Acid.	Solvent.	Temperature.	Soluble in 100 parts.	Melting-point.
Benzylarsonic.	Water.	27	0.39	......
" "	"	97	3.50	......
Phenylarsonic.	"	28	3.25	158.0
" "	"	41	4.82	......
" "	"	52	8.52	......
" "	"	84	24.00	......
" "	Alcohol.	26	15.51	......
" "	"	68	55.40	......
Methylarsinic.	Water.	22	82.90	......
Phenylarsinic.	"	27	0.28	164.0
" "	Alcohol.	22	11.80	......
" "	"	55	57.70	......

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[CONTRIBUTION FROM THE MISCELLANEOUS LABORATORY, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

COPPER SALTS IN IRRIGATING WATERS.[1]

BY W. W. SKINNER.

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THE Miscellaneous Laboratory of the Bureau of Chemistry has for several years past been engaged in a study of the effect of certain waste products from manufacturing operations in regard to their injurious effect upon vegetation and agricultural crops. "The Injury to Vegetation by Smelter Fumes," by J. K. Haywood is the first of a series of bulletins upon this subject. Supplementing this work and as a logical sequence thereto, a study of other waste products from smelters, concentrating plants, and mining operations naturally follows. The data submitted in this paper relate only to copper operations, and the injurious effect upon vegetation from copper salts which, as a waste product from the mining and reduction of copper ores, are frequently carried into and contaminate water supplies which later are used for irrigation purposes.

Toxicity of Copper Salts.—The extremely toxic character of copper salts to plant life is a subject that has received considerable attention both in this country and by foreign investigators. Johnson[2] remarked years ago the injurious effect of salts of copper,

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[1] The second of a series of studies by the Miscellaneous Laboratory on trade wastes in their relation to agriculture. Read at the New Orleans Meeting of the American Chemical Society.

[2] "How Crops Grow," Johnson.

lead and zinc upon plant life. Nageli[1] has found that copper in merest traces is toxic to growing plants, while Low[2] has shown that even the very slight amount of copper which goes into solution during the process of obtaining distilled water from a copper still is injurious to plants when the water is used in culture experiments.

Harter[3] states as a result of his observations that copper is one of the most toxic substances known.

The degree of toxicity of the several salts experimented with varies with the character of the plants, some salts being very much more toxic to some plants than to others, and while all authorities agree that copper salts are extremely toxic, they do not all agree upon the exact coefficient of toxicity. This lack of concordance in results is due no doubt to the different conditions of experiment and to the different plants used. The variation of different plants in respect to their resistance to salts has been clearly demonstrated in the work of Harter above referred to, in which he shows that with several salts, the one that is most toxic for any one plant, say for instance corn, is not necessarily the most toxic for other plants such as wheat or peas.

As to the amount of copper which is toxic, Coupin[4] states that 1 part of copper in 700,000,000 parts of water is sufficient to retard the root growth of wheat seedlings, and that a mere trace of this substance is in many cases sufficient to retard growth. Heald[5] in his experiments demonstrated that seedlings of *Pisum sativum* were killed when the solution contained 1 part of copper in 404,423 parts of water, and that *Zea Mais* seedlings were killed in a solution, the concentration of which was 1 part of copper in 808,846 parts of water.

In all of the above experiments the toxicity was determined in water cultures. The considerations leading to the adoption of water culture methods are purely those of expediency. The results are more definite and the control of disturbing factors are, under such conditions, more easily managed than would be possible with soil cultures. That the toxic coefficients so deter-

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[1] Denkschr. schweizerischen Naturf. Ges. 33, 1.

[2] Land. Jahrb. 20, 235.

[3] U. S. Dept. Agr., Bur. Plant Ind., Bull. 79, p. 40.

[4] Rev. gén. botanique, 10, 180.

[5] Bot. Gaz. 22, 142.

mined do not hold true in their entirety for soil solutions is not to be denied, for it is a well known fact that the other salts found in the soil solution may either by a stimulating action upon plants, or by a partial neutralization of the toxicity of the salt materially reduce the effect of the latter. The mutual effect of some of the so-called alkali salts upon one another has been very carefully worked out by Cameron and Kearney,[1] in some instances with very surprising results. For instance, they found that of the several alkali salts magnesium sulphate was the most toxic to plants, when cultivated in pure solutions of this salt. It was much more toxic than sodium carbonate or sodium chloride. When, however, lime salts were present they found that the relative toxicity of these salts was exactly reversed, magnesium sulphate being the least harmful of the alkali salts. This latter conclusion entirely agrees with actual field observations.

Water cultures, however, do determine the maximum coefficient of toxicity for any particular salt for the particular plant experimented upon, and as it is the maximum factor which must be considered when arriving at any practical conclusion, the knowledge so gained is of the highest importance.

