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THE PREPARATION AND PROPERTIES
OF
DIPHENYLTHIOCARBAZONE

A THESIS SUBMITTED TO
THE DEPARTMENT OF CHEMISTRY
OF
BRIGHAM YOUNG UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF
MASTER OF ARTS

BY
FLOYD C. MCINTIRE

1937

This Thesis by Floyd G. McIntire is accepted in its present form by the Department of Chemistry as satisfying the Thesis requirement for the degree of Master of Arts.

Date, _____ . Signed

Major Professor

Thesis Committee

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PREFACE

At present the chemical literature offers no method for the preparation of diphenylthiocarbazono, or dithizone, sufficiently detailed to guide the average laboratory technician in an economical and successful preparation of this compound. The high price of dithizone and the limited number of dispensers of it emphasize the need of such a method.

The original research reported in this thesis was done primarily in an attempt to formulate a satisfactory detailed method for the preparation of dithizone. The suggestions of Emil Fischer were followed and an attempt was made to improve his outline and to note the possible errors so that they might be brought to the attention of the readers of this work. The research work included, in addition, a brief study of the nature of the melting point of dithizone. An attempt was made to compare the cost of producing it by this method with the commercial price of the compound.

The first part of this thesis is devoted to a survey of the literature which consists of the history, uses, and reactions of dithizone, a summary of the analytical methods in which it is used, and a summary of the available literature on the preparation of it. The remaining part is a report of the research done.

May I express appreciation to Dr. C. E. Maw and to the entire staff of the Chemistry Department of the Brigham Young University for their kind interest and advice.

Floyd C. McIntire


THE PREPARATION AND PROPERTIES

of

DIPHENYLTHIOCARBAZONE

SURVEY OF LITERATURE

HISTORICAL

Diphenylthiocarbazone, or dithizone, is a weak organic acid, the structural formula of which is . Emil Fischer (1) is accredited as being the first man to prepare and study dithizone. He made it in 1876 as a part of his study of the structure and reactions of phenylhydrazine. He noted that dithizone had acid properties and that its zinc salt had a bright red color. Until 1925, however, dithizone was not used as an analytic reagent. In that year Hellmut Fischer began to study the reactions of dithizone and the possibilities of using it as a reagent in qualitative analysis. In 1933 and 1934 he and Leopoldi (2A, 2B) announced colorimetric methods for using it to determine small amounts of lead and copper quantitatively. Since 1935 dithizone has become increasingly popular as a reagent in quantitative analysis; it is used most extensively in determining small amounts of lead particularly in spray residues. Methods have been developed by H. Fischer (3) for the qualitative separation of Pb, Au, Hg, Ag, Cu, Zn, Co, Ni, Cd, CN^- , Sn(ous), Tl(ous), and Bi, using dithizone as the reagent and controlling the pH value. Dithizone is now used to determine small quantities

of lead and zinc in biological products. It is reported that quantities of zinc and lead as small as 0.001 mg. may be determined by the use of this reagent.

PROPERTIES AND REACTIONS

Pure dithizone will form small, sometimes microscopic, blue-black crystals when a solution of it in chloroform or carbon tetrachloride is evaporated to dryness at about 50° C, preferably under reduced pressure (Fig. 1). When a few of these crystals are dissolved in a drop of chloroform or carbon tetrachloride on a microscope slide and the solvent is allowed to evaporate, microscopic crystals of dithizone are formed (Fig. 2). The melting point of these crystals has thus far not been recorded in the literature. The author has done some work on the melting point which is discussed with the other experimental work.

Dithizone is very soluble in chloroform and carbon tetrachloride giving colors from blue-green to deep red, depending upon the concentration of the solute and upon the depth of the column of liquid observed. The deep red color is observed when the concentration is high or when a long column of the solution is observed. Dithizone is insoluble in water. It is slightly soluble in alcohol giving a deep red color, soluble in alkaline solutions both aqueous and alcoholic, insoluble in acids, and slightly soluble in ether. Since dithizone is a weak organic acid, it usually forms a salt when it dissolves in alkaline solutions. The salt is soluble in either water or chloroform as a rule. When a chloroform or carbon tetrachloride solution of dithizone is extracted with dilute ammonium hydroxide (1:100) a red-brown colored salt is formed which is soluble in water and insoluble in either chloroform or carbon tetrachloride. This fact furnishes a means of purification of impure dithizone. The



Fig. 1. Crystals of dithizone obtained by evaporating a chloroform solution of dithizone in a small beaker at 50°C . Photographic data: one-half-second exposure, red color filter, magnification 500 x.



Fig. 2. Crystals of dithizone obtained by evaporating a solution of dithizone on a microscope slide at room temperature. Photographic data: two-second exposure, green color filter, magnification 940 x.

solubility of dithizone in dilute ammonium hydroxide is decreased by the presence of ammonium citrate in the solution.

