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L. B. Roberts

University of Arkansas at Monticello

Edwin Roberts

University of Arkansas at Monticello

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CRYSTALS OF AN INSOLUBLE CARBONATE OF COPPER GROWN UNDER A
SODA SOLUTION¹

L. B. Roberts and Edwin Roberts, *Arkansas Agricultural
and Mechanical College, Monticello*

When an old fire extinguisher of the soda-acid type was opened and emptied preparatory to recharging, several grams of blue crystals were found in the bottom of the container. Crystals of the same kind were later found in several other extinguishers. Some of these crystals were fairly large, weighing as much as half a gram each. Since the body of the extinguisher was of a copper alloy and the solution in the extinguisher was a practically saturated solution of sodium bicarbonate, the logical conclusion seemed to be that the crystals might be a carbonate of copper. Since the color is blue, and not green like malachite, it was at first assumed that the crystals were similar to azurite, the other common basic copper carbonate. However, the crystal form proved to be different from that of azurite and the color a lighter blue, very much the same shade as copper sulfate crystals.

When the crystals were analyzed qualitatively, they were found to be practically insoluble in water but very readily soluble with effervescence in dilute acids. Copper and sodium were the only metals found and carbonate the only anion (with the possible exception of hydroxyl, for the crystals, although practically insoluble, were found to give a faint basic reaction with litmus). There was, of course, the possibility of water being present as water of crystallization.

This led to the idea that the crystals might be sodium copper carbonate and quantitative determinations were run for copper, sodium, carbonate, and water. Copper was determined volumetrically using Park's modification of the short iodine method. Sodium was determined gravimetrically by precipitating the copper (the only other metal present), converting the sodium to the chloride by boiling to dryness repeatedly with concentrated HCl, heating to remove ammonium salts, and weighing the residue as sodium chloride. Carbonate was determined by loss of weight on liberation of CO₂, and water of crystallization was determined by the loss in weight of a sample when heated to 110°C for an hour.

The results of these analyses show a total of 94.6%. The difference may represent water of crystallization too tightly bound to be driven out at 110°C as in the case of 1/5 of the water in copper sulfate penta-hydrate. The retention in this case of 1/5 of the water of crystallization would account for approximately the difference noted. No attempt was made to test these assumptions of retained water by heating to a higher temperature because of the possibility that some of the carbonate might be decomposed.

On the basis of the assumption that the difference between the sum of the copper, the sodium, and the carbonate found and 100% represents the total water, a formula was calculated to fit the data. The formula $3\text{CuCO}_3 \cdot \text{NaHCO}_3 \cdot 8\text{H}_2\text{O}$ agrees with the data

¹ Presented at the 1940 meeting.

very satisfactorily as is shown by the tabulation following:

Substance	Found (Actual)	Found (Water by difference)	Theoretical
Copper	29.0	29.0	31.8
Sodium	3.7	3.7	3.8
Carbonate	42.0	42.0	40.1
Water	19.9	25.3	24.1
Acid H			.2
Total	94.6%	100.0%	100.0%

The difference between 100% and the total of Cu, Na, and CO₃ found might be thought to be due to hydroxyl except for the fact that the ratio of carbonate to metal demands the assumption that bicarbonate is present. The fact that the crystals were grown in bicarbonate solution lends support to this assumption.

The accuracy of these analyses was limited by the small amount of material available for study and it must be understood that these results are only tentative and may be modified by further studies.