ART. XIV.—*An Application of the Copper Reduction Test to the Quantitative Determination of Arsenic;* by HENRY CARMICHAEL, Ph.D.

ONE milligram of arsenious oxide added to strong chlorhydric acid and digested at the boiling temperature with a clean polished piece of copper having a surface of forty square centimeters imparts to the copper a grayish tint without fully extinguishing the red color of that metal. The color darkens rapidly if a larger quantity of arsenious oxide is supplied, and if the copper is removed as soon as it has assumed a steel gray tint, it will be found that a milligram and a quarter of the oxide has been removed from solution. The transition from reddish gray to steel gray is so marked that the experimenter can readily match a specimen which has been selected as the standard of color.

As the arsenic compounds react more slowly and with less certainty, they should always be reduced to the -ous equivalent by means of sulphurous oxide before the trial is made. Using a standard square of copper as an indicator, the writer has been led to the adoption of a method which is believed to be, for the

estimation of small quantities of arsenic, quicker, simpler, easier, more delicate, and, in the hands of toxicologists, less exposed to fallacy than any other.

A smooth, polished sheet of pure copper, not thicker than $0{\cdot}05^{mm}$, is selected. As the commercial article is usually varnished, it must be cleaned with alcohol or otherwise. A neglect of this precaution is indicated by the irregularity of the arsenical deposit. The copper is cut into pieces 20×21^{mm}. A strip one mm. wide is cut nearly across the longer side of each, and bent at a right angle to the general surface. These are the normal squares, and the bent strips are the handles by which they are manipulated. In applying the method, if the arsenic is possibly present in the substance under examination as an arsenic compound, it is digested with strong sulphuric acid, the solution reduced to a small volume, and after the conversion of the arsenic into arsenious oxide, strong chlorhydric acid is added. If the substance can only contain arsenic in the arsenious form, it is reduced to a small volume if liquid and strongly acidulated with HCl.

The acidulated solution is brought into a small porcelain capsule and a square of copper introduced. The capsule is placed over a small flame, and the square moved back and forth until it has acquired the tint of the standard chosen. The copper is removed, carefully washed and dried. The strength of acid is maintained by occasional additions, and squares are made to succeed one another until there is no further discoloration. The last square is usually lighter than the normal. Multiply the number of squares by the volume of standard arsenious solution which is necessary in coloring equally a single square, and subtract an amount which it is shown by trial the last square has required less than a normal square, and the total amount is given. By altering the concentration, the acidity, or the temperature, the rate of deposition is readily controlled. Two examples will illustrate the method.

(*a.*) A square of wall paper two inches on a side was placed in a capsule and drenched with strong HCl. A small flame was brought under capsule and squares of copper were successively colored to the standard until the exhaustion of the arsenic was marked by the lighter color of a surface long exposed to the acid liquid. The last was matched by a square which was known to have withdrawn $0{\cdot}13^{mgrm}$ and the other five by a square which had withdrawn $0{\cdot}23^{mgrm}$. The total amount, therefore, to the square yard of paper was $414{\cdot}7^{mgrm}$. of arsenious oxide. The analysis, which consumed but a few minutes, was qualitative as well as quantitative. It may be of interest to state that the paper was "warranted strictly free from arsenic."

(*b.*) A human stomach sent for analysis was, after the usual physical examination, quartered. The part taken in the search for inorganic poisons was cut into small pieces and the organic matter destroyed with HCl and $KClO_3$ as usual. Through the filtered solution, which had been partially evaporated, SO_2 was passed and the excess removed. H_2S was passed through the warm solution for twelve hours. The precipitate was thrown on a small filter, and after thorough washing was drenched with NH_4HO. The filtrate was evaporated in small capsule, twice moistened with concentrated HNO at a steam heat, then moistened with fuming sulphuric acid and heated over direct flame until the unoxidized sulphur had run into a single globule and the organic matter had been charred. A little warm water was added, a few bubbles of SO_2 passed through the solution, and the excess removed. Concentrated HCl was added and normal squares successively coated. The total amount of arsenic in the stomach was computed to have been $2{\cdot}76^{mgrm}$.

For verification one square was cut into narrow strips and pushed into a hard glass tube of the size of a quill. One end of the tube had previously been drawn down to a diameter of one mm. and the opposite end, after the introduction of the copper, was sealed with a mouth blowpipe. The bottle-shaped tube thus formed was placed in an air-bath for the expulsion of moisture and the bulb then raised to redness over a small flame. A white cloud formed and condensed in the neck. The sublimate was easily vaporized and driven from point to point. Under the microscope the coating appeared as an aggregation of sharply defined, highly refracting, regular octahedrons. The tube was sealed for future reference. The neck of a second tube, prepared in the same manner, was broken off and the arsenious oxide converted into the sulphide in a current of H_2S. The total exhibit then consisted of:

(1.) A steel gray film on copper which did not rub bright.

(2.) Highly refractive, regular octahedrons produced by the oxidation of said film and by sublimation, and which were easily vaporized, reforming as octahedrons.

(3.) A bright yellow substance formed by the action of H_2S upon the octahedral sublimate.

Confirmatory tests might easily have been applied, but the writer, having taken the customary precautions in testing purity of chemicals and utensils, considered the proof of arsenic preexisting in the material submitted for examination as abundant, and is of the opinion that such proof would, in similar cases, be only weakened and obscured by the employment of Marsh's or other familiar tests.

When the above method was first under trial, and it was not known how much the deposition of the steel gray film was influenced by foreign substances, the course of procedure was as follows:

The arsenious liquid under examination was placed in a burette and fed from this into the capsule containing hot chlorhydric acid and a copper square. After the exhaustion of the arsenic by the successive introduction of squares, the burette was filled with a standard solution of As_2O_3 (1 : 10,000), and this solution fed into the same liquid until the same number of squares were covered. The amount of arsenious oxide was then read directly from the burette. Theoretically superior, the results hardly excel in accuracy the results of the preceding method, while the time and care required are greater.

As a matter of curiosity it may be stated that a copper square one mm. on a side is capable of disclosing and estimating ·0000025 grm. arsenious oxide, a quantity forty times less than that necessary for turning the beam of the ordinary chemical balance.

The above quantitative method is commended for trial as being in the hands of experts free from fallacy; requiring few chemicals and utensils; not interfering with the search for other organic poisons and not interfered with by ordinary impurities, and as intelligible to the ordinary juryman, notwithstanding the quibbles of counsel.

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