

amber glass containers, and it is recommended that they be dispensed on prescriptions in the same type of container, instead of the usual prescription bottle.

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A METHOD FOR THE QUANTITATIVE ESTIMATION OF SULPHUR  
COMBINED AS SULPHIDES IN POTASSA SULPHURATA  
(LIVER OF SULPHUR).\*

BY CHARLES H. ROGERS.

"Sulphurated Potassa is a mixture composed chiefly of potassium polysulphides and potassium thiosulphate and contains not less than 12.8 per cent of sulphur (S) in combination as sulphides."—U. S. Pharmacopœia, Tenth Revision.

PREPARATION AND DESCRIPTION OF POTASSA SULPHURATA.

This product is made by thoroughly triturating one part of sublimed sulphur with two parts of potassium carbonate, placing the mixture in a covered crucible, and heating until the mass is in a state of perfect fusion. The melt is then poured upon a slab and when cool is broken into pieces of convenient size and stored in a well-stoppered bottle.

The composition of the product thus obtained varies according to the amount of heat employed. Any of the following reactions may occur.<sup>1</sup>

1.  $3K_2CO_3 + 6S_2 = 2K_2S_5 + K_2S_2O_3 + 3CO_2$ .
2.  $3K_2CO_3 + 4S_2 = 2K_2S_3 + K_2S_2O_3 + 3CO_2$ .
3.  $4K_2CO_3 + 5S_2 = 3K_2S_3 + K_2SO_4 + 4CO_2$ .

Therefore, it will be noted that sulphurated potassa is not a definite chemical compound but a mixture of the polysulphides, the sulphate and the thiosulphate of potassium.

The synonym, liver of sulphur, alludes to the liver-brown color of the freshly prepared material. Upon exposure to air sulphurated potassa absorbs moisture and carbon dioxide and is changed from a brown to a greenish yellow color, and eventually to a gray mass, which consists of potassium carbonate, potassium thiosulphate and potassium sulphate. This decomposition renders it nearly worthless as a therapeutic agent.

ASSAY OF POTASSA SULPHURATA.

U. S. P. X METHOD.

"Dissolve 1 Gm. of crystallized copper sulphate accurately weighed, in 15 cc. of distilled water and 1 Gm. of Sulphurated Potassa accurately weighed in 10 cc. of distilled water, in a flask. Add the copper sulphate solution to the sulphurated potassa solution in a stoppered flask, shake for a few minutes and filter. Acidulate the filtrate with acetic acid, refilter if necessary and add an equal volume of hydrogen sulphide T. S. No black precipitate is produced."

The result obtained by this method of assay indicates only whether the compound is above or below the official requirement. This test does not give results

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\* Scientific Section, A. Ph. A., St. Louis meeting, 1927.

<sup>1</sup> "Principles of Pharmacy," H. V. Army, Second edition, page 412.

that can be interpreted in terms of sulphur combined as sulphides in the sample. A lesser amount of sulphur combined as sulphides than required by the U. S. P. results in part of the copper sulphate being present in the filtrate, from which the copper ions can be precipitated as black copper sulphide upon the addition of hydrogen sulphide T. S.

#### PROPOSED METHOD OF ASSAY OF SULPHURATED POTASSA.

##### Apparatus required:

1. Two 150-cc. glass-stoppered flasks.
2. Two 400-cc. beakers.
3. One 25-cc. standard pipette.
4. Two 5-cm. chemical funnels and filter paper.
5. Hydrogen sulphide generator.
6. Suction filter, drying oven and muffle furnace.
7. Two Gooch crucibles.

The crucibles must be carefully prepared in order to facilitate filtration. A small quantity of soaked asbestos fibre, sufficient to form a layer of the fibre about one cm. thick on the bottom of the crucible, is placed in a freshly ignited and cooled Gooch crucible, the suction turned on and the fibre pressed down gently to form a cup-shaped layer. If too much pressure is used the layer becomes too firm and the filtration period is greatly lengthened. The asbestos is washed with distilled water, then with alcohol, and ether and finally dried in an oven. The crucibles are placed in a muffle furnace and heated to constant weight.

