[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Diphenylthiocarbazone (Dithizone) as an Analytical Reagent

BY HERMAN A. LIEBHAFSKY AND EARL H. WINSLOW

Diphenylthiocarbazone, $C_6H_5N{=}NC(S)NHNH{-}C_6H_5$, called dithizone and abbreviated D, was discovered by Emil Fischer,[1] who found that it forms certain metal salts (dithizonates), which are brilliantly colored in solution. With this orienting information available, Hellmut Fischer[2] over ten years ago began to explore the use of dithizone as an analytical reagent. Due largely to his efforts, it has become one of the more valuable organic compounds now available for the detection and determination of many metals.

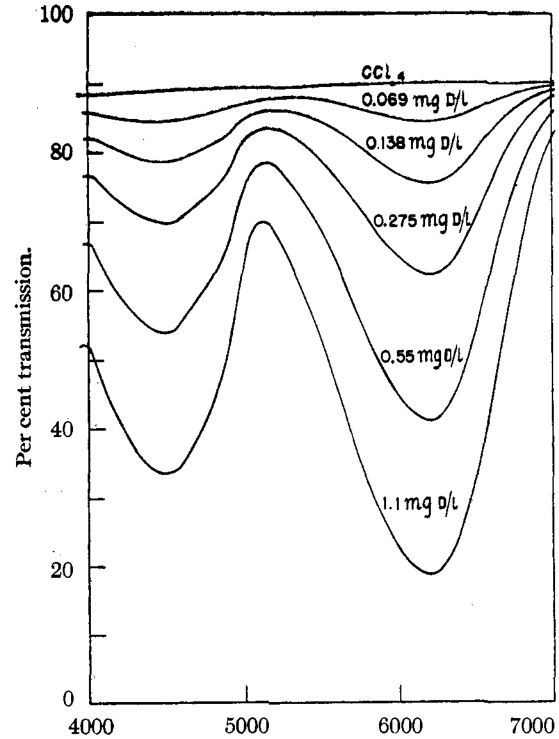

Fig. 1.—Transmission of dithizone in carbon tetrachloride.

To solve the problem of determining quantitatively less then 1 γ (1 gamma = 1 microgram) of copper and lead in cable oil samples containing no other metals, it has been necessary to modify the procedures of Fischer and Leopoldi[2b] so as to achieve greater reliability for small amounts and to measure the spectral transmission in the visible range of the various carbon tetrachloride solutions involved. In this work, a recording spectrophotometer[3] proved an invaluable tool. Although only the determinations of copper and lead have been investigated, the information obtained is of general interest in connection with dithizone and its compounds, apart from the value of the somewhat tedious analytical methods involved. The transmission curves of the (green) carbon tetrachloride dithizone solution are shown in Fig. 1. Beer's law is closely followed at all wave lengths (*cf.* Fig. 2) if the solution is uncontaminated, as by dithizone oxidation products.

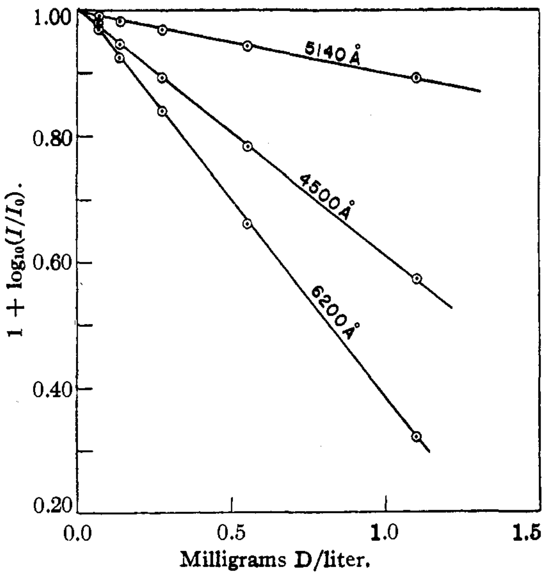

Fig. 2.—Beer's law plot for solutions of Fig. 1.

The molar extinction coefficients, defined by

$$\log_{10} I/I_0 = -\epsilon l(D) \qquad (1)$$

(where l is the length of the cell in centimeters, (D) is the concentration in moles/l. of dithizone, and I_0 is the transmission of carbon tetrachloride) at three wave lengths are 19,000 (4500 Å.); 4740 (5140 Å.); and 30,400 (6200 Å.). The magnitude of these absorption coefficients shows that dithizone solutions are intensely colored.

