THE DETERMINATION OF HYDROGEN IONS IN THE GASTRIC CONTENTS.

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Ever since the discovery of hydrochloric acid in the gastric juice by Prout, various methods have been used for the determination of this hydrochloric acid either in the pure juice or in the gastric contents. Of methods that have been recommended, the use of Gunzburg's reagent might seem the furthest from our present methods of titration since it involves the evaporation of the juice almost to dryness. In fact, there are probably many indicators preferable to Gunzburg's reagent. Töpfer's reagent is an indicator that may be used, and yet, it would probably not be selected by chemists at the present time. Methyl orange is a valuable indicator. To some persons, however, the color change of brom-phenol blue may seem a little more striking, and, therefore, we use brom-phenol blue in the titration of the gastric contents.

Ever since a comparison was made between acetic and lactic fermentations in vitro and gastric digestion, the idea has been expressed or implied that the gastric contents contain other acids than hydrochloric. From what we know now of dissociation constants of weak acids, and particularly of such polyvalent acids (ampholytes) as proteins, an attempt to titrate "the total acidity" of the gastric contents may seem somewhat futile. Even the process of titrating gastric contents back to a hydrogen ion concentration corresponding to the ingested food may seem of less meaning on close scrutiny than at first sight. If the food were placed in a beaker, its hydrogen ion concentration determined, the gastric juice added, and the mixture titrated to the original hydrogen ion concentration, a measure of the amount of acid in the gastric juice would be obtained, but in the stomach, saliva is
continuously poured into this mixture and at certain times duodenal contents are regurgitated. Whereas we may titrate the gastric contents to any desired pH, any titration of "total acidity" is impossible to interpret in quantitative chemical terms. It is therefore hoped that the term "total acidity" of the gastric contents will be dropped from our vocabulary.

Since it was shown by Sörensen and others that it is the pH of the gastric contents which is of significance in the digestion of food, the determination of the pH might seem advisable in routine gastric analysis if the technique is not made too difficult. It is the purpose of this paper to describe a technique which is fairly accurate, which is extremely rapid, and which requires only that apparatus which should be found in every hospital laboratory. The principle of the method is the determination of the percentage dissociation of an indicator by means of the colorimeter. The only valuable indicator which I have found so far for this purpose is quinaldine red.\(^1\)

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\begin{align*}
\text{CH} & \equiv \text{CH} \quad \text{N(CH}_3)_2 \\
\text{C}_2\text{H}_5 & \quad \text{I}
\end{align*}
\]

It is intended to use the colorimeter already in the laboratory. It seems evident, however, that the principle used in the Duboscq has not been supplanted by anything better. There are several instruments on the market using this principle which do not use the Duboscq name. The colorimeter designed by Bürker\(^2\) uses the same principle in matching the fields as used in the Duboscq, but by a different prismatic system made up of a single piece of glass. The apparatus is more rugged. The use of four cups enables the compensation for cloudiness in the gastric contents.

The following account is worded for the use of the small size colorimeters of the Duboscq type. Perhaps the Ewald test meal is very admirably designed for the titration of hydrochloric acid. It is not necessary to use any particular test meal with

\(^1\) Eastman Kodak Co., No. 1361.
this method. If it is desired to test the digestive power of the stomach, a meal containing sufficient nourishment should be used, perhaps the meal that is customary for the individual, or some standard meal of, for instance, 1,000 calories, containing about 35 gm. of protein. The drinking of coffee or of other dark liquids should be excluded. After drawing a sample, it is centrifuged, and the middle portion sucked up with a pipette. 5 cc. of this are placed in the left-hand cup of the colorimeter together with 3 drops of 1 per cent quinaldine red in 95 per cent alcohol, and mixed. The cup is set at 10 mm. (distance between plunger and bottom of cup). In the right-hand cup are placed 10 cc. of distilled water and 6 drops of quinaldine red, and after mixing, some may be transferred to a beaker if necessary. Under the right-hand cup is held a cup with black sides and clear bottom, 10 mm. in depth, filled with the gastric contents without the indicator. The color is now matched by moving the right-hand cup. The reading on the right-hand side in tenths of a millimeter gives the per cent of dissociation of the quinaldine red in the gastric contents. This figure is then found on the left-hand column of Chart 1. For instance, if this is 20, the horizontal line marked 20 is traced to the right until it interesects the diagonal line. It is then traced upward and the pH read on the top, which is in this case, 2.1. If the reading is 50, the pH is 2.7. This means that one-half of the indicator is dissociated. The dissociation constant is $10^{-2.7}$ according to these observations and the formula: 

