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ROGER KIRBY GUILFORD in M.S. in Plant Pathology
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Title FUNGITOXICITY OF SILVER SALTS

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The demand for new fungicides to control plant diseases has led to experimentation with both previously used and newly developed fungicides. Silver, an older but little used fungicide, was selected for evaluation because of its high toxicity to microorganisms. Silver nitrate and a silver electrolytic cell were tested as potential sources of silver ions. The cell discharged 0.17 ppm silver ions into 750 ml of distilled water during a ten-minute period. A bioassay was used to detect silver ion concentrations.

Approximately 1.5 ppm silver ion per 100 ml of cell effluent was lost from the electrode under constant flow conditions. The cost of producing 1000 gallons containing 1 ppm of silver with the silver electrolytic cell was $1.11 vs. $0.20 for silver nitrate. The effluent from the electrolytic cell remained fungitoxic for at least five days after preparation, after which time toxicity gradually diminished.

Ionic silver was not phytotoxic to sword-fern fronds or potato tubers at concentrations much greater than the level required to control dry rots of fern and potato. The concentration of silver nitrate necessary to effectively control the spread of dry rot of fern stored at 34° F was 1.0 ppm. This disease is caused by a complex of a Fusarium sp. and a Pseudomonas sp. and is particularly severe at elevated temperatures. The most effective method of applying silver to fronds was by dip treatment of frond bundles.

Undiluted silver effluent (0.17 ppm) effectively controlled dry rot of potatoes caused by the fungus, Fusarium roseum. However, ionic silver discharged from the silver electrolytic cell was not effective as a pre-harvest treatment for the control of apple scab and peach leaf curl diseases.

FUNGITOXICITY OF SILVER SALTS

by

ROGER KIRBY GUILFORD

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[redacted]

Associate Professor of Plant Pathology

In Charge of Major

[redacted]

Head of Department of Botany and Plant Pathology

[redacted]

Dean of Graduate School

Typed by Nancy Kerley

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FUNGITOXICITY OF SILVER SALTS

INTRODUCTION

Several heavy metals have been used in fungicidal preparations for control of plant diseases. Copper, mercury, and to a lesser extent silver have been most effective primarily due to their high fungitoxicity. Although silver is generally considered the most fungitoxic metal, its use in plant disease control has been limited by the relatively high cost of silver compounds, and the problem of toxic residues.

There still exists a need for new methods for the control of several field and storage diseases. Silver, the most highly toxic heavy metal, was selected for testing as a potential control of these diseases. This metal seemed best suited for meeting the requirements for a highly toxic fungicide that leaves no visible residue or odor. In the past this metal has been used experimentally as a seed disinfectant and foliage spray.

The objectives of this study were: (1) to evaluate the fungitoxicity of silver nitrate and electrolytically produced silver ions, (2) to determine the effectiveness of silver in controlling specific plant diseases, (3) to evaluate the potential of a silver electrolytic cell for use in plant disease control.

LITERATURE REVIEW

The first systematic investigation of the germicidal properties of metals was by the Swiss botanist Carl Nageli in 1893 (11). Somewhat earlier, however, Raulin (15) found that silver was toxic to Aspergillus niger.

The relative toxicities of the various metals as cations has been studied by numerous investigators beginning with Wutrich in 1892 (6). The following descending order of fungitoxicity of metal ions has become fairly well established according to Horsfall (6): Ag> Hg> Cu > Cd > Cr > Ni > Pb > Co> Zn > Fe > Ca. For different organisms the order may differ slightly (14).

Of the silver salts, silver nitrate has been the most successful fungicide; this is primarily due to its high solubility in water. However, other silver compounds have given promising results in certain tests. Nielsen (13) found silver oxide, silver iodide, silver hexacyanoferrate, and silver dichromate to be effective in controlling Phytophthora infestans on potato plants under greenhouse conditions. Miller and McCallan (10) found that the fungitoxicity of silver ions was unaffected by the presence of chloride ions due to the fineness of the precipitate, but bromide ions reduced the toxicity of silver ions and iodide ions prevented the toxicity of silver ions.

Silver ions can be produced electrolytically by passing a

current between electrodes immersed in water. The silver electrode acts as the anode and silver ions are brought into solution by direct current. This method of producing ionic silver is essentially the catadyn process of Krause (1), and has the advantage of producing silver ion in high concentrations.

According to Brandes (3), silver under electrolytic conditions goes into solution in the ionic form, and it is the silver ions that are effective in killing microorganisms. Although the silver concentration may remain unchanged, the solutions are relatively unstable. With time, solutions of ionic silver become blue and finally brown in color. This color change is due to the precipitation of silver as a colloidal dispersion. Ultimately, the metal is deposited on walls of the container in which it is stored (14).

The fungitoxic activity of silver is dependent upon the concentration of the toxicant. Miller and McCallan (10) found that silver interferes with permeability of cell membranes. From 35 to 45 percent of the phosphorus compounds in cells were released into solution in the presence of silver, while killing the spores with heat released only 27 percent of the phosphorus content.

The results of Yudkin (20) demonstrated that only a single silver ion is necessary to produce death of each bacterial cell. Although only one silver ion is required to kill a cell, the cell does not lose its capacity for absorbing additional ions. At low concentrations

of silver, some cells may escape contact with silver ions.

Newton, Hastings and Bosher (12) combined silver nitrate with potassium cyanide in the ratio of one to three by weight to form a stable silver complex. When silver is in the form of this complex $\left[Ag(CN)_2^-\right]$, it is not easily precipitated by chlorides in tap water or in soil clinging to plant material. However, the combination of ionic silver with chlorides does not interfere with toxicity, but may result in loss of the silver ions due to flocculation.

In the laboratory testing of fungicides by the agar plate method, Thornberry (19) found cationic fungicides such as silver were adsorbed and precipitated by the agar media. This he believed was due to the presence of phosphates and other salts in the agar.

