A NOTE ON THE ASSAY OF MASS OF FERROUS CARBONATE.*

BY JOHN C. KRANTZ, JR. AND MANUEL J. VIDAL.[1]

The assay of mass of ferrous carbonate by the pharmacopœial method, as it is generally known, is somewhat different from the assay of other ferrous salts recognized by the Pharmacopœia. The presence of honey and sugar make it impossible to use potassium permanganate in this titration and the alternate use of potassium dichromate makes it necessary to spot the end-point of the titration with potassium ferricyanide as an outside indicator. Certain investigators[2] have experimented with diphenylamine in sulphuric acid solution as an indicator for ferrous iron titrations. It has been found that this substance produces only a pale green color in the ferrous salt solution and a beautiful, intense violet color at the end-point of the titration when an excess of oxidizing agent is added. It has also been shown that the titration results are not materially influenced by the relative quantities of iron or acid present in the solution.

With these facts in mind it occurred to the authors that this indicator might be used advantageously in the assay of mass of ferrous carbonate and would thus eliminate the present official cumbersome spot method with potassium ferricyanide.

EXPERIMENTAL.

Accordingly several samples of crystallized ferrous sulphate were carefully weighed and titrated with potassium dichromate, using the diphenylamine solution as an indicator. In each instance the salt showed more than 99% purity and fairly concordant results were obtained. Following this preliminary step a sample of mass of ferrous carbonate was prepared according to the official formula and an average of three assays by the pharmacopœial method showed 38.46% of ferrous carbonate. The same sample was assayed several times with diphenylamine as an indicator and the following results indicate a series of seven titrations obtained after the details of the method had been worked out: 1, —38.4; 2, —38.42; 3, —38.13; 4, —38.26; 5, —38.11; 6, —38.22; 7, —38.04.

The end-point of this titration is easily seen when the green color of the trivalent chromium sulphate is completly masked by the appearance of the intense violet oxidation product of diphenylamine. It is interesting to note, however, that this blue color is not permanent and fades almost completely within a period of one-half hour. There is some speculation in the literature as to the composition of this substance, but the compound possessing the violet color has apparently never been definitely isolated.

The following experimental procedures were employed:

1. *Preparation of the indicator solution.*—Dissolve 0.2 gram of diphenylamine in enough concentrated sulphuric acid to make 100 cc.

2. *Assay.*—Accurately weigh about 1 gram of mass of ferrous carbonate. Dissolve in 15 cc. of diluted sulphuric acid. Add 35 cc. of distilled water and 0.4 cc. of indicator solution and immediately titrate with potassium dichromate tenth normal volumetric solution to the

* Section on Practical Pharmacy and Dispensing, A. PH. A., Des Moines meeting, 1925.

[1] Technician in the Pharmacy Laboratory, School of Pharmacy, University of Maryland.

[2] W. W. Scott, *J. Am. Chem. Soc.*, 46, 1396 (1924); J. Knop, *Ibid.*, 46, 263, (1924).

appearance of the deep violet color. Each cc. of tenth normal potassium dichromate V. S. corresponds to 0.011584 gram of ferrous carbonate.

CONCLUSION.

The use of diphenylamine as an indicator in ferrous titrations has been successfully applied to the official assay of mass of ferrous carbonate, which method eliminates the troublesome spotting with potassium ferricyanide.

SCHOOL OF PHARMACY,
UNIVERSITY OF MARYLAND,
BALTIMORE, MD.

THE EFFECT OF VARIOUS CONDITIONS ON THE STABILITY OF SOME ESSENTIAL OILS.*

BY R. A. KONNERTH.

It has frequently been observed that Essential Oils are subject to deterioration. Such deterioration usually has been attributed to temperature variation, exposure to light, exposure to air or oxidation, contact with container, etc. In an effort to determine to what extent these factors might be responsible for deterioration, a series of experiments were conducted as follows:

A group of essential oils were placed in different containers and exposed to a variety of storage conditions, carefully observed and compared at intervals over a period of fourteen months. In all, six sets of oils were packaged representing partially filled (1) colorless bottles, (2) amber bottles, (3) tin cans. These were filled under air, and a duplicate set packaged in the same kind of containers with the air replaced by nitrogen.

The six sets consisted of two containers each of the following oils: Anise, Lemon, Lemon (Terpeneless), Orange, Peppermint and Eugenol.

One of each of the containers was kept in a refrigerator, while the other was kept at room temperature, thereby permitting observation of the keeping qualities of the oils in the presence of air, and in the absence of air; at ice box temperature, at room temperature; in glass containers, in tin containers; in the presence of diffused daylight and in the absence of diffused daylight.

In observing the changes which occurred in the oils so stored, great care was taken to note all detectable changes in odor, color and general appearance. The colors were checked against Sheet C of the Milton Bradley Color Standards. ("Mulliken's Identification of Pure Organic Compounds." Vol. III.)

From the observations made, it appears that:

Oxidation is the most active factor in deterioration, hence, it is advisable to avoid contact with air under all storage conditions. This is readily accomplished by the use of nitrogen.

Glass bottles are to be preferred to metallic containers. Tin materially affects the odor and color of the oils.

Light is detrimental to the odor and color of some oils; others are not seriously affected by it if stored under nitrogen.

---

* Scientific Section, A. PH. A., Des Moines meeting, 1925.