

ORGANIC, PROTEIN, AND COLLOIDAL SILVER COMPOUNDS.*

BY P. M. GIESY.

In recent papers,¹ Pilcher and Sollmann have reported their examination of various silver preparations with a view to determining their antiseptic efficiencies and irritating effects under various conditions. The method used was essentially that of determining the concentration of the silver preparation under test required to inhibit the fermentation of sucrose by yeast under definite conditions. Tests were made in water, 0.8% aqueous sodium chloride, and defibrinated blood. Since sodium chloride precipitates silver ions, they argue that the difference in activity in water and saline corresponds to the content of "free silver ions," which they state is a measure of the irritant and astringent effects of the material. In this way they conclude that silver nitrate contains 62.7 per cent. of ionic silver, and 0.8 per cent. of non-ionic silver.

This method is open to several objections. It is questionable whether the inhibitory effects of the materials on yeast growth will parallel their germicidal activities. It is well known that the effects of various germicides on different organisms are not always parallel. The work of Hamilton² shows this very plainly; he finds that acriflavin has the same germicidal power as phenol toward staphylococcus, while it is 1300 times as effective against gonococcus as phenol.

Another objection is that sodium chloride may not destroy entirely the activity of ionic silver, as they assume. It appears to be quite as logical to suppose that this is why they found silver nitrate to have some inhibiting power in the presence of sodium chloride, as to suppose, as they did, that silver nitrate contains 0.8 per cent. of non-ionic silver. In one case, that of "Argyrol y," the presence of sodium chloride actually increased the inhibitory effect of the preparation on yeast growth. It is impossible to explain this if we assume that the only effect of sodium chloride is that of destroying the activity of silver ions.

It would seem that in addition to its precipitating effect on silver ions, sodium chloride may affect the inhibiting power of these preparations by virtue of its effect upon their colloidal nature. It is well known that salts often have a coagulating effect on colloids, and that in other cases they may exert a peptizing action. Certainly we should not overlook the possibility of these effects in this case. Unpublished work of this laboratory has shown that the physical state of these colloidal germicides has immense effect on their germicidal power.

The authors appear to have confused to some extent "ionic" and "ionizable" silver. They draw conclusions as to the amount of "ionic" silver, whereas their method, if their assumptions are correct, will give them rather "ionizable" silver, or, more correctly, silver more ionizable than silver chloride.

Smith and the present author³ have measured electrometrically the actual silver ion concentrations of several colloidal silver germicides, and by following the changes in voltage as the solutions were titrated with a standard solution of hydriodic acid have determined the percentage of silver in these compounds ioniza-

* Scientific Section A. Ph. A., Buffalo meeting, 1924.

¹ *J. Lab. and Clin. Med.*, 8, 301 (1923); 9, 256 (1924); 10, 38 (1924).

² *J. Lab. and Clin. Med.*, 9, 244 (1924).

³ *JOUR. A. PH. A.* (to be published).

ble at each silver ion concentration level. The following table shows how their results compare with the conclusions of Pilcher and Sollmann:

Product.	Pilcher and Sollmann.		Smith and Giesy.	
	Ionic Silver.	Ionic silver.	Silver more ionizable than AgCl.	Silver more ionizable than AgI.
Silver Nitrate	98.7%	81. %	100. %	100. %
Protargentum	70.0	4.9	75.5	81.0
Collargol	1.73	0.00032	0.0	5.0
Solargentum	1.36	0.00014	0.0	5.1

The "Pilcher and Sollmann Ionic Silver" values were obtained by calculating the percentage of "ionic silver" in each preparation from their data by their method, and then dividing this figure by the percentage of total silver in the preparation. The "Smith and Giesy Ionic Silver" values were obtained by converting the p_{Ag} values obtained as described in their paper³ into concentrations, taking the average of these, and dividing by the concentration of total silver. The values for "Silver More Ionizable than AgCl" were obtained from their titration curves by reading off the cc. of $N/10$ HI required to reduce the p_{Ag} to 4.9, the value indicated by the curves for the p_{Ag} of pure saturated AgCl. Since the Ag in the solution was $N/10$, and 100 cc. were titrated, cc. of $N/10$ HI correspond to % Ag. The "Silver More Ionizable than AgI" was found similarly, taking the p_{Ag} of pure, saturated AgI as 7.95. If the values of p_{Ag} for saturated AgCl and AgI are calculated from the solubilities given by Seidell,⁴ 0.0020 and 0.0000028 Gm. per liter respectively, we get for the p_{Ag} values 4.72 and 7.76. The use of these values instead of those taken from the titration curves gives only small changes in the values of the table; the largest is in the Solargentum-AgI value, which is reduced from 5 to 3%.

While there is rough agreement between the "Pilcher and Sollmann Ionic Silver" and the "Smith and Giesy Silver More Ionizable than AgCl" values, it is evident that Pilcher and Sollmann's figures for "Ionic Silver" and those found by the electrometric method do not agree.

Pilcher and Sollmann have given no reasons for believing that the content of ionic silver is a measure of the irritating effect of these materials. It is, of course, true that Protargentum, with 4.9% ionic silver, is more irritating than Solargentum, with 0.00014% of ionic silver, and that silver nitrate is more irritating than either. But since Protargentum gives, for the same amount of silver, 30,000 times as many silver ions as Solargentum, it seems quite obvious that any small differences in silver ion content will have negligible effect.

REMARKS.

P. M. Giesy: May I point out the difference between the curve of protargentum with potassium iodide and with hydrochloric acid. I think that is of some importance. Dr. Kolthoff titrated with potassium iodide, but in the presence of sulphuric acid which would give him the curve corresponding to our curve with hydrochloric acid rather than to our curve with potassium iodide.

RESEARCH LABORATORIES, E. R. SQUIBB & SONS,
BROOKLYN, N. Y.

⁴ "Solubilities of Inorganic and Organic Compounds," 2nd Ed.