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THE FIELD TESTING OF COPPER-SPRAY COATINGS.

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THE PERSISTENCE OF SPRAYS CONTAINING COPPER.

General experience in the use of copper-containing spray mixtures indicates a progressive decrease in the fungicidal effectiveness of the spray coatings which is to a large extent proportional to the relative amounts of spray residue present. A direct decrease in effectiveness is brought about by weathering factors, such as washing by rain or dew, mechanical abrasion by wind, and slow chemical change in the exposed spray coating. An indirect decrease in effectiveness may result from the growth extension of plant parts, either through enlargement of organs already sprayed or through the development of new organs subsequent to the spray application. In practice the interval between spray applications depends on the rates of both weathering and growth extension. The second can be judged by careful observation. In so far as the first is concerned, observations are often misleading. Present-day spray calendars are based only in a general way on the average practical and experimental experience of past years. In any particular season or section or planting the actual requirements for adequate protection may vary widely from such average, necessitating greater or less frequency of applica-

[1] The writers wish to express their appreciation of the cooperation in connection with this work of the staff of the Miscellaneous Division, Bureau of Chemistry, United States Department of Agriculture.

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tion than the standard spray calendar provides. It is difficult to estimate the effects of the complicated set of local factors that determine the effective period of any spray application. A suitable chemical test of the spray coating would seem to be a desirable aid in forming judgment as to the proper time for renewal. Such test should be simple, rapid, and reasonably accurate. The more refined methods of chemical analysis, while very exact, would not well serve the practical purpose, because of the special requirements in professional training, apparatus, and time.

A PRACTICAL METHOD OF FIELD TESTING.

The following method has been used during two seasons and has been found to be reasonably satisfactory in field practice. This is indicated by the consistent results obtained with varying strengths of copper sprays, many of which have been checked by exact chemical analyses of duplicate samples.

A 200-gram fresh weight sample of leaves is washed at least three minutes, with occasional stirring, in 1,000 c. c. of a 0.2 per cent solution of chemically pure nitric acid in water, either distilled or sufficiently pure to give correct results. A convenient amount of this acidulated wash water is treated with a few drops of 2 per cent solution of potassium-ferrocyanid solution, sufficient to precipitate the copper. A color comparison is then made with a series of known dilutions of a standard copper solution, similarly treated with the potassium-ferrocyanid solution. From this comparison the copper content of the wash water is determined. For more exact readings a colorimeter may be used.

The standard copper solution is made by dissolving 3.928 grams of pure crystals of copper sulphate in water to make 1,000 c. c. Each cubic centimeter of such standard solution would then contain 1 milligram of copper, and by proper dilution with water stock solutions may be readily prepared for the comparison series containing one-half to 10 mg. of copper per 100 c. c. of water, in one-half or 1 mg. grades. If the wash water gives readings above 8 or 10 mg. of copper per 100 c. c. it should be diluted for accurate color comparison and account of this taken in figuring results. On the basis indicated above, any direct reading multiplied by 5 will express the amount of copper in the spray residue in milligrams per 100 grams fresh weight of leaves, a convenient unit for tabulation purposes. The solutions of potassium ferrocyanid and of nitric acid may be varied in strength for considerable differences in the copper content of the spray coating, so as to avoid using unnecessarily strong solutions, with consequent reduction in the delicacy of the test. There must always be a sufficient amount of nitric acid to dissolve completely the copper compounds and of potassium ferrocyanid to precipitate them completely.

Due care must be taken to make the leaf samples representative. About three samples of 200 grams each should be taken at various parts of a sprayed planting. Under ordinary conditions collections every three or four days will give satisfactory indication of the persistence of the spray residue. If in the case of any variety of leaf there is a tendency toward discoloration of the wash water from dissolution of organic compounds in such a way as to interfere seriously with the color comparisons, one may titrate a measured quantity of the wash water with a solution of potassium ferrocyanid previously standardized against a copper solution of known strength, using a weak ferric-chlorid solution as the end-point indicator, in small drops on a white porcelain plate. Tests on many kinds of crop plants indicate that this titration method will be seldom needed. Permitting the weighed leaves to dry or to "heat" may interfere with accurate testing.

The coating on the foliage will usually prove to be a fair index to the thoroughness of application to other parts. For convenience, the samples are based on weight, but the spray coating is proportional to area. The different ratios between these, due to difference in species or age of leaves, when considerable, should be given due weight in making comparisons. Obviously, it is possible to secure as high tests from strong sprays unevenly applied as from moderate strengths more evenly and effectively used, but it is believed that the histories of such cases will guard against incorrect interpretations.