According to E. Fischer (4) dithizone forms salts with the alkalies and alkaline earths. The salts of the alkalies are very soluble in water and exhibit various shades of color. The zinc salt will form fine red-violet colored prisms insoluble in water. The lead salt is brown-red, soluble in alkalies and chloroform; the silver salt is a brown-violet, less soluble in alkali and chloroform than in water; the mercury salt is a brown-red, more soluble in chloroform than in water.

According to H. Wolbling and B. Steiger (5):

"Dithizone in carbon tetrachloride yields characteristic color reactions with (a) Ag, Zn, Cd, Sn^{IV}, Pb, Mn; (b) Sn^{II}, Fe^{II}; (c) Sb, Bi; (d) Cu; (e) Au and the Pt metals, and (f) Hg. In acid solutions group (a) gives no reaction with dithizone. When the metals of group (b) are oxidized and are in an acid solution they do not react with dithizone. The addition of tartaric acid prevents the metals of group (c) from reacting with dithizone. Formic acid prevents the reaction between dithizone and copper. Group (e) can be removed by reduction to metals, e.g., by shaking with activated carbon. Hence the reaction can be made specific for mercury; sensitivity 0.01 mg. In a mixed solution the mercury and precious metals can be precipitated with copper and the mercury extracted from the precipitate with nitric acid before making the test."

H. Fischer (6) made the following comments upon the reactions of dithizone as stated by Wolbling and Steiger:

"1. It was not mentioned that oxidizing material with the dithizone reagent will give an orange color very similar to that of the mercury-dithizone reaction. Therefore, oxidizing materials must be avoided. It is possible, however, to distinguish the mercury color from that caused by oxidation by treating the colored material with one per cent potassium cyanide. When the mercury-dithizone complex in chloroform solution is shaken with aqueous potassium cyanide, the complex is broken down and the green color of dithizone appears.

"2. The report that silver will not react with dithizone in the presence of small amounts of acid is not true. Under these conditions silver does not react to give a violet flaky precipitate, however, the green reagent is suddenly changed to yellow, a fact which the author used to detect small traces of silver. When mercury and silver are together in solution the mercury-dithizone color reaction takes place, even in the presence of an excess of silver. When a very dilute solution

of the dithizone reagent is used a confusion of the two colors is possible so that the silver reaction may be misconstrued to indicate the presence of Hg. According to published experiments of the author (H. Fischer) the mercury and silver colors may be distinguished as follows: Carry through the reaction using about 1 cc. of the dithizone reagent; separate the yellow carbon tetrachloride layer; wash it twice with dilute sulfuric acid (1%) and shake well with weakly acidified KONS (1%). The mercury color will remain and the silver color will immediately change to green. When mercury and silver are present, Hg:Ag=1:9000, the mercury can be distinguished.

"3. Contrary to the report of Wöbling and Steiger it has been found that mercury can be detected in the presence of platinum in acid solution. By carrying out the reaction in test tubes the orange color of mercury is detectable in the presence of a 500-fold excess of platinum.

"4. The above mentioned authors report that with the addition of potassium cyanide the copper-dithizone reaction is not sufficiently masked. This is not the case. If the reaction is carried out in a neutral or weakly alkaline solution and a sufficient amount of potassium cyanide is used, the masking is so complete that one can detect 0.01 to 0.001% of lead in the presence of copper colorimetrically with dithizone.

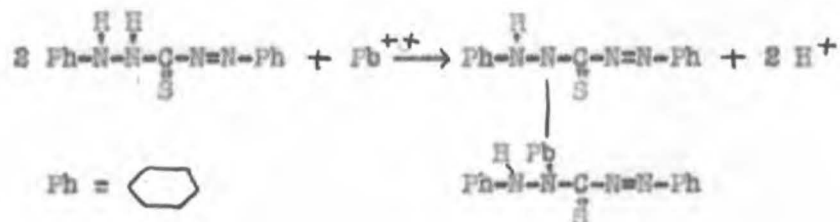
"When dithizone in carbon tetrachloride (as stated by Wöbling and Steiger) gives a red-brown color upon being shaken with potassium cyanide solution, either the dithizone solution or the potassium cyanide solution is impure.

"By using pure solutions the copper-dithizone solution will be decolorized upon being shaken with potassium cyanide. Mercury in neutral or weakly alkaline solutions is as completely masked as copper is by potassium cyanide. In acid solutions the mercury color appears in the presence of potassium cyanide, so with the copper color. This makes a distinction between the two impossible."

Dithizone may be reduced to diphenylthiocarbazine in a cold caustic soda solution treated with zinc dust; by warming the solution further reduction is accomplished and the products are aniline and phenylthiosemicarbazide.

