

At one volume none of the three cohobates deposited any crystals at ordinary temperature but at two volumes the second cohobate was induced to deposit a few; though in every case a turbidity resulted on the first dilution, which increased with the second dilution.

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#### A MORE PRACTICAL ASSAY PROCESS FOR SOME U. S. P. ZINC SALTS.\*

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The burdens of this communication are to emphasize the impracticability of the sulphide method of determining zinc in some U. S. P. zinc salts and to suggest the substitution therefor of the more practical ferrocyanide titration method.

The difficulties surrounding the application of the sulphide method are familiar to every analyst. The chief difficulties are the lack of assurance that the precipitation is complete, the necessity of allowing the precipitate of zinc sulphide to stand with warming for at least eighteen hours in order to complete the precipitation and obtain the precipitate in a sufficiently coagulated form to permit it to be collected on the filter and, most exasperating of all, the difficulty of properly washing the precipitate after it has been collected on the filter. The precipitate is usually so slimy that it is only with the exercise of the most extreme patience that proper washing can be effected at all. In addition to these difficulties, there remain the non-assurance that the treatment of the sulphide with nitric acid is really dissolving out all of the zinc (and that it is not being occluded by the clumps of sulphur formed by the reaction) and the persistence of some of the finely divided sulphur in passing through the filter with the possible production of varying small proportions of sulphate or sulphide in the weighed zinc oxide.

The accuracy of the sulphide method is above question where precise results are required and the proper precautions are observed to obtain these results, but where practical results are desired in a minimum of time the ferrocyanide titration method is infinitely superior.

The U. S. P. zinc salts which are now directed to be assayed by the sulphide method and to the assay of which the ferrocyanide titration method is applicable are the acetate, phenolsulphonate, sulphate and valerate. In addition, it is preferable to assay the chloride and the metal by this method.

The details of the ferrocyanide titration method, as found practicable in this laboratory, are as follows:

*Standard Solution Potassium Ferrocyanide.*—Dissolve 40 Gm., roughly weighed, of potassium ferrocyanide in enough distilled water to obtain a yield of 1000 Cc. Mix well and standardize as follows: Weigh accurately about 0.3 Gm. of chemically pure metallic zinc; place the weighed zinc in a beaker; dissolve it in 10 Cc. of U. S. P. hydrochloric acid; add about 100 Cc. of distilled water; neutralize with ammonium hydroxide; make barely acid with U. S. P. hydrochloric acid and add about 3 Cc. excess of the acid; add 10 Cc. saturated solution of ammonium chloride; heat nearly to boiling and titrate with the standard solution of potassium ferrocyanide, using a 5% solution of uranium acetate or nitrate acidified with

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a few drops of U. S. P. hydrochloric acid, as a "spot" indicator on an opal glass plate. The end reaction is the production of a brown colored "spot" on the plate. Calculate the volume of standard solution used into terms of metallic zinc to which each Cc. of standard solution is equivalent. Time can be saved in standardizing and in making assays for zinc by first running a rough test in order to ascertain the approximate volume of standard solution which will be required, and then in making the actual assay, running in about 1 Cc. less than will be required and finishing the titration by adding 0.1 Cc. at a time and testing by the "spot" test after each addition of the standard solution.

In applying this method of assay to the zinc salts mentioned above, the salts are dissolved in a minimum of water, then 10 Cc. of U. S. P. hydrochloric acid are added and the assay proceeded with as in the determination of the strength of the standard solution.

The application of this method to the assay of metallic zinc merely involves a repetition of the standardization procedure.

The ferrocyanide titration method is extremely short, requiring less than one-half hour for duplicate assays after the standard solution of potassium ferrocyanide has been standardized, contrasted with at least the full day required by the sulphide precipitation method. The ferrocyanide titration method has the additional advantage that the presence of lead exerts no influence on the results, whereas the sulphide method includes any lead which may be present.

The accuracy of the ferrocyanide method is without question, since it is primarily based upon standardization by a definitely known quantity of chemically pure metallic zinc.