The amount of spray residue necessary for adequate protection against any specific disease would doubtless vary with a complex set of factors. There would thus exist a critical transition zone with maximum and minimum limits above which protection would be secured and below which protection would be insufficient. These limits can be determined only from investigations covering a period of years. The best spray practice should aim at keeping the spray coating always above the maximum limit, and ordinarily good practice should never take the risk of falling below the minimum limit.

FIELD TRIALS.

During the two seasons that this method has been in use, something like 75 schedules have been tested by the writers. The following results are selected as being representative.

APPLE LEAVES AT CROZET, VA.

Winesap apple leaves were tested at Crozet, Va., June 23 to July 22, 1917. The orchard was about 5 acres in extent and was sprayed with 3–4–50 Bordeaux mixture on the date of the first collection. Each sample was divided, one portion being sent to the Bureau of Chemistry, United States Department of Agriculture, for exact analysis, and the other tested by the field method outlined above.

The analytical data are based on the dry weight of the samples, and the field tests data have been converted to the same basis by assuming a constant value of 35 per cent for the dry weight of the leaves (fig. 1).

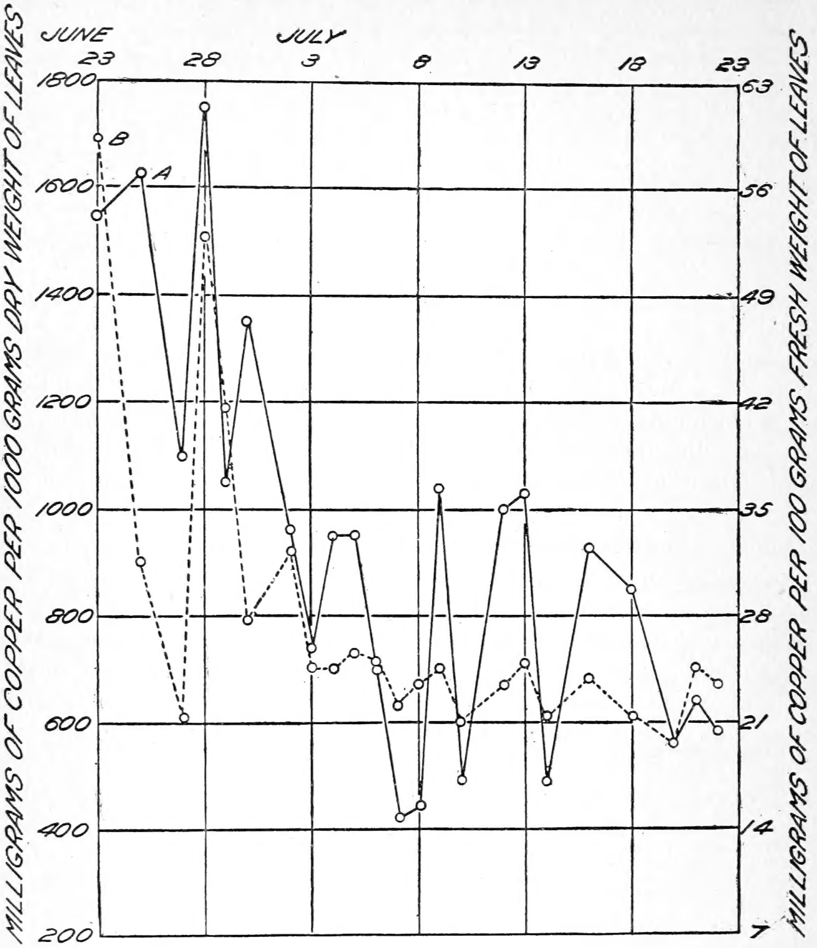

FIG. 1.—Tests for copper on apple leaves sprayed with 3-4-50 Bordeaux mixture. *A* represents the results of chemical analyses on the basis of milligrams per 1,000 grams dry weight of leaves. *B* represents the results of field tests of duplicate samples on the basis of milligrams per 100 grams fresh weight of leaves. The two scales are plotted on an equivalent basis, assuming the dry weight of the leaves to be constantly 35 per cent.

A scale for equivalent readings in milligrams of copper per 100 grams fresh weight of leaves is also indicated in the figure.

At this early period in the work the samples were too small to give the best results for so large a planting. However, there is reasonably close agreement between the graphs secured by the two methods, with the exception of a few of the first determinations.