In measurements of the fungitoxic action of compounds, McIntosh (9) found the speed of killing and ultimate toxicity increased with increasing temperature from 10 to 25° C. This was confirmed by Gibbard (5) and Schioppa (18) who found temperatures below 20° C. retarded the fungitoxicity of silver. Temperatures above 20° C accelerated the action of silver. These workers found that germination of the spores of their test fungus, Botrytis fabae, was unaffected by the temperature changes, and thus, changes in toxicity were most certainly due to differences in susceptibility to the silver ions.

Preliminary trials for testing the adhesiveness and phytotoxicity of a fungicide can be made in the laboratory and greenhouse.

Nielsen and Massey (14) found sprays containing between 100 and 1000 ppm silver were toxic to the leaves of young tomato and bean plants. The injury was most apparent where the drops of the solution dried on the leaves.

Nielsen (13) evaluated over 70 silver spray mixtures for their fungicidal activity and adhesiveness under greenhouse conditions. A silver and iron sulfate mixture was found to be the most adhesive of the several promising fungitoxic silver sprays. The adhesiveness of this mixture was about equal to that of 3:3:50 bordeaux mixture. Field tests of these spray mixtures were not undertaken.

Sandeno (16) identified a Fusarium sp. and a Pseudomonas sp. as the causal organisms of dry rot in stored fern fronds. Using silver effluent from an electrolytic cell for preliminary control tests, he found silver ions gave promising results. Spraying with 20 percent dilution of the silver ion effluent gave over a 50 percent control; dipping fronds in a 50 percent dilution gave 99 percent control, and in undiluted effluent gave complete control of dry rot (17).

MATERIALS AND METHODS

Reagent grade silver nitrate was used in the various treatments of Western sword-fern, Polystichum munitum (Kaulf.) Presl., Kennebec potatoes, Solanum tuberosum L., and in the evaluation of silver as a fungicide. Fresh stock solutions were prepared for each experiment and dilutions were made immediately before use in the experiments.

An electrolytic cell manufactured by the Ster-O-Matic Corporation was used as another source of silver ions for fungitoxicity assays and for plant disease control tests. The cell is composed of a cast metal pot surrounding a silver electrode. The positive side of a 6-volt, 3-ampere direct current power supply was attached to the silver electrode; the negative side was attached to the metal pot (Figure 1). A silver electrode was substituted for the usual poly-electrode composed of several other metals (Figure 2). Therefore, silver was the only metal discharged. Distilled water (750 ml) was placed in the cell, and the current was switched on for ten minutes. During this period silver ions were released into the water from the silver electrode.

Stock solutions of the silver effluent were diluted with tap water for plant disease control on fern fronds, peach leaves, and apple trees. For tests on potato rot, dilutions were made with

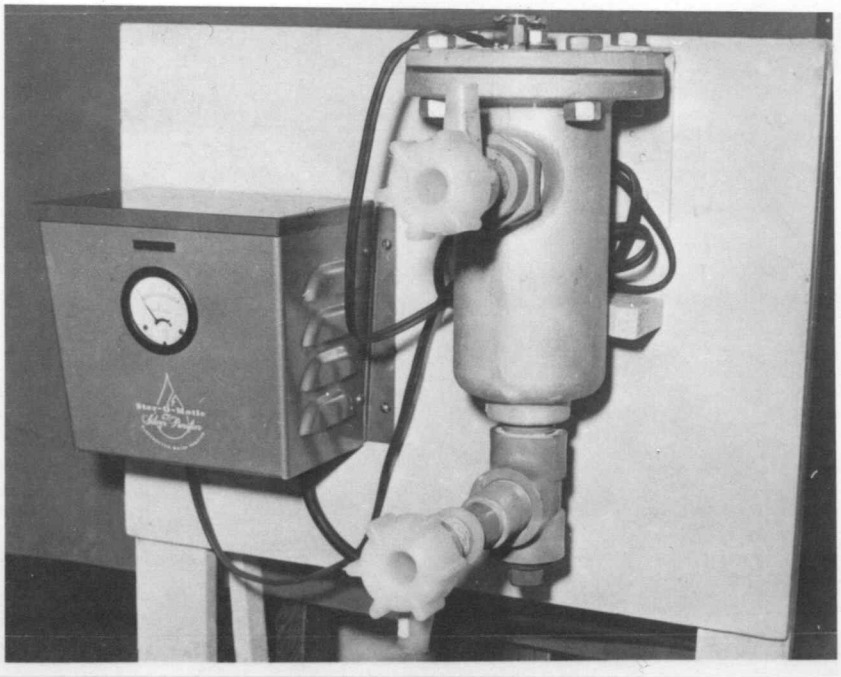

Figure 1. Silver electrolytic cell.

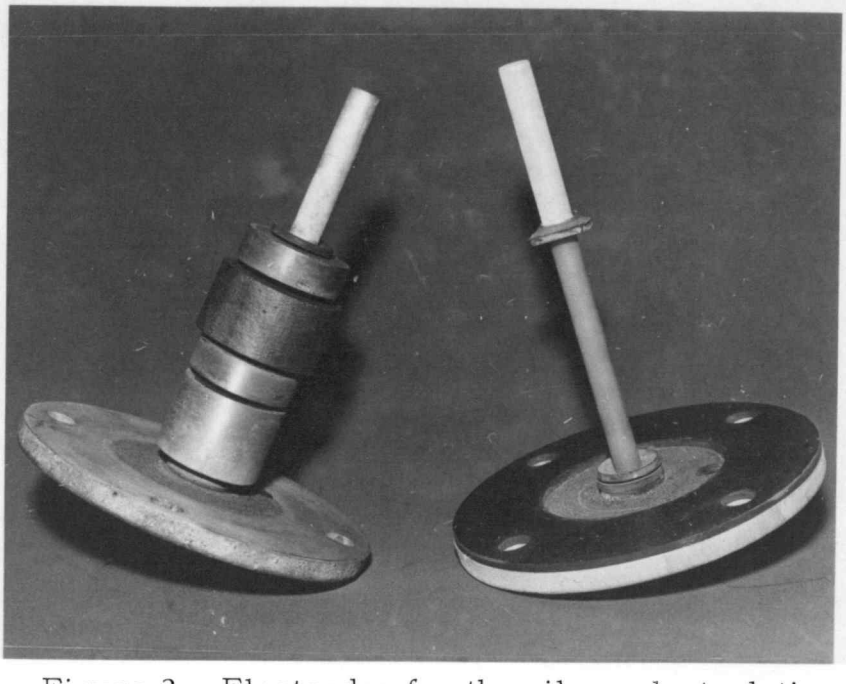

Figure 2. Electrodes for the silver electrolytic cell. Polyelectrode at left and plain silver electrode at right.

distilled water. Distilled water was used exclusively for dilution of silver solutions in laboratory assays for fungitoxicity.