General Experimental Details.—All transmission measurements were made with the General Electric Company recording photoelectric spectrophotometer.[3] The solu-

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[1] Fischer, *Ann.*, (a) **190**, 118 (1878); (b) **212**, 316 (1882).

[2] (a) Fischer, *Wiss. Veröffent. Siemens-Konzern*, **4**, 11, 158 (1926); (b) Fischer and Leopoldi, *Z. anorg. Chem.*, **47**, 90 (1934); (c) Fischer, *ibid.*, **47**, 685 (1934). The complete list of references would be much longer.

[3] Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936).

tions were contained in a cylindrical quartz cell (inside length, 5.15 cm., inside diameter, 2.40 cm.) with nearly plane ends, which was always inserted into the instrument in the same way. After the extraction processes, the substance to be measured was present in 1 cc. of carbon tetrachloride; before the transmissions were measured, these solutions were diluted to 27 cc. (Whenever solutions of dithizone or its derivatives are mentioned below, the solvent is carbon tetrachloride unless another is specified.) Shaking tubes and reagent bottles (all glass-stoppered) of lead-free glass were employed after it was found that lead-containing glass sometimes caused erratic results. Solutions for transmission measurements were not exposed unduly to light and the measurements were made as soon as was feasible. C. P. carbon tetrachloride was distilled before being used. Water was taken from a several-stage laboratory still that had been in operation for some hours; water that had been standing for some days could not be trusted; the ordinary distilled water supply contained far too much lead for this purpose.

All glassware, after being cleaned carefully, was rinsed with a concentrated solution of dithizone in carbon tetrachloride and finally with the pure solvent. This precaution was prompted by the observation that a drop of dithizone solution shaken in each of a series of glass-stoppered graduates that had been cleaned and dried in identical fashion changed color from green to purple in some and not in others. This color change was probably caused by a trace of some metal ion adsorbed on the walls of the graduates. Figure 3 illustrates how vital is scrupulous cleanliness in work of this kind. Just before the curves shown in this figure were taken, the quartz cell had been used to measure the transmissions of a series of ammoniacal copper salt solutions in which the amounts of copper involved were very much larger than the amounts to be determined by the dithizone method. The cell was rinsed perfunctorily, and later used to measure the transmission of a dilute dithizone solution for which 70% transmission at 5140 Å. was known to be correct. As the upper curve in Fig. 3 shows, only 61.8% was obtained. The transmission of this solution was then measured at the times indicated and with the results shown in the figure. It will be clear subsequently that the change with time of the transmission curve was in all probability due to the formation of copper dithizonate (*cf.* Fig. 5), the walls of the cell presumably serving as the source of copper ion.

The Reagent Solution—Its Oxidation.—Oxidation products are the principal impurity in commercial dithizone. Their removal is accomplished by shaking the dithizone solution with ammonium hydroxide, whereupon the dithizone passes into the aqueous layer while the oxidation products do not. To prepare the reagent, 25 cc. of carbon tetrachloride is saturated by shaking with solid dithizone; the solution is filtered, transferred to a separatory funnel and shaken with an equal volume of 0.2 N ammonium hydroxide, whereupon the brownish-yellow carbon tetrachloride layer is discarded. About four additional extractions of the aqueous layer are made, 10 cc. of carbon tetrachloride being used each time and then discarded; the last portion of carbon tetrachloride should show a greenish tint; 25 cc. of carbon tetrachloride is next poured in and the aqueous layer acidified with 3 N perchloric acid added dropwise. After the funnel has been shaken to transfer the dithizone to the carbon tetrachloride layer, the aqueous layer is discarded and the dithizone solution washed twice with distilled water. Water is removed by filtering the solution through a paper moistened with carbon tetrachloride. The solution is finally diluted to about 400 cc., until the proper concentration for analytical work (as shown by transmission measurements) is attained. (Our reagent solution usually contained 0.030 g./l. of dithizone; 1 cc. of this solution diluted to 27 cc. gave 70.0% transmission at 5140 Å.) The solution is kept in a dark bottle. Because of the danger of contamination, we preferred not to protect it against oxidation by an aqueous sulfurous acid or sulfite layer as suggested by Fischer and Leopoldi.[2b]