Generally speaking, there are four facts connected with the properties of dithizone which are to be considered in using it as an analytic reagent: (A) Upon the pH of the solution depend the stability and type of complexes formed, i.e., a dithizonate formed in an acid solution would probably decompose in a basic solution and conversely a dithizonate formed in an alkaline solution would probably decompose in an acid solution. For

example: The lead-dithizone complex which is formed in a slightly basic solution is decomposed by acid to give the lead salt of the acid and free dithizone. The same is true with ammonium dithizonate. (B) The dithizone molecule usually acts as a monobasic acid and metallic dithizonates are formed when a metallic cation replaces one of the hydrogens in the group $\overset{\text{H}}{\text{N}}-\overset{\text{H}}{\text{N}}-\overset{\text{S}}{\text{C}}-$. For example:



(C) In some cases the dithizone radical may have a valence of two. (D) With those metallic ions which are easily reduced--Hg(1c), Au(1c)--oxidation of the dithizone may precede or accompany the dithizonate formation.

DITHIZONE AS AN ANALYTIC REAGENT

The use of dithizone as an analytic reagent depends upon the formation of colored dithizonates which are usually soluble in chloroform. As a rule these complexes, or dithizonates, which are soluble in chloroform are insoluble in water and conversely those which are soluble in water are insoluble in chloroform so that the whole of the dithizonate in any particular analysis may be concentrated in one liquid phase. For example, ammonium dithizonate is insoluble in chloroform and soluble in water. The dithizone may be completely removed from a chloroform solution by extraction with aqueous ammonia. Lead-dithizonate is insoluble in water and soluble in chloroform. Lead can be completely removed from an aqueous solution by extracting with a chloroform solution of dithizone. The colors of the dithizonates range from violet to red and orange. The sensitivity of

any test depends upon (A) the pH of the aqueous solution, (B) the relative volumes of the two liquid phases present, (C) the concentration of the dithizone reagent, and (D) the thoroughness with which the two liquid phases, water and either chloroform or carbon tetrachloride, are shaken together. From this it is obvious that the sensitivity of a test could not be estimated accurately unless the conditions under which the test was made were well known. With ordinary technique and precautions the sensitivity of the reagent is one to five micrograms. With micromethods the sensitivity for zinc is as small as 0.025 microgram.

H. Fischer (3) outlined a group separation which might be used for either qualitative or quantitative analysis of the metals included. This group separation might be summarized as follows: (A) Pd, Au, Hg, Ag, and Cu react with dithizone in an acid solution; (B) in a solution of pH about 6 zinc is most sensitive to dithizone, however, large amounts of Co, Ni, Pb, and Cd might give interfering colorations; (C) Sn(ous) Tl(ous), Pb, and Bi react in a slightly alkaline solution containing CN^- ; (D) in a strongly alkaline solution containing tartrate Co, Ni, and Cd react. Fischer gives methods of separating and identifying the metals within the groups making a complete scheme for the separation and analysis of the metals named.

In quantitative analysis dithizone may be used in either of two ways: (A) for the preliminary extraction of the metal from impurities or from an excess of solvent, (B) for the actual determination of the quantity of a metal.

When dithizone reagent is used as in (A) the group and sub-group separations as outlined by Fischer (3) may be made quantitative as well as qualitative and the value of dithizone in separating a metal from impurities is obvious. All the lead or zinc in 100 cc. of an aqueous

solution may be concentrated into 5 cc. of a chloroform solution of dithizone (provided that there is sufficient dithizone in the 5 cc. of chloroform). By extracting this 5 cc. of chloroform solution with a small volume of acid the metal may be taken back into an aqueous solution. This illustrates that dithizone is valuable as a concentrating agent.

Two types of methods are used in determining the actual quantity of a metal by the use of dithizone: (A) colorimetric, (B) titrimetric.

Of the colorimetric method there are three forms. Probably the first colorimetric method was announced by H. Fischer and G. Leopoldi (25) for lead and copper and may be summarized as follows:

"Dithizone is purified by extraction from carbon tetrachloride with dilute aqueous ammonia (1:200), and reprecipitated into fresh carbon tetrachloride with dilute sulfuric acid. This resultant solution should contain about 20 mg. of dithizone per 100 cc. and is diluted to contain 6 mg. per 100 cc. for use; it is stored in a dark bottle under a layer of sulfurous acid. In lead determination, a solution containing 0.006 to 0.12 mg. of lead is made alkaline with dilute aqueous ammonia. Other metals are held inactive to dithizone by the presence of sodium-potassium tartrate. The solution is shaken with several successive portions of the reagent until no further red color is produced. The separated chloroform solution of the lead-dithizone complex is shaken with 5 cc. of 1% aqueous potassium cyanide and 1:200 ammonium hydroxide to remove excess dithizone. It is washed with water, and shaken with dilute hydrochloric acid. This decomposes the lead dithizonate and leaves the green color of dithizone which is compared with standards made up using known amounts of lead. Many metals interfere. For the determination of copper, the metal content must not exceed the limits 0.004 and 0.050 mg. The copper is extracted by the dithizone reagent from a dilute sulfuric acid solution. The copper-dithizone complex is a violet color. The excess dithizone is removed by dilute ammonia, and the resultant solution compared with standards. Only mercury, silver, and gold interfere with the copper determination, but excess of ferric iron oxidizes the reagent."

