

THE EFFECT OF STORAGE OF DISTILLED WATER IN GLASS AMPULS
ON THE ALKALINITY AND TOTAL SOLIDS CONTENT.*BY A. O. MATTHEUS.¹

The corrosion of glass by distilled water has been investigated on numerous occasions. P. Nicolardot (1), observing the action of cold and boiling water on various glasses, found that Jena glass lost 0.5–2 mg. when exposed to 300 cc. of boiling water for 3 hours and 0.5 mg. when exposed to water under ordinary temperatures for one week. Turner (2) found that various hard glasses behaved in like manner and that the losses in weight varied from 0.01 to 0.07 per cent. F. Mylius (3) subjected hard and soft apparatus glass to water treatments for 7 days at 18° C. and 3 hours at 80° C. He observed that water-resistant glasses liberated 0.000–0.004 mg. of Na₂O at 18° C. and 0.000–0.015 mg. at 80° C. Éwe (4) found flint glass to lose 0–4 mg. per 500 sq. cm. when exposed to boiling for 16 hours. Buhner (5) and Kroeber (6) describe experiments in which precipitation of medicinal substances was caused by the liberation of alkali from the glass. These and other similar investigations bear out the fact that a definite amount of corrosion takes place when a glass surface is exposed to water at elevated temperatures for comparatively short periods and that these losses increase rapidly with temperatures above 80° C.

These losses, sustained by glass, can be looked at as impurity gains in the water and this viewpoint is of considerable interest when such waters are used for intravenous medication. Susceptibility to change in acidity, alkalinity, total solids, together with organic and bacterial contamination of water used for such purposes, is of prime importance. It is quite evident that glasses imparting an alkaline reaction to water would be objectionable as a diluent for alkaloidal solutions aside from the serious tendency of these same alkali-producing glasses to liberate platelets and splints when exposed to water for even short intervals of time.

The behavior of various glasses when exposed to aqueous solutions has necessitated the development of special tests as embodied in the reports of Buhner (5), Kroeber (6), Mylius (3), Foerster (7), Turner (2) and others.

The solvent action of water on glass has been frequently reported in terms of alkali liberated. Experiments with Jena glass have shown that the increase in p_H value of the water has been very little and the solids liberated cannot be composed entirely of alkaline or even acidic substances. Kling and A. Lassieur (8), using a platinum still, prepared a distilled water having a p_H value of 5.8 and this water, on storage in platinum or Jena bottles either open to air or closed, was shown to undergo no change in p_H value. Williams (9), after storing distilled water in flint-glass bottles, noted a lowering of the p_H value from 6.8 to a minimum of 5.23. Experiments, about to be described, with water stored in Jena glass ampuls showed no marked increase in p_H value accompanying an increase in total solids from 1.5 to 6.3 mg.

The distilled water as freshly prepared, using a commercial metal still, possessed a p_H value of 6.2 and at no time was it possible to obtain a water which had the theoretical p_H value of 7. Attempts to prepare water having an index of 7.0,

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using an all-glass distillation system, were not successful nor did distillation over sulphuric acid, phosphoric acid or alkaline permanganate yield any better results. Distilled water for research purposes has been prepared by several investigators but it was invariably of a p_H index lower than 7.

Sample.	p_H .	Investigator.	Reference.
Single distilled	5.8	Kling and Lassieur	<i>Comp. rend.</i> , 181 (1925), 1062-1064.
Distilled	about 7.0	Dewitt and Brown	<i>Ind. Eng. Chem., Analytical Edition</i> , 1 (1929), 109.
Distilled	6.2	Fales	<i>J. A. Chem. Soc.</i> , 37 (1915), 2781.
Distilled over $KMnO_4$	5.8	Fales	<i>Ibid.</i> , 37 (1915), 2781.
Distilled	6.9	Dawson	<i>J. Phys. Chem.</i> , 29 (1925), 554.
Double distilled over H_2SO_4	6.4	Canals	<i>Bull. soc. chim. biol.</i> , 7 (1925), 673-677.
Double distilled	6.2-6.8	Carter	<i>Loc. cit.</i>
Double distilled	6.8	Williams and Sweet	<i>J. A. M. A.</i> , 78 (1922), 1024-1026.
Double distilled	7.0	Acree and Fawcett	<i>Ind. Eng. Chem., Analytical Edition</i> , 2 (1930), 82.

The factors that are responsible for the lower indexes listed are due to causes not definitely understood. Fales and Nelson (10), using the CO_2 content as a basis, calculated the p_H value to be 5.2-5.5 against 5.8-6.2 actual. Kling and Lassieur advanced the contention that the acidity is due to CO_2 . However, using the process described by Dawson, it is relatively simple to obtain a water of p_H 6.9 by simply boiling, for a short time, distilled waters having a p_H value as low as 5.8-6.0. Acree and Fawcett (12), have demonstrated that the removal of CO_2 from water, employing aeration with CO_2 free air, produces a water of p_H 7.0, a fact which supports the view that the acidity is due to CO_2 .

EXPERIMENTAL.

Preparation of Water.—Ordinary tap water was twice distilled, employing a tin-lined, aerated-type, industrial still. This freshly distilled water was collected in washed sterile pyrex bottles and immediately filled into 10-cc. washed Jena ampuls. A sterility test, made on a sample of the water collected just as it came from the still, showed the water to be sterile at this stage in its preparation. All U. S. P. specifications for distilled water were met. The ampuls were inspected for floating material and any that were found in this condition were discarded. The temperature of storage was not absolutely uniform but corresponded to that maintained in the laboratory room which varied from 22° C. in the winter to 27° C. in the summer. The sealed ampuls were sterilized for 1/2 hour at 85° C. on each of 3 successive days.

