cent. higher than those by the magnesium nitrate method. It is not believed, however, that the magnesium nitrate method failed to secure all of the phosphoric acid present in the crop, but rather that there were impurities present in the magnesium pyrophosphate obtained by the acid method; it frequently was of an abnormal color and had a reddish tint, in which case a quite strong reaction for iron was obtained. Furthermore, in a number of instances the magnesium pyrophosphate obtained by each method was dissolved in nitric acid and, upon reprecipitation and ignition, the results by the two methods were more nearly alike.

By a comparison of the results with turnip roots, in which case more than one determination was frequently made by each of the methods, it may be seen that there was more difficulty in obtaining parallel results with the acid method than with the other.

It should be said in explanation of the frequent wide differences in the determinations by a given method, that it was thought advisable to include all of the results as affording an indication of the capabilities of the two methods as followed in the routine analysis of a considerable number of samples, where the time element would preclude reprecipitation for the purpose of increasing the purity of the final product.

It is recognized that a wider experience with the acid method would probably lead to desirable modifications, but for the interest of those who might wish to use the method, the results are presented at this time.

AGRICULTURAL EXPERIMENT STATION,
KINGSTON, RHODE ISLAND.

[CONTRIBUTION FROM THE INSECTICIDE AND WATER LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

COMPOSITION OF THE LIME, SULPHUR AND SALT WASH.[1]

BY J. K. HAYWOOD.

Received November 23, 1904.

SOME two years ago the author received a sample of the lime-sulphur-salt wash, prepared in the usual way from commercial chemicals, from the Division of Entomology, United States Department of Agriculture, with the request that it be subjected

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[1] Credit is due Mr. B. H. Smith who assisted in the analytical work in this paper and to Mr. C. L. Marlatt for suggesting the advisability of the investigation.

to a qualitative examination and a report made as to the probable reason why this mixture gave more satisfactory results in a dry than in a moist climate. The results of this work were published in circular No. 52 (second series) of the Division of Entomology, and are as follows:

"The lime-sulphur-salt wash contains the following substances in solution: A large amount of calcium sulphide, some of the higher sulphides of calcium (as CaS_3 and CaS_5) small amounts of calcium sulphate, and traces of calcium sulphite, and a large amount of calcium thiosulphate; also some of the excess of lime is in solution. The residue is composed of lime.

"On evaporating down a portion of the wash with a blast and at a gentle heat no decided change takes place. Calcium sulphide still remains as does calcium thiosulphate. A small amount of sulphur is deposited (doubtless from the polysulphides of calcium) and the amount of calcium sulphate is increased to a small degree."

Based on the above data a theory as to the action of this wash in moist and dry climates was given.

Recently the author began a new study of this wash, using different periods of boiling and chemically pure reagents. Quantitative methods of examining the wash before and after applying to the tree were also employed, such quantitative methods not having come to the author's notice when making the examination reported above. Based upon this much more extended and complete investigation, certain views expressed above require modification.

The only complete change in regard to the composition of the wash concerns the relative proportions of calcium sulphide and calcium polysulphides, the author's recent work having shown that instead of a large amount of calcium sulphide and a small amount of polysulphide being present in the original wash, a large amount of the polysulphide and little or no sulphide are present. The qualitative results in regard to this point were misleading.

A fractional part of the following formula was used in preparing the lime-sulphur-salt wash, the boiling being carried on in a closed enamel boiler, and the chemicals being chemically pure. The time of boiling was the only variable factor. Lime 10 pounds, sulphur 6⅔ pounds, salt 5 pounds, added to 20 gallons of water in the order named. In one experiment the salt was left out to determine the effect of this constituent on the composition of the wash. After mixing the ingredients as above the total volume was determined and in every experiment thereafter whatever the time of boiling and the consequent reduction in volume, the total volume was made up to the volume as determined above, and aliquot portions of the mixture taken for analysis. Theoretically, each 100 cc. of the mixture prepared as above should contain 5.55 grams of total calcium oxide and 3.89 grams of total sulphur in case there has been no loss by volatilization or mechanically.

