

(about 90 diameters). If all of the paramecia are killed promptly a higher dilution of the disinfectant must be tried. If the paramecia continue alive for a period of three minutes or longer, a stronger solution must be tried. These trials must be continued until the solution strength is found which will kill all of the paramecia present within *three minutes' time* (but not within one minute of time), at a room temperature of approximately 20° C. This dilution shall be known as the minimal killing dose, indicated by M. K. D.

5. *The Phenol Standard*.—Make a 1 per cent. solution of pure phenol (crystals) in distilled water, and determine the M. K. D. as described under (4). This M. K. D. of phenol shall be the standard of comparison, or the phenol standard, given as 1.

6. *The Phenol Coefficient*.—The phenol coefficient of the compared disinfectant is obtained by dividing its killing dilution by the killing dilution of pure phenol. The killing dilution of pure phenol when used in the manner herein described is 1:500.

7. *Determining the Death of the Test Organism*.—The behavior of the test organism toward the test solutions may be stated as follows:

- a. Period of excitation, usually very temporary, followed by,
- b. Retardation of motion; slowing and even complete inhibition of the vesicular pulse; then,
- c. Slow progressive motion with axial rotation, spinning top motion.
- d. Cessation of progressive motion, the cilia still vibrating,
- e. Projection of trichocysts, and,
- f. Protrusion of vacuoles, which invariably means death.

The test solutions of the disinfectants are to be made with distilled water and the mixing done by vigorous shaking. The presence of large numbers of bacteria in the paramecial culture, and of other contaminants, does not materially affect the reaction of the paramecia toward the test solutions. Cover glasses are not required and all of the observations are made under the low power of the compound microscope. Dilutions of liquid disinfectants are to be made volumetrically, and the initial solution of solid but soluble disinfectants is to be made gravimetrically.

HYPOCHLORITE SOLUTIONS.

BY RUTH M. DAVIS AND H. A. LANGENHAN.

(Continued from p. 222, March JOURNAL A. PH. A.)

(NO. 4) PRESERVATION OF HYPOCHLORITE SOLUTIONS.

The alkaline earth hypochlorite solutions are unstable. Their stability may be influenced by the chlorine concentration; by the temperature applied during the preparation and storing of the solution; and by the alkalinity of the finished product.

Faraday was the first to note the importance of the chlorine concentration. He found that by using an excess of chlorine gas a solution was obtained differing from Labarraque's in chemical constituents and reaction. "Labarraque's Solution gave off a slight odor of chlorine, on being heated yielded no chlorine, on being

evaporated gave no salt nor chlorate of soda, and practically all of its chlorine was available for disinfectant purposes; while the solution prepared with excess chlorine gave a powerful odor of chlorine, evolved chlorine when heated, on evaporation gave salt and chlorate of soda, and gave very little chlorine for disinfectant use."

The early experimentors on these solutions noted that controlling the alkali concentration of the solution to be treated with chlorine did not necessarily mean controlling the available chlorine concentration of the finished product but that chlorate and chloride appeared depending upon the amount of chlorine added. Thomas (1922) prepared a concentrated solution keeping the products cold during the reaction. This solution deteriorated rapidly. Mellor explains this by saying that as the solution becomes more concentrated there is sometimes a spontaneous transformation of hypochlorite to chlorate, furthermore, an excess of chlorine might act on hypochlorite, at ordinary temperature, liberating hypochlorous acid. Haskins (1898) claims that more concentrated solutions are less stable than the U. S. P. solution, while Griffin and Hedallen (1915) state that this concentration has very little to do with the stability of the solution. Barnett (1917) states that a 5.5% solution showed no deterioration in thirty days when kept in the dark but did show deterioration in the light. Wische (1917) states that a dilute solution lost 10% in two months while a concentrated solution lost 40%. Another writer reported that the hypochlorite solution lost chlorine steadily until it reached a state of equilibrium at about 1.7% available chlorine. Unfortunately none of the writers included any information relative to the degree of alkalinity of the finished product. Hence a logical interpretation of their information is not feasible.

