

A STUDY ON SOME CALCIUM AND MAGNESIUM SALTS OF COMMERCE.

BY G. G. COLIN.*

Not very long ago, a large number of pharmacies in this city were fined heavily by the Health Department. Inspectors had found that the stock of Magnesium citrate was adulterated, that it contained large amounts of tartrate in some cases, and in others the substance was entirely tartrate instead of citrate. Further investigations disclosed that the adulteration, so-called, had been unintentional on the part of the pharmacists. They had acquired their supply from a European firm and, apparently, there was no special restriction about using one or the other salt in that country. However, the Mexican Pharmacopœia requires absolute freedom from tartrate in magnesium citrate and, therefore, the product was declared misbranded.

Later, other magnesium salts were found impure, the oxide and the carbonate, and calcium carbonate was also found to be unfit for medicinal use in some cases. The Health Department confiscated all of the material from the distributors.

An examination of our stock of magnesium citrate taken from an original, imported, sealed bottle, revealed the large amount of tartrate present. No quantitative estimation was made. A qualitative examination of some samples of our magnesium oxide and carbonate gave the following results:

TABLE I.

Sample.	Amount.	Sol.	Effervesc.	Iron.	Sulph.	Chloride.	Phosph.
1. Carbonate	2.00 Gm.	5 cc.	xxxxx	xx	—	—	—
2. Carbonate	2.00 Gm.	5 cc.	xxxxx	x	—	—	—
3. Carbonate	2.00 Gm.	5 cc.	xxxxx	x	x	—	—
4. Oxide	2.00 Gm.	6 cc.	xx	x	xxx	x	—
5. Oxide	2.00 Gm.	5 cc.	xx	x	x	x	—
6. Oxide	2.00 Gm.	5 cc.	x (slight)	x	—	—	—
7. Oxide	2.00 Gm.	5 cc.	—	xxx	xxx	xx	—

x denotes traces. All samples dissolved to a clear solution using conc. HCl; a yellowish tint was observed in all of them, when in solution.

The magnesium carbonate samples did not show any striking variation from average medicinal product. However, the oxides called our attention, especially Samples 4 and 5. According to the Mexican Pharmacopœia, an F. M. product must yield at least 41.5% MgO upon calcination according to the following, taking basic Magnesium carbonate:

$$\frac{5 \text{ MgO}}{4 \text{ MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}} = \frac{5 \times 40.32}{485.70} \times 100 = 41.50\% \text{ MgO}$$

Samples Numbers 2, 3, 4, 5 and 6 were taken for calcination tests, to determine the fixed residue. The following results were obtained:

TABLE II.

Sample.	Amount.	Residue.	% MgO.	Loss (CO ₂ , H ₂ O, etc.).
2. Carbonate	1.00 Gm.	0.4244	42.44	57.56%
3. Carbonate	1.00 Gm.	0.4300	43.00	57.00%
4. Oxide	1.00 Gm.	0.9400	94.00	6.00%
5. Oxide	1.00 Gm.	0.6160	61.60	38.40%
6. Oxide	1.00 Gm.	0.5980	59.80	40.20%

* Central Chemical Laboratory of the Drogueria y Botica Central, Mexico.

Samples 2 and 3 gave approximately the correct amount of MgO to be expected of magnesium carbonate. Sample 4, an oxide, showed a slightly lower MgO content than that required, 96%. Samples 5 and 6 showed a peculiar behavior towards gentle heat. These two products were labelled "Heavy Calcined Hydrated Magnesia." Very copious effervescence was observed upon addition of acids, more than would be expected from the traces of carbonate allowed by the U. S. P. or the F. M. The determination of fixed residue in these two samples was rather troublesome. A low alcohol flame could not be allowed a very long contact with the crucible without causing a violent effervescence with loss of material. It was necessary to apply the low alcohol flame very cautiously for about 10-20 minutes until all the gas and moisture were driven out; then the calcination could be completed without trouble. Several other samples were tested to see if that low degree of heat would cause decomposition but, of course, neither the ordinary oxides or carbonates were affected at all by that amount of heat. Evidently this kind of material contains an excess of moisture and its fixed residue corresponds to approximately the amount of MgO yielded by $Mg(OH)_2$, about 60%.