Nutrient-yeast-agar (pH 6.8) was used for culture of all bacteria and fungi. The medium contained the following ingredients:

Beef extract	3.0 gm.
Peptone	5.0 gm.
Yeast extract	3.0 gm.
Agar	15.0 gm.
Distilled water	1000.0 ml.

All the constituents were dissolved in distilled water, autoclaved for 20 minutes, and then poured into sterile Petri plates. Twenty ml of medium were added to each Petri plate, and treated fungal spores were mixed into the medium as each plate was poured.

Silver nitrate was used in the various treatments of sword-fern. Stock solutions were prepared in the laboratory at Oregon State University and dilutions were made at the Callison's Incorporated packing plant (Eugene, Oregon) where the experiments were conducted. Tap water was used to dilute the stock solutions to the desired concentrations. Test solutions of silver nitrate were placed in a 55 gallon barrel. The solutions were applied to sword-fern with a small sprayer. An electric pump placed on top of the barrel supplied the pressure to force the liquid through the hose and out the spray nozzle.

The spray nozzle was located at the packing bench where the fern are regularly received. The silver nitrate solutions were applied at the same rate as the water usually sprayed on the incoming fern to increase its storage life.

In addition to spraying, bundles of fronds were dipped individually into silver nitrate solutions. Each bundle was submerged for one minute and then allowed to drain for five minutes before packing in cardboard cartons.

Bundles of fronds were packed in five layers in waxed cardboard cartons of five bundles so that each case contained 25 bundles offronds. To save space, the stem ends of the bundles in one row were placed opposite to those in the preceding row. Before packing, the cartons were lined with a polyethylene plastic sheet to conserve moisture. The cartons were then closed and bound with wire. This method of packing was the same as is used in standard commercial practices.

The cases were then incubated for three weeks either at room temperature or in cold storage at 34° F. The treatments placed at room temperature varied from 62° F to 84° F depending upon the weather and placement in the packing shed.

To obtain a uniform inoculum of the organisms causing dry rot (a Fusarium sp. and a Pseudomonas sp.), one naturally infected frond was added to each bundle. The amount of naturally infected

fern varied widely. The fern originally grew in the coastal range or on the western slopes of the Cascade Mountains. According to Ark (2), the natural occurrence of dry rot is quite variable. Infected fronds were added to give a more uniform disease development during the incubation period.

EXPERIMENTAL RESULTS

Bioassay of Silver Solutions

Because chemical analysis for minute quantities of silver is difficult, a bioassay method was employed to determine the concentrations of silver ions discharged into solution by the silver electrolytic cell. Comparisons of toxicities obtained with dilutions of silver effluent and silver nitrate solutions were used to obtain a quantitative assay of the concentration of silver ions.

Spores of the fungus, Fusarium roseum (Lk. ex Fr.) Snyd. & Hans., were used as the test organism. Spore concentrations were adjusted by use of a hemacytometer (blood cell counter). A dosage-response curve was obtained by placing spores in varying concentrations of silver nitrate. With 100 spores per ml the concentration of silver nitrate for 50 percent inhibition of spore germination (ED_{50}) was 0.0157 ppm (Figure 3) or 0.0099 ppm silver ion on the basis that silver nitrate contains 63.2 percent silver.

A dilution containing 5.8 percent of the silver cell effluent gave 50 percent inhibition of spore germination. Thus, at this dilution, the concentration of ionic silver was 0.0099 ppm, and the silver ion concentration in the original undiluted effluent was about 0.17 ppm.