The exact method of making the analyses in the following table was as follows: First the mixture was boiled the required time, and then made up to the correct volume as determined above. This mixture was then thoroughly shaken up and 100 cc. portions taken for analysis. The 100 cc. portion was weighed, poured through a Gooch filter, sucked dry and the residue dried and weighed. The difference between the total weight and the weight of the residue was taken to be the weight of the liquid portion in 100 cc. of the mixture. An aliquot part of the liquid portion was weighed in order to obtain the weight of 1 cc. The total weight of the liquid divided by the weight of 1 cc. gives the number of cubic centimeters of liquid in 100 cc. of the whole mixture. The total dissolved sulphur and soluble calcium were now determined in 1 cc. of the liquid. The results obtained multiplied by the number of cubic centimeters of liquid in 100 cc. of the mixture gave the weight of the dissolved calcium oxide and sulphur in 100 cc. of the mixture.

The residual sulphur was next determined in the residue as obtained from 100 cc. of the entire mixture. The residual calcium oxide was obtained by subtracting the soluble calcium oxide from the theoretical total calcium oxide. The calcium was determined as oxalate.

Sulphur was determined by oxidizing a small quantity of the sulphur solution with hydrogen peroxide in the presence of potassium hydroxide and with the aid of heat and precipitating the resulting sulphate with barium chloride.[1]

The following results were obtained when the time of boiling was varied:

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[1] For the details of this method see article of S. Avery, in Proceedings of the Association of Official Agricultural Chemists, 1904.

TABLE I.—LIME AND SULPHUR IN 100 CC. OF LIME-SULPHUR-SALT WASH.

Time of boiling.[1]	Sulphur in solution. Grams.	Residual sulphur. Gram.	Total sulphur. Grams.	CaO in solution. Grams.	Residual CaO. Grams.	Total CaO. Grams.
15 minutes	3.03	0.38	3.41	1.64	3.91	5.55
30 "	3.66	0.09	3.75	1.95	3.60	5.55
45 "	3.72	0.02	3.74	1.93	3.62	5.55
60 "	3.75	0.05	3.80	2.13	3.42	5.55
90 "	3.47	0.05	3.52	1.85	3.70	5.55
Theoretical amts.	—	—	3.89	—	—	5.55

From the above table it would appear (1) that the solid sulphur was not completely dissolved by fifteen minutes' boiling, (2) that a thirty-minute boiling period was nearly but not quite enough, (3) that a forty-five- to sixty-minute period of boiling dissolved practically all of the sulphur present, and was consequently the best period to boil the wash in order to get the largest amount of sulphur in solution. By continuing the boiling beyond one hour the mixture became very thick with the quantity of material used, so that some of the sulphur was very likely lost mechanically.

To test the effect of salt on the composition of this mixture the wash was prepared just as before except that salt was left out, a one-hour period of boiling being employed. A comparison of the figures thus obtained with those above, for a like period of boiling, is given in Table II.

TABLE II.

Ingredients.	Sulphur in solution. Grams.	Residual sulphur. Gram.	Total sulphur. Grams.	CaO in solution. Grams.	Residual CaO. Grams.
Lime-salt-sulphur	3.75	0.05	3.80	2.13	3.42
Lime-sulphur	3.85	0.04	3.89	2.02	3.53

From the above it will be seen that salt has no material effect on the composition of the wash, at least in so far as the total soluble sulphur and calcium oxide are concerned.

An attempt was next made to determine what compounds of sulphur are formed in this wash, and also whether they are changed by varying periods of boiling. To do this, the following methods of analysis were used.

Sulphur in Solution as Sulphides.—A measured quantity of the sample was treated with ammoniacal zinc chloride and heated on the steam-bath for about an hour. It was then filtered, the filter and contents treated with potassium hydroxide solution

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[1] The mixture was actually brought to a boil before the time was taken.

and hydrogen peroxide and the resulting sulphates precipitated with barium chloride.