Tests were made during July and August, 1917, in two apple orchards, A and B, at Crozet Va., sprayed by the owners with 3–4–50 Bordeaux mixture according to their usual practices. Both orchards had received a first application of the mixture about the middle of June. The readings indicate the milligrams of copper per 100 grams fresh weight of leaves. Two other orchards, C and D, in the same locality, bore light crops of fruit and for this reason were given rather light spraying of 3–4–50 Bordeaux mixture by their owners.

Tests before and after the second and third spray applications in these orchards gave the results shown in Table I.

TABLE I.—*Field tests in spraying apple orchards A, B, C, and D with 3-4-50 Bordeaux mixture, at Crozet, Va., in July and August, 1917.*

Spray application.	Orchard A.		Orchard B.		Orchard C.		Orchard D.	
	Date sampled.	Reading.	Date sampled.	Reading.	Date sampled.	Reading.	Date sampled.	Reading.
		Milli-grams.		*Milli-grams.*		*Milli-grams.*		*Milli-grams.*
First	July 9	41.6	July 9	35.7	July 19	41.6	July 20	29.4
	July 12	29.4	July 12	21.7				
Second	July 17	125			July 23	62.5	July 24	47.6
	July 19	125	July 20	166.6	July 26	20	July 26	31
	July 23	111.1	July 24	125				
	July 26	76.9	July 26	100				
Third	August 2	100	Aug. 2	125	Aug. 3	55.5	Aug. 2	71.4

BEARING GRAPEFRUIT TREES AT WINTER PARK, FLA.

Two spray applications on a commercial basis were made on plats of bearing grapefruit trees at Winter Park, Fla., the first on March 9 and the second on April 16, 1918, using a power sprayer developing approximately 225 pounds pressure. The plats contained 30 trees each.

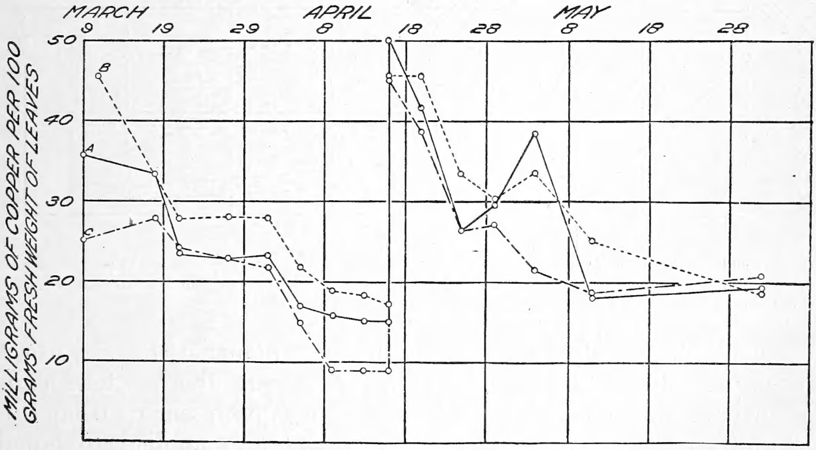

FIG. 2.—Field tests for copper on grapefruit leaves sprayed with 3-4-50 Bordeaux mixture (*A*), 3-4-50 Bordeaux mixture with the addition of a certain oil emulsion (*B*), 3-3½-50 Burgundy mixture (*C*). Each application was renewed on April 17.

Single samples of 200 grams fresh weight were taken from each plat at intervals of about four days until June 1 (fig. 2). In this test 3–4–50 Bordeaux mixture was used with and without a certain oil emulsion, and the Burgundy mixture was also made up with 3 pounds of bluestone. The tests show consistent decreases in copper content of the coatings.

CITRUS NURSERY STOCK AT BRADENTOWN, FLA.

At Bradentown, Fla., comparative tests were made with three strengths of Bordeaux mixture, made up according to 3–4–50, 2–2⅔–50, and 1–1⅓–50 formulas. The applications were made in