A first modification of the method of Fischer and Leopoldi is illustrated by the method of Winter and co-workers (7). This method shortens the Fischer-Leopoldi method by one step. Both methods are fundamentally the same down to and including the extraction of the excess dithizone from the chloroform solution of the red lead complex. At this point Winter and co-workers took a measurement of the intensity of the

red color of the chloroform solution (measured in a colorimeter against a standard of known lead content) as an indication of the quantity of lead present. They found that the intensity of the red color is not a linear function of the amount of lead present. Fischer and Leopoldi found that the intensity of the green color, after the lead had been extracted from the red-colored complex with acid, was a linear function of the quantity of lead present. In using this modification of the Fischer-Leopoldi method it was found, too, that the commercial grade of dithizone gave just as accurate results as that which had been repurified. This same modification is applied to the determination of zinc by Hibbard (8).

The second modification of the Fischer-Leopoldi colorimetric method is generally used in spray-residue analysis. With this method the solution containing an unknown quantity of lead is treated with an excess of the standard dithizone reagent. The same volume of reagent is used for each sample. This excess dithizone gives a color tint varying from blue to red depending upon the amount of excess. By comparing the color tint of a sample of unknown lead content with a series of samples containing the same amount of dithizone and known quantities of lead, the unknown quantity of lead can be closely estimated. This method eliminates the use of a colorimeter and is rapid. The color comparisons may be made with the unaided eye against a white background with ordinary lighting facilities.

A possible simplification of the method used in spray-residue analysis is based upon the fact that dithizone in the presence of ammonia will react with solid lead, lead sulfate, lead arsenate, or lead urcolate. (It is possible that some of the lead from the lead arsenate sprays is held on the fruits as lead urcolate.) This fact provides the possibility

that ammoniacal dithizone solution may be used as the solvent to remove the lead from the fruit, thus eliminating some steps in the usual procedure.

Dithizone produces a coloration in the presence of heated milk. It does not produce a coloration with unheated milk. This fact makes it possible to determine when heated milk has been added to unheated milk in proportions as low as 2 to 3%. The coloration is due to the fact that heated milk oxidizes dithizone while unheated milk does not.

Briefly, the titrimetric method involves the addition of small portions of dithizone reagent of known titer to the lead solution, buffered to a suitable pH, in a separatory funnel. The addition of each portion is followed by a complete shaking to mix the two liquid phases. The chloroform layer is then drawn off. When it is noticed that the lead is nearly all extracted from the aqueous solution (This is indicated by a less rapid and less complete color change of the dithizone reagent.) the portions of dithizone added are made very small. The end point is reached when the color of a very small portion of the dithizone reagent remains green after being shaken with the aqueous solution. The amount of dithizone reagent used is a measure of the quantity of lead determined. This method is sensitive to one microgram of lead.

The following is a review by H. Fischer (3) of the conditions for the use of dithizone as an analytic reagent for the various metals:

*Cadmium may be detected in the presence of copper by precipitating copper with H_2PO_4 ; bismuth in an ammonium chloride-buffered potassium cyanide solution in the absence of Pb, Sn(ous), and Tl; Au, in dilute acid solution, silver being removed with ammonium chloride and mercury with potassium iodide. Palladium forms preferentially a flocculent precipitate in acid solution. A group separation may be effected with dithizone, utilizing the varying solubility of the precipitates in solutions of controlled pH. Metallic Pb, Zn, and Cu react with dithizone

and may be so detected in metals and alloys; solid salts also react. Zinc may be determined colorimetrically as for lead; the reaction is carried out in sodium acetate-buffered solution. Gold may also be determined colorimetrically, using the change in color of a carbon tetrachloride solution of the silver-dithizone complex when shaken with gold. By extraction-titration with dithizone, $(0.5 \text{ to } 100) \times 10^{-6}$ g. of silver may be determined in acid solution in the presence of all other metals except Au, Hg, and Pd; also cadmium and zinc in neutral solutions. Zn, Pb, and Bi may be titrated indirectly, proceeding as for the colorimetric determination, but determining the liberated dithizone by addition of excess silver then titrating back. Alternatively, a measured excess of dithizone may be added to the acid solution, followed by excess of silver and back titration. $(10 \text{ to } 100) \times 10^{-6}$ g. of Cl, Br, I, and S may also be determined by adding excess of Ag, then titrating with dithizone.*

Special methods have been developed for use of dithizone in analysis of biological products for lead and zinc (8) and (9).

