12. — Determination of mercury with dithizone by the mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone. — CCl_4 , - - - - CHCl_3 . A. Absorption of light measured at 620 $m\mu$, B. Absorption determined at 490 $m\mu$.

If the dithizone-reacting metals are arranged according to the pH value at which they first give reaction with the reagent, mercury can be found at the extreme left. Various attempts have proved that the

reaction is immediate, and quantitative already in 12 N sulfuric acid with a carbon tetrachloride solution of dithizone. For this reason, the equilibrium constant for reaction (1):

$$K = \frac{[\text{HgDz}_2]_o [\text{H}^+]_w^2}{[\text{Hg}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

cannot be determined.

Of the metals determined or isolated with dithizone, only silver — and copper present in greater amounts — reacts with the reagent in more acid solution than 1.0 normal. According to Sandell (3) mercury can be quantitatively determined in 1 N acid solutions which are 0.2 N in chloride. Welcher (45), however, points out that extraction of mercury is not prevented by the presence of chloride. Silver should accordingly be eliminated by adding a chloride to the sample solution. Experiments carried out, however, show that the chlorine ion has a highly preventive effect on the extraction of mercury. In the following two graphs, Fig. 13 and 14, this fact is clearly illustrated. The percentage of metal combined with dithizone is given in (a) sulfuric acid of various strengths containing various amounts of sodium chloride and (b) hydrochloric acid of various strengths. The experiments were made with 20 ml. aqueous phase and 10 ml. organic solvent containing 60 micrograms of dithizone.

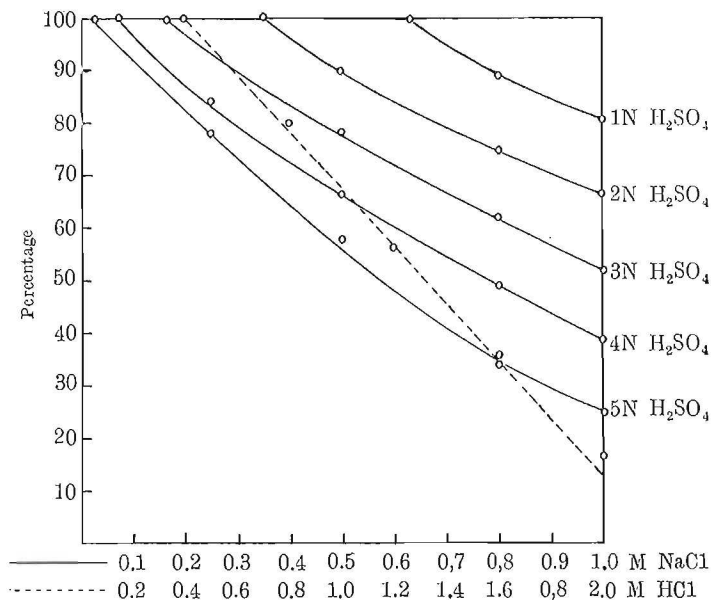


Fig. 13. — Effect of acidity and chloride on the extraction of mercury with a carbon tetrachloride solution of dithizone. 20 ml. aqueous solution and 10 ml. dithizone standard solution. 23.5 μ Hg taken.

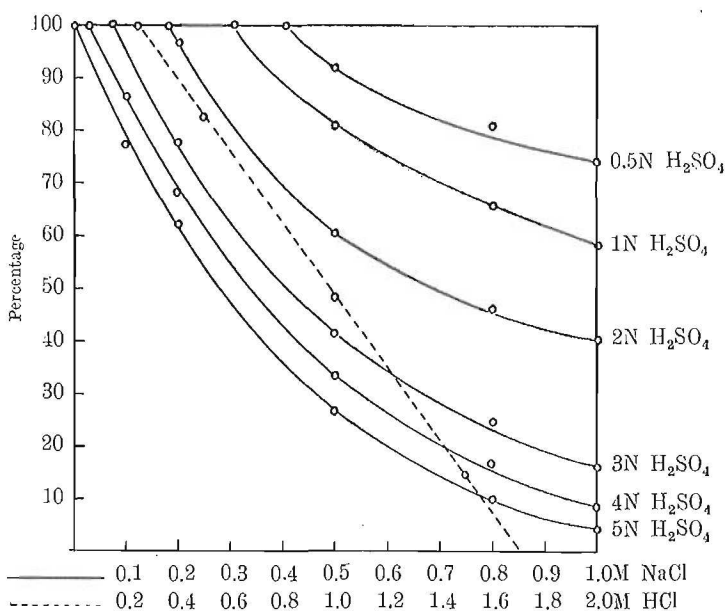


Fig. 14.—Effect of acidity and chloride on the extraction of mercury with a chloroform solution of dithizone. 20 ml. aqueous solution and 10 ml. standard dithizone solution. 23.5 γ Hg taken.

There was present an equivalent amount of mercury to that of dithizone, *i. e.* 23.5 micrograms. The time for extraction was 5 minutes. The amount of metal in organic layer was determined according to the mixed-color method.

It appears from the experiments that mercury with only a slight excess of dithizone can be determined quantitatively in 0.4 and 0.25 N hydrochloric acid, when the reagent is dissolved in carbon tetrachloride and chloroform respectively.

The preventive effect of sodium chloride in sulfuric acid is not as great as that of hydrochloric acid, but this probably depends on the fact that in more acid solution than 0.5 normal, hydrochloric acid has a greater active hydrogen ion concentration than the corresponding sulfuric acid. Because of this, the metal for example can be quantitatively extracted from a solution which is 0.5 M in sodium chloride and 1.2 N (CCl₄) or 0.3 N (CHCl₃) in sulfuric acid.

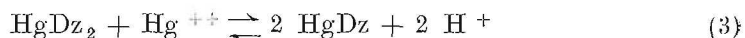
The reason for this is doubtless that mercury combines partly with chlorine in the presence of greater amounts of this ion. Here it is not a question of the influence of a neutral salt, as complete reaction is obtained in 5 N sulfuric acid solution containing 1.0 M potassium sulfate, and if the metal is extracted from a hydrochloric acid solution containing sodium chloride, the amount of mercury in the organic phase is even smaller than the corresponding amount obtained from the graphs.

The low salinity of the sea water round the coast of Finland does not disturb the determination of mercury in water which is for example

2.5 N (CCl_4) in sulfuric acid, and at this degree of acidity the excess of copper can be fairly considerable. In ocean water, however, the metal should be extracted at a pH value of about 1; at this pH fairly large quantities of copper present can be co-extracted with mercury. Barnes (38, 39, 40) accordingly adds potassium cobalti cyanide to the sample solution in order to bind copper as a complex. This salt has no apparent negative effect on the extraction of mercury.

To prevent interference of antimony and bismuth present in greater amounts, Winkler (6) extracts mercury from an acid solution containing tartaric acid; this, also, has no apparent influence, as experiments carried out proved.