Copper Salts as a Waste Product.—In no phase of mining has greater progress been made in recent years than in the working of low-grade copper ores. Deposits of large extent that a few years ago were considered of entirely too low grade to be worked with profit, are now experiencing an unusual development. This is in large part due to the perfecting of mining machinery for working such low-grade ores. Concentrating machinery of both the wet and dry types are in use, but up to the present time only the wet method of concentrating has been entirely satisfactory. For the successful application of this method large quantities of water are necessary. The laws governing water rights in most western states allow the mining and milling companies to use the water of the streams for their operations, but as the water belongs to the land, title to it can only be obtained through title to the land. Hence the mining and milling companies are required to return the water after use to the main waterway, without materially interfering with its use for irrigation purposes. But in the operation of copper concentrating plants this is a difficult matter to accomplish. In such an operation as concentrating

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[1] U. S. Dept. Agr., Rept. 71.

it is generally impracticable to remove all the copper. It may happen therefore that anywhere from 0.25 per cent., or less, to 1.5 per cent. of copper may remain in the tailings which are carried on the dump, or directly into the stream and thence upon the irrigated land. The extremely fine condition of the tailings and the moisture conditions in the dump are such as to render oxidation of the copper therein quite rapid, as is also the case with the fine tailings which are carried upon the land by the irrigating water. It is not unusual therefore, as might be expected, to find the leachings from a dump of sulphide ores to contain large amounts of copper in the form of sulphate. This sulphate, together with the fine tailings introduced directly into the water which is to be used later for irrigating, is a cause for serious consideration to the land owner and irrigator when it is realized, as has been pointed out above, how extremely toxic copper salts are.

The Chemical Problem.—*A priori*, one might assume that with the large amounts of carbonates and bicarbonates of the alkaline earths and sometimes the alkalies found in soils of the arid and semiarid region, the injurious effect of the application of copper salts would not be very great until at least a large portion, if indeed not all, of the carbonates had reacted with these salts to form insoluble compounds of copper. And that it would be only after this reaction was satisfied that the copper would remain in a condition to affect plant life. Actual field observations prove, however, that this is not the case, and that injury does occur even when the soil solutions are known to contain relatively large amounts of bicarbonates of calcium, magnesium, etc. That the injury is due to the effect of copper has further been confirmed by the author and others who have found water-soluble copper in soils under conditions noted above, and an absence of sufficient amounts of alkali salts to produce upon vegetation the toxic effect noted.

There are therefore two distinct features of the problem,—the solubility of copper salts in solutions of normal carbonates and the solubility of copper salts in solutions of bicarbonates. If a solution of a carbonate, for instance sodium carbonate, is added to a solution of a copper salt "normal carbonate of copper does not occur but only the basic salts."[1] The first result is

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[1] Ostwald: "Principles of Chemistry, Inorganic," p. 636.

green basic carbonate of copper having the composition $CuCO_3.Cu(OH)_2$, which corresponds to the mineral malachite. If more of the sodium carbonate is added, the green precipitate is dissolved, forming a deep blue solution. The solubility of the copper salts in solutions of the normal carbonates, while of considerable scientific interest, is not of great importance in our problem, for it is the exception that normal carbonates are found in soil solutions or irrigating waters, but generally the bicarbonates. However, the reaction with the bicarbonates is entirely analogous to that with the normal carbonates. It is frequently true that both the soil solutions and irrigating waters contain large amounts of bicarbonates, usually of calcium and magnesium and sometimes sodium. In regard to the soil solution it is probable that upon the addition of an irrigating water containing carbon dioxide to a soil containing calcium in the form of carbonate, considerable quantities of the carbonate go into solution as $Ca(HCO_3)_2$. The question therefore of how much copper this bicarbonate will hold in solution is vital. To determine this, several grams of pure calcium carbonate were placed in two liters of water and a current of carbon dioxide passed through the solution for twelve hours. This solution was found to contain at the temperature at which the experiment was conducted (23.5° C.), the equivalent of 1.1075 grams $Ca(HCO_3)_2$ per liter. To one liter of this solution a dilute solution of copper sulphate was gradually added until precipitation just began. The solution was allowed to stand until perfectly clear (about forty-eight hours). All the precipitated basic copper carbonate having settled, one liter of the clear solution was then removed, concentrated, and the copper determined electrolytically. The yield of copper was found to be 0.2071 gram per liter.

The reaction between copper salts and the bicarbonates of the alkalies is believed to be, from an irrigation standpoint, of secondary importance as compared to the reaction with calcium and magnesium bicarbonates; however it is not unusual to find the alkali carbonates and bicarbonates existing in both irrigating waters and soil solutions. While both the soil and the irrigating water may contain the normal carbonate, yet in the practice of irrigation it is entirely probable that these salts very rapidly revert, at least in great part, to the bicarbonate. Especially does this seem plausible when it is remembered that the river waters of the west from which irrigation supplies are taken as a rule carry large amounts of dissolved carbon dioxide.

