# A RAPID METHOD FOR THE ASSAY OF SILVER PROTEINATES.*

BY MARGARET C. SWISHER.[1]

The U. S. P. assay for silver proteinates directs the carbonization of the weighed sample, the solution of the residue in nitric acid, the filtration of the diluted solution and the titration of the silver salt with standard ammonium thiocyanate. This is a time-consuming procedure, requiring the use of four containers and the transfer of the sample four times.

Other methods for the analysis of silver proteinates have been reported in which, for oxidizing agents, are used an acid solution of potassium permanganate (1), fuming sulfuric acid and thirty per cent hydrogen peroxide (2), mixtures of nitric and sulfuric acids (3) and perchloric acid (4).

Experience with the foregoing methods for analysis suggested that a simple and more rapid, but just as accurate a procedure for the assay of silver proteinates might be developed. With this purpose in mind, samples of silver proteinates were subjected (*a*) to analysis by the previously reported methods and their possible variations, (*b*) to treatment with other oxidizing agents and catalysts and (*c*) to methods requiring less cumbersome apparatus and technique until the following method was developed.

## METHOD.

About 5 Gm. of the sample are weighed and transferred to a 50-cc. volumetric flask containing 25 cc. of water. When solution is complete, the volume is made to 50 cc. with water and mixed. To a 250-cc. wide-mouthed Erlenmeyer flask are added an accurately measured 10-cc. sample of the silver proteinate solution, 15 cc. of $H_2SO_4$ (sp. gr. 1.83), 1.5 cc. of fuming $HNO_3$ and some glass beads or broken glass tubing. The mixture is boiled over a free flame, with continuous shaking, until dense white fumes are evolved. After cooling for from one to three minutes (the solution is usually a dark red color), 1 cc. of fuming $HNO_3$ is added and the mixture boiled again to white fumes. If the hot solution is a lemon-yellow color, it will usually become colorless when cooled to room temperature, and the oxidation is complete. If the solution is not colorless when cold, 1 cc. of fuming $HNO_3$ is added, and the boiling to the white fume stage repeated. When the oxidation is complete, 50 cc. of water is added, and the solution is boiled to remove the oxides of nitrogen. The volume is brought to 100 cc. with water, the solution is cooled to room temperature, 3 cc. of ferric alum T.S. is added and the silver salt titrated with standard ammonium thiocyanate.

The entire oxidation period requires from five to twenty minutes, depending almost entirely upon the will of the operator. Weighed samples of the solid may be used in place of the solution, thus eliminating the time required to remove the solvent. The time can be further shortened if, after reaching the white fume stage the first time, the fuming $HNO_3$ is added drop by drop to the boiling solution while it is continuously shaken.

Although it was found that the addition of 0.2 Gm. of selenious acid to the oxidizing mixture increased the rate of oxidation, it was not generally used for the analyses in this report since the difference in time is small.

Inabinette (5) reports that samples of silver proteinate boiled with nitric acid, cooled and titrated with thiocyanate, gave results identical with those obtained by the U. S. P. method. This is true with some products, but with others Inabinette's method gives results three per cent lower than that of the U. S. P. Without the use of heat, results comparable to those by Inabinette's method can be obtained. The proteinates dissolve in and are decolorized by cold nitric acid. The results are, however, from five-tenths to three per cent low.

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Since the method of the Association of Official Agricultural Chemists gives the same results as that of the U. S. P., and is easier to use, the analyses by the new method were checked against it. Over one hundred and fifty analyses were run by this method. Six different preparations of silver proteinates, which represent three of the four different types, were used. No work was done on the electric type of solution.

TABLE I.

| Method Used, Time for Digestion. | A. O. A. C. 45–90 Min., % Ag. | New Method 5–20 Min., % Ag. |
|---|---|---|
| Strong Silver Protein (Merck) | 8.19 | 8.21 |
| Mild Silver Protein (Merck) | 19.54 | 19.59 |
| Argyrol | 20.95 | 20.95 |
| Silloid | 17.67 | 17.67 |
| Collargol | 78.22 | 78.42 |

A ten per cent Argyrol ointment (Norwich Pharmacal Co.) was analyzed by this method. For complete oxidation it required from one to two hours and the use of 50 cc. of $H_2SO_4$ and 50 cc. of fuming $HNO_3$. The results indicated the presence of 2.15% silver, $\pm 0.02\%$. Samples of the same ointment were treated by the A. O. A. C. method. After heating for two days and repeatedly adding $HNO_3$ and $H_2SO_4$, the samples were discarded.

SUMMARY.

1. An accurate method, considerably less involved than that of the U. S. P., has been developed for the assay of silver proteinates.

2. It has the following advantages over that of the U. S. P. and other methods reported in the literature:

(a) It gives the same or slightly higher percentage of silver.

(b) The oxidation is complete in from one-tenth to one-third of the time.

(c) The complete analysis is made in one container, a 250-cc. Erlenmeyer flask.

3. It can be used for the analysis of oil solutions and of ointments of silver proteinates.

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# COMPARATIVE SENSITIVITY OF THE TOAD AND THE FROG TO CYMARIN AND COUMINGINE.*

BY K. K. CHEN, CHSETER C. HARGREAVES AND WILLIAM T. WINCHESTER.[1]

In a previous report (1), it was concluded that the nebulous toad, *Bufo valliceps*, was many times more tolerant to *G*-strophanthin and scillaren B than the common frog, *Rana pipiens*. It was also noted that the tolerance of the toad is confined to the cardiac muscles. Of a large number of crystalline cardiac principles studied

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