Sulphur in Solution as Thiosulphates.—A measured quantity of the solution was treated with ammoniacal zinc chloride and filtered to get rid of sulphides. The filtrate was titrated to neutrality, with standard hydrochloric acid, using methyl orange as indicator, and then titrated with standard iodine solution. The reading thus obtained gave the thiosulphates and sulphites. Since the sulphites are present in such small amounts, however, the number of cubic centimeters of iodine used may be considered to represent only the thiosulphates.

Sulphur as Sulphates and Sulphites Combined.—The solution remaining from the determination of thiosulphates in which both thiosulphates and sulphites had been oxidized was acidified with hydrochloric acid and precipitated with barium chloride.[1]

Working by the above method of analysis the following results were obtained with several samples of the lime-sulphur-salt wash,[2] where the time of boiling was the only variable factor.

TABLE III.—SULPHUR COMPOUNDS IN 100 CC. OF THE LIQUID PORTION OF THE LIME-SULPHUR-SALT WASH.

Time of boiling.	Sulphur as thiosulphates. Gram.	Sulphur as sulphides and polysulphides. Grams.	Sulphur as sulphites and sulphates. Gram.	Total sulphur. Grams.
15 minutes	0.63	2.59	0.004	3.224
30 "	0.76	2.91	0.004	3.674
60 "	0.84	2.91	0.01	3.76
90 "	0.86	2.92	0.01	3.79
60 " (without salt)	0.88	2.92	——	3.80

Four points are brought out by the above results, (1) a one-hour period dissolves practically all of the sulphur, (2) the thiosulphates are somewhat increased by a more prolonged period of boiling, (3) the combined sulphates and sulphites are somewhat increased by a more prolonged period of boiling, and (4) salt has practically no effect on the composition of the wash in so far as the sulphur compounds are concerned.

It is probable that the primary reaction followed in the above combination of sulphur and lime is as follows:

$$3Ca(OH)_2 + 12S = CaS_2O_3 + 2CaS_5 + 3H_2O \qquad (1)$$

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[1] The above methods of analysis and those to follow are combinations of Avery's method for determining sulphur and certain methods of determining sulphur as given in Sutton's "Volumetric Analysis," modified to suit the conditions here presented.

[2] Different samples from ones previously examined.

Such a reaction, however, would lead to the formation of less sulphur as thiosulphate, and more sulphur as pentasulphide, than is indicated in most cases in the above table. It is therefore probable that either or both of the two following secondary reactions take place, both of which would lead to the formation of more thiosulphate and less polysulphide, thus approximating the figures as found above:

$$3Ca(OH)_2 + 8S = CaS_2O_3 + 2CaS_3 + 3H_2O \qquad (2)$$

and

$$CaS_5 + 3O = CaS_2O_3 + 3S. \qquad (3)$$

The sulphur set free in this last reaction would on further boiling combine with more lime to form thisoulphate and polysulphide. If the boiling were continued, it will be seen that more thiosulphate would constantly be formed at the expense of the pentasulphide. Since the figures as given above indicate that more thiosulphate and less polysulphide are formed than is indicated by theory for equation (1), it is probable that reaction (3) is the principal or only secondary reaction which leads to the increased formation of thiosulphate.

It is well known that thiosulphates in solution change slowly to sulphites, which in turn change to sulphates according to the following reactions:

$$CaS_2O_3 = CaSO_3 + S. \qquad (4)$$

$$CaSO_3 + O = CaSO_4. \qquad (5)$$

It is therefore probable that sulphates and sulphites are found in this wash because of the above reactions.

