[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A STUDY OF SUPERACID SOLUTIONS. II. A CHEMICAL INVESTIGATION OF THE HYDROGEN-ION ACTIVITY OF ACETIC ACID SOLUTIONS

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RECEIVED AUGUST 16, 1927 PUBLISHED DECEMBER 10, 1927

The preceding paper of this series has demonstrated that the hydrogen-ion activity of glacial acetic acid solutions may be estimated by means of the chloranil electrode. In this paper we shall show that the halochromism of triarylcarbinols, the halochromism of unsaturated ketones and the rate of inversion of cane sugar are controlled by the hydrogen-ion activity as measured electrochemically. The general agreement between the four independent methods seems to us to establish beyond doubt the possibility of measuring in this solvent hydrogen-ion activities which have the same general significance as those measured in water.

The Halochromism of Arylcarbinols and Unsaturated Ketones

Triarylcarbinols such as triphenylcarbinol and certain diarylcarbinols give intensely colored salts when treated with acid in suitable media. Some of the derivatives of triphenylcarbinol which contain a number of methoxy groups form halochromic salts even in aqueous solutions. A careful quantitative study of these compounds has recently been made by Lund[1] and by Kolthoff[2] who have shown that they may be used as indicators in aqueous and alcoholic solutions. From this work of Lund and from that of Hantzsch[3] it seems quite clear that the triarylcarbinols are pseudo bases of varying strength. Indeed this was essentially Baeyer's original idea. The equilibrium involved in the formation of the colored ion may be represented as follows

$$\underset{\text{Colorless}}{R_3COH + H^+} \rightleftharpoons \underset{\text{Colored}}{R_3C^+ + H_2O}$$

If we use a medium in which the carbinol and salt are both soluble, the appearance of color will be a function both of the hydrogen-ion activity and the water activity. If the latter is constant in a series of solutions the appearance of color may be used as a method of estimating the hydrogen-ion activity.

Unsaturated ketones such as benzalacetophenone ($C_6H_5CH{=}CHCOC_6H_5$) also give intense colors with concentrated mineral acids. Hantzsch[4] be-

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[1] Lund, THIS JOURNAL, **49**, 1346–1360 (1927).

[2] Kolthoff, *ibid.*, **49**, 1218–1221 (1927).

[3] Hantzsch, *Z. physik. Chem.*, **61**, 257 (1907); *Ber.*, **55**, 953 (1922).

[4] Hantzsch, Ref. 2 and *Zeit. Elektrochemie* No. 6 (1923) in which the use of dibenzalacetone as an indicator is discussed.

lieves this to be also an example of salt formation and we may write the equilibrium

$$\underset{\text{Slightly colored}}{\mathrm{RCH{=}CHCOR} + \mathrm{H}^+} \rightleftharpoons \underset{\text{Intensely colored}}{[\mathrm{RCH{=}CHCOHR}]^+}$$

The unsaturated ketones are thus anhydro bases which form a colored ion. They would be expected to differ from the carbinols only in that the appearance of color is a function solely of the hydrogen-ion activity; the activity of the water *per se* should not affect the composition of the equilibrium mixture.

In order to investigate the halochromism of a number of carbinols and unsaturated ketones we prepared a series of acetic acid solutions of graded hydrogen-ion activity and with a constant and small water content. With the exception of the two most acidic they were mixtures of sulfuric acid and very weak bases dissolved in acetic acid. Thus, they were "buffered" in respect to both the increase and decrease of hydrogen-ion activity.

The results are summarized in Table I, which is self-explanatory. The data are remarkably consistent with each other and with the e.m.f. measurements. It seems certain from these more than 100 experiments that the halochromism of both the carbinols and the unsaturated ketones is determined within at least 0.5 of a $(P\mathrm{H})^{\mathrm{HAc}}$ unit by the hydrogen-ion activity of the solution as found from e.m.f. measurements.