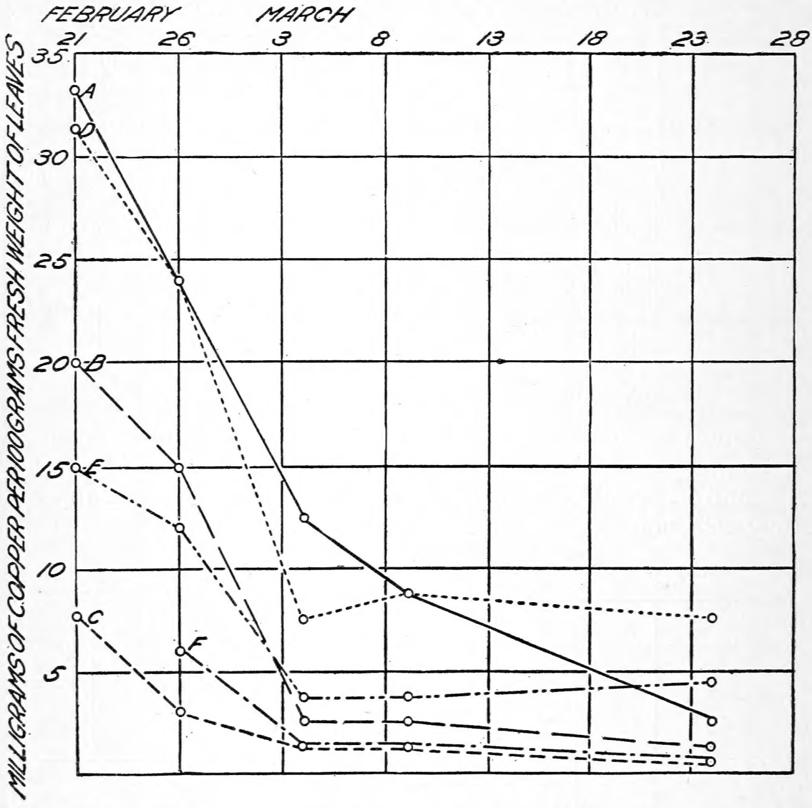

FIG. 3.—Field tests for copper on sour-orange leaves. *A* and *D* were sprayed with 3–4–50 Bordeaux mixture; *B* and *E*, with 2–2⅔–50 Bordeaux mixture; and *C* and *F*, with 1–1⅓–50 Bordeaux mixture. *A*, *B*, and *C* were in Nursery I; *D*, *E*, and *F* in Nursery II.

February and March, 1918, on two nursery plantings of overgrown sour-orange stock. In Nursery I the trees were about 6 feet high; in Nursery II about 3 feet. A bucket spray pump was used, and in each nursery measured amounts of spray were applied to equal lengths of the nursery rows to secure a distribution of the spray as equal as possible. The fresh weight of each leaf sample approximated 100 grams. Figure 3 shows the relative agreement of the field test results with the strengths of spray applied. Plat F was sprayed with the others on February 21, but the first sample was lost.

CELERY AT BRADENTOWN, FLA.

Figure 4 shows the behavior of Bordeaux mixture on celery at Bradentown, Fla., in February and March, 1918. Each grower prepared and applied the mixture in his own way to plantings of