Analysis of Water.—The ampuls, after storage, were scratched with a file at the constricted neck, and thoroughly washed with running distilled water. When dry, they were carefully opened and the contents removed with a syringe. Approximately 100 ampuls were used to supply the 1000-cc. sample used in the test for total solids.

The sample to be analyzed was evaporated from a three-inch platinum dish. The dish, heated to constant weight at 110-115° C., was allowed to cool in a calcium

chloride desiccator, a procedure which was followed identically in the final weighing. A two-inch sand bath, made from an ordinary jar cover and heated with a small electric hot plate, supplied the heating surface. A glass funnel lowered over the dish prevented contamination from extraneous dust particles. Boiling was avoided at all times in order to eliminate spattering. Loss of weight on ignition was determined by carefully heating over a free flame with subsequent heating at 110–115° C. for one hour.

Determination of p_H Value.—The p_H values were determined colorimetrically using an adjusted brom thymol blue indicator. Four hundredths gram (0.04) brom thymol blue was wetted with 5 cc. (95%) alcohol and 5 cc. water. To this 0.2–0.3 cc. of *N*/10 sodium hydroxide was gradually added and the solution well stirred until dissolved. This solution was made up to 100 cc., then adjusted to a p_H value of 6.9. To adjust the indicator to a p_H of 6.9, *N*/10 sodium hydroxide was added dropwise to the total indicator solution until the color produced when 0.05 cc. of the indicator added to 1 cc. of water, prepared by Dawson's (11) method, produced the same color as obtained when a similar amount of indicator was added to a 6.9 buffer. Dawson was able to prepare a water of a constant p_H value of 6.9 by evaporating $\frac{1}{3}$ of the volume of an ordinary distilled water sample, transferring the remaining water to a flask of a capacity sufficiently large to permit of completely filling and allowing the water to cool out of contact with air.

Condition of Ampuls after Aging.—The great majority of the ampuls after aging 18 months were perfectly clear. Whatever damages or corrosion resulted during the storage period, the dissolving away of soluble material did not liberate any splints or flakes so often noted as a sediment in bottles, similarly exposed. A random selection of ampuls, when carefully cut and microscopically examined on the inner surface, showed pitted, segregated areas. These areas appeared to be more plentiful on the water-aged glass; however, the difference, if any, was slight. The outlines of the pitted areas were quite irregular, the pitting was uniform over the area and this condition would account for the absence of whole segments of liberated material.

TABLE II.

	Start Oct. 8, 1929.	Jan. 8, 1930.	April 8, 1930.	Aug. 15, 1930.	April 1931.
Total solids per liter	0.0015 Gm.	0.0047 Gm.	0.0045 Gm.	0.0049 Gm.	0.0063 Gm.
Loss on ignition	None	0.0030	0.0025		0.0026
Inorganic solids	0.0015	0.0017	0.0020		0.0037
p_H value	6.2	6.6	6.4–7.0

Discussion of Results.—The total solids content of sterile distilled water, stored in Jena glass ampuls for 18 months, had increased from 1.5 to 6.3 mg. per liter. Of this amount 2.5–3.0 mg. was represented by organic matter which appeared at an early date and showed no increase. The origin of this organic matter is not definitely known, particularly when it is recalled that only glass surfaces were exposed to the water and that the conditions of handling which insured a sterile state at all times, eliminated any accumulation of bacterial débris. The inorganic portion of the total solids has been slowly increasing at an apparently constant rate as the aging progresses and has risen from 1.5 to 3.7 mg. per liter.

The p_H values of the water contained in the individual ampuls show a little variation due to differences in the glass. Over a short period not much difference is noted but after 18 months about 70 per cent of the ampuls show a p_H of 6.6; about 15 per cent, a p_H of 6.8; and 15 per cent, a p_H value of 7.0. This condition existing in the individual ampuls is in close agreement with the behavior of similar ampuls when heated with water at 100° C. for one hour, a test which was resorted to, to determine the uniformity of the glass. The initial p_H value of 6.2 has gradually increased to 6.6 with a small percentage as high as 7.0 but the average change was well within the limit of 6.2 to 6.6.

CONCLUSIONS.

The increase in alkalinity of distilled water was so slight that its use as a diluent would not be incompatible with any alkaloidal solutions. The contamination due to inorganic matter when pro-rated among the individual ampuls amounted to only 0.037 mg. per 10-cc. ampul. No glass splints or platelets were liberated. These data seem to indicate that the corrosion of the glass by distilled water at room temperature is a relatively slow reaction and no deleterious effects are produced which would be of any consequence in the use of water, so stored, for medicinal purposes.

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ESSENTIAL OIL EXTRACTION INDUSTRY IN THE NETHERLAND EAST INDIES.

The extraction of essential oils in the Netherland East Indies, as an industry, has been developed largely in connection with the processing of citronella, and the majority of estates having large areas planted to citronella operate steam-distilling apparatus to handle the output. They also frequently buy citronella grass from native plantings in their vicinity, but concentration of the extraction industry is impracticable since cintronella grass must be processed soon after it is harvested. Three or four distilleries handle such products as lemongrass, palmarosa, patchouli or vetivert, in addition to citronella.

There is also an extensive, but crudely developed, native extraction industry. All cajuput oil produced in Boeroe and Ceram, all of the cananga oil distilled in Bantam and most of the champaca, wintergreen, ambrette, clove and cinnamon oils, and similar products processed for local consumption are put through primitive native stills. According to the only statistics available there were in operation in 1927 under the Factory Safety Ordinance 151 essential oil factories—141 in Java and 10 in the Outer Possessions. (Trade Commissioner Don C. Bliss, Batavia.)