The second mercuric dithizonate is Fischer's enol modification and is formed in neutral and alkaline solution in the presence of an excess of metal:



This dithizonate imparts to the organic solvent a red-violet color. The composition was determined at that given in reaction (3) by the following procedure: After the dithizonate was formed, the organic layer was discarded and the aqueous phase acidified with sulfuric acid, and then the amount of mercury remaining was determined according to the mixed-color method.

Like CuDz , HgDz is not formed by treating HgDz_2 with alkali, so the mono-color method can be used. On the other hand this violet mer-

TABLE 18
EFFECT OF PH ON THE FORMATION OF HgDz IN THE PRESENCE OF AN
EXCESS OF MERCURY

20 ml. aqueous solution containing 80 γ Hg and 10 ml. dithizone standard solution.

	pH	$\epsilon_{490} \text{ m}\mu$	$\epsilon_{535} \text{ m}\mu$	HgDz %
CCl_4	1.00	0.905	0.099	0
	3.90	.861	.136	8
	4.31	.802	.221	21
	4.87	.658	.405	52
	5.30	.524	.576	81
	7.00	.432	.690	100
CHCl_3	1.00	0.791	0.158	0
	6.90	.753	.216	13
	7.31	.700	.304	33
	7.83	.637	.428	64
	8.07	.566	.549	85
	9.00	.524	.620	100

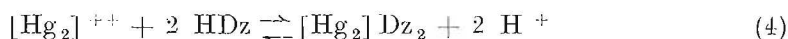
cury dithizonate is not as stable as CuDz towards acids; by treating with dilute acid it decomposes into yellow mercuric dithizonate and metal.

The formation of HgDz is partly prevented by neutral salts being present, but the following experiments (Table 18) made with 20 ml. dilute acetate buffers containing 80% of mercury and 10 ml. standard dithizone solution give the formation range. The time for extraction was 5 minutes, and the percentage of HgDz was calculated from the values of the extinction coefficients.

B. Mercurous mercury

Mercurous mercury can be determined colorimetrically with dithizone, but in most cases this ion is oxidized to the mercuric state. The mercurous salts of dithizone, however, like the cuprous dithizonates, are of interest from a theoretical point of view. In the following investigation a standard solution made by dissolving mercurous sulfate in water was used. The mercurous ion content was determined gravimetrically with hydrochloric acid.

In acid solution mercurous mercury reacts with dithizone to form a yellow-orange dithizonate soluble in the organic solvents according to the reaction:



The composition was checked by extractive titration. The formation conditions are the same as for HgDz_2 , and the absorption curve shows also an almost identical course with maximum at 490 m μ wave length.

In the presence of an excess of mercurous ions in alkaline solution the yellow dithizonate is converted to a violet salt which is almost insoluble in carbon tetrachloride and chloroform. With a carbon tetrachloride solution of dithizone the formation begins at a pH of about 3.5 and in conformity with copper and silver the reaction probably is as follows:



An exact determination of the composition, however, could not be made because of analytical difficulties.

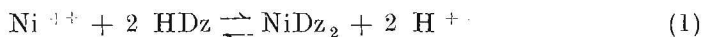
Summary: There are four mercury dithizonates which have the following compositions and characters:

A. Mercuric mercury	HgDz_2	orange	soluble in organic solvents
	HgDz	red-violet	» » » »
B. Mercurous mercury	$[\text{Hg}_2] \text{Dz}_2$	yellow-orange	» » » »
	$[\text{Hg}_2] \text{Dz}$	violet	partly insoluble in organic solvents

The value of the equilibrium constant for the orange mercuric dithizonate could not be determined. From the investigations it appears that the chlorine ion has a great preventive effect on the extraction of the metal in acid solution. Any influence from other salts used has not been observed.

7. Nickel

In weak alkaline solution, nickel forms a brownish dithizonate soluble in carbon tetrachloride and chloroform. The reaction takes place according to the usual equation for divalent metals:



A confirmation of the composition of the dithizonate and standard curves was obtained in the usual manner, but immediate reaction occurs first at pH 8.0 (CCl_4) and 9.0 (CHCl_3). A part of the dithizone amount is at this stage passed to the aqueous layer, but by lowering the pH to 6 after the extraction, followed by a vigorous shaking for a few seconds, this amount is retransferred to the organic phase. Nickel dithizonate is not decomposed by this treatment, as, according to Sandell (3), it is scarcely affected by acids — like cobalt dithizonate.

Standard nickel solution, 0.02 per cent. The stock solution was made by dissolving $\text{NiSO}_4 \times 7 \text{H}_2\text{O}$ in 0.1 N sulfuric acid. This solution was diluted with metal-free water to 0.001 per cent.

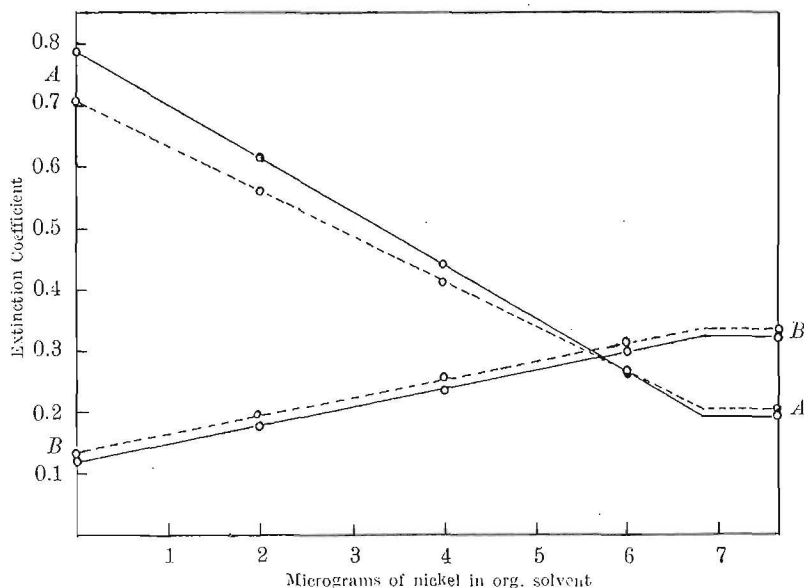


Fig. 15. — Determination of nickel by the dithizone mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . A. Absorption of light measured at 620 m μ . B. Absorption determined at 505 m μ .

Spectrophotometer readings were made at 490 and 620 m μ , which correspond to regions of strong absorption by nickel dithizonate and dithizone respectively. NiDz₂ has a maximum absorption of light at 460 m μ , but readings are uncertain at this wave length. The curves are reproduced in Fig. 15.

The equilibrium constant for reaction (1) is as follows:

$$K = \frac{[\text{NiDz}_2]_o [\text{H}^+]_w^2}{[\text{Ni}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

As the reaction is slow the time for extraction must first be established. This took place with 20 ml. acetate buffer pH 6.0 (CCl₄) and borax-boric acid buffer pH 7.4 (CHCl₃) containing 10 γ of nickel and 10 ml. dithizone working solution. The results are given in Table 19, and they show that shaking for one and a half hours is sufficient for reaching equilibrium.