A further test of the general consistency of the results is made possible by the fact that the titration curves of a number of the very weak bases lie close together (Fig. 1, preceding paper). Since this is the case it should be possible to titrate with an indicator a given weak base with sulfuric acid to the same color as that shown by the same indicator in one of the buffered solutions. The result should agree with the e.m.f. titration data. Thus, the acetamide buffer (No. 5, $(P\mathrm{H})^{\mathrm{HAc}} = -1.0$) was used as a standard, and benzamide was titrated with sulfuric acid, using indicator F′ in both the standard and the titrating solution. The same relative concentration of indicator was used and the same concentration of base (0.2 *M*). A color match was obtained when 0.1 cc. of *M* sulfuric acid was added (1 cc. required for total neutralization); from the e.m.f. titration curve the calculated quantity for $(P\mathrm{H})^{\mathrm{HAc}} = -1.0$ would be 0.1 cc. The other results were as follows: Urea titrated to match $(P\mathrm{H})^{\mathrm{HAc}} = -1.0$ (indicator F′) required 0.9 cc., calcd. 0.9 cc.; acetamide to match $(P\mathrm{H})^{\mathrm{HAc}} = -0.5$ (indicator F′) required 0.2 cc., calcd. 0.2 cc.; benzamide to match $(P\mathrm{H})^{\mathrm{HAc}} = -2.0$ (acetanilide buffer) (indicator C) required 1.4, calcd. 0.9; titrating acetanilide to match $(P\mathrm{H})^{\mathrm{HAc}} = -1.5$ (benzamide buffer) with indicator D′ required 0.1 cc., calculated 0.2 cc.

The differences between the required and the calculated amount of acid in titrating acetanilide or comparing benzamide with the acetanilide buffer amount to 0.3 of a $(P\mathrm{H})^{\mathrm{HAc}}$ unit. This is an indication of the magni-

TABLE I

TURNING RANGE OF UNSATURATED KETONE AND CARBINOL INDICATORS IN GLACIAL ACETIC ACID SOLUTION[a]

	Buffer solution	$(P_{\mathrm{H}})^{\mathrm{HAc}}$ predicted from composition	$(P_{\mathrm{H}})^{\mathrm{HAc}}$ measured directly	Indicator (see below) A′	B	C	D′	E	F′	G′	H′	I	J
1	1.0 M H_2SO_4		−3.22	+	++++	++++	++++	+++	++	+++	++	+	+
2	0.064 M H_2SO_4	−2.7	−2.78	−	+	+	+	+	+	+	+	+	+
3	Acetanilide 0.76 neutralized	−2.0	−2.03	−	+	+	+	+	+	+	+	+	+
4	Benzamide 0.40 neutralized	−1.5	−1.5	−	−	−	−	(+−)	+−	+−	+−	+−	+
5	Acetamide 0.55 neutralized	−1.0	−1.0	−	−	−	−	−	+−	+−	+−	+−	+
6	Urea 0.75 neutralized	−0.5	−0.55	−	−	−	−	−	(+−)	(+−)	+−	+−	+
7	Urea 0.44 neutralized	−0.0	−0.0	−	−	−	−	−	−	−	(+−)	+−	+
8	Urea 0.14 neutralized	+0.5	+0.42	−	−	−	−	−	−	−	−	+−	+
9	Hexamethylenetetramine 1.20 neutralized	+2.05	+1.99	−	−	−	−	−	−	−	−	−	+−
10	Hydrobenzamide 0.85 neutralized	+2.5	+2.85	−	−	−	−	−	−	−	−	−	+−
11	Hexamethylenetetramine 0.15 neutralized	+3.6	+3.62	−	−	−	−	−	−	−	−	−	−

[a] Col. 1. Each buffer, except the first two, contained the base named in 0.2 M concentration, dissolved in glacial acetic acid. To this had been added sufficient sulfuric acid to neutralize the stated fraction of the base, on the assumption that one mole of the base was neutralized by one mole of acid. The acetic acid was "P. W. R. analytical, complying with dichromate test." The sulfuric acid was "P. W. R. analytical 94 to 97%." It was assumed to contain 95% H_2SO_4. The acetanilide showed an extremely faint brownish color. The benzamide left a very slight white residue on dissolving. The hexamethylenetetramine "1.20 neutralized" contained a large amount of white precipitate (sulfate or hydrosulfate). The hydrobenzamide developed a pronounced yellow color on standing, smelt of benzaldehyde, and formed a slight precipitate when treated with sulfuric acid. The other solutions were clear and colorless.

Col. 2. The "$(P_{\mathrm{H}})^{\mathrm{HAc}}$ predicted" was read from titration curves previously obtained (see Fig. 1 preceding paper).