PUBLISHED MATERIAL ON THE PREPARATION OF DITHIZONE

The author has been unable to learn of any detailed methods published for the preparation of dithizone. The work of E. Fischer (1) on the preparation of this compound is apparently the only such work published. This work consists of a mere outline with details lacking. The preparation of dithizone consists of preparing diphenylthiocarbamide and oxidizing it to dithizone.

E. Fischer's outline for the preparation of dithizone may be stated as follows: Prepare the diphenylthiocarbamide from phenylhydrazine in one of two ways. (A) Add carbon disulfide to a solution of phenylhydrazine in ether. Heat the product of the ensuing reaction at about 90° (or $100\text{--}110^{\circ}$ --He indicated the two different temperature ranges in different papers.) until the evolution of hydrogen sulfide ceases and the evolution of ammonia begins. Dissolve the blue-green mass in hot alcohol and allow it to cool. The diphenylthiocarbamide will crystallize out since it is insoluble in cold alcohol. (B) Add an ether solution of thiophosgene to an ether solution of phenylhydrazine. Purify the product by crystallizing from alcohol. Dissolve the carbamide in moderately strong alcoholic potassium

hydroxide; boil for about fifteen minutes. Cool; add dilute sulfuric acid until precipitation is complete. The precipitate of dithizone may be purified by dissolving it in a dilute alkali and reprecipitating it with an acid (HCl or H_2SO_4). It may be further purified by dissolving in chloroform, evaporating off most of the chloroform, and adding alcohol to precipitate the dithizone.

The information to be found in the literature on the preparation of dithizone is obviously not sufficiently detailed to guide the average laboratory technician to a successful preparation of the compound. This is emphasized by the high price of dithizone which is sold only by a few dealers. A detailed guide to the preparation of dithizone is needed.


EXPERIMENTAL

PREPARATION OF DIPHENYLTHIOCARBAZONE

EQUIPMENT

The apparatus required is relatively simple. The author used an oil bath with an electric stirrer, arranged to accommodate ten 185 cc. Erlenmeyer flasks. The bath was heated with a bunsen burner. It was possible to control the temperature of the bath within 0.5° C. All operations of the preparation except the last were carried out in the same flask; 600 ml. beakers were used for the precipitation of the dithizone. 500 ml. separatory funnels and 600 ml. beakers were used in the purification process. 150 ml. pear-shaped separatory funnels and a colorimeter were used in the process of determining the purity of the product colorimetrically. A round-bottomed melting-point flask and a thermometer calibrated to tenths of a degree were used to determine the melting points. All samples were prepared using 5 ml. or 5.458 gm. of phenylhydrazine as a standard amount. A technical grade of chemicals was used throughout. Wherever the use of chloroform is mentioned carbon tetrachloride could be used as well.

PREPARATION OF DIPHENYLTHIOCARBAZIDE

Diphenylthiocarbazide was prepared from phenylhydrazine and carbon disulfide according to the following reactions: Ph = 



The carbazide was purified by crystallizing from an alcohol-water solution. As regards this preparation four main points were studied.

(A) Proportions of Carbon Disulfide and Phenylhydrazine

Since the first reaction above is spontaneous and results in the formation of a solid and the evolution of heat, it was found that the carbon disulfide must be added very slowly and in excess. When the theoretically required quantity of carbon disulfide is added quickly to a given quantity of phenylhydrazine in ether and the mixture stirred well, the ensuing reaction (which takes about 5 seconds to start) is so spontaneous that an appreciable loss of the product results. The best results were obtained when the carbon disulfide was added a drop at a time until some of the solid product formed. From then on the carbon disulfide could be added more rapidly.

For the data of Table I each sample contained 10 ml. of ether to 5 ml. of phenylhydrazine. To insure the strength of the phenylhydrazine-ether solution, 5 ml. of phenylhydrazine was added to 10 ml. of ether just before the sample was used. Table I shows that an excess of carbon disulfide is required to give the best yield of dithizone. Beyond a certain excess additional carbon disulfide does not increase the yield. 1.93 g. or 1.528 ml. of carbon disulfide should react with 5.458 g. or 5 ml. of phenylhydrazine. The following table shows that 4 ml. or 5.052 g. carbon disulfide per 5 ml. or 5.458 g. phenylhydrazine gave the maximum yield of dithizone.