TABLE 19
EFFECT OF TIME ON THE EXTRACTION OF NICKEL
20 ml. aqueous solution pH 6.0 (CCl₄) and 7.4 (CHCl₃).
10 ml. dithizone standard solution. 10 γ Ni taken.

Time of shaking in minutes	Micrograms of Nickel found in organic phase	
	Carbon tetrachloride	Chloroform
5	1.3	2.6
15	2.6	3.4
30	3.8	3.9
60	4.1	5.7
90	5.3	6.3
120	5.2	6.3

The value of the constant was then determined in the usual manner. The result is given in Table 20.

Determinations of traces of nickel are usually made with dimethylglyoxime, but Young, Strickland and Leibowitz (48) use the reaction of nickel with dithizone for determining the metal in steel. The metal is first isolated as glyoxime, which is dissolved in hydrochloric acid, and then extracted from basic solution containing about 25 per cent of a mixture of 3 parts saturated sodium acetate solution and one part saturated ammonium thiocyanate solution. To ascertain any possible effect of anions, the equilibrium constant was determined in the mixture mentioned and also in sodium chloride solution and sea water. The value of K, however, remained unchanged.

TABLE 20
NICKEL — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Ni added γ	ϵ_{620} m μ	ϵ_{505} m μ	Ni in org. phase γ	K	
Carbon tetrachloride			0	0.785	0.122			
			NiDz ₂	.193	.327	6.9		
		10	5	.456	.234	3.8	6.7×10^{-2}	
		10	10	.331	.282	5.2	6.1	
		20	5	.652	.171	1.6	7.0	
		20	10	.397	.258	4.3	6.5	
		20	50	.252	.306	6.1	6.0	
		¹⁾ 4.83	20	10		5.9	6.7	
		5.37	50	5	.696	.153	1.1	6.7
		5.58	50	10	.557	.201	2.7	6.4
							M. 6.4×10^{-2}	
Chloroform			0	0.707	0.132			
			NiDz ₂	.208	.332	6.9		
		10	5	.504	.208	2.6	1.0×10^{-3}	
		10	10	.335	.279	5.1	1.3	
		20	5	.438	.340	3.7	1.0	
		20	10	.355	.269	4.8	1.3	
		20	50	.292	.301	5.7	1.2	
		¹⁾ 5.70	20	10		6.2	1.4	
		6.29	50	5	.616	.173	1.3	1.3
		6.62	50	10	.449	.236	3.5	1.2
							M. 1.2×10^{-3}	

¹⁾ The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

Nickel dithizonate, like the cobalt salt, is not as stable towards acids as stated in literature. The decomposing begins at a pH of about 2, but the time of shaking is conclusive in this case also, which can be seen from the following experiments (Table 21) made at pH 2.0 with 20 ml. buffer solution and 10 ml. nickel dithizonate solution, obtained by converting the dithizone in the standard solutions into dithizonate.

TABLE 21
EFFECT OF pH AND TIME OF SHAKING ON DECOMPOSING OF NICKEL
DITHIZONATE

20 ml. aqueous solution and 10 ml. organic solvent containing 6.85 γ Ni combined with dithizone.

pH	Time of shaking in minutes	Micrograms of Nickel found in organic phase	
		Carbon tetrachloride	Chloroform
2.07	5	5.25	4.1
2.07	30	2.40	1.2
1.50	5	4.65	3.2
1.50	30	0.00	0.0

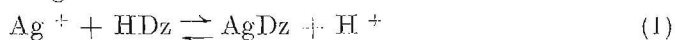
Summary: The value of the equilibrium constant for nickel dithizonate was determined both in carbon tetrachloride and in chloroform. The reaction between the metal and dithizone proceeds, as for cobalt and copper, very slowly and under normal working conditions one should take into account the distribution constant after vigorous shaking for 5 minutes, which can be calculated from Table 19. Further, it has been proved that the decomposing of the nickel dithizonate occurs at a higher pH value than usually stated in literature.

Any eventual effect of anions used on the extraction of nickel has not been observed.

8. Silver

Silver gives two complex salts with dithizone. The one of analytical importance occurs in mineral acid solution and is soluble in chloroform and carbon tetrachloride, imparting to them a yellow color. The other salt is formed in neutral and basic solution through the conversion of the yellow one; it has a red-violet color and is almost insoluble in carbon tetrachloride, and only partly soluble in chloroform. As already mentioned, the composition of these two dithizonates has gravimetrically been determined by Buch and Koroleff (16) at AgDz and Ag_2Dz respectively.

According to Fischer, the yellow dithizonate is the keto tautomer and is formed according to the reaction:



The standard curves (Fig. 16) were constructed in the manner already described for the determination of the amount of dithizone in standard solution, (page 17).

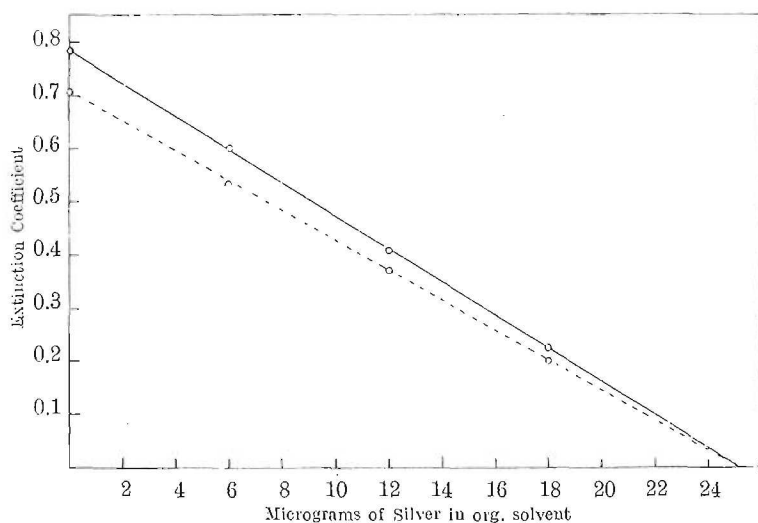


Fig. 16. — Determination of silver with dithizone by the mixed-color method. 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . Absorption of light measured at 620 $m\mu$.

From reaction (1) the equilibrium constant is given by

$$K = \frac{[\text{AgDz}]_o [\text{H}^+]_w}{[\text{Ag}^+]_w [\text{HDz}]_o} \quad (2)$$

but its value has not been definitely determined before, although Sandell (3) mentions that it is about 10^7 .

The reaction between silver and dithizone is immediate; 5 minutes was sufficient time to establish equilibrium. The determinations, however, have to be made in acids of various strengths; which naturally gave less exact results. In the experiments carried out, sulfuric acid was used instead of nitric acid, as the latter may contain oxides which could oxidize the dithizone solutions. The hydrogen ion concentration was taken as equal to the normality of the acid. The acid was titrated after the extraction with 0.1 N sodium hydroxide. As AgDz is formed in such an acid solution, the determination of its decomposition was left out of consideration. The results are given in Table 22.