To recapitulate then, we may say that the lime-sulphur-salt wash is probably formed in the following way: First, the lime and sulphur react and calcium thiosulphate and pentasulphide are formed; second the calcium pentasulphide is partly changed to calcium thiosulphate and free sulphur; third, the sulphur set free recombines to a large extent with the calcium hydroxide according to reaction (1); fourth, the calcium thiosulphate formed is changed to a slight extent to calcium sulphite and sulphur; fifth, the calcium sulphite is partly oxidized to calcium sulphate. All of the above reactions are well known and can be found in the leading books of reference such as Mendeléeff's "Principles of Chemistry," Thorp's "Dictionary of Applied Chemistry," Frémy's "Chemical Encyclopedia," etc. It will be thus seen that we may expect to find and do find in the lime-salt-sulphur wash, comparatively large quantities of pentasulphide and thiosulphate, and extremely small quantities of sulphates and sulphites.

An attempt was next made to determine what changes take place in the sulphur compounds of the wash when it is sprayed upon the tree. To imitate as closely as possible actual spraying conditions, measured samples of the wash (5 cc. usually) were soaked up by a large quantity of filter-paper which had been cut in slips and placed in large porcelain dishes. These dishes were immediately put in the open air in direct sunlight and the paper allowed to dry. This usually took about one hour. The dishes were then placed in the open air and allowed to stand varying lengths of time. In one series of experiments the paper was moistened each morning to represent dew, in another series they were allowed to remain undisturbed until analyzed. From the reactions already given above we would expect that the following changes in the wash would take place, when it was allowed to dry in the open air: (1) The pentasulphide would be oxidized to thiosulphate and sulphur, according to $CaS_5 + O_3 = CaS_2O_3 + S_3$. This would result in the formation of more thiosulphate than was already present and to the deposition of free sulphur in a very finely divided form. (2) The total thiosulphate would then be changed, to some extent, to sulphite and deposit free sulphur according to $CaS_2O_3 = CaSO_3 + S$. (3) The sulphite would then be partly oxidized to sulphate according to, $CaSO_3 + O = CaSO_4$. We would finally expect to find in the wash, then, after it had dried on the tree, free sulphur, calcium thiosulphate and small quantities of calcium sulphate and sulphite. The longer the action of the air and dew continued the less calcium thiosulphate we would expect to find present, and the more sulphites and sulphates. Of course, calcium hydroxide would be present, which would be gradually changed to carbonate. The sodium chloride appears to have no effect on the composition of the wash and would very likely remain as such on the tree. For experimentation a wash was prepared by boiling the constituents together one hour. Its composition was as follows:

	Grams per 100 cc. of solution.
Sulphur as thiosulphate	0.85
" " polysulphide	2.93
" " sulphate and sulphite	0.02
Total	3.80

The following methods were used to determine the composition of the wash after drying on filter-paper.

Total Free Sulphur.—The filter-paper was extracted in a Soxhlet extractor with carbon bisulphide. The carbon bisulphide was evaporated off, the residual sulphur dissolved in concentrated potassium hydroxide by boiling and the sulphur determined as sulphate according to Avery's method. The filter-paper remaining from the above treatment was allowed to stand until all carbon bisulphide had evaporated and then all soluble sulphur compounds extracted with water.

Sulphur as Sulphides.—These were tested for, but none were found present. The whole of the filtrate was now titrated to neutrality with standard hydrochloric acid, using methyl orange as indicator, made to a definite volume and aliquot portions used for analysis.

Sulphur as both Sulphates and Sulphites.—These were determined by the method already indicated earlier in this paper except that a previous precipitation of the sulphides was not necessary.

Sulphur as Sulphites and Thiosulphates.—A measured quantity of standard iodine was placed in a beaker and the neutral filtrate was added till all the iodine had been used up. From the quantity of filtrate used the quantity of iodine corresponding to the whole filtrate could be calculated. The solution was titrated by adding to the iodine rather than adding the iodine to the solution, because it has been found by many investigators that more constant results are obtained in this way.

Sulphur as Sulphite.—The solution remaining from the determination of sulphites and thiosulphates was now titrated with standard sodium hydroxide to neutrality. The method of calculating sulphite from this figure is given on page 353 of Sutton's "Volumetric Analysis," eighth edition.

Sulphur as Sulphates.—Determined by subtracting the sulphur as sulphites from the total sulphur as sulphates and sulphites.