The effect of the alkalinity, of the finished product, on the stability of the available chlorine content, has been commented upon by many. Balard first called attention to the effect of the degree of alkalinity. "The presence of a certain excess of base, prevents the conversion of the hypochlorite into chlorate and chloride, whereas it is rapidly effected when the acid is in excess." Cowley (1906), Brown (1909), Éwe (1920), and Thomas (1922) are only a few of the many who have stated that an increase in the alkalinity of the solution increases the stability since it retards the hydrolysis of the hypochlorite. However, the alkalinity being undesirable, attempts were made to eliminate this factor. Éwe suggested that a non-caustic alkali, such as lime, be used. Dakin and Carrel introduced the solution neutralized with boric acid. Dakin states that a so-called neutral solution of sodium hypochlorite is alkaline due to the production of sodium hydroxide by reaction between water and hypochlorites but nevertheless a solution neutralized with boric acid deteriorated very rapidly.

The other factor of importance influencing the stability of hypochlorite solutions that has been discussed at great length, is the temperature employed during the preparation and storing. Thus the components of the finished product may be influenced by the temperature at which the solution was prepared. The speed of deterioration depends upon the temperature at which it is stored and the temperature at which a solution is evaporated controls the purity of the resulting crystals. Mellor states that the optimum temperature at which a hypochlorite solution should be prepared is 27 degrees C. Above this temperature chlorates and chlorides are formed, proportionately to the degree of heat applied. In storing the solution it is generally required that it be kept in brown glass bottles in a

dark, cool place. Johanneson gives evidence to the wisdom of this rule. He reported that a 0.516% sodium hypochlorite solution lost 0.011% per week when stored in amber colored bottles at 18 degrees C., but only lost 0.006% when stored in a refrigerator at zero degree C.

Most of the work has been done on heating the prepared solution for use in applying to wounds and in attempting to prepare a crystalline hypochlorite. Durand states that no chlorine is lost on boiling the solution. LaWall (1895) tried evaporating the solution on a water-bath and in an air oven, and obtained a large percentage of hypochlorite loss both times. Éwe (1922) warmed a solution to 70 degrees C., reporting a loss of from 0.002% to 0.005% in available chlorine. Mellor states that if an excess of the alkali be present the solution can be dried *in vacuo* at ordinary temperature without much decomposition, may then be crystallized at -10 degrees C. with a resulting product of the following analysis: 37.6% sodium hypochlorite, 3.7% salt, and 58.7% water, and no chlorate. This particular analysis was made upon crystals from a solution prepared by passing chlorine into sodium hydroxide.

Whether the preparation of pure sodium hypochlorite crystals to be dissolved in water for extemporaneous solutions would eliminate some of the problems of decomposition is still to be determined.

REFERENCES (NO. 4).

- Cowley, PROC. AM. PHARM. ASSOC., 55, 673, 1907.
- Brown, *Brit. and Col. Drug.*, 55, 178, 1909.
- Elvoe, *Am. Jour. Pharm.*, 82, 161, 1910.
- Higgins, *Chemical News*, 109, 21, 1914.
- Dakin, *Brit. Med. Jour.*, 11, 318, 1915.
- Éwe, JOUR. AM. PHARM. ASSOC., 9, 46, 1920.
- Thomas, JOUR. AM. PHARM. ASSOC., 11, 940, 1922.
- Cohen, *Am. Jour. Pharm.*, 4, 205, 1833.
- Durand, *Am. Jour. Pharm.*, 4, 271, 1833.
- LaWall, *Am. Jour. Pharm.*, 67, 203, 1895.
- Mellor, "Inorganic Chemistry," 1922.
- Éwe, *Practical Drug.*, Dec. 1922.
- Lloyd, *Am. Jour. Pharm.*, 68, 298, 1896.
- Lauer, *Pharm. Ztg.*, 52, 954, 1907.
- , *Am. Jour. Pharm.*, 87, 590, 1911.
- Johanneson, *L. Arch. d' Pharm. et d' Chem.*, 27, 77, 1920.
- Haskins, PROC. AM. PHARM. ASSOC., 693, 1898.
- Griffin & Hedallen, *Jour. Soc. Chem. Ind.*, 34, 530, 1915.
- Bouret, *Bull. Sc. Pharmacol.*, 24, 347, 1917.
- Ursicho & Freiburger, *Münch. Med. Wochenschr.*, 64, 1528, 1917.
- Mulford & Co., *Drug Cir.*, 62, 25, 1918.
- Richter, *Chem. Zentrabl.*, 2, 306, 1919.
- Lauer, *Ibid.*, 52, 954, 1907.
- "A. M.," *Ibid.*, 79, 994, 1908.
- Graham, *Am. Jour. Pharm.*, 3, 148, 1832.
- Higgins, *Proc. Chem. Soc.*, 29, 302, 1913.