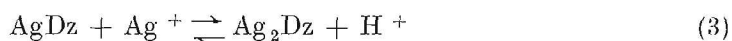
TABLE 22
SILVER — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	H ⁺	aq. phase ml.	Ag added γ	ϵ 620 m μ	Ag in org. phase	K
CCl ₄			0	0.785		
			AgDz	.000	25.3	
	10	10	15	.350	14.0	1.3×10^7
	5	20	20	.216	18.3	1.7
	8	20	25	.158	20.2	1.4
	4	50	30	.114	21.6	1.5
						M. 1.5×10^7
CHCl ₃			0	0.707		
			AgDz	.000	25.3	
	1.5	10	15	.339	13.2	1.0×10^6
	1.5	20	20	.287	15.0	0.95
	2.0	20	25	.241	16.7	1.0
	2.0	50	30	.284	15.1	1.1
						M. 1.0×10^6

If gold, palladium and platina are excluded, mercury and greater amounts of copper are the only metals which disturb the determination of silver with dithizone in acidic solution. For this reason no complex-forming substances required to be added. According to Fischer *et. al.* (4), if copper in moderate amounts is present, a solution of cupric dithizonate is used as the reagent. The mixed color varies from violet to yellow and this process is recommended for general use since no special

purification of acids, distilled water and other reagents is necessary to remove traces of copper and other metals. In the presence of small quantities of mercury, this metal is co-extracted with silver and the organic layer is then shaken, according to Fischer (49), with a weak acid solution of potassium cyanide, which reverts the silver to the aqueous phase.

Silver also forms, as already mentioned, another complex salt with dithizone. The formation takes place in neutral and basic solution in the presence of excess metal according to the reaction:



In conformity with copper, Ag_2Dz is not formed if AgDz is treated with alkali. The mono-color method, therefore, can be used in the determination of silver with dithizone.

The equilibrium constant for reaction (3) has not been determined, but to give a picture of the formation conditions the percentage of Ag_2Dz formed after extraction for 5 minutes is given in Table 23. The percentage was calculated from the extinction coefficients. The experiments were carried out with 20 ml. aqueous solution containing 60 γ of silver and 10 ml. dithizone standard solution.

TABLE 23

EFFECT OF pH ON THE FORMATION OF Ag_2Dz IN THE PRESENCE OF AN EXCESS OF SILVER

20 ml. aqueous solution containing 60 γ Ag and 10 ml. dithizone standard solution.

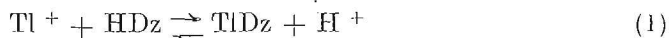
	pH	$475 \frac{e}{m\mu}$	$\frac{\text{Ag}_2\text{Dz}}{\%}$
CCl_4	1.0	0.635	0
	3.7	.495	24
	4.2	.413	38
	4.9	.197	75
	7.0	.050	100
CHCl_3	1.0	0.617	0
	4.1	.503	22
	4.6	.415	39
	5.2	.281	65
	8.0	.100	100

9. Thallium

Among the metals reacting with dithizone, thallium is the only one which does not give reaction with the reagent until in more basic solution.

Both univalent and divalent thallium combine with dithizone. The thallic ion, however, gives an incomplete reaction only, and moreover it has an oxidizing influence on dithizone solutions.

Thallos thallium forms a red dithizonate soluble in chloroform and carbon tetrachloride according to the reaction:



In the experiments to ascertain at which pH the extraction of thallium is quantitative, it was observed that a complete one was still not obtained at pH 11 when a carbon tetrachloride solution of dithizone was used. This is contrary to a report by Fischer (9). With a chloroform solution of the reagent, however, a complete extraction was obtained at this pH-value. Because of the formation of water-soluble alkali dithizonate at this stage, if there is an excess of dithizone present, the standard curves were constructed for determinations by the mono-color method. As Beer's law holds for thallos dithizonate both in carbon tetrachloride and in chloroform, a curve was obtained also for the reagent dissolved in carbon tetrachloride. Excess of dithizone was removed by shaking the organic layer separated with a few portions of dilute ammonia solution.

Standard thallium solution, 0.02 per cent, was made by dissolving recrystallized Tl_2SO_4 in 0.1 N sulfuric acid. The working solution containing 100 γ thallium per ml. was obtained by diluting the stronger solution with metal-free water.

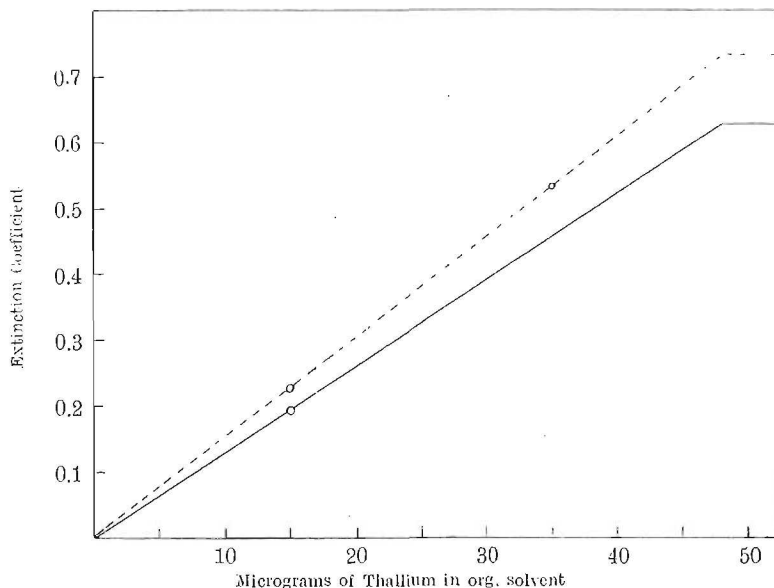


Fig. 17. — Determination of thallium by the dithizone mono-color method. 10 ml. organic solvent containing 60 γ of dithizone, — CCl_4 , - - - CHCl_3 . Absorption of light measured at 505 $m\mu$.

The extractions were made with 20 ml. dilute buffer of pH 11 and 10 ml. dithizone standard solution. The absorption of light was measured at $505\text{ m}\mu$, the maximum wave length by the dithizonate. The curves are given in Fig. 17 and from these it can be seen that the salt has the composition TIDz.

Because of the incomplete reaction with dithizone dissolved in carbon tetrachloride and also because of the formation of water-soluble dithizone during the extraction, the value of the equilibrium constant for the reaction (1) was not determined, but the following series of experiments (Table 24) shows the formation range. The extractions were made with 20 ml. aqueous phase containing 40γ thallium and 10 ml. dithizone standard solution. The time of shaking was 5 minutes, as the reaction is almost immediate.

TABLE 24
EFFECT OF pH ON THE EXTRACTION OF THALLIUM
20 ml. aqueous solution containing 40γ Tl and 10 ml. dithizone standard solution.

pH	Micrograms of Thallium found in organic phase	
	Carbon tetrachloride	Chloroform
8.60	6.0	12.0
9.15	8.0	18.0
10.0	10.6	38.0
10.5	15.2	40.0
11.0	22.0	40.0

It can be seen from the table that thallium is extracted more completely with a chloroform solution than with a carbon tetrachloride solution of the reagent; this is contrary to all of the other metals investigated.