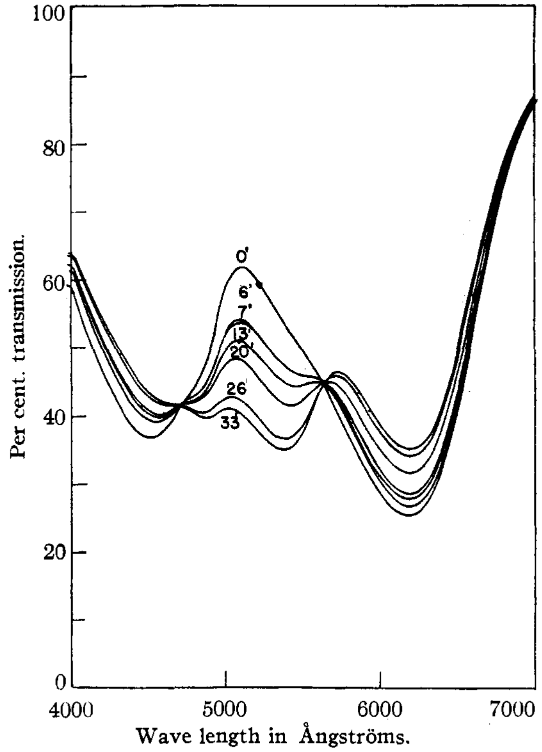

Fig. 3.—Effect of cell wall contamination on dithizone transmission.

The reagent solution prepared in this way gradually deteriorates, presumably because of oxidation by the air, but it can be used for at least three weeks. Different solutions do not always give identical results, probably because of differences in the (small) amounts of oxidation products they contain. Curves 1–4, Fig. 4, show the transmission measurements for carbon tetrachloride containing various concentrations of the oxidation products. Obviously, the presence of these oxidation products will lead to incorrect analytical results, especially at the shorter wave lengths.

The Copper Determination.—The sample for the copper determination should have a volume of 1.5 cc., be 0.3 N in perchloric acid, and contain not over 3 γ of copper. This sample is placed in a 5 cc. well-ground glass-stoppered cylinder, 1 cc. of the dithizone reagent is added, and the tube shaken by hand for two minutes. (The presence of copper is indicated by a color change toward the violet.)

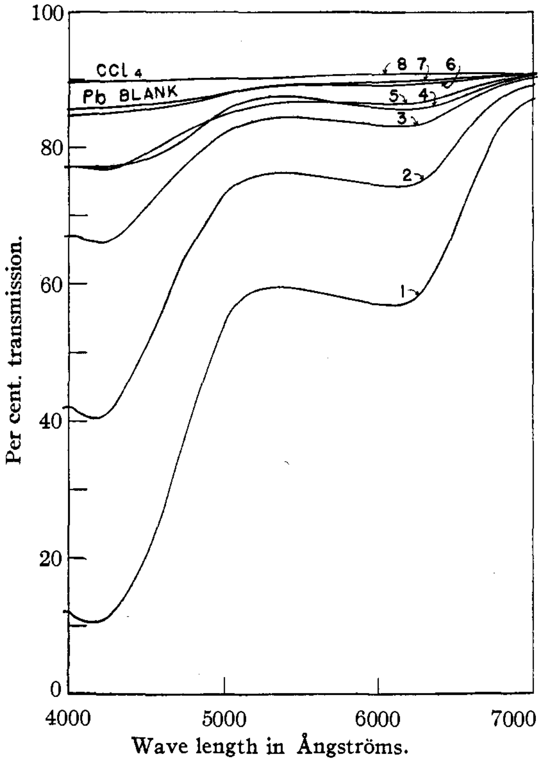

Fig. 4.—Transmission of dithizone oxidation products.

The aqueous phase is removed carefully with a dropper, 0.5 cc. of 0.3 *N* perchloric acid is added, the tube is shaken for another minute, and the aqueous phase is again withdrawn. (The aqueous phases are combined for a lead determination if one is to be made.) The carbon tetrachloride layer, containing the copper compound and the excess dithizone, is diluted with carbon tetrachloride and transferred quantitatively to a glass-stoppered cylinder, then diluted further (in our case to 27 cc.) for the transmission measurements.