##### Reagents:

1. *Copper Sulphate Solution.*—Dissolve about 15 Gm. of crystallized copper sulphate accurately weighed, in sufficient distilled water to make 250 cc. at 20° C., using a standard volumetric flask.

##### Procedure:

The method given below permits two or more determinations being run at the same time. Dissolve about 1 Gm. of sulphurated potassa, accurately weighed, in 15 cc. of distilled water in a stoppered flask. Add 25 cc. of the standard copper sulphate solution, stopper the flask, agitate for a few minutes and filter. Rinse the flask thoroughly with warm distilled water and pass the rinsings through the filter. Wash the precipitate and filter thoroughly with warm distilled water until all of the excess copper sulphate has been removed. Test the washings with ammonium hydroxide for the presence of copper ion. When they no longer contain any copper ion, slightly acidulate the filtrate with diluted acetic acid and warm to about 70° or 80° C. Slowly pass hydrogen sulphide through the filtrate until the copper ions have been completely precipitated as black copper sulphide and which collect at the bottom of the container. This operation requires at least ten minutes for the complete precipitation of the copper ions. It should be noted that copper ion is not precipitated by thiosulphate ion. With concentrated solutions a small amount of free sulphur is precipitated which, as will be shown later, does not affect the accuracy of the determination. Filter off the precipitate through a tared Gooch crucible and wash thoroughly with distilled water. Test the filtrate with ammonium hydroxide for the presence of copper ion and, if absent, wash the precipitate first with alcohol and then with ether. If a positive test is obtained it is quite evident that the copper ions have not been completely precipitated and more hydrogen sulphide should be passed into the liquid. When the precipitation is complete, dry the washed copper sulphide in a hot-air oven to remove moisture. Ignite the dried precipitate to constant weight in a muffle furnace at dull red heat. From two to three hours are required for the complete conversion of the copper sulphide to copper oxide.

In the method described all of the sulphur combined as sulphides in the sample is precipitated as copper sulphide by the copper ions. The excess copper ions then pass through the filter and are precipitated as copper sulphide by hydrogen sulphide. At this point free sulphur is also thrown down, a condition which makes it impossible to dry and weigh the copper sulphide obtained from the excess copper ions. The very tedious task of washing the precipitate free from sulphur leads to many errors and loss of time. Therefore, it was thought expedient to convert the copper sulphide to copper oxide by ignition and burn up the sulphur during the operation.

In order to express the per cent of sulphur combined as sulphides in a sample of sulphurated potassa, it is necessary to obtain the copper sulphide equivalent of 25 cc. of the standard copper sulphate solution. The number of Gm. of copper sulphate in 25 cc. of the standard solution is multiplied by the factor 0.3829, thus giving the equivalent in terms of copper sulphide. The copper sulphate content of the standard copper sulphate solution was also determined quantitatively and, where clean, uneffloresced crystals had been used in making the solution, was found to check very closely with the weighed amount used in making the standard solution. The copper oxide from which the final weighing is obtained also must be expressed in terms of copper sulphide and hence the weight of the residue is multiplied by the factor 1.2018. This weight is subtracted from the copper sulphide equivalent of the 25 cc. of standard copper sulphate solution and the difference is the amount of copper sulphide which has been precipitated by the interaction of copper ions of the standard copper sulphate solution and the sulphide ions present in the solution of sulphurated potassa. This amount of copper sulphide is then calculated to combined sulphur by multiplying by the factor 0.33525, the product being the actual amount of sulphur combined as sulphides in the sample. The per cent of sulphur combined as sulphides is obtained by multiplying the weight of sulphur combined as sulphides by 100 and dividing the product by the original weight of sulphurated potassa used for analysis.

*Example:* 1.0988 Gm. sulphurated potassa taken for analysis.

1.50274 Gm. copper sulphate present in 25 cc. of standard copper sulphate solution.

$1.50274 \times 0.3829 = 0.5754$  Gm. equivalent in terms of copper sulphide.

