

CONCLUSION.

1. A modified colorimetric procedure has been presented based upon Smith's Quantitative Colorimetric Reaction.

2. Data obtained while comparing the modified colorimetric procedure, the Cock's Comb and the Broom and Clark methods of physiological standardization have been given.

3. The presence of hydrochloric and tartaric acids, sodium hydrosulphite, sodium acid phosphate or sodium hyposulphite does not interfere with the modified colorimetric procedure.

The author is indebted to Mr. Clarence E. Powell for the Broom and Clark and to Mr. C. C. Hargreaves for the Cock's Comb assay results appearing in this paper. He also wishes to express his appreciation to Mr. W. J. Rice and Mr. E. J. Hughes for their friendly criticism.

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THE BUFFER CAPACITY OF TINCTURE OF DIGITALIS.*

BY JOHN C. KRANTZ, JR.

INTRODUCTION.

Hydrogen-ion concentration and buffer capacity of various extractive preparations have received the attention of the pharmacist and physical chemist during the past few years. The buffer capacity of the extractive preparations of ergot was studied by Wokes and Elphick (1) in 1930. In addition, Thompson (2) in his comprehensive study of ergot mentioned the buffer value of ergot in his efforts to adjust the hydrogen-ion concentration of the fluidextract. In studying the work of Joachimaglu and Bose (3), the author (4 and 5) observed the rather striking buffer capacity of the extractive substance obtained in the percolation of digitalis leaves with hydroalcoholic menstrua.

Wokes (6) examined the relationship between the total solids of various tinctures of digitalis and their potency and found the relationship to be of no significance. With Munch (7) the author showed that there existed a great variation in the potency of tinctures prepared with absolute alcohol and those prepared

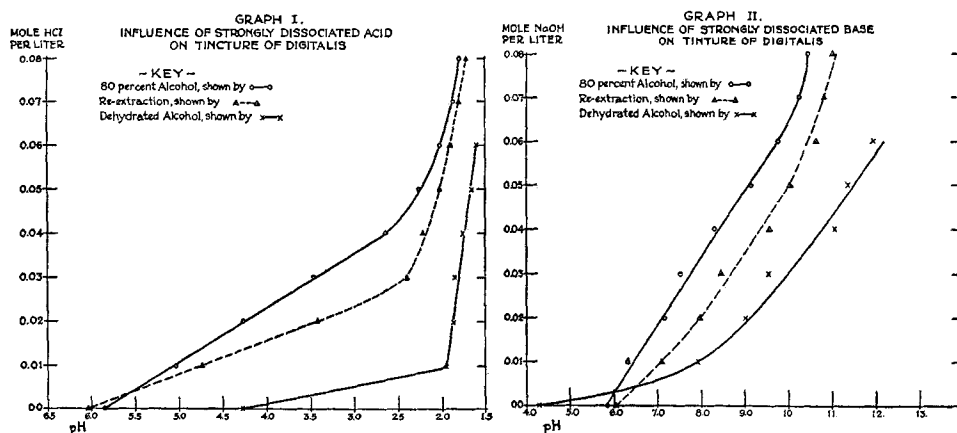
* Scientific Section, A. P. H. A., Toronto meeting, 1932.

with 80 per cent alcohol. This difference in heart- tonic value is accompanied by a marked difference in hydrogen-ion concentration. On account of the differences in heart- tonic value and hydrogen-ion concentration existing between these tinctures it was decided to measure their buffer capacities.

EXPERIMENTAL.

Tinctures of digitalis were prepared from six specimens of digitalis leaves using 80 per cent alcohol as a menstruum. These tinctures were mixed to obtain a composite sample. From the same specimens of leaves tinctures were prepared using dehydrated alcohol as a menstruum: likewise a composite sample of tincture was prepared. The marcs obtained from the preparation of the tinctures with dehydrated alcohol were re-percolated with 80 per cent alcohol. The composite tincture prepared by this extraction was studied also.

To a definite volume of each of the three tinctures was added definite Gm. equivalents of hydrochloric acid and sodium hydroxide, respectively. The hydrogen-ion concentration of these tinctures to which strongly dissociated acid and base were added was measured electrometrically using a hydrogen electrode Wilson (8) type. The results expressed in p_H were reproducible within ± 0.1 unit.



The differential ratio suggested by Van Slyke (9) $\frac{dB}{dp_H}$ was employed as a unit of measurement. This ratio expresses the relationship between the increment in Gm. equivalents of strong base added to the buffer solution and the resultant increment in p_H . If an acid is added the value of each term in the expression is negative, and the buffer capacity represented by " β " retains its positive value.

The results of these measurements are shown in Tables I and II and plotted in Graphs I and II.

TABLE I.—STRONGLY DISSOCIATED ACID.

No.	Cc. 0.1 N HCl per L.	Mole HCl per L.	p_H Menstruum, 80 Per Cent Alcohol.	p_H Tincture, 80 Per Cent Alcohol.	p_H Tincture, Dehydrated Alcohol.	β Tincture, Re-extraction.
0	0.00	0.00	6.35	5.85	4.28	6.03
1	100	0.01	2.18	5.03	1.96	4.74
2	200	0.02	1.89	4.27	1.87	3.42
3	300	0.03	1.71	3.46	1.86	2.41

TABLE I.—STRONGLY DISSOCIATED ACID. (Continued.)

