

playing an important role. There are no striking relations between the formation of bands and the physical properties of the dye solutions (Table I). It is probable that by using different papers from ours and different concentrations it would be possible to form bands in still other cases than those indicated.

Summary

Rhythmic bands of dyes have been made on filter paper, cotton cloth, and unglazed porcelain by regulated evaporation. Several varieties of filter paper were used with both 0.04% and 0.005% solutions of each of 62 dyes. A table gives measurements of the following physical properties of the 0.04% solutions: refractive index for light, surface tension, conductivity, viscosity, Brownian movement, Tyndall cone, and band formation. Uniform temperature and a gradual decrease in the rate of flow are the important factors in the formation of bands. It is probable that just before the band forms we have a film of oriented molecules.

In conclusion I wish to thank the National Aniline and Chemical Company of New York for samples of the dyes used in these experiments.

MORGANTOWN, WEST VIRGINIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, CASE SCHOOL OF APPLIED SCIENCE]

THE USE OF MALIC, MALEIC AND FUMARIC ACIDS IN VOLUMETRIC ANALYSIS

BY N. A. LANGE AND HARRY KLINE

Received June 12, 1922

Malic, maleic and fumaric acids¹ are now available in large quantities and at comparatively low prices, and an investigation was, therefore, made to determine whether they might replace the more costly succinic acid² for standardizing basic solutions. A. Astruc³ has shown that when phenolphthalein is used as the indicator many of the dicarboxylic acids, including the acids mentioned above, behave as though they have 2 replaceable hydrogen atoms, whereas with methyl orange the end-point is uncertain. No methods of purification nor data of titrations were given for these acids.

In the experiments below, the sodium hydroxide solutions free from carbon dioxide were prepared in the usual manner by the addition of barium chloride and then standardized against hydrochloric acid, the normality of which was determined by precipitation of silver chloride; the normality of the sodium hydroxide was also determined by titration with pure succinic acid.

¹ U. S. pat. 1,318,631-2, -3.

² Phelps and Weed, *Am. J. Sci.*, **26**, 138 (1908); *Z. anorg. Chem.*, **59**, 114 (1908).

³ Astruc, *Z. anal. Chem.*, **40**, 418 (1901); *Compt. rend.*, **130**, 253 (1900).

Maleic Acid.—Commercial maleic acid was found to be too impure to use directly. The acid was, therefore, purified by crystallization in four different ways: (1) a single crystallization from water; (2) two crystallizations from water; (3) one crystallization from 200 cc. of water to which had been added 4 drops of conc. nitric acid; (4) crystallization as in 3 and then once more from pure water. After air-drying, the crystals were dried to constant weight over sulfuric acid or in an oven at 90° for 2 hours. Definite amounts of the acid were dissolved in distilled water, which was previously boiled to expel carbon dioxide and allowed to cool to about 50° before addition of the acid. In each case the standard sodium hydroxide solution was then added until the end-point with phenolphthalein was obtained. The normality of the base against standard hydrochloric acid was $0.1087 N$; 4 titrations with succinic acid gave an average value of $0.1087 N$ with an extreme variation of $\pm 0.0001 N$; the normality determined with 16 samples of maleic acid dried over sulfuric acid and varying in weight from 0.1696 to 0.2642 g. averaged $0.1088 N$ with an extreme variation of $+0.0001$ to $-0.0003 N$; titration with 4 samples of maleic acid dried at 90° and varying in weight from 0.1987 to 0.2339 g. gave an average value of $0.1087 N$ with an extreme variation of $\pm 0.0001 N$. It was found that maleic acid after one crystallization from water or from water with a few drops of nitric acid will give results as accurate as obtainable with succinic or hydrochloric acids. Several determinations with samples of maleic acid dried at 105° and 120° showed that a small amount of maleic anhydride is formed; such samples after standing in the open air for 24 hours are hydrolyzed giving accurate results after drying again in a desiccator over sulfuric acid or in an oven at 90° and reweighing before titration.

Fumaric Acid.—Commercial fumaric acid was found to be too impure to use directly; any one of the four methods given above may be used to purify it. The normality of the base determined with 16 samples of fumaric acid dried to constant weight over sulfuric acid and varying in weight from 0.1280 to 0.4249 g. gave an average value of $0.1082 N$ with an extreme variation of $+0.0003$ to $-0.0001 N$; the normality of the base determined with 4 samples of succinic acid averaged $0.1081 N$ and with hydrochloric acid $0.1082 N$. The results with fumaric acid dried for 2 hours in an oven at temperatures from 90 – 120° gave an average value of $0.1082 N$ with an extreme variation of $+0.0002$ to $-0.0001 N$. The results show that fumaric acid may serve as a standard in alkalimetry after one crystallization from water, although a higher temperature of the solution must be maintained during the titration because of the lower solubility.