(NO. 5) CHEMISTRY.

Much has been offered on the chemistry of hypochlorite solutions, and a review of the literature leaves one still unsatisfied as to a complete understanding of the subject. Inasmuch as Labarraque's solution is practically the precursor to the more modern hypochlorite solutions, and has been official since 1840, a survey of the reacting ingredients as prescribed in the U. S. P. formulas with a possible theory of the chemistry involved is of interest.

1. *Sodium Carbonate as an Ingredient.*—The revisions of 1840 to 1870 inclusive, each prescribed carbonate of soda, which was described as "colorless crystals." The U. S. Dispensatories of 1843, 1854, 1865, and 1870 each give the formula of sodium carbonate as $\text{Na}_2\text{CO}_3 \cdot 12\text{H}_2\text{O}$. The 1880 and 1890 revisions of the U. S. P.

describe sodium carbonate, the official formula for this being given as $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The revisions of 1900 and 1911, however, direct the use of monohydrated sodium carbonate ($\text{Na}_2\text{CO}_3\text{H}_2\text{O}$).

"Twenty-four troy ounces" of the crystalline sodium carbonates were directed to be used in the revisions of 1840-70 inclusive representing eight troy ounces and 422 grains of anhydrous sodium carbonate. "One hundred parts" and "150 grams" of the crystalline sodium carbonate as prescribed by the revisions of 1880 and 1890, represent 37 parts and 55.5 Gm. of anhydrous sodium carbonate, respectively; and 65 Gm. and 70 Gm. of the monohydrated salt prescribed by the 1900 and 1910 revisions, represent 55.51 Gm. and 59.78 Gm. of anhydrous salt, respectively. Summarizing this, we have the following:

1840-70 (incl.)	24 troy oz. cryst.	8 troy oz. 422 grains of anhyd. salt
1880	100 parts	37 parts of anhydrous salt
1890	150 Gm.	55.5 Gm. of anhydrous salt
1900	65 Gm.	55.1 Gm. of anhydrous salt
1910	70 Gm.	59.78 Gm. of anhydrous salt

2. *Chlorinated Lime as an Ingredient.*—"Chlorinated lime" is directed to be used by all of the U. S. P. revisions containing Labarraque's solution. The revisions of 1840-70 inclusive prescribe "12 troy ounces;" the revision of 1880, prescribes 80 parts; that of 1890, 75 grams; that of 1900, 90 grams; and the 1910 revision prescribes 100 grams.

No purity rubric for chlorinated lime is given in the revision of 1840, and none is given in the U. S. Dispensatory of 1843. The revision of 1850-60-70, each state that chlorinated lime shall contain "at least 25% of chlorine." The revision of 1880 states "at least 25% of available chlorine," that of 1890, "at least 35% of available chlorine," and the last two revisions, *viz.*, 1900 and 1910, require not less than "30% of available chlorine."

The following table indicated the amount of available chlorine in the quantity of chlorinated lime prescribed:

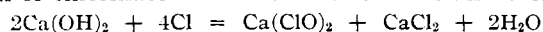
1840*-70 (incl.)	12 troy oz. chlor. lime	3 troy oz. of avail. Cl.
1880	80 parts chlor. lime	20 parts of avail. Cl.
1890	75 grams chlor. lime	26.25 Gm. of avail. Cl.
1900	90 grams chlor. lime	27 Gm. of avail. Cl.
1910	100 grams chlor. lime	30 Gm. of avail. Cl.

* Based on the assumption that the chlorinated lime used in 1840 was of the same strength as that of the three succeeding additions.

3. *Ratio of Ingredients.*—Due to the fact that chlorinated lime is a mixture of several compounds rather than one definite compound; and also that the sodium carbonate added may react, and undoubtedly does react with more than one of the ingredients of the chlorinated lime, the ratio of ingredients, because of the possible interpretation as to the compounds formed, may be computed in several ways, *viz.*:

- A. Based on the assumption that chlorinated lime is a compound of calcium chlor-hypochlorite CaOCl .
- B. Based on the quantity of available chlorine in chlorinated lime.