The explanation of this fact is probably that the formation of the enol modification of dithizone begins at a higher pH value when the reagent is dissolved in chloroform, and that it is dithizone in keto form which reacts with the metal, not the enol tautomer.

As thallos dithizonate is not formed unless in alkaline solution, it can be supposed that it decomposes easily and experiments have shown that the metal can be retransferred quantitatively to the aqueous phase at pH 7.0. This holds irrespective of the use of organic solvent. The reaction between thallos thallium and dithizone is then simply reversible and this fact, not observed earlier, offers a simple method for separating thallium from all other metals co-extracted.

Dithizone has been used by Bambach (50) in the determination of thallium in pharmaceutical chemicals and also by Kamerman (51), who has used a titrimetric method for the toxicological examination of vis-

cera for the metal. Both of them extract thallium together with lead from an alkaline cyanide-citrate solution. The influence of these anions on the extraction was therefore investigated. It appeared therefrom that citrate partly prevents the extraction. The equilibrium is displaced about 0.5 pH units to the right, and for this reason a double extraction with a chloroform solution of dithizone at pH 11 is to be recommended.

Bambach does not separate thallium from lead, but determines the combined amounts of the metals, as both thallous and lead dithizonate are of the same color. Kamerman, again, retransfers the metals to the aqueous phase by shaking at pH 3, converts them to sulfates, and separates them by adding alcohol, which precipitates lead sulfate. Finally, he titrates at pH 9.0, but according to this investigation the reaction is not quantitative at this value. Taking into account the fact that TIDz decomposes already at pH 7.0, both of the methods mentioned can be simplified and made more exact.

The influence of sea water and sodium chloride on the extraction of thallium was studied also as for the other metals. A preventive effect like that of citrate was observed. Thallium solutions containing greater amounts of chloride should therefore be extracted several times at pH 11 with a chloroform solution of dithizone.

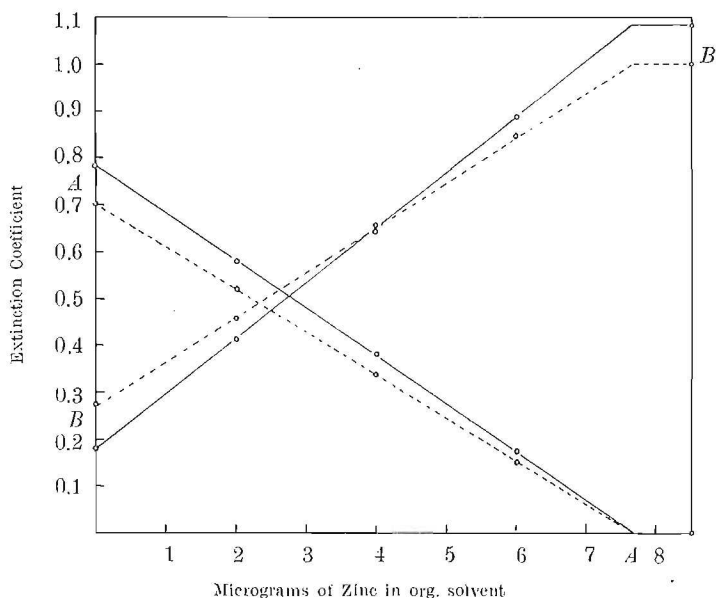
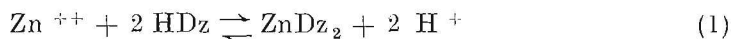


Fig. 18. — Determination of zinc with dithizone by the mixed-color method. 10 ml. organic solvent containing 60 γ of dithizone, ——— CCl₄, - - - - - CHCl₃. A. Absorption of light measured at 620 m μ . B. Absorption determined at 535 m μ .

10. Zinc

When Emil Fischer (1) first prepared dithizone, he observed already then its reaction with zinc. He also prepared the zinc dithizonate and determined its composition at $\text{ZnDz}_2(\text{H}_2\text{O})$. Dithizone combines with zinc in acidic, neutral and alkaline solution to give a purplish-red salt soluble in chloroform and carbon tetrachloride. The reaction takes place according to the equation:



The standard curves in Fig. 18 are made in the manner already described for the determination of the dithizone content (page 17) with 10 ml. organic solvent containing 60 micrograms of dithizone.

Up to now, dithizone is the only organic analytical reagent for direct colorimetric determination of zinc, and for this reason the equilibrium constant for reaction (1):

$$K = \frac{[\text{ZnDz}_2]_o [\text{H}^+]_w^2}{[\text{Zn}^{++}]_w [\text{HDz}]_o^2} \quad (2)$$

has been determined earlier. Kolthoff and Sandell (13) found K equal to 3.2 with a chloroform solution of the reagent, and a preliminary determination by Buch (15) gave the value $1.96 \cdot 10^2$ for zinc dithizonate in carbon tetrachloride. To verify these values, the equilibrium constant was determined in this investigation also, using the same method as for all other metal dithizonates.

In fixing the time needed for extraction, it was observed that the reaction between dithizone and zinc is somewhat faster in carbon tetrachloride than in chloroform. This is in accordance with the observations by Hibbard (35, 52). The results are shown in Table 25. Attempts were made with 10 ml. dithizone standard solution and 20 ml. acetate buffer

TABLE 25
EFFECT OF TIME ON THE EXTRACTION OF ZINC
20 ml. aqueous solution pH 3.7 (CCl_4) and 4.65 (CHCl_3)
10 ml. dithizone standard solution. 20 γ Zn taken.

Time of shaking in minutes	Micrograms of Zinc found in organic phase	
	Carbon tetrachloride	Chloroform
5	3.2	0.4
15	3.2	1.2
30	3.1	2.2
60	3.2	3.8
90	3.2	3.8

of pH 3.7 (CCl_4) and 4.65 (CHCl_3), containing 10 micrograms of zinc. Metal in the organic layer was determined in the usual manner, following the mixed-color method.

The reaction in carbon tetrachloride is not immediate, as, for example, the formation of lead dithizonate, but equilibrium is attained in about 5 minutes. The tests with the reagent dissolved in this solvent, therefore, were extracted during this time. In chloroform, however, the time for shaking-out was one hour. The results are given in Table 26.