A typical family of transmission curves for the copper determination is given in Fig. 5, which shows clearly how dithizone is consumed (decreasing absorption at 4500 and 6200 Å. with increasing amounts of copper) as copper dithizonate (maximum absorption near 5080 Å.) is formed. Figure 5 illustrates in striking fashion how the spectrophotometer is able to circumvent color interference that makes it difficult or impossible to obtain accurate results by simple visual comparison. Fischer and Leopoldi[2b] attempted to reduce this difficulty through the removal of excess dithizone by shaking with ammonium hydroxide; our experience indicates that this procedure can introduce serious complications due in part to oxidation of the reagent, and is therefore to be avoided. The Beer's law plot for 5080 Å. (Fig. 6) with the transmission of carbon tetrachloride as I_0 shows that no blank correction is necessary in the copper determination since no systematic deviations from linearity occur. (Curves corresponding to the solid circles in Fig. 6 are not shown in Fig. 5.)

The Lead Determination.—For the lead determination, the sample should have a volume of about 3 cc., be alkaline with ammonium hydroxide, and preferably contain no other metals. In our work, 1 cc. of 1 *N* ammonium hydroxide was added to the shaking tube containing the 2 cc. of aqueous solution 0.3 *N* in perchloric acid remaining from the copper determination; 1 cc. of dithizone reagent was then added, the tube shaken for two minutes, the aqueous phase (which will be at least faintly brownish) removed with a dropper and discarded. One cc. of 1% potassium cyanide solution was next added, and the aqueous phase again discarded after a fifteen-second shaking. This step was repeated, the shaking time being reduced to ten seconds; the carbon tetrachloride phase was next shaken for ten seconds with 1 cc. of water, and the aqueous layer discarded. At this point, the carbon tetrachloride will be pink and should contain lead dithizonate only. Dithizone was liberated from this compound by shaking with 1 cc. of 0.3 *N* perchloric acid and the aqueous layer discarded. As in the case of copper, the carbon tetrachloride layer was transferred to a glass-stoppered cylinder and diluted to 27 cc. for the transmission measurements. A typical family of lead curves is shown in Fig. 7, the corresponding Beer's law plot for 6200 Å. in Fig. 8. The transmission of the solution from a blank test (one was run to accompany each series of lead determinations) at 6200 Å. was taken as I_0.

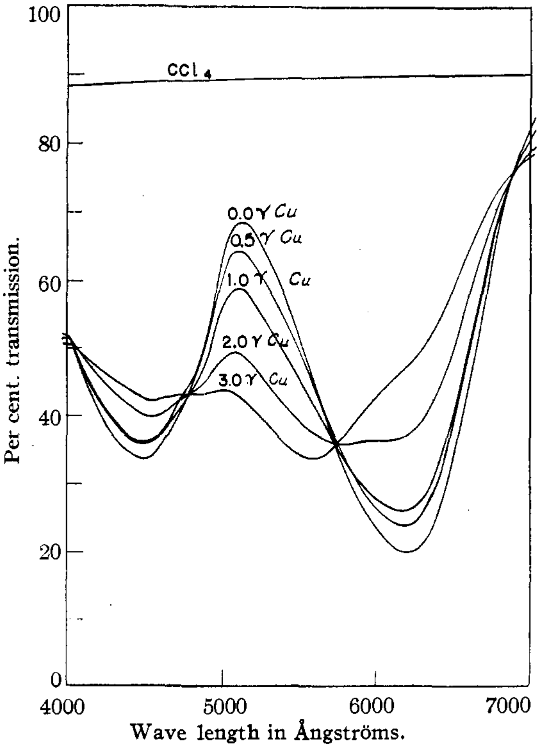

Fig. 5.—Transmission of solutions for the copper determination.

Precise results are much more difficult to obtain for lead than for copper; the variability of the blank and a greater danger of contamination appear to be responsible. Comparison of Figs. 1, 4 and 7 indicates that the decreased transmission of the blank below that of carbon tetrachloride is due not to lead but to dithizone oxidation products. (Our earlier experience with the lead analysis

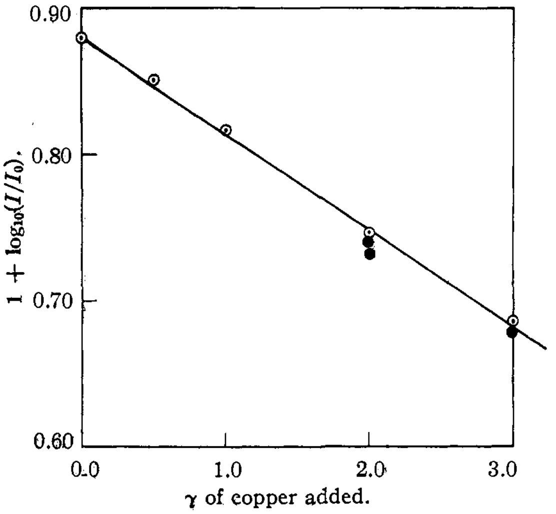

Fig. 6.—Beer's law plot for the copper determination.