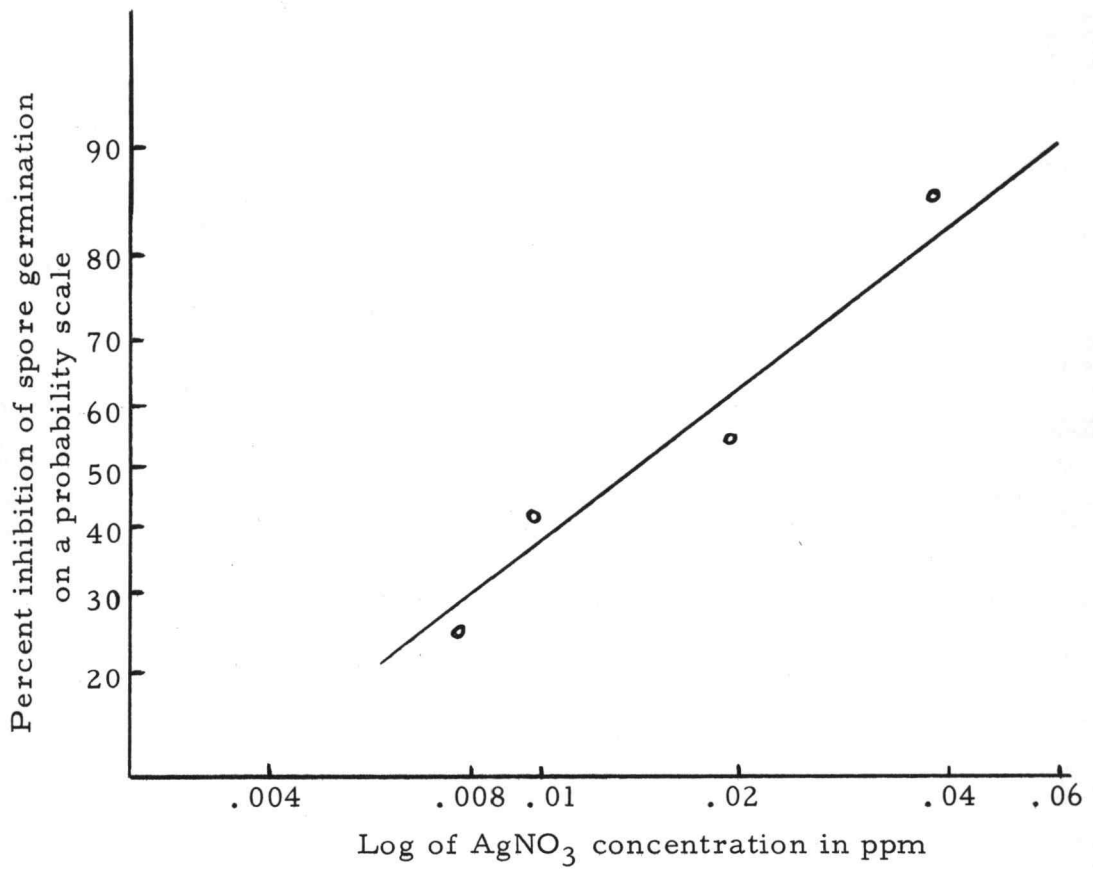

Figure 3. Inhibition of spore germination of F. roseum by $AgNO_3$.

Effect of Temperature on Fungitoxicity of Silver

Five ml of spore suspension of F. roseum containing 100 cells per ml was placed in test tubes, and a dilution series of silver nitrate were placed in a similar series of tubes. Both sets of tubes were placed in a range of temperatures in incubators for 45 minutes to allow for temperature adjustment. The spore suspensions and the silver nitrate dilutions were mixed together, and incubated 30 minutes. One ml of treated spores was pipetted into Petri plates and 20 ml of nutrient-yeast-agar were immediately poured into the plates. The molten medium was swirled to distribute the spores in the medium. This sequence was repeated for each treatment, and the plates were incubated at 25° C for three days before colony counts were made as an index of spore germination.

The fungitoxicity of silver nitrate was significantly inhibited at temperatures below 20° C (Table 1). At temperatures above 20° C, silver gave complete inhibition of Fusarium at concentrations of 0.5 and 1.0 ppm. Higher concentrations of silver were required for complete inhibition at temperatures below 20° C.

Fungitoxic Stability of Silver Solutions

A series of tests were conducted to determine the effect of aging on the fungitoxicity of silver from the silver electrolytic cell.

Table 1. Influence of temperature on fungitoxicity of silver nitrate to spores of Fusarium roseum.

Temperature in degrees C.	Percent inhibition of spore germination at various concentration of silver nitrate (ppm)			
	0	0.1	0.5	1.0
5	0	1	66	90
10	0	13	96	99
15	0	15	99	100
20	0	26	100	100
25	0	38	100	100
30	0	39	100	100

Spore suspensions of F. roseum (100 cells per ml) were placed in fresh, 4, 8 and 12 day-old dilutions of the effluent. The spores were incubated in the silver solution for 30 minutes. One ml of treated spores was then swirled into 20 ml of cool nutrient-yeast-agar in Petri plates. The plates were incubated at 20° C for three days before colony counts were made.

These tests indicated that the silver effluent would retain its toxicity for at least eight days (Table 2). By the 12th day a significant loss in fungitoxicity occurred. Loss of fungitoxic activity was associated with the production of a precipitate on the walls of the containers. Undoubtedly, silver was removed from solution and

Table 2. The effect of aging of silver effluent on its fungitoxicity to spores of Fusarium roseum.

Percent silver effluent	Percent inhibition of spore germination Number of days silver effluent aged before assay			
	0	4	8	12
20	100	100	100	69
18	100	100	100	46
16	100	100	100	37
14	100	100	95	19
12	99	99	89	4
10	97	96	71	1
8	82	83	59	0
6	66	65	37	0
4	16	17	9	0
2	11	11	1	0
1	5	16	0	0
0 (control)	0	0	0	0

converted to a less available form.

Effect of Inoculum on Fungitoxicity of Silver

An experiment was designed to determine the toxicity of silver to various concentrations of F. roseum spores. Five ml of a spore suspension were placed in test tubes, and a dilution series of silver nitrate was placed in the same tubes to give the desired concentrations. Spore concentrations of 100, 200, and 300 spores per one ml were treated with 0.04, 0.05, 0.07, 0.1, 0.2, and 0.3 ppm of silver nitrate. After a 30 minute incubation, one ml of treated spores was pipetted into Petri plates, and 20 ml of cooled nutrient-yeast-agar was immediately poured into the plates. The molten medium was swirled to distribute the spores. The plates were incubated at 25° C for three days before colony counts were made.

The position but not the slope of the dosage-response curve was shifted slightly by increasing the spore concentration (Figure 4). The amount of inoculum influenced the ED_{50} value when the spore concentration of 100 cells per ml was doubled or tripled. Each higher spore concentration required more silver ions for a 50 percent inhibition of spore germination.