Col. 3. The $(P_{\mathrm{H}})^{\mathrm{HAc}}$ of each solution was measured directly with the technique previously described (p. 3049 preceding paper). The benzamide values showed a slight drift with time, a phenomenon previously observed. Acetanilide, whether alone or in the presence of sulfuric acid, gives an orange color with chloranil.

Indicators. These were unsaturated ketones (denoted by "primed" letters) or substituted carbinols. They were all 0.05 M in glacial acetic acid as a solvent. The meaning of the signs used is as follows: +, halochromic color; ++, +++, ++++, etc., very intense color; −, no halochromic color; +−, transitional color; (+−), doubtful color.

The comparison was carried out by adding the stated number of drops to 5 cc. of each buffer. The tubes were shaken slightly to mix the solutions.

A′ Benzalacetophenone. 10 drops. Buffer No. 1, pale yellow; all others colorless.

B Triphenylcarbinol. 10 drops. No. 1, full yellow; 2 and 3, pale yellow; all others colorless.

C Diphenyl-α-naphthylcarbinol, 5 drops. No. 1, inky greenish-blue; 2 and 3, clear greenish-blue. All others colorless.

D′ Piperonalacetophenone. 8 drops. No. 1, red-orange; 2 and 3, strong yellow; all others very pale yellow.

E Dianisylcarbinol. 5 drops. No. 1, pinkish-orange; 2 and 3, pale salmon; 4, almost invisible salmon; all others colorless.

F′ Anisalcinnamalacetone. 1 drop. No. 1, carmine; 2 and 3, full red; 4, orange-red; 5, orange; 6, orange-yellow. All others clear yellow.

G′ Dipiperonalacetone. 2 drops. No. 1, purplish-red; 2 and 3, full red; 4, salmon; 5, orange-yellow; 6 full yellow; all others pale yellow.

H′ Dianisalacetone. 2 drops. No. 1, pinkish-red; 2 and 3, full red; 4 and 5, orange-red; 6, reddish-orange; 7, brownish-yellow. All others pale yellow.

I Diphenylanisylcarbinol. 5 drops. 1 to 3, brown-orange; 4 and 5, orange; 6, yellow-orange; 7, yellow; 8, pale yellow; others colorless.

J Phenylxanthydrol. 1 drop. 1 to 8, clear yellow with greenish fluorescence; 9 and 10, pale yellow; 11, colorless.

tude of the discrepancy which may be expected to arise from time to time in determining the hydrogen-ion activity by different methods in glacial acetic acid. Similar errors, often referred to as salt errors, have been found frequently in using indicators in aqueous solutions. Undoubtedly if we had varied our concentrations of base and experimented with the addition of considerable amounts of neutral salt, still larger discrepancies would have been found between the indicators and the e.m.f. measurements.

The difference in behavior of the two types of indicators in regard to the influence of the water activity was shown by several experiments. Both diphenyl-α-naphthylcarbinol (C) and piperonalacetophenone (D′) show a color change at about $(P_{\rm H})^{\rm HAc} = -2.0$. When 5 drops of acetic anhydride were added to one of two 5cc. portions of the buffer containing the carbinol indicator (C), the color rapidly became much deeper. The unsaturated ketone (D′) color was unaffected. We interpret this difference as showing that the acetic anhydride combined with the small amount of water present in the solution and therefore the equilibrium with the carbinol shifted. In the case of the unsaturated ketone there was no shift as water is not involved in the reaction. In a similar experiment with diphenylanisylcarbinol in the series of 11 buffers there was no noticeable effect after several days on adding the acetic anhydride. This may be due to the fact that the reaction between small amounts of water and acetic anhydride is slow in solutions of $(P_{\text{H}})^{\text{HAc}} = -0.5$ to $+0.5$ where this indicator turns.