According to the National Standard Dispensatory, p. 382, the reaction, in the preparation of chlorinated lime from slaked lime and chlorine, is as follows:

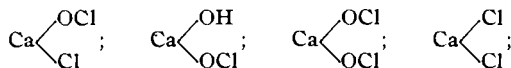


This reaction is based upon that between potassium hydroxide and chlorine, *viz.*:



However, it was found that chlorinated lime upon treatment with alcohol did not yield calcium chloride. Likewise it was noticed that chlorinated lime was not hygroscopic to the degree expected of a mixture containing calcium chloride. Hence it was concluded that the dry chlorinated lime consisted of mixed compound, *viz.*, CaOCl_2 or $\text{Ca} \begin{smallmatrix} \text{OCl} \\ \text{Cl} \end{smallmatrix}$. It is apparent that two molecules of this are equivalent to $\text{Ca}(\text{ClO})_2 + \text{CaCl}_2$. When chlorinated lime is treated with water, it is found to decompose, and, it is assumed into $\text{Ca}(\text{ClO})_2$ and CaCl_2 .

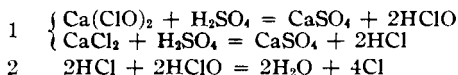
Erdman ("Anorg. Chem.") states that the following compounds are present:



and sometimes, but not always,



Schorloemer, Lunge and others (N. S. D., p. 382) have shown that after exhausting chlorinated lime with a little water, the resulting solution contains calcium and chlorine uniformly in the proportion required by the formula CaOCl_2 . Upon treatment with acids the following reactions take place;



If there is a larger percentage of CaCl_2 present than is represented by $[\text{Ca}(\text{ClO})_2 + \text{CaCl}_2]$ or 2CaOCl_2 , its chlorine will not be liberated, and therefore is not available chlorine. Hence, it follows that the amount of $\text{Ca} \begin{smallmatrix} \text{OCl} \\ \text{Cl} \end{smallmatrix}$ or CaOCl_2 may be computed from the percentage of available chlorine in the chlorinated lime.

Based on the requirement for available chlorine, the amounts of the compound $\text{Ca} \begin{smallmatrix} \text{OCl} \\ \text{Cl} \end{smallmatrix}$ present in the pharmacopœial quantities of chlorinated lime used would be as follows:

1840-70 (incl.)	188	Gm. CaOCl_2
1880	40.3	parts CaOCl_2
1890	52.9	Gm. CaOCl_2
1900	54.4	Gm. CaOCl_2
1910	60.4	Gm. CaOCl_2

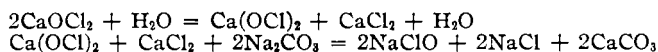
The quantities of anhydrous sodium carbonate representing the prescribed amounts of crystalline or monohydrated sodium carbonate used are as follows:

1840-70 (incl.)	276.2	Gm. anhyd. Na_2CO_3
1880	37	parts anhyd. Na_2CO_3
1890	55.5	Gm. anhyd. Na_2CO_3
1900	55.51	Gm. anhyd. Na_2CO_3
1910	59.78	Gm. anhyd. Na_2CO_3

Hence the ratio of chlor-hypochlorite to anhydrous sodium carbonate is as follows:

Chlor-hypochlorite : anhydrous sodium carbonate.		
1840-70.....	188	276.2
1880.....	40.3	37
1890.....	52.9	55.5
1900.....	54.4	55.51
1910.....	60.4	59.78

In the preparation of chlorinated soda solution, Sadtler and Trimble (Med. Chem.) state that the following reactions take place;

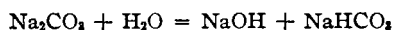


The computed weights of CaOCl_2 represented by the quantities of chlorinated lime prescribed by the U. S. P. and the weights of anhydrous sodium carbonate required in each case to complete the reaction are as follows:

	CaOCl_2	Anhyd. Na_2CO_3	Excess, Na_2CO_3
1840-70 (incl.).....	188 Gm.....	163.1 Gm.....	113.1 Gm.
1880.....	40.3 parts.....	34.9 parts.....	2.1 parts
1890.....	52.9 Gm.....	45.0 Gm.....	9.6 Gm.
1900.....	54.4 Gm.....	47.2 Gm.....	8.3 Gm.
1910.....	60.4 Gm.....	52.4 Gm.....	7.38 Gm.