0.1310 Gm. weight of copper oxide residue.

$0.1310 \times 1.2018 = 0.1574$  Gm. equivalent in terms of copper sulphide.

0.5754 Gm.

0.1574 Gm.

0.4180 Gm. copper sulphide precipitated by sulphide ions present in the solution of potassa sulphurata.

$0.4180 \text{ Gm.} \times 0.33525 = 0.13401$  Gm. sulphur combined as sulphides in the sample.

$\frac{0.13401 \text{ Gm.} \times 100}{1.0988 \text{ Gm.}} = 12.75$  per cent of sulphur combined as sulphides in the sample of sulphurated potassa.

#### EXPERIMENTAL RESULTS OBTAINED.

##### SAMPLE 1.

Determination 1. 15.88 per cent of sulphur combined as sulphides.

Determination 2. 15.91 per cent of sulphur combined as sulphides.

Determination 3. 15.26 per cent of sulphur combined as sulphides.

Determination 4. 15.19 per cent of sulphur combined as sulphides.

## SAMPLE 2.

Determination 1.	14.11	per cent of sulphur combined as sulphides.
Determination 2.	14.12	per cent of sulphur combined as sulphides.
Determination 3.	14.19	per cent of sulphur combined as sulphides.
Determination 4.	14.44	per cent of sulphur combined as sulphides.
Determination 5.	14.17	per cent of sulphur combined as sulphides.
Determination 6.	14.29	per cent of sulphur combined as sulphides.
Determination 7.	14.35	per cent of sulphur combined as sulphides.
Determination 8.	14.39	per cent of sulphur combined as sulphides.

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### A SOURCE OF ERROR IN THE ASSAY OF BELLADONNA PLASTER.\*

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Assays of belladonna plasters having yielded low results, samples of the same lot were submitted to me for analysis and the results showed that the material fully met the U. S. P. standard of "not less than 0.25 per cent and not more than 0.30 per cent of the alkaloids of belladonna leaves." I conducted a series of experiments to determine the cause of the low results obtained by the other analyst.

The following method for the assay of Belladonna Plaster official in U. S. P. X, page 129, was employed in making the analyses:

Introduce 10 Gm. of Belladonna Plaster into a 100-cc. flask. (If the plaster is spread on fabric, cut the portion to be assayed into strips, weigh accurately and introduce it into the flask.) Now add 50 cc. of chloroform, and shake the mixture until the plaster is dissolved. Pour the chloroform solution into a 250-cc. beaker, and wash the cloth upon which the plaster was spread with two successive portions of 25 cc. each of chloroform, adding the washings to the chloroform solution in the beaker. Then wash this cloth with 80 cc. of alcohol containing 1 cc. of ammonia T. S., and pour the washings into the chloroform solution in the beaker. Stir the mixture gently, and allow it to stand until the rubber has separated into a compact mass. Dry the cloth upon which the plaster was spread, weigh it, and subtract its weight from the first weight of the plaster. Pour the chloroform-alcohol solution into a 250-cc. separator, rinse the beaker and rubber with 10 cc. of alcohol, and add the rinsing to the separator. Completely extract the alkaloids from the chloroform-alcohol solution by shaking out repeatedly with weak sulphuric acid. Collect the acid washings in a separator, and add ammonia T. S. until the solution is decidedly alkaline to litmus paper, and completely extract the alkaloids by shaking out repeatedly with chloroform. Filter the chloroform solution through a pledget of purified cotton, evaporate it to dryness and dissolve the alkaloids from the residue in exactly 5 cc. of tenth-normal sulphuric acid and titrate the excess of acid with fiftieth-normal potassium hydroxide.

The U. S. P. on page 453, "Proximate Assays," "General Directions for Alkaloidal Assays," under the heading "Shaking Out with Acid," states that

"After extracting with the several portions of acid, test a few drops of the last portion used, for the presence of alkaloid. Extraction must be continued until not more than a very faint cloudiness results upon the addition of a drop of mercuric potassium iodide T. S. or, in the case of hydrastis or colchicum, upon the addition of a drop of iodine T. S."

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