To determine the solubility of copper salts in the alkali bicarbonates the following experiment was conducted. To about 2 liters of water was added pure sodium bicarbonate until several grams remained in the solid phase. Through the saturated solution a current of pure carbon dioxide was passed for twelve hours, the solution allowed to settle until clear, when it was tested and found to contain no normal carbonate. A portion was drawn off and a dilute solution of copper sulphate added until a permanent precipitate just occurred. The solution was then allowed to settle until clear, requiring about forty-eight hours, and the copper determined in the clear solution as before by the electrolytic deposition from a nitric acid solution. The copper held in solution was found to be 953 parts per million. It may be objected that in actual irrigation practice the soil solution never reaches anything like the concentration of the solution with respect to sodium bicarbonate given above, and it is undoubtedly true that if a soil solution should, at its maximum dilution, contain anything like this amount of the bicarbonate, plant life would be inhibited. When, however, water is added to a soil the soluble salts very soon go into solution, and as capillarity brings the water to the surface and evaporation proceeds, the concentration gradually increases until, if the loss of moisture continues to completeness, it is readily seen that the saturation point of every salt held in solution is reached. It is apparent therefore that the solution of any toxic salt in a saturated solution is of vital interest and must be considered as well as the solubility in more dilute solutions.

To determine, however, the amounts of copper held in solution by a dilute solution of sodium bicarbonate, which more nearly approached conditions as sometimes met in the soil, the following experiments were made. A solution was made of sodium bicarbonate of a strength corresponding to a soil solution which would result from adding one-third of an acre foot of irrigating water to one acre of soil containing 0.05 per cent. of sodium carbonate, assuming that the latter would be converted to the bicarbonate, and also another solution of half this strength or representing a soil containing 0.025 per cent. of sodium carbonate.

These amounts of sodium bicarbonate were taken because they are respectively one-half and one-quarter of that quantity of this salt, which under ordinary irrigation practice has been demonstrated to be about its toxic limit for most farm crops. The results are tabulated with those preceding and are as follows:

	Solution $NaHCO_3$.	Parts per million of copper held in solution.
A.	Saturated	953.00
B.	Solution equivalent to soil containing 0.05 per cent. Na_2CO_3	1.70
C.	Solution equivalent to soil containing 0.025 per cent. Na_2CO_3	0.40
	Solution containing $Ca(HCO_3)_2$ 1.1075 grams per liter	207.10

An inspection of this table reveals the fact that even with a dilute solution of sodium bicarbonate, where the amount, if present in a soil solution, would not condemn the land for most agricultural crops, there was held in solution a quantity of copper entirely sufficient to be toxic to plants and in some cases sufficient to inhibit plant growth. The results, however, with calcium bicarbonate are believed to be of more importance than those with sodium bicarbonate, for the former may exist in a soil solution in very much greater quantities without any effect upon plants, than is the case with the bicarbonates of the alkalies. And, furthermore, as most arid soils contain large amounts of calcium in the form of carbonate, as before stated it is entirely reasonable to assume that where the irrigating water contains much dissolved carbon dioxide the soil solution soon becomes relatively highly charged with this salt. The fact that a solution of this salt of the strength before given should hold in solution 207.1 parts of copper per million, is believed therefore to be of considerable significance and offers an explanation of the phenomenon observed in actual field practice as to the destruction of vegetation when irrigated with a water containing soluble copper salts, even though the application be made to soils containing calcium, magnesium and other carbonates.

SUMMARY.

(1) It has been demonstrated by Coupin, Nageli, Löw, Harter and others that for most plants, copper is one of the most toxic substances known.

(2) For wheat seedlings 1 part of copper to 700,000,000 of

water has been found to retard growth, and 1 part in approximately 800,000 was fatal to the growth of corn.

(3) One part of copper per million of water should condemn the water for irrigation purposes.

(4) Copper salts are not rendered entirely insoluble when brought into contact with solutions containing carbonates and bicarbonates, and there may be held in solution under such conditions sufficient copper to be toxic to plants.

(5) That the solubility of copper in solutions of bicarbonates probably explains the observed injury produced by irrigating waters carrying copper, even when applied to soils containing large amounts of carbonates and bicarbonates.

THE DETERMINATION OF SMALL QUANTITIES OF COPPER IN WATER.

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BY EARLE B. PHELPS.

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DURING the past few years the question of the addition of small quantities of copper salts to water supplies as a preventative of algal growths and as an emergency disinfectant against typhoid fever germs, has received much discussion and led to many important investigations in this country as well as abroad. One result of all this work has been to indicate the need of some simple yet accurate method for the determination of the small amounts of copper with which the investigator has to deal. The method recommended by the Committee on Standard Methods of Water Analysis of the Laboratory Section of the American Public Health Association,[1] is essentially that of Clark and Forbes.[2] It involves the concentration of a sufficient amount of the water to yield a weighable amount of copper, the precipitation of the copper as well as of certain other metals which may be present, as sulphides, and the separation from the mixed sulphides of the lead and iron by the usual methods. The copper is then deposited electrolytically and weighed. Quantities of copper as small as 2 or 3 mg. are thus determined by Clark and Forbes with a mean probable error of about 5 per cent., while the de-

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[1] "Report of the Committee on Standard Methods of Water Analysis," Jour. Inf. Dis. 1905, Sup. No. 1, p. 1.

[2] Mass. State Board of Health, 32d Ann. Rep. for 1900, p. 487.