Malic Acid.—Malic acid is very soluble in water and was therefore recrystallized by dissolving in hot acetone, filtering and then adding carbon

tetrachloride to the hot solution and allowing the acid to crystallize on cooling. The crystals were dried in air for about 24 hours and then dried in a desiccator over sulfuric acid for an equal length of time, or for 2 hours in an oven at temperatures from 90° to 120°. The normality of the base determined with 4 samples of malic acid dried over sulfuric acid and varying in weight from 0.2071 to 0.2742 g. gave an average value of 0.1081 *N* with an extreme variation of +0.0001 *N*; the normality of the base determined with hydrochloric acid and with succinic acid was 0.1081 *N*; the determination with samples of malic acid dried at 90–120° gave an average value of 0.1082 *N* with an extreme variation of +0.0002 to --0.0001. It is evident that malic acid can easily be obtained pure and because of its greater solubility would be more valuable as a standard than either maleic or fumaric acids.

Maleic and fumaric acids are oxidized by potassium permanganate according to the following equation:⁴ $C_4H_4O_4 + 5O \longrightarrow 3CO_2 + H_2O + HCOOH$. Conflicting statements are made by previous investigators concerning the quantitative course of this reaction. This work was repeated and it was found that although these acids may be used as standards for permanganate solutions, they are not as accurate nor as convenient as sodium oxalate. This is due to the low hydrogen equivalent of the acids which necessitates using very small samples with the consequent greater effect of any small errors in weighing and the difficulty of titrating boiling solutions. Titrations of malic acid were conducted in the same manner but the results were too variable and inaccurate to be of any value. Experiments with maleic or fumaric acid as titrating agent with 0.1 *N* iodine solution using starch as indicator did not give accurate results.

Attempts to standardize a 0.1 *N* ammonium hydroxide solution by titrating against known weights of malic, maleic, fumaric and succinic acids using either cochineal or methyl red as indicator were not successful. Although it is evident for theoretical reasons that a sharp end-point cannot be obtained in titrating a weak acid with a weak base, nevertheless conflicting statements have been made by previous investigators on the use of succinic acid in the standardization of ammonium hydroxide solution with cochineal as an indicator.⁵

Summary

It is evident that malic, maleic and fumaric acids may be used with great accuracy as standards for sodium hydroxide solutions; it is further obvious that all 3 acids may be obtained in a pure form very readily

⁴ Perdrix, *Bull. soc. chim. Paris*, [3] **23**, 645 (1900). Clarke, *Am. Chem. J.*, **3**, 201 (1881). Micko, *Z. anal. Chem.*, **31**, 465 (1892). *Z. allgem. österr. Apotheker Ver.*, **30**, 197 (1891).

⁵ Phelps and Hubbard, *Z. anorg. Chem.*, **53**, 361 (1907); *Am. J. Sci.*, **23**, 211 (1907). Peters and Sauchelli, *Am. J. Sci.*, **41**, 244 (1916).

and all may be dried over sulfuric acid; malic and fumaric acids may be dried for 2 hours at temperatures from 90° to 120°; because of the formation of the anhydride, samples of maleic acid should not be dried above 100°. As standards in alkalimetry and acidimetry these acids, in the pure state, are as accurate as hydrochloric acid determined gravimetrically as silver chloride. The most serviceable of these organic acids are those most soluble in water—malic and maleic acids—although they are no more accurate than fumaric acid. Although maleic and fumaric acids may be used as standards for potassium permanganate solutions, they are neither as accurate nor as convenient as sodium oxalate for this purpose. Succinic, malic, maleic and fumaric acids cannot be used as standards for ammonium hydroxide solutions; the last 2 acids cannot be used for iodine titrations.

CLEVELAND, OHIO

[CONTRIBUTION FROM THE CERAMIC EXPERIMENT STATION, UNITED STATES BUREAU OF MINES]

THE PURIFICATION AND ANALYSIS OF ZIRCONIUM DIOXIDE¹

By F. G. JACKSON² AND L. I. SHAW³

Received June 23, 1922

In preparation for an investigation of refractories to be later conducted at this Station, 1 or 2 kg. of very pure zirconium dioxide was needed. Low-melting impurities were especially undesirable. The subject of purification was, therefore, investigated.

Marden and Rich⁴ have covered the subject of zirconium oxide very thoroughly and give a variety of methods of both dissolving and purifying the ores and oxide. They recommend fusion, either with caustic soda or with soda ash. Washburn⁵ has approached the complete removal of impurities from the commercial oxide by heating in a current of carbonyl chloride. Venable's new book, "Zirconium and Its Compounds," has appeared since this work was completed.

Zirconium oxide, which has been ignited, resists attack of fusion mixtures more strongly, the higher the previous ignition temperature. The commercially purified sample obtained as a starting point for this work was very resistant. Neither caustic soda, nor soda ash, nor borax, alone, attacked it markedly; hence the method of Marden and Rich would not serve. However, an equal mixture of borax and soda ash proved more

¹ Published with the permission of the Director of the U. S. Bureau of Mines.

² Assistant Chemist.

³ Assistant Chief Chemist.

⁴ Marden and Rich, "Investigations of Zirconium with Especial Reference to the Metal and Oxide," *U. S. Bur. Mines Bull.*, **186** (1921).

⁵ Washburn and Libman, *J. Am. Ceramic Soc.*, **3**, 634 (1920).