seemed to show that lead is present everywhere; most of this "lead" may have been dithizone oxidation products.) For dithizone alone, the transmission at 4500 Å. is never less than the transmission at 6200 Å.; for the oxidation product, the converse is true. The curve for the lead blank (Fig. 7 and Fig. 4, Curve 7) resembles the oxidation products curves; the curves for the smaller amounts of lead are intermediate at the lower wave lengths between those of the oxidation products and those for dithizone. The oxidation products may have existed in the reagent solution but more probably were formed during the shaking of this solution with the alkaline aqueous phases.

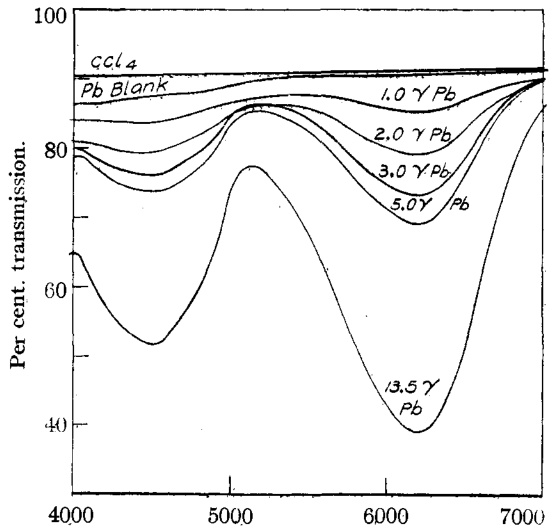

Fig. 7.—Transmission of solutions for the lead determination.

Fischer and Leopoldi[2b] state that a procedure not essentially different from ours can be used for lead when other metals are present, provided these metals (*e. g.*, copper) form complex cyanide ions. We have found that small amounts of lead cannot be estimated accurately by the above procedure when copper is present, presumably because the presence of copper accelerates the oxidation of dithizone in contact with an alkaline solution. Curve 5, Fig. 4, shows the transmission of a blank test for lead carried through the regular procedure with 5 γ of copper in the aqueous layer. The close resemblance of this curve to the oxidation products curves is apparent. Curve 7 results from a similar test carried through with the ammonium hydroxide shaking omitted; it corresponds closely to Curve 8, which is a lead blank obtained in the regular manner without copper present. It appears, therefore, that the oxidation of dithizone occurs principally during the shaking with ammonium hydroxide when the copper ion concentration is relatively high and when some copper dithizonate is present. These results indicate that copper preferably should be removed before lead is determined, or that cyanide should be introduced immediately after the aqueous phase is made alkaline, in order to prevent oxidation of the dithizone. This conclusion may well apply also in the cases of metals other than copper.

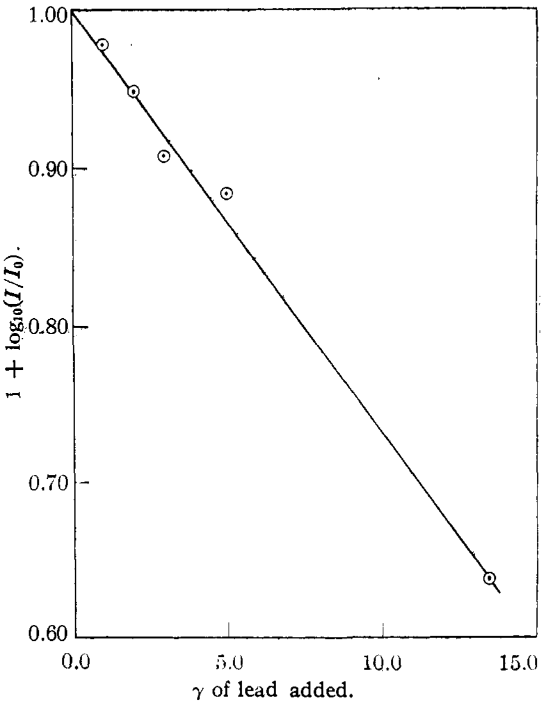

Fig. 8.—Beer's law plot for the lead determination.

