AQUEOUS EXTRACTS OF SEEDS AS AGENTS IN THE PREPARATION OF SILVER SOLS

E. V. MILLER AND R. P. HIBBARD

Introduction

Many methods have been suggested for the preparation of colloidal metals by condensation with the use of organic compounds as stabilizers (1). Among these compounds may be mentioned gum arabic, gelatin, sugar, glycerol, sodium citrate, saponin, barium arabinate, sodium protalbinate, and sodium lysalbinate.

Probably colloidal silver has received as much attention as has colloidal gold. Wool-fat has been employed as a stabilizing agent in preparing colloidal silver from organic solutions. Kohlschütter (2) reduced AgOH by means of hydrogen. Lüppo-Cramer (4) obtained a series of beautifully colored silver sols by the reduction of AgNO₃ with hydrochinone in the presence of gelatin. Carey Lea (3) reduced AgNO₃ with ferrous citrate, dissolving the deposit in water and reprecipitating with ammonium nitrate.

Svedberg (6) observed that a silver plate submerged in water or alcohol produced a silver colloid when illuminated by ultra-violet light or by X-rays. According to Traube-Mengarini (7) a certain amount of silver colloid may be produced by boiling silver in water.

Nordensen (5) showed that silver is oxidized by both water and alcohol and is dissolved as AgOH or some other compound. This silver solution, Svedberg has shown, may be reduced by illumination, while Traube-Mengarini produced similar results with traces of reducing agents. The dissociation (or oxidation) is accelerated by light, especially ultra-violet light.

The method for preparing colloidal silver described in this paper depends upon the ability of aqueous extracts of seeds to reduce AgNO₃ solutions. A number of methods for preparing colloidal silver have already been mentioned. This is an addition to the list and is highly recommended because of its simplicity of manipulation. It should therefore be of more than passing interest to plant physiologists, botanists, and chemists.

Methods

One gram of timothy seeds is stirred into 100 cubic centimeters of distilled water and allowed to stand about an hour. The solution is filtered and two drops N/10 AgNO₃ added. If the solution is then permitted to stand in diffused light for about half an hour a dark brown color will appear, this being due to colloidal silver. The speed of this reaction may
be increased by exposure to sunlight. However, too great exposure will precipitate the silver. If the aqueous extract is placed over a Bunsen burner and heated as soon as the AgNO₃ has been added, the colloidal silver will form within a few minutes.

If the colloidal silver solution is not placed in the strong sunlight the sol remains indefinitely stable. A solution in the laboratory at present has held up for over nine months.

**Seeds investigated**

The following seeds were later employed for reducing the silver, positive results being obtained in all cases except clover: Pea, bean, tomato, corn, wheat, buckwheat, grass, clover, sunflower, lettuce and beet. Later investigation revealed that though there was a precipitate formed in the clover solution, the supernatant liquid was colored a faint brown like that of other sols.

In a subsequent experiment colloidal silver solutions were prepared from the following: Corn, oats, wheat, rice, peas, beans, soy beans, cotton, beet, and gladiolus (bulb). In this case 50 and 100 seeds were soaked in 100 cubic centimeters of water. These were all placed under the ultramicroscope and were found to exhibit Brownian movement. In the sol prepared from the oats the particles were so numerous that the field presented the appearance of a confused mass of seething particles.

The particles of course are electrically charged, as was demonstrated by use of two platinum electrodes, placed on each side of the ultra-microscopic field and connected to storage batteries by means of a key. If the circuit were closed while the field was being observed the charge of the particles could be determined by their behavior in the electric field. All of the sols described possessed negative charges.

An outstanding feature of these colloidal solutions is the elaborate coloring. Colors varying from a dark amber to a rich rose or orchid were obtained. It is possible that different classes might be characterized by the color of their colloidal solutions. Corn, wheat, oats and rice all produced colloidal silver in a rose-colored suspension. Peas, beans, and soy beans were all characterized by a brown color. Other seeds were examined but could not be compared because no other closely related groups were included. These differences in color, especially the roseate hues, may depend in part on adsorption by the colloidal silver particles, as the usual color of silver sols is.

In an effort to locate the exact source of this reducing substance different parts of bean seeds were soaked in water and the solutions treated with AgNO₃. Beans were soaked in distilled water over night. The next morning they were taken from the water, the seed coats removed, and the plumule
and hypocotyl cut out of the cotyledons. These three parts (seed coat, cotyledons, and hypocotyl and plumule) were again soaked over night. On the following morning AgNO₃ was added to the extracts.

The intensity of the colloidal silver color was greatest with the seed coats, next with the cotyledons, and least with the hypocotyl and plumule. In the last the color did not form at all until after several hours.

