

627; through *Chem. Abst.*, 29 (1935), 8233.

(13) Vieböck, F., and Fuchs, K., *Pharm. Monatsh.*, 15 (1934), 39.

(14) Schulek, Elemer, and Rozsa, Pal, *Magyar Gyógyszerész. Társaság Értesítője*, 14 (1938), 96; through *C. A.*, 32 (1938), 3901.

(15) Schulek, Elemer, and Rozsa, Pal, *Z. Anal.*

Chem., 112 (1938), 404; through *Squibb Abstract Bull.*, 11 (1938), 1157.

(16) "The National Formulary," Sixth Edition, Mack Printing Company, Easton, Pa., 1935.

(17) "The British Pharmacopoeia," Published for the General Medical Council by Constable & Co. Ltd., London, 1932.

The Effect of Age upon the pH of Dilute Solutions of Zinc Sulfate and Solutions of Mild Silver Protein*

By Charles V. Netz

Physicians use very dilute solutions of zinc sulfate, alone and with other agents, as ophthalmic astringents. A 0.22 per cent solution of zinc sulfate appears to be the most popular. The astringency of zinc sulfate solutions is due to the zinc ion. Astringent substances will irritate the delicate corneal membrane; hence dilute solutions of zinc sulfate are somewhat irritating to the eye, and the irritation is proportional to the concentration of the zinc ion. A number of local physicians have reported that solutions of zinc sulfate, as they become older in office use, appear to cause increased corneal irritation. Since zinc sulfate is completely ionized in solution, the concentration of the zinc ions should not increase with time, hence there should be no increase in the astringency of such a solution with age, providing there is no evaporation of the solvent.

Dilute solutions of zinc sulfate are weakly acid due to the slight hydrolysis of the zinc ions which causes an excess of hydronium ions. Although hydronium ions are irritating to the cornea they are reasonably well tolerated because a half-saturated solution of boric acid with a pH of 4.8 is only mildly irritating. Observations were made over a period of fifteen months on three 0.22 per cent solutions of zinc sulfate. A 1500-cc. portion of the solution was prepared and from this were filled three pint bottles of ordinary clear glass. Bottles of this type were used to simulate the conditions under which such solutions are usually found in physicians' offices. The bottles were kept in daylight but not in direct sunlight. The pH values of the solutions were determined at intervals with a Coleman Electrometer and glass electrode. A very slight pre-

cipitate which slowly formed was not filtered out. The temperatures of the solutions ranged from 21° to 23° C.

The distilled water used to make the solution had a pH of 6.74. The freshly prepared 0.22 per cent solution of zinc sulfate had a pH of 6.70. The pH values of the solutions uniformly decreased (solution became more acid) until at the end of the fifteen months of observation each had a pH of 6.38. Obviously the slight increase in acidity over that period could hardly be the cause of additional corneal irritation. Five people who dropped in their eyes on alternate days a freshly prepared 0.22 per cent solution of the salt and the fifteen-month-old solution could discern no difference in the astringency of the solutions.

The increased irritation of old solutions of zinc sulfate as reported by a few physicians is certainly not due to increased acidity. It may be due to an increase in zinc ions caused by loss of solvent from containers which are poorly stoppered or are opened for brief periods during routine office use.

The pH of a 5 per cent solution of mild silver protein was determined at intervals over a period of twelve months, using the same general procedure as outlined above for zinc sulfate solutions. The pH of the solution in each bottle decreased (became less alkaline) from 9.65 at the time of preparation to 9.05 after twelve months of standing.

SUMMARY

1. The pH of three 0.22 per cent solutions of zinc sulfate decreased from 6.70 to 6.38 over a fifteen-month period.

2. The pH of two 5 per cent solutions of mild silver protein decreased from 9.65 to 9.05 over a twelve-month period.

* Received July 30, 1943, from the College of Pharmacy, University of Minnesota, Minneapolis.