Formulas of the Dithizonates.—The extreme sensitivity of the dithizone reactions makes it possible to determine the formulas of the resulting dithizonates when only a few γ of the metals react. Stoichiometric measurements are not often possible with such minute amounts of reactants.

Since the transmission measurements in the case of lead are made on dithizone derived from the lead dithizonate, the formula of this compound can be calculated if the transmission of dithizone solution as a function of its concentration is known. The reagent solution on which the data of Figs. 1 and 2 were obtained was used to determine the formula of lead dithizonate with the results given below.

γ Pb (taken)	1	2	3	5	13.5
Moles D/moles Pb	1.09	1.09	1.21	0.90	0.97

These figures indicate that the lead dithizonate in our analytical method is PbD; Fischer[2c] gives the formula PbD_2 but we have not discovered upon what experimental evidence this formula is based. It was found that 1.1 γ of lead remained in the ammoniacal solution in the last experiment, 12.4 having passed into the carbon tetrachloride; if 12.4 γ Pb is used for the calculation, 1.05 instead of 0.97 is obtained as the molar ratio. This experiment obviously indicates that the extraction by the reagent of lead from an aqueous solution is not quite complete.

The formula of the copper compound is more difficult to establish because copper is less completely extracted than lead and excess dithizone is not removed. The results of a series of measurements made with varying amounts of copper and 1 cc. of reagent solution by the standard method are given below, together with the amounts of copper remaining in some of the aqueous layers, as determined by the same method.

TABLE I

γ Cu (taken)	2	3	4	5	5	10	100
γ Cu (CCl_4)	2.2	3.1	3.1	3.8	3.6	4.2	4.2
γ Cu (H_2O)	0.25	0.65	1.3	1.4	1.0	(7)	

Comparison of the first two lines shows that the 30 γ of dithizone present in 1 cc. of reagent solution cannot extract more than 4.2 γ of copper; if this copper dithizonate is CuD_2 as Fischer reports, compound formation is complete when 3.7 γ of copper has been removed. Our results therefore confirm this formula, and the incomplete extraction of larger amounts of copper (which fixes the upper limit of the sample for our analytical method near 3 γ) results because there is insufficient dithizone compound formation.

The incomplete extraction when less than 3 or 4 γ is present (third line of the table) has another cause; the proportion of copper remaining in the aqueous layer increases with the amount of copper added, as the amount of dithizone uncombined after shaking decreases. This suggests that the rate of removal of copper from the aqueous layer is proportional to the uncombined dithizone in the carbon tetrachloride layer. (In agreement with this explanation, it was found that increasing the time of shaking from two to five minutes removed very little additional copper; and that shaking of copper dithizonate in carbon tetrachloride with water did not remove copper, showing that the incomplete extraction does not result from a reversible reaction.) Because of this incomplete extraction, Beer's law may not be obeyed precisely and the abscissas of the points for a calibration curve (Fig. 6) will exceed the amounts of copper actually in the carbon tetrachloride layer. Neither of these considerations vitiates the analytical method; the latter explains why the limiting value in the second line of the table was reached at 4.2 γ instead of 3.7 γ.

The formula CuD_2 is confirmed by the two 5 γ experiments. The amount of copper combined with 30 γ of dithizone is $5 - 1.4 = 3.6$ γ in the one and 4.0 γ in the other, in good agreement with 3.7 γ, the theoretical value. The result from the 10 γ experiment is less accurate.

With the formula of copper dithizonate established, Beer's law applied to experimental results like those plotted in Fig. 6 takes the form

$$\log_{10} I/I_0 = -[\epsilon_1(a - 2x) + \epsilon_2(x)] \qquad (2)$$

for an absorbing layer 1 cm. thick. Here a is the (constant) initial concentration of dithizone; x, the concentration of copper dithizonate; $(a - 2x)$, the concentration of dithizone remaining when compound formation has occurred; all concentrations are moles/l. ϵ_1 and ϵ_2 are the molar extinction coefficients of dithizone and of copper dithizonate; I_0 and I are the transmissions of carbon tetrachloride and of the D–CuD_2 solutions. The differential form of Eq. 2 shows that $\log_{10} I/I_0$ when plotted against x should give a straight line of slope $[-2\epsilon_1 + \epsilon_2]$. For the dithizone of Fig. 5, $\epsilon_1 = 5470$ at 5080 Å.[4] From $\log_{10} I/I_0$ for the 100 γ experiment (Table I), in which all the dithizone was consumed so that $(a - 2x) = 0$, $\epsilon_2 = 35{,}600$ was obtained. If copper extraction were complete below 3 γ so that all the copper added appeared as copper dithizonate, a slope of 24,660 would therefore be expected for the Beer's law plot (Fig. 6), provided the necessary conversions to unit thickness and to the proper concen-