**Nature of the reducing substance**

About ten cubic centimeters of the aqueous-extract of timothy seed were enclosed in a collodion sack and lowered into a beaker of distilled water. Two or three drops of N/10 AgNO₃ were added to this distilled water and in a few days the extract within the collodion sack had assumed a brown color characteristic of the colloidal silver. This would indicate non-diffusibility on the part of the reducing substance.

A more concentrated solution of the timothy extract presents a dark brown color, indicative of tannin. In the presence of ferric chloride a faint blue-black precipitate is formed, the intensity of the color resembling that produced by a .001 per cent. tannin when treated in the same way.

Following this a timothy extract was treated with lead acetate to remove the proteins. The excess lead was removed with H₂S. A few drops of AgNO₃ were added and a brown colloid, similar to the original, was formed. However, the colloid soon settled out.

The experiment was repeated, first adding enough tannin to make it a .001 per cent. solution. The same brown colloid was formed, appearing permanent at first, but settling out after a longer interval. The filtrate did not reduce Fehling's solution.

The instability of this last colloid was no doubt largely due to the presence of acid formed by the method employed for removing the excess lead. Later sodium carbonate was used instead of the hydrogen sulphide and the filtrate treated with AgNO₃. This time a colloidal silver formed which was not quite the same color as the original. This colloid lasted longer than the others (about a week) but finally settled out like the rest.

Difficulty in identifying this reducing substance arises from the fact that many substances are extracted from the seeds by both water and alcohol. In some instances sugar has been found present and in others it has not.

An alcoholic (90 per cent.) extract of corn meal has been found to reduce the silver nitrate, producing a colloid identical in appearance with the original one. In previous cases the reduction has been brought about by an aqueous extract. Furthermore, this alcoholic extract has produced a silver sol which thus far rivals the aqueous extract in stability.
In another experiment an alcoholic extract of corn meal was evaporated and the alcohol replaced with water as the alcohol evaporated. The zein was precipitated in this process. This impure zein was dissolved in ethyl alcohol and AgNO₃ added to the solution. A silver sol, very similar to the original, was formed. After a period of a week this sol became cloudy and appeared to be precipitating.

From the above results it seems possible that both zein and sugar would be extracted by the alcohol. When the alcohol is replaced by water the sugar would go into solution, leaving the zein to be precipitated. Hence it might be surmised that the silver can be reduced by either the alcohol- or water-soluble proteins and the sol stabilized by sugar or vice versa.

An aqueous extract of corn meal was made after the meal had first been extracted with 90 per cent. alcohol. This aqueous extract reduced Fehling’s solution when tested for sugars. There were also proteins present which were removed before testing for sugars. A colloidal silver solution was produced by this aqueous extract but the sol was unstable.

The zein mentioned in this paper has been designated as "impure zein." It was prepared by extracting corn meal with alcohol, evaporating off the alcohol, replacing the alcohol with water as the alcohol evaporated, and collecting the zein as it precipitated.

A little later some pure zein was prepared. An alcoholic extract of corn meal was made, the zein salted out with dilute NaCl, and the NaCl removed by dialysis. It is possible that some of the carotinoid pigments were carried down with the zein but we shall distinguish between the two by calling this last one "pure zein."

A stable colloid has been prepared by dissolving this "pure zein" in alcohol and adding the AgNO₃. With the impure zein the colloid was not stable unless a small amount of arabinose was added.

Summary

A simple method has been described for preparing colloidal silver from aqueous extracts of seeds. The process is essentially one of reduction or condensation.

Further investigation revealed three other methods for preparing colloidal silver. They are as follows: (1) Alcoholic extract of seeds; (2) Alcoholic solution of pure zein; (3) Alcoholic solution of impure zein plus arabinose.

The reducing substances are not as yet known but it seems probable that they might be alcohol- and water-soluble proteins with sugar as the stabilizer.
The work on this problem has been made possible by the encouragement
and financial aid of the D. M. Ferry Seed Company of Detroit.

MICHIGAN STATE COLLEGE,
EAST LANSING, MICHIGAN

LITERATURE CITED

2. KOHLSCHÜTTER, B. On the reduction of silver oxide by hydrogen and
5. NORDENSEN, H. The spontaneous formation of colloids of metals in
6. SVEDEBERG, THE. The formation of dispersed systems through the action
of ultra-violet and Röntgen rays on metals. Zeitsehr. Chem. Ind.
7. TRAUBE-MENGARINI, M., and SCALA, A. The formation of colloidal solu-
tions of the noble metals in boiling distilled water. Zeitsehr.