$$\frac{[H^+] \times [\text{Indicator}^\text{-}]}{[\text{H Indicator}]} = k$$

becomes $10^{-2.7} \times \frac{1}{2} = 10^{-2.7}$. To show the limits of the method it is easy to distinguish the color change from a setting of 0.3 to 0.4 mm. of the right-hand cup which should mean a change in pH from 1.2 to 1.3. It also would be easy to distinguish the color change from a setting of 4.4 to 5.0 mm. which would denote a change in pH from 2.6 to 2.7. In the upper part of the chart the sensitivity per 0.1 on the pH scale is about uniform. In the lower part of the chart, however, the sensitivity decreases because of the fact that the percentage change of color per unit pH decreases. In the distinguishing of color the sensitivity depends upon the percentage change according to Weber's law within certain limits. For instance, we can easily dis-
tistinguish between 5.0 and 5.6 mm. in the setting of the right-hand cup which denotes a pH change of 2.7 to 2.8, but we cannot as easily distinguish a color change between 9.8 and 9.9 mm. in the setting of the right-hand cup, which denotes a change of 4.4 to 4.7 in the pH. In fact, if our eyes are sensitive only to a .5 per cent change in color, the best we can do is to distinguish between 9.4 and 9.9 in the setting of the right-hand cup which denotes a pH change of 3.9 to 4.7. Since, however, a titratable amount of
hydrochloric acid in the gastric contents would denote a pH between 1 and 4, about all we can say as a result of this examination, if the reading of the right-hand cup is greater than 9.5, is that there is no free hydrochloric acid in the gastric contents. Since many foods and drinks contain acetic and lactic acids, and often small quantities of phosphoric acid, the determination of the pH of the adult's stomach between 4 and 7 is difficult to interpret. It has already been shown that most foods are acid. In fact, with the exception of a few alkaline mineral waters, and milk immediately from the lacteal glands, perhaps all foods and drinks are acid. Therefore, the method is not designed for the detection of these very slight acidities. The mode of construction of the chart has already been described. The advantage of this method is that by making the curve a straight line, new curves are easily drawn. They should be drawn parallel to the diagonal line on the chart, which can easily be done by means of parallel rules. The addition of salt will change the dissociation constant of quinaldine red, and it is merely necessary to find the logarithm of the reciprocal of the dissociation constant under the given conditions, and having determined this on the pH scale, trace this coordinate to the 50 per cent dissociation line and draw the diagonal through the point of intersection. If the dissociation constant is not determined, all that is necessary is to determine a single value of pH corresponding to a known percentage dissociation, find this point on the chart, and draw the diagonal through this point. It is possible that the admixture of some other red dye in the quinaldine red as an impurity might be dealt with approximately by determining a single point on the chart, and drawing a new diagonal in this way.

By means of the micro colorimeter made by Bausch and Lomb, it is possible to make this determination on 0.5 cc. of gastric juice in the left-hand cup together with 0.5 cc. of gastric juice or fluid of equal opalescence in a cup held beneath the right-hand cup. Phosphates shift the average wave-length of the color of quinaldine red, and hence if the gastric contents contain a high concentration of phosphates, it is necessary to put some alkaline phos-

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phates in the distilled water standard. I have not encountered a sufficiently high concentration of phosphate in any sample of gastric content so far studied to cause detectible effect on the color.
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