No.	Cc. 0.1 N HCl per L.	Mole HCl per L.	p_H Menstruum, 80 Per Cent Alcohol.	p_H Tincture, 80 Per Cent Alcohol.	p_H Tincture, Dehydrated Alcohol.	p_H Tincture, Reëxtraction.
4	400	0.04	1.60	2.65	1.77	2.22
5	500	0.05	1.49	2.27	1.66	2.03
6	600	0.06	1.39	2.03	1.60	1.91
7	700	0.07	1.36	1.88	..	1.81
8	800	0.08	1.33	1.81	..	1.72

TABLE II.—STRONGLY DISSOCIATED BASE.

No.	Cc. 0.1 N NaOH per L.	Mole NaOH per L.	p_H Menstruum, 80 Per Cent Alcohol.	p_H Tincture, 80 Per Cent Alcohol.	p_H Tincture, Dehydrated Alcohol.	p_H Tincture, Reëxtraction.
0	0.00	0.00	6.35	5.85	4.28	6.03
1	100	0.01	12.66	6.32	7.93	7.10
2	200	0.02	12.78	7.16	9.01	7.97
3	300	0.03	12.79	7.52	9.55	8.45
4	400	0.04	12.74	8.30	11.04	9.57
5	500	0.05	12.76	9.16	11.35	10.05
6	600	0.06	12.77	9.77	11.94	10.65
7	700	0.07	12.80	10.25	...	10.82
8	800	0.08	12.78	10.45	...	11.09

From Graph I the following relationships may be calculated:

$$\begin{aligned} \text{80 per cent alcohol tincture} & \quad \frac{-\Delta B}{-\Delta p_H} = \frac{0.012}{1} = 0.012 \\ \text{Reëxtraction tincture} & \quad \frac{-\Delta B}{-\Delta p_H} = \frac{0.010}{1} = 0.010 \\ \text{Dehydrated alcohol tincture} & \quad \frac{-\Delta B}{-\Delta p_H} = \frac{0.004}{1} = 0.004 \end{aligned}$$

From Graph II the following relationships may be calculated:

$$\begin{aligned} \text{80 per cent alcohol tincture} & \quad \frac{\Delta B}{\Delta p_H} = \frac{0.016}{1} = 0.016 \\ \text{Reëxtraction tincture} & \quad \frac{\Delta B}{\Delta p_H} = \frac{0.010}{1} = 0.010 \\ \text{Dehydrated alcohol tincture} & \quad \frac{\Delta B}{\Delta p_H} = \frac{0.003}{1} = 0.003. \end{aligned}$$

These values represent measurable increments of acid and base, respectively, necessary to change the p_H of the tinctures one unit. In order to obtain the differential ratio $\frac{dB}{dp_H}$ or β it is necessary to draw a tangent to the curve at a definite point. Values on the ordinate axis above and below this point are taken and the base line intercepts of the tangent at these points are determined. For these tinctures over a considerable p_H range the curves are essentially straight lines, and for practical purposes the ratio obtained by the use of measurable increments is practically the same as the differential ratio.

SUMMARY.

1. The buffer capacities of composite tinctures of digitalis made according to the foregoing description have been determined.
2. The buffer capacity of the tincture prepared with dehydrated alcohol is comparatively negligible.

3. The sum of the buffer capacities of the dehydrated alcohol and the re-extraction tinctures is essentially the same as the buffer capacity of the 80 per cent alcohol tincture.

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SIGNIFICANCE OF STEARIN CONTENT OF COD LIVER OIL.*

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Stearin is a normal constituent of the oil obtained upon rendering cod livers with steam in the manufacture of cod liver oil. Stearin congeals to a solid at only a moderately low temperature at which the other constituents of the oil remain quite fluid and it is the general practice to remove more or less of the stearin during the process of refining the oil by chilling the oil and filtering off the hardened stearin.

The object of removing this stearin is to produce a cod liver oil which will not become cloudy or thick from separation of stearin when the oil is subjected to practical low temperatures.

Removal of the stearin from cod liver oil has, in general, no significant effect upon the vitamin A potency of the oil. Crude cod liver oil and the refined oil and stearin all possess relatively high vitamin A potency, the refined oil sometimes having the higher potency of the three substances, although usually there is no significant difference between the potency of the crude cod liver oil and the refined oil made from it.

Prof. E. Poulsson of Oslo, Norway, in a private communication to the Tailby-Nason Co., writes on this subject, the following being a translation by S. Hammer, an employee of the Tailby-Nason Co.:

"Minute quantities of stearin present in refined cod liver oil have no influence on the digestive organs. Minute quantities of stearin present in cod liver oil do not lower the vitamin content in the oil. It has been shown by research work both here, and in other laboratories, that the separated stearin contains the same quantities of vitamins as the liquid oil. In earlier times, the refrigeration of cod liver oil was almost always done by exposing containers of cod liver oil to the cold in the winter. At present, as far as I know, refrigerating plants are in use, and the temperature of the oil varies between zero and 4 below zero Centigrade. This is sufficient for all practical uses; at a lower temperature, the oil will undoubtedly be cloudy, but we presume that oil exported from this country, very seldom is exposed to a lower temperature. I do not know of any literature bearing on the above questions. The above information is built partly on our own research work, partly on what I have read in different journals, and partly on my own experience (in regard to temperature), from producers."

* Scientific Section, A. PH. A., Toronto meeting, 1932.