A few experiments in which absolute alcohol was added to the buffer solutions containing the indicators are of interest. Equal quantities (2.22 cc.) of absolute ethyl alcohol were added to 5cc. portions of buffer solution No. 4 ($(P_{\text{H}})^{\text{HAc}} = -1.5$) containing, respectively, indicator F′ (an unsaturated ketone) and I (a carbinol). Both solutions showed a diminution in color corresponding to a decrease in hydrogen-ion activity as would be expected from the results reported in the preceding paper. The carbinol indicator, however, showed a decrease amounting to 2 $(P_{\text{H}})^{\text{HAc}}$ units (as determined by matching colors) while the change with the unsaturated ketone was only about 1 unit. Similarly 0.3 cc. of alcohol in 5 cc. of buffer No. 3 was sufficient to discharge the color of indicator C (diphenyl-α-naphthylcarbinol). With D′ (an unsaturated ketone) 1.3 cc. of alcohol was necessary to produce a corresponding decrease in hydrogen-ion activity as measured by the color.

These experiments illustrate the caution which must be employed in attempting to use these indicators in solvents containing varying amounts of alcohol. Apparently alcohol can produce an alcoholysis of the carbinol salt in addition to its effect in diminishing the acidity of the solution.

In this connection it should be emphasized that the data in Table I permit of only a very rough estimation of the basicity of each carbinol or unsaturated ketone used as an indicator. As we have employed them, the turning point of the indicator is a function both of its basicity and the intensity of color of the ion. The turning point must be at such an acidity that only a fraction of the base is present as salt but what that fraction may be depends on the sensitivity of the eye for that particular color. The true measure of the basicity can only be obtained by carrying out an e.m.f. titration curve (cf. phenylxanthydrol, Fig. 1, preceding paper) or by careful colorimetric measurements in which the intensity of color is determined. Baeyer's method[5] of determining the basicity of the halochromic salts by titration with alcohol suffers from this error. In his method alcohol is added until the solution is colorless; the amount of alcohol added would be a true measure of the basicity only if the sensitivity of the eye were the same for all the colored ions. It also is in error since there is not an absolute proportionality between the amount of alcohol added and the hydrogen-ion activity (cf. Fig. 4, preceding paper).

The Catalytic Effect of the Hydrogen Ion in Glacial Acetic Acid Solution

Some rough measurements were made of the rate of inversion of cane sugar in the buffer solutions listed in Table II to which a small amount

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[5] Baeyer, *Ber.*, **35**, 1189, 3013 (1902).

of water was added. To 5 cc. of each buffer was added 0.1 cc. of a solution of cane sugar in water containing 7 g. in 11 cc. (7 g. of sucrose and 7 g. of water). The mixtures were kept at 25 ± 2° and after a given time diluted with water, neutralized with sodium carbonate and the amount of reducing sugar determined by the titration of Benedict's solution. It was assumed that the inversion was complete in 1 *M* sulfuric acid in acetic acid after five minutes; the titration of such a reaction mixture corresponded approximately to the amount of invert sugar that would be formed from the sucrose employed. Duplicate experiments agreed within 20%. Enough determinations were made in each buffer solution so that a curve representing the rate of reaction could be plotted. From this curve the time for half reaction was determined. This half reaction time is given in Table II for solutions 5 to 9 inclusive; the data were not of sufficient accuracy to warrant the calculation of a reaction constant. It is evident that the rate of inversion of the sucrose parallels in a general way with hydrogen-ion activity of the solutions. In the measurable range, $((P\text{H})^{\text{HAc}} = -0.8$ to $+2.2)$, the rate increases 2.5 to 4.5 fold per 0.5 $(P\text{H})^{\text{HAc}}$ unit. If the rate were directly proportional to the hydrogen-ion activity the change would be 3.2-fold per half unit. The small amount of water added with the sucrose in each experiment made the water concentration in each experiment about 1.4 g. per 100 cc.; it is presumably this water which is involved in the inversion of the sucrose, though the acetic acid itself might take part in the reaction. The $(P\text{H})^{\text{HAc}}$ of the reaction mixture (Col. 3, Table II) was estimated on the basis of the experiments in the preceding paper in which water was added to various solutions (Fig. 4). Since the effect is approximately the same for all the buffer solutions except those containing sulfuric acid, the exact value for this correction is not of great importance in our preliminary work. In the range represented by solutions 4–9, the scale of hydrogen-ion activity as determined by the e.m.f. and colorimetric measurements in 99.5% acid is obviously a close measure of the rate of inversion of sucrose in the presence of small amounts of water.