A comparison of this table of the theoretical ratios with the above table of the ratios actually employed, shows that in every case an excess of sodium carbonate is employed. This accounts, in part at least, for the alkalinity of the solution.

4. *Solution of Sodium Carbonate.*—It is well known that when sodium carbonate is dissolved in water, the resulting solution does not contain sodium carbonate as such; but the products of hydrolysis. (Treadwell, "Anal. Chem.") The hydrolysis can be indicated by the following reaction:



Furthermore, heating the solution tends to decompose the bicarbonate forming carbonate, carbon dioxide and water;

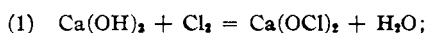


Inasmuch as hot water is used to effect the solution of sodium carbonate, the above reaction takes place to a certain degree. Hence it may be assumed that the solution prepared according to the U. S. P. directions contains:

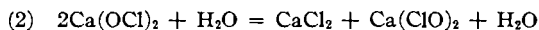
Na_2CO_3 , NaOH , NaHCO_3 besides trace of CO_2 . The latter may be considered negligible.

5. *Solution of Chlorinated Lime.*—Chlorinated lime is prepared by passing chlorine over dry freshly slaked lime. The exact chemical composition of the resulting compound is a matter of uncertainty. It is known that only part of it is soluble in water.

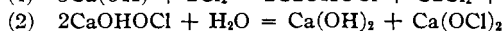
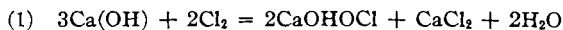
Sadtler and Coblentz (Pharm. Chem.) give the following reaction for the preparation of chlorinated lime:



upon dissolving the finished product in water, the following takes place:



Roscoe and Schorlemmer give the following reaction for the preparation and the subsequent solution in water:



In either case the substances assumed to be in solution are calcium hypochlorite, calcium chloride and undoubtedly traces of calcium hydroxide. Hence, upon mixing the solution of sodium carbonate with the "solution" of chlorinated lime the following are some of the possibilities that may result:

1. $\text{Ca}(\text{OCl})_2 + 2\text{NaOH} = 2\text{NaOCl} + \text{Ca}(\text{OH})_2$
2. $\text{Ca}(\text{OCl})_2 + \text{Na}_2\text{CO}_3 = 2\text{NaOCl} + \text{CaCO}_3$
3. $\text{Ca}(\text{OCl})_2 + 2\text{NaHCO}_3 = 2\text{NaOCl} + \text{Ca}(\text{HCO}_3)_2$
4. $\text{CaCl}_2 + 2\text{NaOH} = 2\text{NaCl} + \text{Ca}(\text{OH})_2$
5. $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 = 2\text{NaCl} + \text{CaCO}_3$
6. $\text{CaCl}_2 + 2\text{NaHCO}_3 = 2\text{NaCl} + \text{Ca}(\text{HCO}_3)_2$

Inasmuch as the insoluble calcium salts would be removed by filtration, the possible compounds in solution would be NaOCl; $\text{Ca}(\text{HCO}_3)_2$; NaCl; traces of $\text{Ca}(\text{OH})_2$ besides any excess of NaOH; Na_2CO_3 and NaHCO_3 that may have been used. Kavanagh claims that "oxychloride of sodium" and bicarbonate of sodium are found in this solution and not the hypochlorite and chloride of sodium. (*Am. J. Ph.*, 17, p. 226.)

LABORATORY EXPERIMENTS.

In Berthollet's original bleaching fluid the available chlorine content was the factor of prime importance. Later on as this, and especially *Labarraque's Solution*, became popular as an antiseptic and disinfectant the alkalinity of the product became an important factor because it was undesirable. With the development of the weak hypochlorite solutions for medical use the presence of other constituents called for comment as influencing the therapeutics of the solution. The principal one was the calcium salt, although a manganese salt was reported present at one time and its irritating effect on the tissues noted.