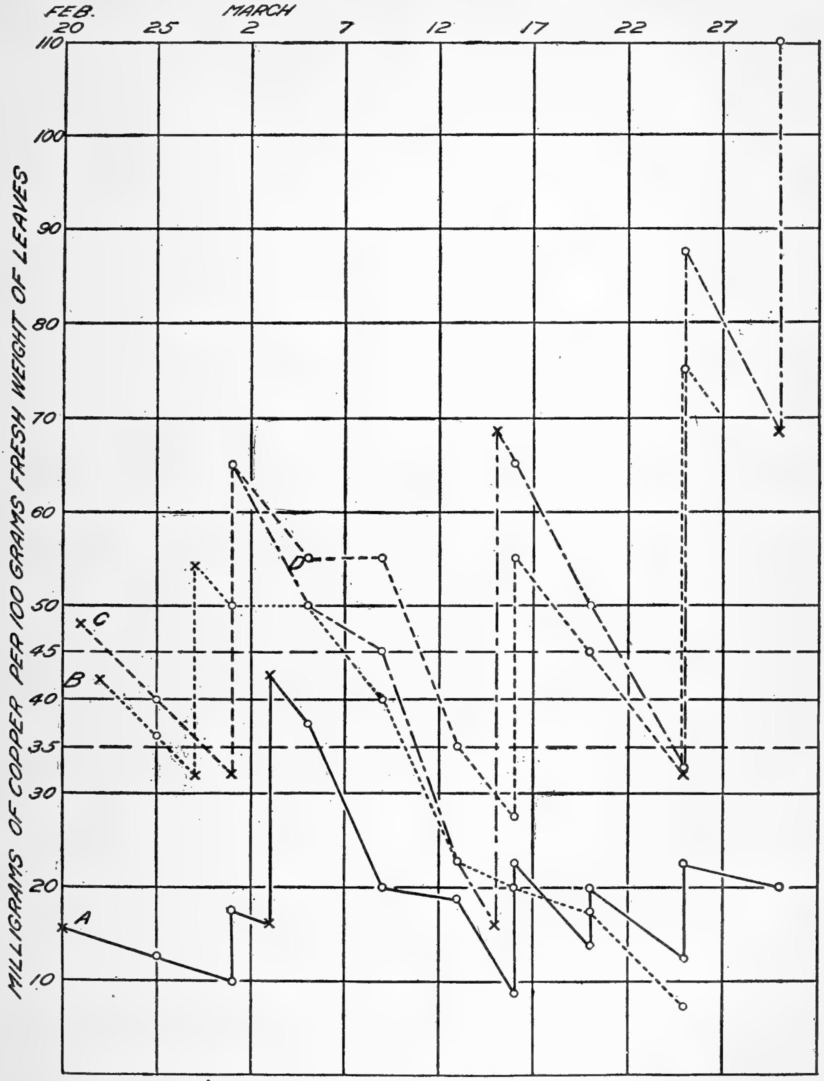

Fig. 4.—Field tests for copper on celery leaves. Four fields were sprayed by the owners with Bordeaux mixture supposedly made up in each case with 6 pounds of bluestone in 50 gallons. A hypothetical safety zone is indicated between the 35 and 45 milligram tests. The actual determinations are indicated by O, the estimated interpolations by X.

1 or more acres. In every case the grower claimed that 6 pounds of bluestone were used in 50 gallons of the Bordeaux mixture. Knapsack sprayers were used. With the exception of field D one or

more applications had been made before testing began. When samples could not be taken immediately before and after a spray application, estimates have been made from the previous or subsequent direction of the graph to determine the probable values, and such approximations are indicated by X rather than by O in plotting.

The owner of field A, besides guessing at the quantities of ingredients, followed a faulty method of mixing the spray. In spite of frequent applications, the results were very unsatisfactory. If it is assumed that adequate protection from some specific celery disease is secured by spray residues testing between 35 as a minimum and 45 as a maximum for a transition zone, it will be seen that this field was really protected for only 3 out of 38 days by 6 applications.

Field B, with two applications, dropped below this theoretical transition zone 10 days after the second application and stood with insufficient protection during the remaining 15 days of the test period.

Field C, with four applications, was insufficiently protected during a total of five days, but this could have been prevented by slight shortening of the intervals between applications.

Field D was late celery sprayed first on March 1. On the basis of the limits assumed for the critical zone, the second application should have followed the first in 10 days, and the interval between the third and fourth might have been considerably prolonged provided large growth development had not occurred.

DIRECTIONS FOR USE.

As a guide in the practical use of this method, a condensed statement of the successive steps may be outlined, as follows:

Dissolve 3.928 grams of pure crystals of copper sulphate in distilled water and make up to 1,000 c. c.

Prepare in well-stoppered bottles stock dilutions of the above solution containing one-half c. c., 1 c. c., 1½ c. c., 2 c. c., and so on up to 10 c. c., in 100 c. c. of distilled water. These dilutions would then contain from one-half to 10 milligrams of copper per 100 c. c.

Prepare a weak solution of potassium ferrocyanid, about 2 grams in 100 c. c. of distilled water.

All of the above may be prepared in advance, by a pharmacist if desirable, and kept for a season's use.

Collect at least three representative samples of sprayed leaves, each of 200 grams fresh weight.

Wash each sample separately in 1,000 c. c. of pure water to which has been added 2 c. c. of chemically pure nitric acid, being careful to use glass or chinaware vessels and stirring occasionally for at least three minutes.

Pour into test tubes or vials of uniform size about 5 c. c. portions of the graded stock solutions of copper sulphate, and add to each a few drops of the potassium-ferrocyanid solution, sufficient to develop the maximum color reaction.

Treat similarly 5 c. c. portions of the washings from the leaf samples. Compare the color developed in these with the graded series. Take for a reading the number expressing milligrams of copper per 100 c. c. in the stock dilution that matches closest in color intensity. Simply multiplying this reading by 5 will then give a value in milligrams of copper per 100 grams fresh weight of leaf sample, a convenient unit for finally expressing the amount of copper in the spray coating. The results from the several samples may be compared and averaged.

CONCLUSION.

This field method of following the persistence of copper-containing sprays promises to be of service to pathological investigators, agricultural experts, and commercial growers along these lines: (1) To secure data showing the persistence of copper-containing sprays as it may be influenced by method of preparation, weathering, or other factors; (2) to determine the minimum and maximum limits of working safety zones, as measured by evenly distributed residues, effective for the practical control of specific diseases; (3) to secure prompt correction of faulty spraying practices, either in the preparation of mixtures or in the times or modes of application, with a view to insuring more effective and economical protection of crops; and (4) to serve as a practical guide in timing new applications, especially after rainy periods.

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