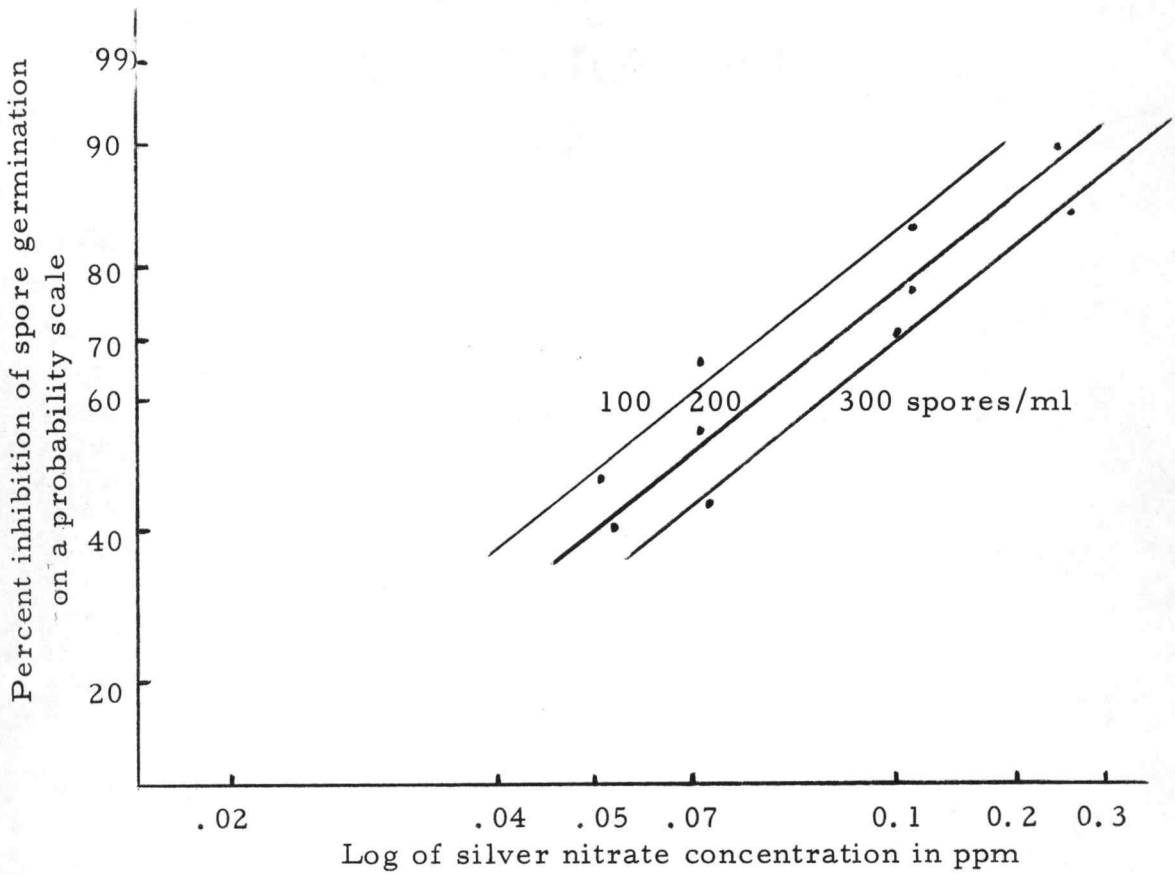

Figure 4. Effect of F. roseum spore concentration on the position of the dosage-response curve for silver nitrate.

Silver Output by the Silver Electrolytic Cell

The silver electrolytic cell was connected to a source of tap water to evaluate silver ion production by the cell under continuous flow conditions and to determine the loss of silver from the electrode. A flow meter was added to the discharge side of the electrolytic cell to measure total flow. Samples of the silver effluent were bioassayed for silver content and silver nitrate was used as a standard.

The electrolytic cell was equipped with a silver electrode weighing 160.4 grams at the start of the experiment. The electrode was 1/2 inch in diameter and 4-7/8 inches in length. At the completion of the test (25 days after initiation of the experiment), the electrode weighed 93.6 grams. During this period about 42,197 liters of tap water had passed through the cell, and 67.1 grams of silver were lost from the electrode. Thus, the effluent contained about 1.6 ppm silver.

Four 100-ml samples of the silver effluent were collected at five-day intervals for bioassay to determine the silver concentration. A dilution containing approximately 0.6 percent of the silver effluent gave a 50 percent inhibition of spore germination (Table 3). The concentration of silver nitrate to inhibit germination of 50 percent of the spores was 0.0157 ppm or 0.0099 ppm silver ion. Thus, the average concentration of silver ions from the four samples of silver effluent

Table 3. Percent inhibition of F. roseum spores by silver effluent produced in a silver electrolytic cell under continuous flow conditions.

Number of days after initiation of experiment 1/	Silver effluent concentration in percent	Inhibition of spore germination in percent 2/
5	1.0	92
	0.8	86
	0.6	51
	0.4	39
	0.2	23
	Control	0
10	1.0	96
	0.8	81
	0.6	52
	0,4	36
	0.2	20
	Control	0
15	1.0	96
	0.8	84
	0.6	48
	0.4	31
	0.2	14
	Control	0
20	1.0	92
	0.8	80
	0.6	49
	0.4	30
	0.2	21
	Control	0

1/ 100-ml samples were collected at five-day intervals and bioassayed for amount of silver within 24 hours.

2/ Average of three replications.

was 1.5 ppm. This result is consistent with the value obtained by calculation of the weight lost by the electrode during the experiment.

Effectiveness of Silver in Plant Disease Control

Control of dry rot of potato.

Dry rot of potato causes serious losses of stored potatoes according to Loring (7). Silver from the silver electrolytic cell was tested as a possible means for controlling dry rot caused by F. roseum.

The silver cell was filled with about 750 ml of distilled water, and the rectifier was switched on for ten minutes to discharge silver ions into solution. The silver effluent was then diluted immediately with distilled water and used to treat F. roseum spores. The spores were incubated with various concentrations of silver effluent for ten minutes. Pieces of quartered Kennebec potato tubers were dipped in the treated spore suspension for one minute immediately following spore treatment.

Inoculated tubers were placed in paper bags and kept at room temperature (72° F) for two weeks. Eight tuber pieces were placed in each bag, and the bags were then stapled across the top. At the end of the incubation period, the bags were opened, and the tuber pieces were inspected for visible dry rot. No dry rot occurred when the spores of the pathogen were treated with undiluted effluent (Table 4), and ten-fold reductions in the silver content of the

Table 4. Incidence of dry rot of Kennebec potatoes inoculated with F. roseum spores treated with silver effluent.