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[4] The dithizone of Fig. 1 gave $\epsilon_1 = 4920$ at 5080 Å. Comparison with $\epsilon_1 = 5470$ (Fig. 5) shows how the reagent solutions prepared at different times vary in transmission.

tration unit (moles/l.) are made. The slope actually obtained from Fig. 6 is 21,900. The ratio 24,660/21,900 is within 1% of the ratio 4.2/3.7 (Table I), which shows clearly that incomplete extraction alone is responsible for the difference in these two slopes.

That dithizone is acid in character and may consequently be expected to form salts was demonstrated by its discoverer,[1b] who isolated from acid solution a zinc dithizonate of the formula $ZnD_2 \cdot H_2O$. As Hellmut Fischer[2c] has pointed out, the reactions which dithizone undergoes as an analytical reagent can all, with the possible exception of its oxidation, be explained on the assumption that enolization to give an H—S—C=N linkage occurs. He has also given plausible structural formulas of the dithizonates, according to which D^- is present in the keto form in CuD_2, and in the enol form in PbD. The essential difference between the two structural formulas is that a divalent metal is bound to both nitrogen and sulfur in the latter but only to nitrogen in the former.

Summary

With the aid of a photoelectric recording spectrophotometer, the spectral transmission in the visible range of carbon tetrachloride solutions of dithizone, its oxidation product, and of copper dithizonate have been measured.

The dithizone analytical methods for copper and lead have been modified so as to make them more reliable for small amounts; 1γ of either element can now be determined with reasonable accuracy.

The two chief difficulties encountered in securing results of high precision with these small amounts were incomplete extraction by the reagent solution of the aqueous layer containing the metals, and the oxidation of the reagent, which appears to be catalyzed by copper ion.

Transmission measurements involving only a few γ of either metal gave the formulas PbD and CuD_2 for lead and copper dithizonates.

Our experience with dithizone as an analytical reagent indicates that satisfactory quantitative results on small samples can be obtained only through painstaking and somewhat tedious manipulation. For this reason, it often will be advisable to use other methods of analysis when these will achieve the desired result.

SCHENECTADY, N. Y. RECEIVED JULY 23, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Ester Formation and Some Structural Relationships

BY S. GERALDINE TOOLE AND FRANK J. SOWA

Bergmann, Engel and Wolff[1] in their work on the dipole moments of substituted methane derivatives showed that the tetrahedral angle caused by a chloro substitution was about the same as that of a phenyl group; or, in other words, the chlorine atom and the phenyl group possess about the same spacial requirements.

This investigation was undertaken to study the relationship between spacial requirements and chemical reactivity as applied to the formation of esters.

The process of ester formation suggests itself to determine this relationship using compounds that contain phenyl and chloro substituents in the acids and amides, for example, phenyl-, chloro-, dichloro-, and trichloroacetic acids and acetamides. In the case of the acetamides a relationship not involving acidity was introduced. The same agent, boron fluoride, was used to transform both acids[2,3] and amides[4] with alcohol into esters in this study.

Experimental Part

Amides with Methyl Alcohol.—Into a one-liter flask was weighed 0.75 mole of an acetamide and 1.5 moles of absolute methyl alcohol. The flask was fitted with a two-holed stopper containing an inlet and outlet tube. Boron fluoride was passed into the solution until it had absorbed 0.75 mole of the gas. The flask was cooled in an ice-bath during the total absorption. The solution was then refluxed for forty-five minutes. During this period the solution became cloudy due to the separation of monoamminoboron fluoride. After distillation directly from the reaction flask the ester was purified in the usual manner and fractionated. With the exception of methyl formate,

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(1) Bergmann, Engel and Wolff, *Z. physik. Chem.*, **17B**, 81 (1931).

(2) Hinton and Nieuwland, THIS JOURNAL, **54**, 2017 (1932).

(3) Sowa and Nieuwland, *ibid.*, **58**, 271 (1936).

(4) *Idem*, **55**, 5052 (1933).