The agents for the manufacturers of this product were called to give us some data regarding the composition of their product. They claimed that their product was a special one, a derivative of MgO containing water of hydration. The manufacturers submitted an analysis of their product claiming the following composition:

Hydrate of Magnesia ($Mg(OH)_2$).....	96.97%
Magnesium Oxide (MgO).....	66.67%
Basic Magnesium Carbonate.....	1.30%
Iron Oxide.....	0.02-0.08%

This product is not specified either in the F. M. or in the U. S. P. where we see Heavy and Light Magnesium Oxides and Magnesium Carbonate with 96% and 40% MgO respectively. Magnesium hydroxide is recognized in the pharmacopœias as magnesia magma or milk of magnesia, not as heavy or light $Mg(OH)_2$ powder.

The solubility tests confirmed the excess of carbonate (more than 1.30%), for both $Mg(OH)_2$ and MgO are rather insoluble products. The tests carried out as specified in the U. S. P. IX gave residues of about 0.18 Gm., checked volumetrically by titrating the alkalinity of the solution and calculating as $MgCO_3 \cdot 3H_2O$. The maximum amount of soluble salts according to the U. S. P. IX is 0.01 Gm. for the carbonate, and 0.02 Gm. for the oxide, heavy or light, per Gm., and in this case we have almost ten times the maximum limit of soluble salts.

Both pharmacopœias allow a slight alkalinity in the hot water extract of the sample and a slight effervescence upon addition of acids. In this case we had a marked alkalinity and production of gas, indicating an appreciable amount of carbonate. It was not determined whether a sample of $Mg(OH)_2$ powder is capable of taking up from the air an excessive amount of CO_2 inside of a well-sealed tin can, such as the manufacturers use as containers for their product.

CALCIUM CARBONATE.

Calcium carbonate had also been found by the Health Authorities to be an impure product. This was true of certain European brands, for there is still pref-

erence for them in spite of the fact that American-made products are as good, and in many cases better than the European similars. A qualitative examination, using two Gm. samples of seven different brands, dissolved in HCl and HNO₃ plus 10 cc. distilled water, gave the following results:

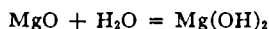
TABLE III.

Sample.	Solution.	SO ₄ .	P ₂ O ₅ .	Cl.	Fe.	H ₂ S.
1. CaCO ₃	Opales	x	xxxx	—	xx	—
2. CaCO ₃	Clear	xxx	xx	—	xxx	—
3. CaCO ₃	Clear	xxx	xxx	—	xx	—
4. CaCO ₃	Clear	xxx	xxx	—	xx	—
5. CaCO ₃	Clear	x	x	—	x	—
6. CaCO ₃	Clear	xxxx	x	—	xxxxx	xx
7. CaCO ₃	Clear	xx	xxx	—	xxxxx	—
8. CaCO ₃ (Pptd.)	Clear	x	—	—	x	—

Sample No. 1 was an impure product for industrial use and was used as a basis for comparison, and Sample 8 was pure precipitated calcium carbonate. The others were samples of so-called prepared chalk. All of them except No. 1 were taken from original packages purchased in the open market. One "x" denotes traces of the impurity sought. All the solutions in HCl, except the one from No. 8, had a slight yellowish tint indicating Fe, and gave strong reactions with potassium ferro and sulphocyanides. It will be noticed that some of the prepared chalk samples contained more Fe than the crude industrial product. The same will be noticed about sulphates. The crude salt and the precipitated sample contained considerably less SO₄ than any of the others. With exception of No. 8 nearly all the other samples contained almost as much phosphate as the crude calcium carbonate. And the worst of all: a very handsomely wrapped product labelled "Pure, for Medicinal Use" contained a very appreciable amount of sulphide as shown by the evolution of H₂S when dissolving the sample. In many cases the only difference between the crude product and some of the "pure" ones was the insoluble matter contained in the former; if this was filtered, the solution contained impurities in smaller amounts.