In concordance with the development of the requirements, and because of the feasibility of the order of additional requirements from the viewpoint of assay, laboratory investigations were conducted, first, on permanency of the available chlorine, second, on the degree of alkalinity; and, third, on the preparation of solutions in which an alkaline sodium salt was used, a neutral sodium salt, and a mixture of an alkaline and acid sodium salt, with subsequent determinations of hypochlorite, chlorite, chloride and alkalinity.

(1ST) AVAILABLE CHLORINE CONTENT.

Hypochlorite solution of zinc, lead, aluminum, magnesia, and sodium were prepared according to the U. S. P. process substituting in each case an equivalent amount of salt to react with the prescribed amount of chlorinated lime as follows:— to 100 Gm. of chlorinated lime (available Cl. 22%), 70 Gm. Sodium Carbonate, monohydrated, 112.7 Gm. Zinc Sulphate, 76 Gm. Magnesium Sulphate, respec-

tively, were added. To 150 Gm. of chlorinated lime 100 Gm. of Aluminum Sulphate was added and a 152.7 Gm. of chlorinated lime to 72.8 Gm. magnesium sulphate formed a second ratio. Basic lead acetate as well as other soluble metallic salts were used but the products were discarded as unsatisfactory for the time being. Determinations for available chlorine were made according to the U. S. P. method when the product was first prepared (November) and in January and May.

The following table presents a summary of the results:

TABLE I.

No. 1.		No. 4.	
Chlorinated lime	100 Gm.	Chlorinated lime	152.7 Gm.
Sodium carbonate	70 Gm.	Magnesium sulphate	72.8 Gm.
No. 2.		No. 5.	
Chlorinated lime	100 Gm.	Chlorinated lime	100 Gm.
Sodium carbonate	70 Gm.	Magnesium sulphate	76 Gm.
No. 3.		No. 6.	
Chlorinated lime	100 Gm.	Chlorinated lime	150 Gm.
Zinc sulphate	112.7 Gm.	Aluminum sulphate	100 Gm.

TABLE II.—AVAILABLE CHLORINE.

Solution.	Nov.	Jan.	May.	Alk. <i>N</i> /10 acid—1 cc.
No. 1	2.2	2.26	2.24	10.9
No. 2	0.73	0.73	0.12	10.6
No. 3	0.2	0.03	0	Neutral
No. 4	1.5	1.50	0.03	Neutral
No. 5	2.3	2.32	1.50	5
No. 6	0.18	0	0	15.5 (alk.)

(2ND) DEGREE OF ALKALINITY.

The alkalinity was determined according to Wesener and Teller's method, *vis.*:

To 2 cc. of the solution of sodium hypochlorite add 10 cc. of 10 per cent. potassium iodide solution and 25 cc. *N*/10 hydrochloric acid. To this add *N*/10 sodium thiosulphate until the brown color just disappears. Then titrate the excess acid with *N*/10 sodium hydroxide and report alkalinity in 1 cc.

The results were as follows:

Solution.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Degree of Alkalinity <i>N</i> /10 Acid 1 cc.	10.9	10.6	Neutral	Neutral	5	15.5 <i>N</i> /10 alk.

(3RD) COMPARABLE SODIUM HYPOCHLORITE SOLUTIONS.

Sodium hypochlorite solutions were prepared using (1) sodium carbonate, (2) sodium sulphate (3) mixture of sodium carbonate and sodium bicarbonate. Primary, secondary, and tertiary sodium phosphates were also used but the solutions obtained were rejected for the time being. The first three named solutions were assayed for hypochlorite, chlorate, chloride, and degree of alkalinity. For the preparation of the solutions the U. S. P. 1880 method was slightly modified, as follows:

Triturate the chlorinated lime with 500 mls of water; transfer the magma into a liter flask, agitate at intervals during a period of twelve hours, keeping the temperature at or below ordinary room temperature.

Dissolve the reacting salt in 500 mls of hot water, cool and add to the lime magma. Allow the mixture to stand for one hour shaking occasionally. Filter and wash the magma with sufficient water to collect 900 mls of finished product.

For assaying the solutions Carnot's Method (*Chemical News* (1896)), slightly modified, was used. It consisted of determining the hypochlorite content by measuring its oxidizing power on As_2O_3 (Penot's Method), the chlorate content by its action on ferrous sulphate and total chlorides by Volhard's silver nitrate method. The details of the technique are as follows:

TABLE III.