TABLE 26
ZINC — DITHIZONE EQUILIBRIUM
10 ml. organic solvent containing 60 γ of dithizone.

	pH	aq. phase ml.	Zn added γ	$\epsilon_{620} \text{ m}\mu$	$\epsilon_{535} \text{ m}\mu$	Zn in org. phase γ	K
Carbon tetrachloride			0	0.785	0.180		
			ZnDz ₂	.000	1.085	7.6	
	3.39	10	5	.626	0.360	1.5	2.0×10^2
	3.53	10	10	.463	.545	3.1	2.0
	3.82	20	5	.514	.486	2.6	2.1
	4.05	20	10	.292	.746	4.8	1.9
	4.17	20	50	.085	.981	6.8	2.0
	¹⁾ 3.08	20	10			6.0	2.1
	3.65	50	5	.658	.324	1.2	2.0
	3.59	50	10	.602	.377	1.7	2.0
	²⁾ 3.11	10	ZnDz ₂	.691	.290	0.9	1.9
	²⁾ 3.92	20	"	.410	.604	3.6	1.7
							$M. 2.0 \times 10^2$
	Chloroform			0	0.707	0.275	
			ZnDz ₂	.000	1.010	7.6	
4.57		10	5	.441	0.552	2.9	4.7
4.38		10	10	.410	.579	3.2	4.4
5.09		20	5	.341	.655	4.0	4.2
4.94		20	10	.231	.767	5.1	4.6
5.06		20	50	.071	.932	6.9	4.2
¹⁾ 3.67		20	10			3.7	4.8
4.43		50	5	.614	.371	1.0	4.2
4.52		50	10	.501	.482	2.2	4.6
²⁾ 4.04		10	ZnDz ₂	.598	.389	1.2	4.0
²⁾ 4.48		20	"	.476	.510	2.5	4.3
							$M. 4.4$

¹⁾ The organic solvent contained 300 γ of dithizone. Amount of metal in org. phase determined as described for bismuth on p. 24.

²⁾ Decomposing of zinc dithizonate. Procedure on p. 24.

Many other metals reacting with dithizone do so under the same optimums as zinc. It is necessary, therefore, to use complex-formers to eliminate their influence.

TABLE 27

ZINC — DITHIZONE EQUILIBRIUM IN THE PRESENCE OF VARIOUS ANIONS.
10 ml. organic solvent containing 60 γ of dithizone.

	Anions present in aqueous phase	pH	aq. phase ml.	Zn added γ	ϵ 620 $m\mu$	ϵ 535 $m\mu$	Zn in org. phase γ	K
Carbon tetrachloride	Sea water, Cl = 12 ‰	3.60	10	5	0.556	0.439	2.2	1.8×10^2
	» »	4.46	50	10	.214	.831	5.5	1.7
	1M NaCl	4.14	10	5	.402	.614	3.7	1.0
	» »	4.11	50	10	.424	.593	3.5	1.0
	0.1M KCN	3.42	10	5	.616	.370	1.6	2.0
	» »	4.77	50	10	.113	.950	6.5	2.3
	0.1M Na thiosulf.	4.29	10	5	.476	.534	3.0	0.20
	» »	4.62	50	10	.348	.675	4.2	0.19
	Carbamate 0.005 ‰	5.41	10	5	.601	.396	1.8	2.7×10^{-2}
	» »	6.47	50	10	.198	.858	5.7	2.1
Chloroform	Sea water, Cl = 12 ‰	4.97	10	5	0.331	0.666	4.1	4.3
	» »	4.89	50	10	.349	.650	3.9	4.1
	1M NaCl	4.38	10	5	.568	.415	1.5	2.2
	» »	5.21	50	10	.280	.713	4.6	1.8
	0.1M KCN	4.29	10	5	.550	.436	1.7	4.1
	» »	4.46	50	10	.531	.460	1.9	4.6
	0.1M Na thiosulf.	4.68	10	5	.498	.493	2.3	1.4
	» »	5.28	50	10	.310	.686	4.3	1.0
	Carbamate 0.005 ‰	7.24	10	5	.278	.714	4.6	4.3×10^{-4}
	» »	7.34	50	10	.181	.820	5.7	3.9

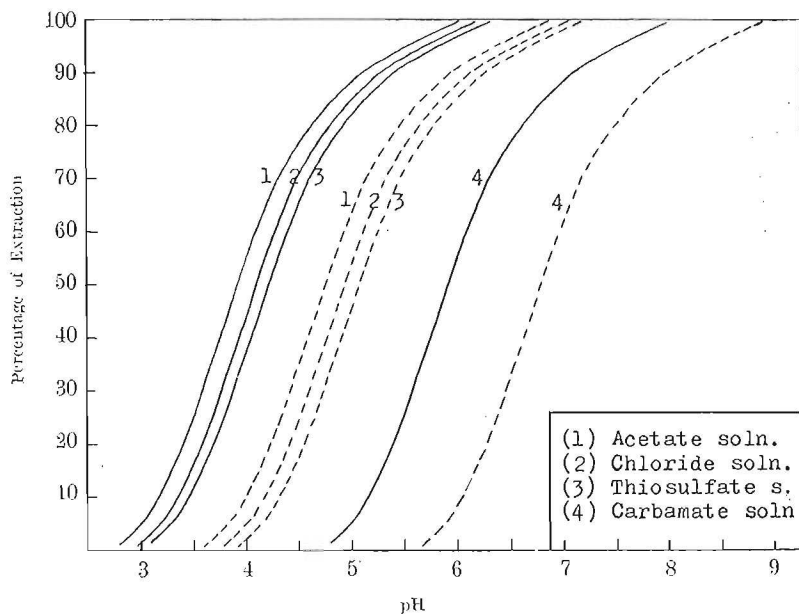


Fig. 19. — Equilibrium curves for zinc dithizonate in carbon tetrachloride (----) and chloroform (-----). No excess of dithizone.

According to Fischer and Leopoldi (53) thiosulfate at pH 4—5.5 prevents the reaction of the following metals with dithizone: bismuth, copper, gold, mercury, lead and silver. Further, they use potassium cyanide in weak acid solution to convert cobalt, nickel and palladium into their cyanide complexes. Ritchie and Holland (54, 55) use sodium diethyldithiocarbamate in alkaline solution as a general complex-former. Cowling and Miller (56), however, state that zinc in the presence of carbamate cannot be quantitatively extracted with a carbon tetrachloride solution of dithizone. As for the other metals, the equilibrium constant has been determined in the presence of the above-mentioned complex-forming substances, and also in sea water and sodium chloride solution. The results are given in Table 27 and Fig. 19.

Conclusions. If zinc is to be determined in weak acid solution, a carbon tetrachloride solution of the reagent has to be used. With this solvent, equilibrium is attained after a few minutes' extraction.

In the presence of thiosulfate the determination must be made at a higher pH than usual, and if other reacting metals are converted to their carbamate complexes, the extraction should be made in alkaline solution. Contrary to what Cowling and Miller state, a quantitative reaction was obtained at pH 8.5 with dithizone dissolved in carbon tetrachloride.

VI. SUMMARY AND CONCLUSIONS

On the basis of the results obtained in this investigation, the following table (No. 28) can be prepared. It contains the most important information regarding the composition, formation and description of the metal dithizonates investigated.

To give a clear picture of the formation range for the various metal dithizonates in carbon tetrachloride, the corresponding equilibrium curves are shown in Fig. 20. The curves are calculated from the values of the equilibrium constants and for twice as much aqueous phase as organic solvent. It is supposed that an equivalent amount of metal against dithizone is present.

Similar equilibrium curves are obtained with a chloroform solution of dithizone, but they are in general displaced 1.0 pH units to the right. As under normal working conditions an excess of dithizone is most often used, it can be mentioned that with a 50 per cent excess of dithizone, for example, the curves are displaced 0.3 pH units to the left.