Concentration of silver ion per liter of effluent 1/	Severity of Dry Rot 2/			
	Replicate 1	Replicate 2	Replicate 3	Average
0.17	0	0	0	0
0.017	2	1	1	1
0.0017	3	3	2	3
0.00017	3	4	3	3
0.000017	4	4	4	4
0.0000017	4	4	4	4
0.00000017	4	4	4	4

1/ Silver ion concentration of the effluent was determined in a bioassay using inhibition of spore germination. Results with the effluent were compared with the results obtained with silver nitrate.

2/ 0 - no dry rot
1 - trace of dry rot
2 - moderate dry rot
3 - moderately severe dry rot
4 - severe dry rot

treatment solution caused decreasing control of dry rot (Figure 5).

Control of dry rot of sword-fern. To prevent the spread of dry rot of fern in the cartons during storage, silver nitrate solution was applied as a possible control. The fronds were dipped in different concentrations for five minutes. Dipping bundles of fronds in silver nitrate solutions was more effective in controlling dry rot than spraying the silver solutions on the fronds (Table 5). However, there were some difficulties with the dip method. The main disadvantages were the increase in shipping weight and the addition of the dipping step to the packing schedule. Because fern fronds are normally sprayed with water to prolong their storage life, spraying would be the most economical method of applying fungicides. Additional spray trials were made at higher silver concentrations, and it was found that spraying with concentration of silver of 0.8 and 1.0 ppm caused a significant decrease in the incidence of dry rot (Table 6).

To determine the best method of spraying fern fronds with silver solution, frond bundles were sprayed individually or the layers of bundles were sprayed in the packing cartons.

Spraying individual bundles was more effective in controlling dry rot than spraying the layers of bundles (Table 6). The former method apparently provided a more uniform coverage of the fronds. The spread of dry rot was completely controlled by a concentration

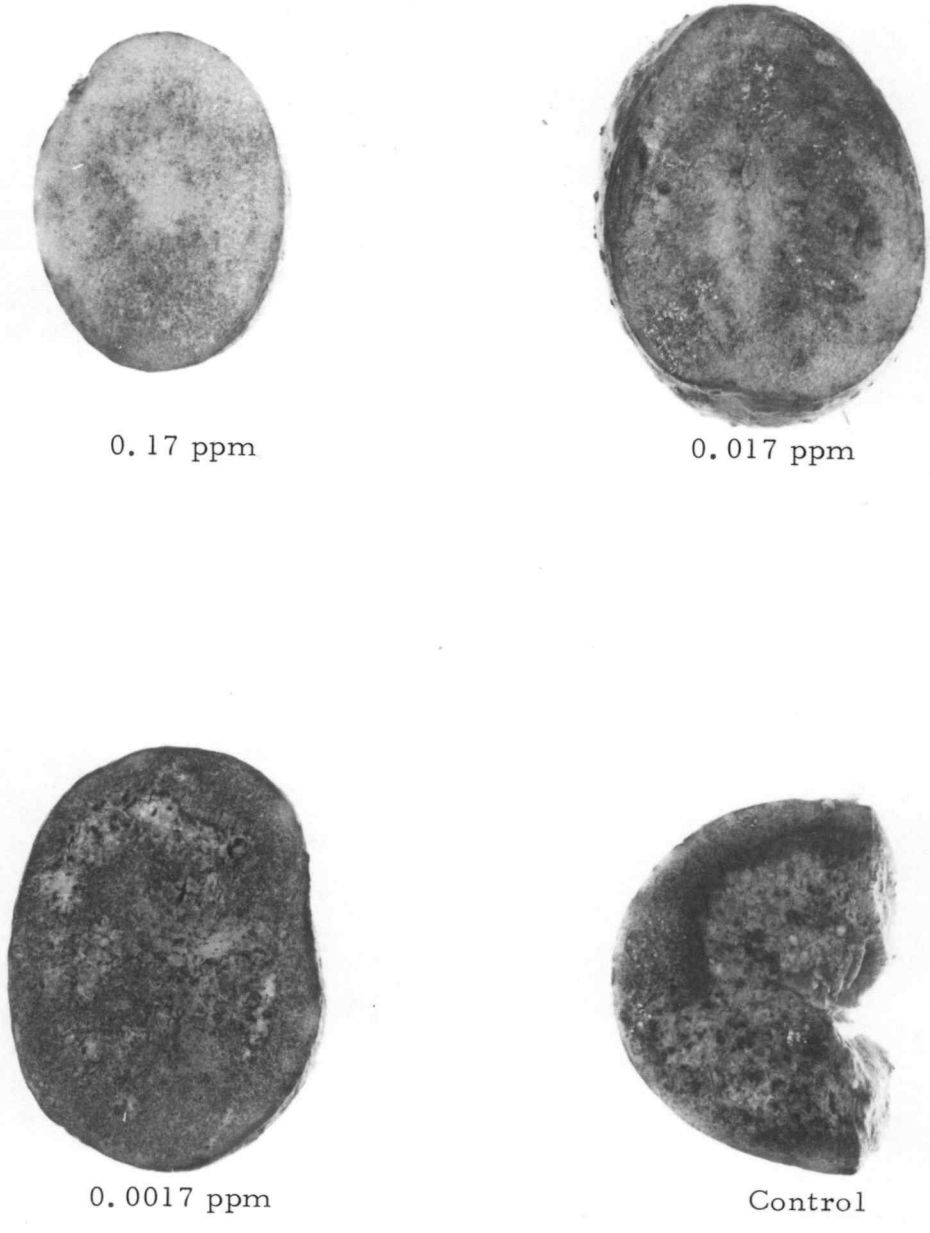

Figure 5. Severity of dry rot of Kennebec potato caused by F. roseum two weeks after dipping in spores treated with silver effluent.

Table 5. Effect of spray and dip treatment with silver nitrate on dry rot of sword-fern.

Silver nitrate treatment (ppm)	Percent fronds with dry rot 1/	
	Spray treated	Dip treated
0.05	99	30
0.07	94	16
0.09	89	9
0.11	82	2
Control	100	100

1/ 250 fronds per treatment incubated three weeks at 34° F.