In order to ascertain if the acetic, hydrochloric, phenolsulphonic, sulphuric and valeric radicles of the U. S. P. salts of zinc, to which it would be desirable to apply this method, would have any appreciable influence on the accuracy of the method, the following experiments were conducted:

*Zinc Acetate.*—Definite weights of Baker's chemically pure metallic zinc were dissolved in hydrochloric acid and acetic acid, in small excess of the theoretical proportion which would be present if zinc acetate equivalent to the metallic zinc used were present, was added. Triplicate assays yielded 100.3% of the weight of metallic zinc employed, so that it can be safely stated that the acetic radicle of zinc acetate exerts no appreciable influence on the results obtained by the ferrocyanide titration method and therefore this method is applicable to the assay of zinc acetate.

*Zinc Chloride.*—The present U. S. P. method for the assay of this salt is inaccurate, since only the chloride radicle is determined and calculated into terms of zinc chloride. Since free hydrochloric acid is usually present in zinc chloride, determination of the chloride radicle yields high results. The ferrocyanide titration method is applicable to the assay of this salt since it merely duplicates the method of standardizing the standard solution of potassium ferrocyanide and is preferable to the present method, since it is based upon direct determination of the zinc.

*Zinc Phenolsulphonate.*—A commercial lot of U. S. P. zinc phenolsulphonate assaying 100.6% of crystallized salt by the U. S. P. sulphide method yielded 100.4% crystallized salt by the ferrocyanide titration method. Four other com-

mercial lots of this salt assayed 104.5%, 99.43%, 98.7% and 99.25% crystallized salt, respectively. It appears likely that the lot which assayed 104.5% had lost some of its water of crystallization. Three experiments with chemically pure metallic zinc dissolved in hydrochloric acid to which sufficient phenolsulphonic acid was added to represent that which would be present if the zinc had originally been present as phenolsulphonate, yielded 99.5% of the amounts of metallic zinc used. Therefore the ferrocyanide titration method appears to be applicable to the assay of this salt.

*Zinc Sulphate.*—The experiments outlined above under zinc acetate were repeated, using sulphuric acid in place of acetic acid. Several assays yielded 99.6% of the weight of metallic zinc used. A commercial lot of this salt assayed 102.9% crystallized salt by this method; the high assay indicating a loss of water of crystallization. Therefore, the ferrocyanide titration method appears to be also applicable to the assay of zinc sulphate.

*Zinc Valerate.*—The experiments outlined above under zinc acetate were also repeated using valeric acid in place of acetic acid. Triplicate assays yielded 100.4% of the amount of metallic zinc employed. This method is, therefore, applicable also to the assay of zinc valerate.

*Zinc U. S. P.*—Since the determination of the strength of the standard solution of potassium ferrocyanide is based primarily upon the use of a definite amount of chemically pure metallic zinc, the ferrocyanide titration method, of course, is perfectly applicable to the assay of U. S. P. metallic zinc.

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#### MEXICAN HERBS AND DRUGS.\*

Noticing in the pharmaceutical press that a number of medicinal vegetable raw products have been received from the secretary of the British Trade Board of Mexico, and were on view at the chemical section of the Overseas Trade Department, at 35 Old Queen Street, Westminster, the writer paid a visit there in order to see if any of them presented possibilities of use in this country. Mr. T. W. Rogers, the gentleman in attendance, most courteously permitted me to peruse all the information that had been provided concerning the specimens, but unfortunately this information was of the scantiest character, even the names of the plants being in several cases incorrectly spelt, and the specimens apparently selected without the advice of either a scientific or trade expert, or without intelligent supervision. The specimens consist of seventy boxes, about 3 by 3 by 2 in., containing about an ounce of herb or root in each, and consequently insufficient material for botanists in this country to identify them with certainty if previously unknown to them. A small number occurring also in Europe, such as *Ocimum basilicum* (Albahaca), *Foeniculum vulgare* (Hinojo), *Matricaria chamomilla* (Manzanilla comun, or M. del Pais), *Ruta graveolens* (Ruta), *Rosa centifolia* (Rosa de Castile), were so badly prepared that they certainly could not compete with the same herbs as sold in Europe. The majority of the samples of purely Mexican drugs exhibited had nothing to recommend them as superior to the drugs or herbs of other countries.

\* E. M. Holmes, F.L.S., in *Chemist and Druggist*, January 8, 1921, p. 52.