	Chlorinated lime (22% Cl)	112 grams
Sol. 1.	Sodium carbonate (monohyd.)	78 grams
Sol. 2.	Sodium sulphate	90 grams
Sol. 3.	{ Sodium carbonate (monohyd.) }	{ 46 grams
	{ Sodium bicarbonate }	{ 38 grams

The same amount of chlorinated lime was used in each solution.

ASSAY.

(1) *Hypochlorites*.—An aliquot portion of a known alkaline arsenic trioxide solution was titrated with the hypochlorite solution using starch iodide solution as the indicator.

(2) *Chlorates*.—The solution from (1) was made strongly acid with sulphuric acid and a definite amount of standardized ferrous sulphate added. This was then heated to 100° C., cooled, and the excess ferrous sulphate titrated with *N*/10 potassium permanganate solution V. S.

(3) *Chloride*.—The rose tint of the solution from (2) was removed with a trace of ferrous sulphate, an excess of *N*/10 silver nitrate V. S. added, and the excess titrated with *N*/10 ammonium thiocyanate V. S.

(4) *Alkalinity*.—This was determined as already outlined.

The results of these assays are as follows:

TABLE IV.

Solutions From.	Hypochlorites. Per cent.	Chlorates. Per cent.	Chlorides. Per cent.	Alkalinity <i>N</i> /10 acid—1 cc.
Sodium carbonate	2.21	0.27	2.54	7.9
Sodium sulphate	2.11	0.30	2.33	7.7
Sodium carbonate and Sodium bicarbonate	2.22	0.36	2.70	10.4

PREPARATION OF CRYSTALLINE SODIUM HYPOCHLORITES.

Attempts to obtain sodium hypochlorites in crystalline form were carried out as follows:

Based upon Mellor's Method 100 cc. portions of the solution, prepared from the mixture of sodium carbonate and sodium bicarbonate with chlorinated lime, were evaporated in a vacuum oven at room temperature until almost entirely crystallized. Then the mother liquor was filtered off and subjected to a freezing mixture at -10° C. when a second lot of crystals was obtained. The mother liquor was removed and the crystals analyzed. The mother liquor was then

evaporated in the oven until entirely crystallized and analyzed. The results are as follows:

TABLE V.

Crystals.	Hypochlorites.	Chlorates.	Chlorides.	Alkalinity % NaOH.
Crystals (10° C.)	14.83	0.02	5.58
Crystals (10° C.)	11.60	1.93	9.13	36.07
Crystals (10° C.)	11.61	1.99	9.25	26.77
Crystals from mother liquor	15.87	3.69	4.19
Crystals from mother liquor	20.38	3.66	3.58
Crystals	2.89	5.36	46.19	8.53
Crystals	3.12	5.35	57.72	8.88

The crystals prepared at -10° C. were very hygroscopic and dissolved in their own water of crystallization. No effort was made to purify them.

REFERENCES (NO. 5).

Mellor, "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," Longmans & Co., 1922.

Canot, *Chemical News*, 73, 157, 1896.

Wisener and Teller, *Am. Jour. Pub. Health*, 11, 613, 1921.

Elledge, *Chemical News*, 116, 64, 1917.

Williams, *Chemical News*, 107, 109, 1913.

Ruyz, *Jour. Chem. Soc. Lond.*, 114, 125, 1918.

Rideal, *Jour. Soc. Chem. Ind.*, 40, 64, 1921.

MacMillan, *Chem. Met. Eng.*, 23, 1064, 1920.

Coblentz and Vornik, "Volumetric Analysis," 1909.

Schimpf, "Manual of Volumetric Analysis," 1909.

(To be continued.)

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UNSOLVED PROBLEMS OF U. S. P. REVISION.*

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Some of the unsolved problems of the U. S. P. Revision are concerned with the organization, and methods of working, of the Convention and of the Revision Committee. Among these I know of nothing more important than the present-day method of spasmodically attacking the problem of revision. Every ten years a new committee is elected and it works very energetically for four or five years and then gives no further thought to the subject of revision until the next convention time rolls around. It would seem to me far better that the Committee should continue to work throughout the period of ten years and when this period comes to an end they should have the Pharmacopœia in proper condition for presentation to the Convention for its approval. This would avoid, I think, many of the imperfections which are bound to creep in under the present plan. We now base our

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