

tional to the absolute amount of carbon monoxide in the sample tested. For these tests a standard mixture of CO-O₂ was used. The carbon monoxide was prepared by the action of sulfuric acid on pure formic acid. The gas was liquefied and fractionated: the mixtures with oxygen were prepared for us by weight by Dr. Leo I. Dana of the Linde Air Products Company of Buffalo.

Procedure: Fill a 1000-cc. volumetric flask with distilled water and invert it over distilled water. Displace the water in the flask with the oxygen until less than 1 cc. of water remains in the inverted flask. Rapidly introduce 2 cc. of a saturated solution of palladious chloride, re-stopper and twirl the flask in order to bring the liquid and gas into intimate contact. The shaking is repeated intermittently for an hour and the mixture is then set aside for 12 hours in subdued light. Now add 2 cc. of ammonium molybdate solution (5 Gm. in 100 cc.), shake thoroughly and add 2 cc. of diluted hydrochloric acid. Allow the mixture to stand for one hour and then transfer to a suitable Nessler tube. Holding the tube over a white background and looking down through the liquid a bluish hue is observed in contradistinction to the yellowish green of a blank test.

DISCUSSION.

Using the foregoing procedure 10 p. p. m. of carbon monoxide in oxygen may be easily detected and in concentrations of 25 p. p. m. the deposit of metallic palladium prior to mixing with the ammonium molybdate solution is plainly visible. In applying this test many of the principal difficulties of the iodine pentoxide method are obviated. Nevertheless the non-specificity of the iodine pentoxide method obtains with the palladium procedure. Scrubbing with fuming concentrated sulfuric acid will easily remove one of the greatest offenders in this regard, namely, acetylene. As yet we have been unable to selectively absorb hydrogen, which if present in the oxygen tested in a concentration of 0.5 per cent gives a positive test.

Further experiments are being conducted to increase if possible the specificity of the test and to reduce the time required in which to perform it.

SUMMARY.

1. A procedure has been set forth for the purpose of detecting carbon monoxide in oxygen based upon the reduction of palladious chloride by the former. The sensitivity is of the order of magnitude of 10 p. p. m.

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A STUDY OF THE FACTORS INFLUENCING THE STABILITY OF LIQUOR MAGNESII CITRATIS, U. S. P. XI.*¹

BY GEORGE E. CROSSEN AND CHAS. H. ROGERS.

Osol and Tice, in a recently published paper (20), report that stable samples of Solution of Magnesium Citrate can be prepared from 15 Gm. of an official magnesium carbonate and 33 Gm. of citric acid if the potassium or sodium bicarbonate is withheld until the product is dispensed. Such solutions, of course, contain nei-

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ther carbon dioxide nor alkali citrate during their time of storage. In addition, the quantity of citric acid necessary for the formation of these substances is still present in the solutions and available for combination with the magnesium. From the fact that precipitation did not occur in these unfinished solutions, it might be inferred that the stability of the finished official solution is influenced by the presence of the carbon dioxide or the alkali citrate, or by the lesser concentration of acid that results when these substances are formed. A number of variations of Solution of Magnesium Citrate were prepared for the purpose of determining the effect of these and other factors upon the stability of the official solution.

Six series of solutions were prepared, each series consisting of 20 solutions. Each solution within a series was made to contain a concentration of magnesium salt or salts differing from that of any other solution in the same series. Solutions bearing the same number and appearing in different series were made to contain the same equivalent quantity of magnesium oxide. The magnesium oxide used in the preparation of the solutions was analyzed and a quantity used which was calculated to make the solutions contain the MgO equivalents indicated in Table I.

TABLE I.—MgO EQUIVALENTS USED IN THE PREPARATION OF SOLUTIONS.

Solution Number.	MgO Used in 350 Cc. of Solution, Grams.	MgO Equivalent in Each 100 Cc. of Solution, Grams.
1	5.6000	1.6000
2	5.6735	1.6210
3	5.7820	1.6520
4	5.9045	1.6870
5	5.9430	1.6980
6	5.9745	1.7090
7	6.0305	1.7230
8	6.0550	1.7300
9	6.0655	1.7330
10	6.0865	1.7390
11	6.0914	1.7404
12	6.1085	1.7453
13	6.1338	1.7525
14	6.1530	1.7580
15	6.2055	1.7730
16	6.2580	1.7880
17	6.3175	1.8050
18	6.4190	1.8340
19	6.5415	1.8690
20	6.6500	1.9000

The weight of citric acid used in the preparation of those solutions that were not to be carbonated by the addition of a bicarbonate was calculated by subtracting the amount of acid necessary to form the normal alkali citrate by reaction with the bicarbonate (1.75 Gm.) from the quantity of acid which U. S. P. XI directs for the preparation of each bottle of the solution (33 Gm.).

Each solution was prepared by adding an accurately weighed quantity of magnesium oxide to a solution containing the required amount of citric acid, making the solution up to volume, heating, filtering, etc., as directed in the U. S. P. To prevent the growth of molds, a small crystal of thymol was added to each solution that was not to be carbonated.