Sulphur as Thiosulphates.—This figure was found by subtracting from the total iodine figure obtained above for thiosulphates and sulphites together, an amount of iodine corresponding to the sulphites as determined above, the resulting figure being the iodine used up by thiosulphates.

Following are the results obtained on allowing four samples of the above-mentioned wash to stand in the open air for varying lengths of time, after being soaked up by the slips of filter-paper. The samples were *not* watered to represent dew.

TABLE IV.

(Expressed in grams per 100 cc. of the solution.)

	Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
(*a*)	5 days	1.71	1.97	0.11	0.01	3.80
(*b*)	5 "	1.72	1.97	0.10	0.01	3.80
(*c*)	8 "	1.74	1.94	0.137	0.01	3.83
(*d*)	8 "	1.77	1.94	0.12	0.02	3.85

Following are the results obtained on four samples which were dampened each morning to represent the dew.

TABLE V.

(Expressed in grams per 100 cc. of the solution).

	Time of standing.	Free sulphur.	Sulphur as thiosulphate.	Sulphur as sulphite.	Sulphur as sulphate.	Total sulphur.
(*e*)	10 days	1.94	1.66	0.22	not det.	3.82
(*f*)	10 "	1.93	1.69	0.20	"	3.82
(*g*)	4 weeks	2.11	1.42	0.29	0.15	3.97[1]
(*h*)	4 "	2.13	1.41	0.27	0.16	3.97[1]

From Tables IV and V it is evident that just those changes take place in the wash when it dries on the tree that would be expected. Analyses (*a* and *b*) after five days, indicate that the following reaction has taken place, (1) $CaS_5 + O_3 = CaS_2O_3 + 3S$, resulting in a deposit of sulphur and an increased formation of calcium thiosulphate. These two analyses also indicate that the following reaction has begun, (2) $CaS_2O_3 = CaSO_3 + S$, resulting in the formation of more calcium sulphite and more free sulphur.

Analyses (*c*) and (*d*), after eight days, indicate that the reaction represented by reaction (2) has gone still further, and that now the following reaction has commenced, (3) $CaSO_3 + O = CaSO_4$ resulting in the formation of more calcium sulphate.

Analyses (*e*) and (*f*), made after ten days, indicate that the rapidity of reactions (2) and (3) has been much increased by wetting the paper every day (or in practice by the dew wetting the branches each day).

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[1] The rather high results obtained for total sulphur in these two determinations is doubtless owing to errors in analysis especially in the thiosulphate figures. The method of analysis as outlined above is very difficult of execution even under the best circumstances. In these two determinations six extracts of 500 cc. each were necessary to extract all soluble sulphur compounds. This resulted in very small amounts of material being present in the last four 500-cc. filtrates, and consequent increased chances of error in the determinations.

Analyses (*g*) and (*h*), after four weeks, indicate that the above reactions, (2) and (3), have gone still further, resulting in the breaking-up of about one-fourth of the thiosulphate and the consequent increase of sulphur, sulphates and sulphites. If the decomposition of the wash continued at the same rate as is indicated above, it would take it about four or five months to completely decompose (at least under these artificial conditions). When decomposition of the thiosulphate was complete a very large amount of free sulphur would still be upon the tree, calcium sulphite would be present and calcium sulphate. Still further along, the sulphite would be oxidized to sulphate so that finally only sulphur and calcium sulphate would be present after perhaps four or five months. In case of a very hot sun shining upon the tree the sulphur itself might be volatilized, leaving only calcium sulphate.

From the above data a theory can be formed as to the action of this wash. We will first take the case where the wash, after being sprayed upon the trees, remains practically untouched by rains for several months (as in the dry climate of California) so that the products of decomposition remain upon the tree for a long time. First the excess of lime in the wash is quite caustic, so loosens the scales from the tree and exposes the insects. Almost at once the pentasulphide, on decomposing, deposits sulphur in a very finely divided condition which has its usual insecticidal action (just how is not known). Now the thiosulphate already present in the wash together with the thiosulphate formed by the decomposition of the pentasulphide commences to decompose and set free more sulphur and a sulphite. This decomposition of the thiosulphate very likely extends over several months. It is a well-known fact that calcium sulphite and other sulphites act as antiseptic agents. There is reason to believe that they would also act as insecticides. We therefore have, from the decomposition of the wash, sulphur which is in a very finely divided state and sulphite which is gradually set free. The author is of the opinion that these are the two active agents in killing insects. This theory of the action of the wash would also explain why the action is not immediate and also why it continues over a great length of time.