The reaction between metal and dithizone usually proceeds more slowly when the reagent is dissolved in chloroform than in a carbon tetrachloride solution, but for the following metals equilibrium is attained after vigorous shaking for only a few minutes: mercury, silver, bismuth, zinc (CCl_4), cadmium, lead and thallium. On the other hand,

TABLE 28
THE DITHIZONATES INVESTIGATED

Cation	Complex form	Color (CCl ₄)	pH for quant. reaction	Equilib. constant		Wavelength of max. absorption
				CCl ₄	CHCl ₃	
Bi ⁺³	BiDz ₃	orange	weak acid soln	5.6 × 10 ⁹	2.3 × 10 ⁵	490
Bi ⁺³	1) Bi ₂ Dz ₃	red-orange	basic soln			490
Cd ⁺²	CdDz ₂	red	neutral soln	38.5	3.4	515
Co ⁺²	CoDz ₂	red-violet	basic soln	39	3.2 × 10 ⁻²	535
Cu ⁺	CuDz	brown	dil. acid soln			
Cu ⁺	1,2) Cu ₂ Dz	violet	neutral soln			
Cu ⁺²	CuDz ₂	violet	weak acid soln	3.4 × 10 ¹⁰	3.2 × 10 ⁶	545
Cu ⁺²	1) CuDz	green-yellow	neutral soln			460
Pb ⁺²	PbDz ₂	red	neutral soln	2.4	0.13	515
Hg ⁺	[Hg ₂]Dz ₂	yellow-orange	dil. acid soln			490
Hg ⁺	1,2) [Hg ₂]Dz	violet	neutral soln			
Hg ⁺²	HgDz ₂	yellow-orange	dil. acid soln			490
Hg ⁺²	1) HgDz	violet	neutral soln			535
Ni ⁺²	NiDz ₂	brownish	basic soln	6.4 × 10 ⁻²	1.2 × 10 ⁻³	460
Ag ⁺	AgDz	yellow	dil. acid soln	1.5 × 10 ⁷	1.0 × 10 ⁶	460
Ag ⁺	1,2) Ag ₂ Dz	violet	neutral soln			
Tl ⁺	TlDz	red	basic soln			505
Zn ⁺²	ZnDz ₂	purplish	neutral soln	2.0 × 10 ²	4.4	535

1) Formed in the presence of an excess of metal only.

2) Insoluble in the organic solvents.

the reaction of copper, cobalt and nickel with dithizone is rather slow and equilibrium is first attained in this case after shaking for 1—2 hours. The reason for the facts mentioned above could not be ascertained.

In addition to the keto form the enol modification has also been found for the dithizonates of the following metals: bismuth, copper, mercury and silver. The enol tautomer is formed in nearly neutral or alkaline solutions and in the presence of an excess of metal only. According to

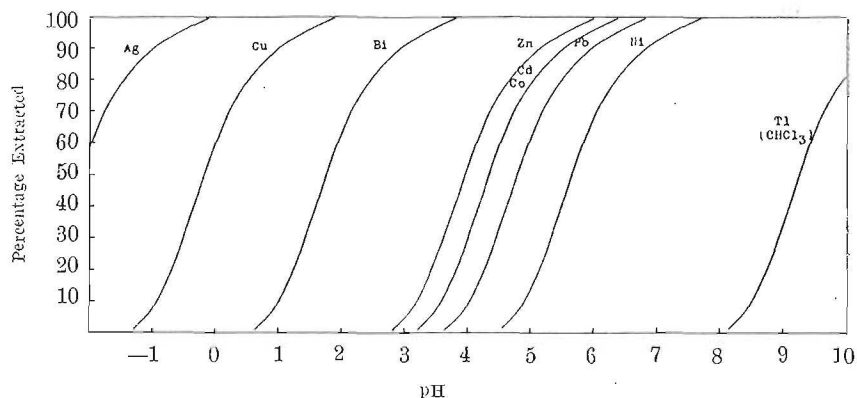


Fig. 20. — Equilibrium curves for some metal dithizonate in carbon tetrachloride. No excess of dithizone.

Hellmuth Fischer this tautomer should also be formed by treating the keto form with alkali, but this has not been confirmed during the present experiments. If desirable, therefore, the mono-color method can be used in the final determination of these metals also.

The metal dithizonates once formed are generally decomposed in a simply reversible manner and this probably holds for mercury, silver and copper dithizonate also if they could be treated with sufficient acid solutions. It is stated in literature that the cobalt and nickel dithizonates should be exceptions, but the results obtained show that the dithizonates of these metals decompose at a higher pH value than hitherto supposed, and a sufficient time of shaking would probably prove that their reaction with dithizone is simply reversible also.

With regard to the constitution of the various metal dithizonates, no conclusive evidence was forthcoming during the investigation that the suggestions made by Fischer were in any way incorrect. The enol forms of the univalent metal dithizonates with the composition M_2Dz , however, have probably no ring structure, as they are without exception insoluble in organic solvents, and accordingly differ from all other dithizonates for which this structure must be supposed as the right one.

As this investigation was made in the first place to obtain a foundation for the determination of traces of heavy metals in sea water, it can be stated that in practice the salinity of the water round the coast of Finland does not have any impeding influence on the extraction of the metals. In ocean water, however, the extraction should be made at a higher pH value than the equilibrium constant would presuppose.

The influence of other anions on the extraction, especially cyanide, citrate and tartrate, differs from one metal to another and is often rather remarkable, due to the fact that the metals — especially in more acid solutions — combine with them to form complexes stronger than the dithizonates.

On studying the analyses existing at present for the amount of heavy metals in sea water it has been observed that among the metals investigated there are only three (*viz.*, zinc, copper and lead) to be found in quantities greater than one microgram per liter. From this, therefore, it would appear that the metals should be concentrated from sample waters of 5 to 10 liters in order to obtain a sufficient amount for a reliable analysis.

As all of the dithizone-reacting metals do so in weak alkaline solution, a pH value of 8.5 is the most suitable one in this case; similarly for a carbon tetrachloride solution of the reagent also. At this pH, however, thallium cannot be extracted quantitatively; the determination of this metal must accordingly be excluded.

The metals should be extracted from one liter of water at a time, so that a sufficiently vigorous shaking can take place. As the values of the equilibrium constants are known, the combined organic extracts should be shaken with a water solution of pH 3.0. Lead, zinc and cadmium enter the aqueous phase at this pH; these metals are finally separated from one another and are determined by using various complex-formers.

The extracts are then treated with 1 N sulfuric acid, which procedure passes bismuth, cobalt and nickel to the aqueous phase, leaving copper, mercury and silver in the organic layer. The aqueous phase is almost neutralized with ammonia (pH 4.5) and bismuth extracted. At this pH value the equilibrium between the cobalt- and nickel-ions and the dithizonates of these metals is replaced entirely in favor of the former if a shorter time of shaking-out is used.

As it was apparent from the investigation that dithizone is not a suitable reagent for determination of traces of nickel and cobalt; these metals should be finally determined more exactly with dimethylglyoxime and Nitroso-R-salt respectively.