TABLE I

Relation Between Proportion of Carbon Disulfide
and Yield of Dithizone

cc. CS ₂	1.75	3.00	4.00	5.00	6.00
g. CS ₂	2.185	3.789	5.052	6.315	7.578
Grams of dithizone produced					
Sample No.					
1	1.167	1.941	2.251	2.091	2.233
2	1.253	1.651	2.115	2.094	2.386
3	1.833	2.085	2.349	2.306	2.495
4	1.594	2.203	2.305	1.194	1.223
5	1.191	1.052	1.779	1.996	1.824
6	0.940	1.817	1.939	1.759	1.751
7	1.959	2.275	2.437	2.516	2.526
8	1.08	2.409			
Average	1.377	1.954	2.165	1.994	1.919

(B) Concentration of Phenylhydrazine in the Ether Solution

There seems a possibility that the first reaction might be slowed down by making the solution of phenylhydrazine in ether more dilute, thus giving a better yield of dithizone. This, however, is not the case. A series of samples was run. Part of the samples contained 20 ml. ether per 5 ml. phenylhydrazine, the remaining part contained 10 ml. ether per 5 ml. phenylhydrazine. No appreciable difference in yield was caused by the dilution.

(C) Evolution of Hydrogen Sulfide

Some references give 100-110° as the temperature at which the hydrogen sulfide should be evolved; others give 90°. Samples were heated

at 90, 95, and 100-110°. Best results were obtained when the temperature was kept at 90° during the evolution of hydrogen sulfide.

E. Fischer said;

"Heat until hydrogen sulfide is all evolved and evolution of ammonia begins."

The author found that using lead acetate paper to test for hydrogen sulfide and red litmus to test for ammonia there was no definite point where the hydrogen sulfide ceased to be evolved and evolution of ammonia began. As a matter of fact, ammonia was liberated at times while the evolution of hydrogen sulfide was still strong. If one watches the color of the solid material during the heating, he will notice that it changes from a yellow to dull green. The best results were obtained when the heating was stopped just as soon as the last trace of yellow color had disappeared.

(D) Addition of Water to Crystallize Diphenylthiocarbazine From the Alcoholic Solution

To purify the diphenylthiocarbazine the green mass which remains after the evolution of hydrogen sulfide is dissolved in hot alcohol. 25 ml. alcohol was required for the size sample used. E. Fischer states that the carbazine will crystallize out when the alcohol cools. The author found, however, that the crystallization from 95% alcohol is very slow and incomplete. The carbazine is slightly soluble in the alcohol. The addition of water hastened the crystallization and increased the yield. This is probably due to a lowering of the solubility of diphenylthiocarbazine in the alcohol due to the addition of water. Table II shows how much the yield was increased when 20 ml. of water was added to the solution of the carbazine in 25 ml. of 95% alcohol. In obtaining the data for Table II, the green mass was dissolved in

25 ml. of hot alcohol. The carbazide was allowed to crystallize out for ten hours. The supernatant liquid was then decanted and 20 ml. of water was added to it. The diphenylthiocarbazide was allowed to crystallize from the water-alcohol mixture for about five hours. Column (a) represents the weight of dithizone produced from the first crystallization. Column (b) shows the yield of dithizone produced from the additional crystals obtained after the water had been added. The irregularity of the results of Table II is probably due to the fact that the first crystallization in some samples was slower than in others. If this were true the crystallization at the end of the ten hours would not be as complete in some samples as in others. Table II shows that the average increase in yield due to the addition of water is 26.36. The important fact is that the crystallization of the carbazide is hastened and the yield is definitely increased by the use of water at this point.

TABLE II

Increase in Yield of Dithizone by Addition of Water to
Crystallize Diphenylthiocarbazide
from Alcohol

Sample No.	(a)	(b)
1	1.506 g.	0.725 g.
2	1.486	0.629
3	1.724	0.625
4	1.844	0.461
5	1.236	0.543
6	1.725	0.214
7	1.549	0.172
8	2.033	0.074
Average	1.6376	0.4304

There should be a relation between the concentration of water in the water-alcohol mixture and the yield of dithizone. Table III shows in a rough way the relation between the amount of water added and the total yield obtained. Each sample contained 25 ml. of alcohol.

TABLE III

Relation Between Amount of Water Used
and Yield of Dithizone

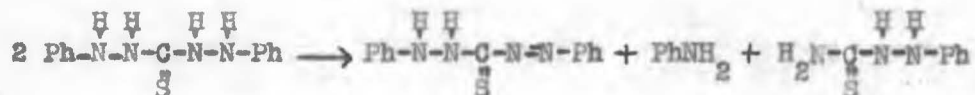
Sample No.	Weight of Dithizone Produced		
	5 ml. H ₂ O	10 ml. H ₂ O	20 ml. H ₂ O
1	2.082 g.	1.831 g.	1.832 g.
2	1.924	1.925	1.915
3	1.992	1.924	1.996
4	2.171	2.087	2.133
5	1.899	2.096	1.895
6	1.897	2.081	1.643
7	1.850	2.157	1.942
8	1.896	1.999	1.786
Average	1.964	2.010	1.854

This table shows that 10 ml. of water to 25 ml. of alcohol will produce the maximum yield. It should be mentioned that the data for Table I was obtained using 20 ml. of water to complete the crystallization of the diphenylthiocarbazine.