DISCUSSION.

A discussion was raised as to what "Heavy, calcined, hydrated magnesia" meant. This product has great demand in pharmacy on account of its smaller volume when used in cachets, papers, etc., and for some reason or other, most probably on account of its lower price, is mostly used by pharmacists. As a laxative, there is not much difference between the oxide, the carbonate and the hydrate. The result is that this particular product is used whenever heavy magnesium oxide or heavy magnesium carbonate is called for in a prescription. There is very little difference, if any, between magnesium hydroxide and a "heavy or light calcined hydrated magnesia." The alleged hydration takes place according to the equation:



These two Magnesias, says Arny (Principles of Pharmacy), and referring to Magnesii Oxidum and Magnesii Oxidum Ponderosum, are prepared by the calcination of light and heavy magnesium carbonates from cold dilute solutions or from

hot concentrated solutions. The medicinal use of light and heavy magnesia is identical, both being laxative and antacid; the advantage of the heavy magnesia depending entirely upon its greater density, the average heavy magnesia occupying only about one-quarter the bulk of the light magnesia. In some cases the same substance can be precipitated in a light, flocculent form or in a heavy, granular form, giving rise to the distinction between "light" and "heavy" precipitates.

It is evident then, that "Heavy, calcined, hydrated magnesia" is some kind of "heavy magnesium hydroxide" containing appreciable amounts of magnesium carbonate of the "heavy" kind. It is worth while noticing that heavy magnesias, except this particular kind, are more expensive and scarce in this market so that their use is rather limited.

Regarding calcium carbonate it is astonishing to find products for medicinal use with impurities such as observed in this rather elementary study. The presence of sulphides is inexcusable and dangerous. Other impurities were found in larger amounts than in crude industrial chalk. It is hoped that the present campaign initiated and carried out by our Health Department will put an end to the introduction of drugs and drug-products unfit for medicinal use.

August 20, 1927.

A PHARMACOLOGICAL NOTE ON BAPTISIA TINCTORIA.

BY DAVID I. MACHT AND JAMES A. BLACK.

INTRODUCTORY.

Baptisia Tinctoria is a plant which has been described in the United States Dispensatories of all the older editions and is still to be found mentioned in the latest 21st edition of the Dispensatory of the United States published in 1926. While the value of this drug is open to question all kinds of extravagant claims have been made in regard to its medicinal virtues in all of the works. Thus we read of its being used as an emetic, cathartic, "hepatic and intestinal stimulant" and of its having been recommended in the treatment of Typhus, Scarlet Fever, Dysentery, and also of its virtues as a nervous stimulant, antipyretic, etc. Locally, preparations of this drug have been used for the treatment of laryngitis and applications to foul ulcers. The U. S. Dispensatory mentions the following N. F. preparations: **Dentifricium** N. F. and **Fluidextractum Baptisiæ** N. F. Perhaps the commonest use of this drug which is still prevalent is as an ingredient of certain mouth washes and dentifrices on account of its peculiar stinging and tingling taste to the buccal mucous membranes. Inasmuch as very little is known concerning the pharmacology of this drug a brief pharmacological examination was made of it by the authors and is here reported.

HISTORICAL.

The drug *Baptisia Tinctoria* or wild indigo comes on the market as the **Radix Baptisiæ Tinctoriæ** and is the dried Rhizome and roots of *Baptisia Tinctoria* a perennial herb growing in the eastern United States and Canada (1). The taste of the root is extremely bitter and acrid, producing a tingling sensation of the mucous membranes of the lips, mouth and tongue. While the pharmacology of the sub-