Table 6. Effect of spraying individual bundles of fronds and layers of bundles in the packing carton on subsequent dry rot development.

Silver nitrate treatment (ppm)	Percent fronds with dry rot			
	Individual bundles sprayed		Layers of bundles sprayed	
	77° F 1/	34° F 2/	77° F 1/	34° F 2/
0.2	-	43	-	80
0.4	34	32	37	36
0.6	26	20	33	29
0.8	22	9	31	24
1.0	17	0	28	21
Control	100	100	100	100

1/ 250 fronds per treatment stored at 77° F for two weeks.

2/ 250 fronds per treatment stored at 34° F for three weeks.

of 1.0 ppm silver nitrate when the treated fronds were continuously incubated at 34° F (Figure 6).

The spread of dry rot in the cartons is influenced by temperature (Table 7). One carton of fronds treated with various concentrations of silver nitrate was incubated at 34° F, while another treated carton was held at room temperature (77° F) for 24 hours before it was stored at 34° F.

Bundles of fern were sprayed with 1.0 ppm of silver nitrate and then held at room temperature for varying time periods to determine the influence of storage temperature on control of dry rot. Temperatures within the packing cases were measured and recorded periodically during the experiment.

The internal temperature of the cases increased slightly after eight hours of incubation, but after 24 hours of incubation at 60 - 80° F, the internal temperature of the cases increased significantly (Table 8). There was no dry rot development until the internal temperature of the carton made a significant rise.

Control of peach leaf curl. To further evaluate the disease control potential of silver, orchard plots were treated on the Oregon State University farm using a single spray application. Five year-old Lovell peach (Prunus persica Batsch.) trees naturally infected with Taphrina spp. were selected. Silver effluent (0.34 ppm) from the silver electrolytic cell was compared with some commercially

Treated Frond Untreated Frond

Figure 6. Control of dry rot of sword-fern using 1.0 ppm silver nitrate and a storage temperature of 34° F.

Table 7. Effect of incubation temperature on dry rot development in fronds dip-treated with silver nitrate.

Silver nitrate treatment (ppm)	Percent fronds with dry rot 1/	
	Incubated at 34° F except for 24 hours at 77° F	Incubated at 34° F
0.05	69	34
0.07	61	16
0.09	42	9
0.11	18	2
Control	100	100

1/ 250 fronds per treatment incubated for two weeks.

Table 8. The effect of external temperature on heat build-up in packing cases and subsequent dry rot of fronds sprayed with 1.0 ppm silver nitrate.

Hours exposure at 60 - 80° F	Internal case temperature degrees F	Percent fronds with dry rot 1/
24	68	46
8	43	0
4	39.5	0
0 2/	38	100

1/ 25 bundles of fern per case and two cases per treatment.

2/ Unsprayed control.

available fungicides. Tag (phenylmercuric acetate) applied at 1.5 pt/100 gal and Cyprex (dodecyl guanidine acetate) applied at 1 lb/ 100 gal were applied as a single application.

The spray materials were applied with a jeep-mounted sprayer. To prevent washing off by rainfall, two materials were added to the silver effluent; a commercial "sticker," (Triton) and an inorganic mixture composed of iron sulfate and calcium hydroxide. The components of the latter material were added simultaneously to the silver effluent. Upon dilution of the spray material, the concentration of the sticker was about 5.0 ppm, and the concentration of the silver effluent was 0.34 ppm. The iron sulfate-calcium hydroxide mixture gave the greatest increase in the adhesion of silver under greenhouse and laboratory conditions in trials conducted by Nielsen (13).

The results of this experiment (Table 9) indicate that silver effluent gives poor control of peach leaf curl. The iron sulfate-calcium hydroxide mixture decreased the effectiveness of silver effluent in comparison to the control or to the treatment containing Triton. Leaves showing visible symptoms of curling were counted as infected, while leaves showing no visible symptoms were counted as healthy.

Control of apple scab. An orchard plot of ten year-old Richared Delicious apples (Malus domestica Barkh.) grafted on Malling 1V rootstocks was selected for further tests of the

Table 9. Peach leaf curl control with silver effluent and other fungicides.

Spray material	Concentration	Percent leaf infection			
		Trial 1	Trial 2	Trial 3	Average
Silver effluent	0.034 ppm	99[1/]	65[2/]	59[3/]	74
Tag	1.5 pt/100 gal	62	69	41	57
Cyprex	1 lb/100 gal	53	14	51	38
Control	--	92	89	97	93

1/ 5.0 ppm $FeSO_4 \cdot 7 H_2O$ - $Ca(OH)_2$ mixture.

2/ No sticker.

3/ Triton.

effectiveness of silver effluent for plant disease control. The apple trees were naturally infected with Venturia inaequalis (Cke.) Wint., the causal organism of apple scab.

The effectiveness of silver effluent was compared with Stauffer MV - 119A, an experimental organic spray material. Spray applications were made at the pre-pink, calyx, and first and second cover stages. All four applications were made with a jet-mounted sprayer at a pressure of 300 pounds per square inch. The leaves of the apple trees were sprayed to run-off.

Counts were made of both leaves and fruit showing symptoms of the disease. Infected leaves had lesions, and infected fruit had

visible scab. Silver effluent gave little, if any, control of apple scab, while Stauffer MV - 119A was quite effective in the control of this disease (Table 10). It is apparent that either the fungitoxicity of silver effluent was inadequate or that weathering inactivated the silver ions.

Phytotoxicity of Silver Sprays

To determine possible injury to plant tissue by silver sprays, sword-fern, salal (Gaultheria Shallon Pursh.), and Bountiful beans (Phaseolus vulgaris L.) were sprayed with silver nitrate solutions and silver from the electrolytic cell. Concentrations of silver ions were increased until phytotoxicity occurred.

Bean leaves were more sensitive to silver than were leaves of salal or pinnae of sword-fern. Darkening of the bean leaves began at 100 ppm and was severe at 1000 ppm silver nitrate. Discoloration of the salal leaves and sword-fern pinnae occurred at 500 and 1000 ppm (Table 11). No darkening occurred at 1, 10 or 50 ppm on salal or fern which could be considered safe concentrations for control of diseases on these species.