OXIDATION OF DIPHENYLTHIOCARBAZIDE TO DIPHENYLTHIOCARBAZONE

According to Fischer's outline the dithizone was produced by an auto-oxidation process in which two molecules of diphenylthiocarbazine participated. One molecule was oxidized to dithizone, the other

reduced to aniline and phenylthiosemicarbazide according to the following equation:



This auto-oxidation was accomplished by boiling the carbazide in alcoholic potassium hydroxide for fifteen minutes. The author used a saturated solution of alcoholic potassium hydroxide.

Another scheme was tried which consisted of dissolving the carbazide in cold alcoholic potassium hydroxide and adding the calculated amount of hydrogen peroxide which would be required to oxidize all of the carbazide to dithizone. If this were feasible the yield of dithizone should be twice as great as that produced by the auto-oxidation. This oxidation method produced a greater amount of crude dithizone, but purification showed that the auto-oxidation method produced a greater amount of pure dithizone. Time did not permit further work on this point. The author is of the opinion, however, that oxidation by hydrogen peroxide or some other oxidizing agent offers a fruitful field for further investigation, especially oxidation by hydrogen peroxide in dilute ammoniacal solutions. Table IV shows the quantity of crude and purified dithizone obtained when each method of oxidation was used.

TABLE IV

Effect of Oxidation Method on
Yield of Dithizone

Weight of Dithizone Produced

	Auto-oxidation		H ₂ O ₂ oxidation	
	crude	purified	crude	purified
1	1.899 g.	1.34 g.	2.63 g.	1.215 g.
2	1.85	1.405	2.279	0.858
3	2.087	1.27	2.221	0.88
4	2.081	1.36	2.887	0.647
5	1.999	1.32	2.967	1.100
Average	1.963	1.339	2.597	0.94

PURIFICATION OF THE CRUDE PRODUCT

Purification by precipitating dithizone from chloroform by the addition of alcohol was found to be inefficient chiefly because dithizone is slightly soluble in alcohol and appreciably soluble in a chloroform-alcohol mixture.

The best method of purification is that given by H. Fischer (2B). The crude dithizone is dissolved in chloroform, the solution extracted with 1:99 or 1:200 ammonium hydroxide, and the ammonia extract acidified with either hydrochloric acid or sulfuric acid. The dithizone is either filtered off or extracted back into fresh chloroform. Pure dithizone may be preserved in a dark bottle dissolved in chloroform, under an aqueous layer of sulfurous acid. The sulfurous acid prevents oxidation of the dithizone.

PURITY OF THE PRODUCT

Two methods of determining the relative purity of the product were attempted--melting point and a colorimetric method.

Colorimetric method: A sample of dithizone was purified three times and taken as arbitrarily 100% pure. From this a standard solution was made, 25 mg. per liter of chloroform. Chloroform solutions were made containing 90, 80, 70, 60, 40, and 20 per cent as much pure dithizone per unit volume as the standard. An aliquot of each solution was extracted with an excess of lead solution in the presence of a potassium cyanide-ammonium citrate solution. The intensity of the resulting red color of the standard solution was measured in a colorimeter against the intensity of the red color of each of the more dilute solutions. From the data thus obtained a graph was plotted to show the relation between the concentration of dithizone in the chloroform solution and the reading of the colorimeter. The curve obtained was not a linear function.

An attempt to determine the relative purity of a crude sample of dithizone was made as follows: A solution was made containing 25 mg. of the sample per liter of chloroform; an aliquot was extracted with excess lead solution in the presence of potassium cyanide-ammonium citrate solution; the intensity of the red color thus obtained was measured against that of the standard in the colorimeter; the colorimeter reading was referred to the graph to determine the per cent of pure dithizone in the sample.

This method was not applicable to the determination of the purity of samples of crude dithizone. There was an interfering color which prevented accurate measurement of the intensity of the red color of the lead-dithizone complex in chloroform. The interfering color was rather yellow and was observed also in the green dithizone solution before the lead extraction. This interfering color was assumed to be due to some impurity in the crude dithizone. It was found that if the

crude samples were purified as were those of Table IV the interfering color was removed. This purification was as follows: Dissolve 0.5 g. impure dithizone in 50 ml. chloroform; extract with six successive 100 ml. portions of 1:99 ammonium hydroxide; acidify the ammonium extract with dilute hydrochloric acid (1:4); filter off the precipitated dithizone, and dry it at 50° C. This purification gave a product which was suitable for the analytic method of Winter and co-workers (7) and which should be suitable for use in any method of analysis.