The solutions in series A were prepared by dissolving the required amount of magnesium oxide in 100 cc. of a solution containing 312.5 Gm. of citric acid per liter. This solution was then made up to 350 cc. with distilled water and treated as described above.

It was calculated that 2.5 Gm. of potassium bicarbonate would form 2.55 Gm. of normal potassium citrate. Therefore, this amount of anhydrous salt was added to each of the solutions in Series B. In all other respects, these solutions were the same as those in Series A.

The solutions in Series C were prepared by dissolving the magnesium oxide in 100 cc. of a solution containing 330 Gm. of citric acid per liter, making the solution up to volume with distilled water, and adding 2.5 Gm. of potassium bicarbonate to the cooled solution immediately before the bottle was stoppered.

Series D, E and F were prepared in the same manner as were series A, B and C, respectively, with the exception that 60 cc. of official syrup were added to each solution before it was made up to volume.

The quantities of dibasic and tribasic magnesium citrates that would be formed by the complete reaction of each amount of magnesium oxide used with 31.25 Gm. of official citric acid and which, therefore, should be contained in the solutions prepared, were then calculated. The results of these calculations are given in Table II.

TABLE II.—CALCULATED QUANTITIES OF MAGNESIUM CITRATES CONTAINED IN SOLUTIONS PREPARED.

Solution Number.	Gm. of Salt in Each 100 Cc. of Solution.	
	$MgHC_6H_6O_7 \cdot 5H_2O$.	$Mg_3(C_6H_5O_7)_2 \cdot 14H_2O$.
1	12.0800
2	12.2500
3	12.5000
4	12.7500
5	12.8500
6	12.9100
7	12.7500	0.2000
8	12.6900	0.3011
9	12.6500	0.3360
10	12.6000	0.3930
11	12.5350	0.4670
12	12.4365	0.5535
13	12.3500	0.6970
14	12.2250	0.8295
15	12.0500	1.0310
16	11.8140	1.5000
17	11.5500	1.6690
18	11.0750	2.1320
19	10.6000	2.7160
20	10.0000	3.2850

After the solutions had been prepared, they were set aside and allowed to age. During this period of aging, they were inspected regularly and the appearance of a precipitate was noted. All of the solutions remained clear for three days after their preparation. After the expiration of this time, however, several of the more concentrated samples began to show definite signs of precipitation. This was first noted in solution F 20, and then spread rapidly to the more concentrated solutions in Series D and E as well as to other members of Series F. It was not until after two weeks of standing that precipitation was noted in any of the solutions that did not contain syrup, and then only in the most concentrated of these, solution C 20. The following table (Table III) shows the results of a survey of the solutions six weeks after their preparation. In this table, those samples in which a precipitate was found are marked +, whereas those in which no precipitation had occurred are marked —.

TABLE III.—RESULTS OF EXAMINATION OF SIX-WEEK-OLD SOLUTIONS.

Solution Number.	MgO in 100 Cc., Grams.	Series.					
		A.*	B.**	C.′	D.″	E.†	F.††
1	1.6000	—	—	—	—	—	—
2	1.6210	—	—	—	—	—	—
3	1.6520	—	—	—	—	—	—
4	1.6870	—	—	—	—	—	—
5	1.6980	—	—	—	—	—	—
6	1.7090	—	—	—	—	—	—
7	1.7230	—	—	—	—	—	+
8	1.7300	—	—	—	—	—	+
9	1.7330	—	—	—	—	—	+
10	1.7390	—	—	—	—	—	+
11	1.7404	—	—	—	—	—	+
12	1.7453	—	—	—	+	+	+
13	1.7525	—	—	—	+	+	+
14	1.7580	—	—	—	+	+	+
15	1.7730	—	—	—	+	+	+
16	1.7880	—	—	+	+	+	+
17	1.8050	—	—	+	+	+	+
18	1.8340	—	—	+	+	+	+
19	1.8690	—	—	+	+	+	+
20	1.9000	—	—	+	+	+	+

* Plain aqueous solutions of the citrates of magnesium.

** Aqueous solutions with potassium citrate.

′ Carbonated aqueous solutions with potassium citrate.

″ Solutions to which syrup had been added.

† Solutions with syrup and potassium citrate.

†† Carbonated solutions with syrup and potassium citrate.

In Table III, the influence of the sucrose contained in the syrup is shown in Series D and E. In both of these series, the more concentrated solutions precipitated; whereas the solutions in Series A and B, to which no syrup had been added, remained clear even after six weeks of storage. The effect of carbonation is shown in Series C, in which the more concentrated solutions precipitated whereas the solutions in Series A and B did not; and in Series F, in which more solutions contained precipitates than in either Series D or E. As a result of these observations, it can be stated that sucrose and carbon dioxide each contributed to the instability of the solutions studied.

The table also shows that the presence of an alkali citrate had no appreciable effect upon the stability of the solutions, since neither series B nor E showed any more precipitation than Series A or D, respectively.

The most important observation, however, is that none of the less concentrated solutions precipitated, regardless of the influence of the factors already mentioned. This indicates that the factor primarily responsible for the precipitation is the concentration of magnesium contained in the solution. Since the solutions in Series F resemble the official Solution of Magnesium Citrate very closely, the stability of the official solution can be predicted by a consideration of the behavior of the solutions in this series.