Table II

Rate of Inversion of Cane Sugar in 98% Acetic Acid Buffer Solutions

Solution	$(P\text{H})^{\text{HAc}}$ buffer	Est. $(P\text{H})^{\text{HAc}}$ of reaction mixture	Rate of inversion %	Time in minutes
1	−3.22		100	2
2	−2.7		100	2
3	−2.0	−1.8	100	2
4	−1.5	−1.3	90	2
5	−1.0	−0.8	50	2
6	−0.5	−0.3	50	7
7	0.0	+0.2	50	20
8	+0.5	+0.7	50	90
9	+2.0	+2.2	50	1400

The Behavior of Acids and Bases in Different Solvents

In themselves the results presented in this paper throw no light on the hydrogen-ion activities of acetic acid solutions compared to aqueous solutions. The excellent agreement between the electrochemical measurements and the three other methods just described only shows that each method is satisfactory for determining the relative hydrogen-ion activities in a series of acetic acid solutions. That certain acids are "stronger" in acetic acid solutions than in water rests on the electrochemical evidence presented in the last paper (with the admitted uncertainties in regard to the liquid junction) and on certain chemical facts. This chemical evidence will now be briefly reviewed.

Many very weak anhydro bases which do not form salts in aqueous solutions are neutralized by perchloric or sulfuric acids in glacial acetic acid solutions. This is shown by the titration curves which can be obtained by using the chloranil electrode or by the use of indicators. It should be noted that in the formation of salts from anhydro bases, no water is eliminated and the water activity is not involved except in so far as it affects the hydrogen-ion activity. In the second place, although perchloric, sulfuric and trichloro-acetic acids are all strong acids in water, they are of widely different strengths when dissolved in glacial acetic acid. This fact again rests not only on the electrochemical evidence but on the use of two different types of indicators.[6] Thus whether we define the strength of acids in terms of the relative hydrogen-ion activities of their equimolal solutions or in terms of salt formation with anhydro bases, the evidence is clear that perchloric and sulfuric acids are stronger acids in acetic acid than in water. The reader of Hantzsch's papers[7] will be familiar with the mass of evidence which he has accumulated dealing with the behavior of strong acids in non-aqueous solvents. We should like to stress Hantzsch's point that the classification of acids into strong and weak on the basis of their behavior in water is inadequate. Much important chemistry (particularly important to the organic chemist) has been obscured by our slavish devotion to water.

At present we have some information about the behavior of acids and bases in at least four common solvents, ammonia (liquid), alcohol, water and glacial acetic acid. All the facts point to a close resemblance between alcohol and water as regards the strength of acids and bases dissolved in them. We may, therefore, consider them together. Following Brönsted,[8] we may imagine that in water the hydrogen ion (the proton) is largely hydrated. In liquid ammonia probably no one would contend that there

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[6] The determination of the $(P\text{H})^{\text{HAc}}$ value of 0.2 M trichloro-acetic acid gave: electrometric −0.1; colorimetric +0.5 with both types of indicators.

[7] Ref. 4 and other papers.

[8] Brönsted and Guggenheim, THIS JOURNAL, 49, 2554 (1927).

was any large proportion of free hydrogen ion in equilibrium with the solvated hydrogen ion which is the ammonium ion. We are thus led to imagine that the essential difference between glacial acetic acid and water is similar to that between water and liquid ammonia. The acetic acid molecule has less affinity for a proton than water; the ion $CH_3COOH_2^+$ more readily gives up its extra proton than the ion H_2OH^+.

The formation of a salt from an anhydro base is the reverse of the dissociation of an acid. Indeed, if we accept Brönsted's definition of a base, the anhydro base (B), the anion of an acid ($\overline{X}$) and the solvent molecule (S) may all be regarded as bases competing for the proton (H^+). We may, therefore, write the following equations

$$\overline{X} + H^+ \rightleftharpoons HX \qquad (1)$$
$$B + H^+ \rightleftharpoons BH^+ \qquad (2)$$
$$S + H^+ \rightleftharpoons SH^+ \qquad (3)$$

Probably in most solvents the amount of unhydrated hydrogen ion (free proton) is very small[8] but this does not prevent our formulating the reaction

$$SH^+ + B \rightleftharpoons BH^+ + S \text{ (salt formation of B)}$$

in terms of the competing reactions 2 and 3 above. A very weak base, **B**, (corresponding to a very strong acid BH^+) will only form stable salts in a solvent which has considerably less affinity for the proton than B itself. Obviously salt formation can only take place with an acid whose anion ($\overline{X}$) will release the proton to B.