In a wet climate, on the other hand, we will suppose that a heavy rain occurred a day or two after the wash was applied.

This would tend to wash out all thiosulphate which was originally present, together with that which had been formed by a decomposition of the pentasulphide. No sulphite could then be formed. There would therefore be left upon the tree sulphur as the only compound having insecticidal properties. The efficacy of the wash would therefore be reduced. Again, suppose light rains occurred only occasionally after the wash had been applied: this would reduce its efficacy just in proportion to the thiosulphate they washed out, and the consequent reduction in the amount of sulphite formed.

It is possible that the thiosulphate itself has some value as an insecticide. If so, it would be manifested much more strongly in a dry climate than in a wet climate, where the thiosulphate would be gradually or at once washed off.

It was suggested to the author by Mr. F. H. Pough, the manager of the Bergen Port Sulphur Works, of New York City, before the above paper was prepared, that the efficiency of the lime-sulphur-salt wash was due almost entirely to the finely divided sulphur which was set free on the decomposition of the calcium pentasulphide. In support of this he cited the wide-spread use of sulphur as a fungicide and insecticide. More particularly its use for the prevention of the powdery mildew in the vineyards, where it is often sprinkled on the hot ground to the windward of the plants as well as on them. Also to the recently discovered value of sulphur dusting as a remedy against the red spider of citrous trees.

He believes that the action of the wash is to be attributed to the gradual oxidation of sulphur which gives rise to sulphur dioxide or sulphurous acid where moisture is present, and that it is these constituents which do the work. In support of his theory he cites cases where an odor resembling sulphur dioxide is plainly discernible on hot, sunny days in the vicinity of orchards sprayed with the above mixture.

While the author does believe that the finely divided sulphur is one of the active insecticidal agents in the wash (just how he is not prepared to say), he is inclined to doubt whether this oxidization of the sulphur would be rapid enough to be of great value.

In regard to the second point brought out by Mr. Pough, those who have sublimed sulphur know that during sublimation a smell resembling sulphur dioxide can plainly be observed, so that the odor observed in the vicinity of orchards on a hot, sunny day might be due to the sulphur subliming.

The following points are all against this theory:

(1) If the action were at all considerable, we would expect that the total sulphur on the tree would decrease, since not all would be likely to be absorbed by the calcium hydroxide or calcium carbonate present, these being only mechanically mixed with the sulphur. In our paper experiments (which to be sure are artificial), no loss of sulphur was shown after four weeks.

(2) We would expect the free sulphur to decrease during the course of four weeks: instead of this it increases to a slightly greater extent than corresponds to the amount of thiosulphate broken up according to the following equation: $CaS_2O_3 = CaSO_3 + S$.

On the whole, then, while the author is not prepared to say that under certain conditions some of the sulphur might not be oxidized sufficiently to give enough sulphur dioxide to be of value, he is very much inclined to doubt whether this action is the major factor in determining the efficiency of the wash.

It should be borne in mind that the above results were obtained not by boiling the whole 20 gallons mixture of lime, sulphur and salt, but by boiling a small fraction of this formula (about one quart). While this might, to some extent, influence the time necessary for all sulphur to go into solution, it would not influence the final composition of the wash. The author is of the opinion that in cases where the samples are brought to a boil, before the time of boiling is taken, the size of the sample has very little influence on the amount of sulphur going into solution in a given time.

In giving the methods of analysis used in this work the author has confined himself to the barest outline at the request of the editor. The details will gladly be furnished to those who may be interested.