Melting point: Dithizone was found to have a very peculiar melting point. When pure, it melts sharply if the temperature is raised slowly. The temperature at which the melting occurs depends upon the rate at which the temperature is raised as well as upon the degree of purity of the compound. For example, a sample which melted at 143° when the temperature was raised one degree in two minutes, beginning three degrees below the melting point, melted at 148° when the temperature was raised one degree per minute. Another sample which melted at 141° when the temperature was raised one degree in two minutes, beginning three degrees below the melting point, melted at 138° when the temperature was kept at 130° for about ten minutes and then raised at the rate of one degree in two minutes. Samples which melted at 128°--130° before purification melted at 144°--146° after they had been purified once. All these melting points were taken at the same rate of heating--one degree rise in temperature in two minutes. A sample purified three times melted at about 151° at the same rate of heating. Another fact to be noted is that dithizone seems to decompose upon further heating after it has melted. A gas is liberated in the decomposition.

Samples which were purified as were those of Table IV were compared to the product sold by Eastman Kodak Company by taking their

melting points when all were heated at the same rate (one degree rise in temperature in two minutes). The results of Table V were thus obtained.

TABLE V
Relative Melting Points of
Purified Samples and of
Eastman's Product

Sample No.	Melting Point °C
1	145.1
2	146.1
3	144.6
4	144.9
5	144.9
6	143.6
7	144.8
8	145
9	144.8
10	142.6
Eastman's	143

It might be concluded that the purified samples listed in Table V are of a slightly higher grade than the product sold by Eastman.

SUMMARY

The experimental work may be summarized as follows:

1. In preparing diphenylthiocarbazide from phenylhydrazine and carbon disulfide, an excess of carbon disulfide is required for best results. 4 ml. carbon disulfide to 5 ml. phenylhydrazine will give the maximum yield.

2. Best results are obtained when the carbon disulfide is added very slowly to the ether solution of phenylhydrazine.

3. The yield of dithizone is not increased by diluting the ether solution more than 5 ml. phenylhydrazine to 10 ml. ether.

4. In heating the product of the reaction between phenylhydrazine and carbon disulfide to evolve hydrogen sulfide, the best point at which to stop the heating is the point at which the entire solid mass becomes a dull green color.

5. In purifying the diphenylthiocarbazine by crystallization from alcohol, the crystallization can be hastened and made more complete by adding water to the solution. 10 ml. water for every 25 ml. alcohol gives the maximum yield of dithizone.

6. The auto-oxidation method of oxidizing the diphenylthiocarbazine to dithizone gave the best yield. Oxidation by some oxidant such as hydrogen peroxide offers a very fruitful field for further investigation, especially oxidation in slightly ammoniacal solutions with hydrogen peroxide.

7. The melting point of dithizone depends greatly upon the rate of heating as well as upon the purity of the compound.

8. From 5.458 g. of phenylhydrazine, 1.34 g. of pure dithizone can be prepared. This is a 50% yield. This product is shown by melting point measurements to be of a slightly higher quality than the product sold by the Eastman Kodak Company. The cost of chemicals for the preparation is approximately \$36.00 per pound of dithizone produced. In calculating this cost it was assumed that 75% of the chloroform used could be recovered.

BIBLIOGRAPHY

- (1). Fischer, K. Berichte, Vol. 9, (1876). p. 884.
- (2A). Fischer, H. and Leopoldi, G. Weiss-Veroff. Siemens-Konz., Vol. 12, (1933). No. 1, p. 44-52, p. 52-60. British Abstracts, (1933). p.923.
- (2B). Fischer, H. and Leopoldi, G. Angew. Chemie, Vol. 47, (1934). p. 90-92. British Abstracts, (1934). p. 361.
- (3). Fischer, H. Angew. Chemie, Vol. 47, (1934). p. 685-692. British Abstracts, (1934). p. 1191.
- (4). Fischer, K. Berichte, Vol. 15, (1882). p. 2252.
- (5). Wölbling, H. and Steiger, B. Angew. Chemie, Vol. 46, (1933). p. 279-281. British Abstracts, (1933). p. 796.
- (6). Fischer, H. Angew. Chemie, Vol. 46, (1933). p. 517.
- (7). Winter, O. B., Robinson, Helen M., Lamb, Frances W., and Miller, E. J. Ind. & Eng. Chem. Anal. Ed. Vol. 7, (1935). p. 265-271.
- (8). Hibbard, P. L. Ind. & Eng. Chem. Anal. Ed. Vol. 29, (1937). p. 127-131.
- (9). Hibbard, P. L. Ind. & Eng. Chem. Anal. Ed. Vol. 6, (1934). p. 423-425.