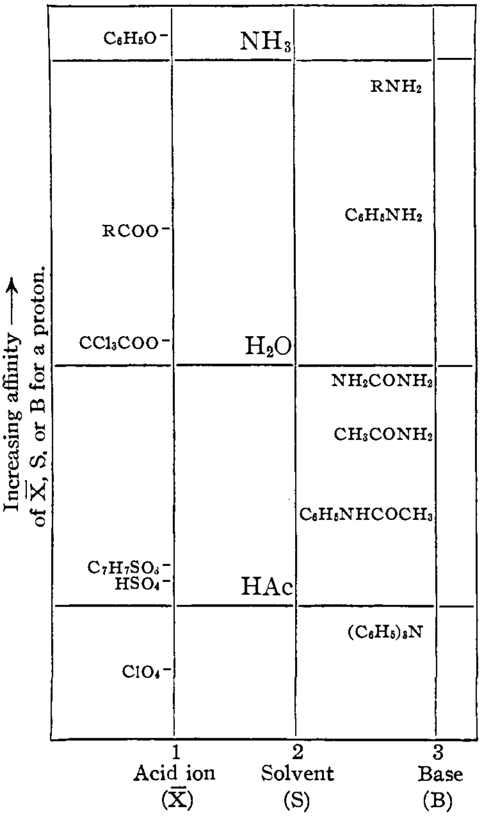

Fig. 1.—Diagram illustrating the relationship of acids and anhydro bases in a variety of solvents.

The inter-relation of the three competing reactions can best be illustrated qualitatively by a diagram. This is shown in Fig. 1; the affinities of the three competing bases ($\overline{X}$, S and B) are plotted vertically on lines 1, 2 and 3, respectively. The position of some common acids, anhydro bases and three solvents are indicated by their formulas. The scale is arbitrary and no attempt has been made to evaluate the exact relationships as this would involve data in regard to the activities which are lacking. According to the general scheme which is roughly outlined in Fig. 1, acids are "strong" only in the solvents which lie above them on the diagram. Thus perchloric acid is strong in all three solvents; sulfuric and hydrochloric acids in ammonia and water and RCOOH only in ammonia. Anhydro bases are neutralized by one equivalent of any acid which is a stronger acid than their "onium ions," provided the action takes place in a solvent which lies below the position of their ions on the scale. Thus an amide ($RCONH_2$) will be neutralized only in acetic acid and only by perchloric or sulfuric acid. We have not yet found a solvent in which triphenylamine can be titrated even with perchloric acid. If such a solvent is found it will lie below acetic acid in the diagram.

We take pleasure in expressing our indebtedness to Mr. N. M. Bigelow for assistance in carrying out the experiments on the inversion of sucrose.

Summary

1. Five arylcarbinols and five unsaturated ketones have been tested for the appearance of halochromic color by introducing them into eleven buffer solutions in glacial acetic acid. The results are all consistent with the determination of the hydrogen-ion activities of the solution by means of the chloranil electrode. The ten substances form a graded series of indicators suitable for use in superacid solutions.

2. The rate of inversion of sucrose in 98% acetic acid solutions of definite acidity has been studied. The rate is approximately proportional to the hydrogen-ion activity as measured by the chloranil electrode or by the use of indicators.

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[CONTRIBUTION FROM THE CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

APPLICATION OF THE INTERFERENCE REFRACTOMETER TO THE MEASUREMENT OF THE CONCENTRATION OF DILUTE SOLUTIONS[1]

BY RUDOLPH MACY

RECEIVED AUGUST 19, 1927 PUBLISHED DECEMBER 10, 1927

In this Laboratory an extended series of measurements has been made involving accurate determinations of the concentrations in water of various types of organic compounds. A more accurate, more general and more rapid method of determining concentrations in liquid solvents was sought than is afforded by the usual methods of analysis. The instrument selected for this purpose is the interference refractometer designed by Professor F. Haber and made by the Zeiss Company. Although measurements can be made very quickly by means of this instrument, and with a high degree

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[1] Published by permission of Chief, Chemical Warfare Service.