Table 10. Apple scab control with silver effluent and other fungicides.

Spray material	Percent Infection							
	Trial 1		Trial 2		Trial 3		Average	
	leaf	fruit	leaf	fruit	leaf	fruit	leaf	fruit
Silver effluent[1/]	72	81	79	98	73	97	75	92
Stauffer MV119[2/]	0	1	4	6	3	2	2	3
Control	81	91	76	87	84	96	80	91

1/ 0.1 ppm 2/ 1.5 pounds per 100 gallons.

Table 11. Phytotoxicity of silver nitrate and effluent from the silver electrolytic cell.

Concentration (ppm)	Degree of phytotoxicity[1/]		
	Bountiful Bean	Salal	Sword-fern
Silver nitrate 1000	severe	moderate	moderate
Silver nitrate 500	moderately severe	slight	slight
Silver nitrate 100	slight	none	none
Silver nitrate 10	none	none	none
Silver nitrate 0.17	none	none	none
Untreated control 0.0	none	none	none

1/ 250 leaves or fronds per treatment. Phytotoxicity as discoloration of the foliage.

DISCUSSION

Silver has had limited use as a fungicide due to the relatively high cost of silver compared to other heavy metals. Because of its high fungitoxicity and the availability of a silver electrolytic cell, silver was considered to possess a potential as a control for several field and storage diseases occurring in Oregon.

Two sources of silver ions were evaluated for controlling several plant diseases. Silver ions from silver nitrate and an electrolytic cell were selected as the two most promising sources. Until a cost comparison was made between the two sources, it was believed that the electrolytic cell might provide a more economical and in particular a more convenient source of silver ions than silver nitrate. However, ionic silver output by the electrolytic cell was considerably more costly than ionic silver from silver nitrate.

A cost comparison was made of silver in silver nitrate versus silver from a silver electrode. On the basis of producing 1000 gallons at a concentration of one ppm silver, the cost of using silver nitrate at $16.00 per pound would be $0.21 versus $1.11 for the electrolytic cell at $0.31 per gram of silver electrode. In addition to the $1.11 per 1000 gallons, the initial cost of the silver cell of approximately $150.00 would have to be pro-rated over a serviceable period of not more than ten years. It seems apparent that the silver

cell is a more expensive source of silver ions in the concentration range required for the effective control of plant diseases.

In the development of a fungicide, the working concentrations must be known. This presented no problem when silver nitrate was used, but did present one when silver was discharged from an electrode. Because of the complexity of chemical analysis for minute quantities of silver ions, a bioassay method was used.

Ionic silver gave promising control of dry rot of potato in laboratory trials. Undiluted silver effluent (0.17 ppm) gave complete control of dry rot. Although no visible residue was apparent, the chance of toxic residues of silver on potato tubers makes commercial use of silver doubtful. Applications of ionic silver on non-edible plants was then pursued.

One advantage of ionic silver as a fungicide is its relatively low phytotoxicity. Dry rot of fern is a disease requiring a control method, but because the fronds are used for decorative purposes they must not be discolored or damaged by the control treatment.

Silver was tested as a means of controlling dry rot of fern, and a concentration of 1.0 ppm silver nitrate spray was completely effective. At this concentration no phytotoxicity occurred. The dip method of application was more effective than the spray method.

Trials using silver ions were conducted in orchard plots. These trials showed silver ions to be ineffective in controlling apple

scab and peach leaf curl. Apparently ionic silver was inactivated on the foliage.

The use of ionic silver seems to be limited to the control of certain diseases where the fungitoxicity of silver ions is not destroyed. The use of commercially available "stickers" only slightly improved the field performance of ionic silver. It appears that the use of ionic silver in plant disease control will be limited in scope.

SUMMARY

1. The fungicidal activity of silver was reduced at temperatures below 20° C.
2. Using distilled water and a ten-minute discharge, approximately 0.17 ppm of silver ion was released from a silver electrolytic cell.
3. Approximately 1.5 mg of silver were lost from the electrode per liter of tap water. This occurred under continuous flow of water through an electrolytic cell equipped with a silver electrode.
4. Silver effluent retained its fungitoxicity for at least five days after preparation. After eight days the effluent had lost some of its fungitoxicity, and after 12 days a significant loss of toxicity had occurred.
5. On the basis of producing 1000 gallons of a solution of one ppm silver, the cost using silver nitrate would be $0.20 versus $1.11 for silver from an electrolytic cell.
6. Silver effluent obtained by using a ten-minute discharge and distilled water was toxic to spores of F. roseum, the cause of dry rot of potato. A ten-fold dilution of the effluent did not give complete control, and greater dilutions gave only slight control of the disease.

7. The amounts of silver required to cause phytotoxic responses are much greater than the amount of silver necessary to control dry rot of sword-fern and Kennebec potato. No phytotoxicity or visible residue occurred when less than 100 ppm of silver nitrate was sprayed on sword-fern fronds and salal leaves. No phytotoxicity or visable residue occurred when less than 50 ppm silver nitrate were sprayed on bean leaves.

8. The use of a sticker to increase the adhesion of silver was only slightly effective in increasing the disease control potential of silver.

9. The concentration of silver nitrate necessary to effectively control the spread of dry rot of fern at 34° F was 1.0 ppm. At lower concentrations, dry rot developed even under cold storage conditions (34°F). However, concentrations up to 100 ppm can be used without danger of phytotoxicity.

10. The best method of application was the dip treatment of individual fern frond bundles. Although effective in controlling dry rot of fern, this method of application increased the moisture content of the packed fronds.

11. If the cartons of fern fronds are allowed to remain at room temperature for 24 hours following treatment, the internal case temperatures increase significantly and dry rot development is enhanced.

12. Ionic silver discharged from the silver electrolytic cell was not effective as a pre-harvest spray in the control of apple scab and peach leaf curl diseases.

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