The combined extracts contain now not only a large excess of dithizone but also the dithizonates of copper, mercury and silver. These metals cannot be separated from one another except by retransferring to the aqueous phase. This is accomplished by treating the extracts with 1 N sulfuric acid and a few drops of a 1 % KMnO_4 solution; before this, however, the overwhelming excess of dithizone should be removed by shaking with very dilute ammonia. Excess of permanganate in the aqueous solution is reduced with hydroxylamine hydrochloride, for example, and both mercury and silver extracted with dithizone. By treating the dithizonates obtained with a weak acid solution of potassium cyanide, only silver dithizonate is decomposed. After the removal of mercury and silver, the pH of the solution is increased with ammonia to about 3, and the copper present determined with dithizone.

This outline of procedure, drawn up on the basis of the results hitherto obtained, has already been partly checked, but will of course be examined more closely in the second part of the complete investigation. This second part will give the analyzing procedure in detail, along with its application in the determination of traces of heavy metals in sea water samples collected from the Gulf of Finland, the Gulf of Bothnia, the Baltic Sea and the North Sea.

LITERATURE CITED

1. E. Fischer, *Ann.*, **190**, 118 (1878); E. Fischer and E. Besthorn. *ibid.*, **212**, 316 (1882).
2. H. Fischer, *Wiss. Veröffentlich. Siemens-Konzern*, **4**, 158 (1925).
3. E. B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Pub. New York 1944.
4. H. Fischer, G. Leopoldi and H. von Usler, *Z. anal. Chem.*, **101**, 1 (1935).
5. W. O. Winkler, *J. Assoc. Off. Agr. Chem.*, **18**, 638 (1935).
6. W. O. Winkler, *ibid.* **21**, 220 (1938).
7. M. K. Horwitt and G. R. Cowgill, *J. Biol. Chem.*, **119**, 553 (1937).
8. H. Fischer and G. Leopoldi, *Wiss. Veröff. Siemens-konzern*, **12**, 44 (1933).
9. H. Fischer, *Angew. Chem.*, **50**, 919 (1937).
10. H. J. Wichmann, *Ind. Eng. Chem., Anal. Ed.*, **11**, 66 (1939).
11. H. Fischer, *Angew. Chem.*, **47**, 685 (1934).
12. H. Fischer and G. Leopoldi, *Chem.-Ztg.*, **64**, 231 (1940).
13. I. M. Kolthoff and E. B. Sandell, *J. Am. Chem. Soc.*, **63**, 1906 (1941).
14. P. L. Hibbard, *Ind. Eng. Chem., Anal. Ed.*, **10**, 179 (1938).
15. K. Buch, *Finska Kemistsamfundets Medd.*, **1-2**, 25 (1944).
16. K. Buch and F. Koroleff, *ibid.*, **3-4**, 98 (1945).
17. F. F. Martens and F. Grünbaum, *Ann. d. Phys.*, (4) **12**, 984 (1903).
18. P. A. Clifford, *J. Assoc. Off. Agr. Chem.*, **21**, 695 (1938).
19. H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **119**, 168 (1940).
20. L. J. Snyder, *Ind. Eng. Chem., Anal. Ed.*, **19**, 684 (1947).
21. D. A. Biddle, *ibid.*, **8**, 99 (1936).
22. L. P. Biefeld and T. M. Patrick, *ibid.*, **14**, 275 (1942).
23. W. W. Clark and H. A. Lubs, *J. Biol. Chem.*, **25**, 479 (1916).
24. E. J. Cohn, F. F. Heyroth and M. F. Menkin, *J. Am. Chem. Soc.* **50**, 696 (1928).
25. S. Palitzsch, *Biochem. Z.*, **70**, 333 (1915).
26. I. M. Kolthoff and J. J. Vleeschhouwer, *ibid.*, **189**, 191 (1927).
27. P. A. Clifford and H. J. Wichmann, *J. Assoc. Off. Agr. Chem.*, **19**, 130 (1936).
28. C. A. Greenleaf, *ibid.*, **24**, 341 (1941).
29. D. M. Hubbard, *Ind. Eng. Chem., Anal. Ed.*, **11**, 343 (1939).
30. J. F. Reith and C. P. van Dijk, *Chem. Weekblad.* **36**, 343 (1939).
31. L. A. Haddock, *Analyst.* **59**, 163 (1934).
32. Yu-Lin-Yao, *Ind. Eng. Chem., Anal. Ed.*, **17**, 114 (1945).
33. H. Fischer and G. Leopoldi, *Mikrochim. Acta*, **1**, 30 (1937).
34. E. B. Sandell, *Ind. Eng. Chem., Anal. Ed.*, **11**, 364 (1939).
35. P. L. Hibbard, *ibid.*, **10**, 615 (1938).
36. E. B. Sandell and R. W. Pehrlich, *ibid.*, **11**, 309 (1939).
37. H. R. Marston and D. W. Dewey, *Australian J. Exptl. Biol. Med. Sci.* **18**, 343 (1940); *C. A.* **35**, 3557 (1941).

38. H. Barnes. *Analyst*. **71**, 578 (1946).
39. H. Barnes. *J. Marine Biol. Assoc. U. K.* **26**, 203 (1946).
40. H. Barnes. *Analyst* **72**, 469 (1947).
41. R. Vesterberg and O. Sjöholm. *Arkiv för kemi, mineralogi och geologi*, **22 A**, N:o 22 (1946).
42. E. P. Laug and K. W. Nelson. *J. Assoc. Off. Agr. Chem.*, **25**, 399 (1942).
43. S. L. Morrison and Harriet L. Paige. *Ind. Eng. Chem., Anal. Ed.*, **18**, 211 (1946).
44. R. M. Mehurin, *J. Assoc. Off. Agr. Chem.*, **18**, 192 (1935).
45. F. J. Welcher, *Organic Analytical Reagents, part III*, D. Van Nostrand Company, Inc. (1947).
46. G. D. Sherman and S. Mc Hargue, *J. Assoc. Off. Agr. Chem.*, **25**, 510 (1942).
47. P. A. Clifford, *ibid.*, **26**, 26 (1943).
48. R. S. Young, E. H. Strickland and A. Leibowitz, *Analyst* **71**, 474 (1946).
49. H. Fischer, *Angew. Chem.*, **46**, 517 (1933).
50. K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **12**, 63 (1940).
51. P. A. E. Kamerman. *J. S. African Chem. Inst.*, **27**, 22 (1944); *C. A.* **39**, 1370 (1945).
52. P. L. Hibbard. *Ind. Eng. Chem., Anal. Ed.*, **9**, 127 (1937).
53. H. Fischer and G. Leopoldi. *Z. anal. Chem.*, **107**, 241 (1937).
54. W. S. Ritchie, *J. Assoc. Off. Agr. Chem.*, **21**, 204 (1938).
55. E. B. Holland and W. S. Ritchie. *ibid.*, **22**, 333 (1939).
56. H. Cowling and E. J. Miller, *Ind. Eng. Chem., Anal. Ed.*, **13**, 145 (1941).