Comparison of the results obtained by the study of the solutions in Series F (Table III), with the calculated quantities of magnesium citrates in the solutions prepared (Table II), shows that all of those solutions that were calculated to contain tribasic magnesium citrate deposited a precipitate under the conditions encountered in the official solution. On the other hand, no precipitation occurred in those solutions calculated to contain only dibasic magnesium citrate. These calculations were based upon the complete reaction of the citric acid with the amounts of magnesium oxide listed in Table I. From this it becomes apparent that those official solutions prepared from 33 Gm. of citric acid and a quantity of magnesium oxide varying from 5.6 Gm. to 6.0 Gm. would be stable after the bicarbonate had been added, and would be within the official concentration range for Solution of Magnesium Citrate.

U. S. P. XI directs that the solution be prepared from 15 Gm. of magnesium carbonate, which is defined as "equivalent to not less than 39.2 per cent and not more than 41.5 per cent of MgO" (23). An accurately weighed 15-Gm. portion of this substance, therefore, is the equivalent of from 5.880 Gm. to 6.225 Gm. of MgO. The data given in Table III shows, however, that solutions containing the equivalent of more than 6.0 Gm. of magnesium oxide are unstable. In order to produce a stable solution by the use of 15 Gm. of an official magnesium carbonate, therefore, a sample which is equivalent to between 39.2% and 40.0% of MgO must be used. Obviously, it is not always possible to obtain magnesium carbonate having a magnesium oxide equivalent within this rather limited range. However, a stable solution can be prepared from any sample of magnesium carbonate of known MgO equivalent by using that quantity of the sample calculated to make each 350 cc. of the finished solution contain the equivalent of from 5.6 Gm. to 6.0 Gm. of MgO.

The calculated quantities of various magnesium carbonates equivalent to 5.8 Gm. of magnesium oxide are given in Table IV. Use of the weight of magnesium carbonate indicated opposite the MgO equivalent of the sample will yield a solution which conforms to the U. S. P. XI requirement with regard to magnesium concentration, and which is stable and can be stored without fear of precipitation.

TABLE IV.—QUANTITIES OF VARIOUS MAGNESIUM CARBONATES TO BE USED IN THE PREPARATION OF 350 CC. OF LIQUOR MAGNESII CITRATIS.

MgO Equivalent of Carbonate, Per Cent.	Wt. of Carb. to Be Used, Gm.	MgO Equivalent of Carbonate, Per Cent.	Wt. of Carb. to Be Used, Gm.
37.0	15.67	40.6	14.28
0.2	15.59	0.8	14.21
0.4	15.50	41.0	14.15
0.6	15.42	0.2	14.08
0.8	15.34	0.4	14.00
38.0	15.26	0.6	13.95
0.2	15.18	0.8	13.87
0.4	15.10	42.0	13.81
0.6	15.02	0.2	13.74
0.8	14.95	0.4	13.68
39.0	14.87	0.6	13.61
0.2	14.80	0.8	13.55
0.4	14.72	43.0	13.49
0.6	14.64	0.2	13.43
0.8	14.57	0.4	13.36
40.0	14.50	0.6	13.30
0.2	14.43	0.8	13.24
0.4	14.36	44.0	13.18

SUMMARY AND CONCLUSIONS.

(1) The influence of syrup; of potassium citrate; of carbon dioxide; of varying magnesium concentration; of a lesser concentration of citric acid; and of

combinations of two or more of these factors upon the stability of solutions of the citrates of magnesium was studied.

(2) The stability of these solutions was dependent upon the quantity of magnesium oxide used in their preparation, and was influenced by the presence of sucrose and carbon dioxide.

(3) Stable samples of Solution of Magnesium Citrate can be prepared according to the official formula if the magnesium carbonate used is the equivalent of from 39.2% to 40.0% of MgO. Since it is impractical, if not impossible, to obtain magnesium carbonate having an MgO equivalent within this range, the use of calculated quantities of magnesium carbonates having other equivalents is suggested and a table is given by means of which the necessary quantities of these carbonates can be ascertained

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PROFESSOR KARRER, NOBEL PRIZE WINNER.

The Nobel prize for chemistry has been divided between Prof. Dr. Paul Karrer of Zurich and Prof. W. N. Haworth of Birmingham, England. Professor Karrer, a native Swiss, is 48 years old. He served a year as assistant to Professor Werner at Zurich and then for six years was associated with Paul Ehrlich. In the spring of 1918 he was called to Zurich University as special professor and in the following year he was appointed ordinarius in the entire field of chemistry. In 1923 Karrer received the Marcel Benoist prize, a Swiss award, for his research on carbohydrates. In recent years Karrer's investigations of vegetable coloring matter and the vitamins have gained him an international reputation. The Nobel prize was awarded him in recognition of his research on the carotenoids, the flavins and vitamins A and G. A few years ago he also received the degree of doctor honoris causa from the medical faculty of Breslau University.

Professor Haworth received the prize in recognition of his research on carbohydrate and vitamin C.—*J. A. M. A.* (January 1, 1938).