

ART. XXIX.—*On the preparation of Cylinders of Zirconia for the Oxy-hydrogen Light*; by JOHN CHRISTOPHER DRAPER, M.D., LL.D., Professor of Natural History in the College of the City of New York.

SUCCESS in the use of the microscope for the purpose of projecting magnified representations of microscopic objects on a screen depends primarily upon the light employed, especially when high powers are used, as for example, a quarter inch objective. To answer the purpose in question the light must possess: 1st, intrinsic brilliancy; 2d, the brilliancy must be as nearly as possible invariable; 3d, it must retain its fixity of position in the optical axis of the apparatus.

If the experimenter has a good heliostat, the light from the sun fulfills these conditions better than any artificial light; but, experience teaches the unwelcome lesson that though sunlight is preferable to any other, it scarcely ever happens that it is available at the time it is wanted. The weather is almost certain to be either cloudy or hazy just at the hour when it is desired to make an important demonstration, and the lecturer is obliged to postpone it, thereby lessening its value, and often entirely losing its effect. The selection of the best artificial light therefore becomes a matter of importance to those who desire to secure the advantages to be derived from the successful demonstration of such microscopic objects as preparations of animal and vegetable tissues, animalcules, the circulation of the blood, etc.

The artificial lights possessed of sufficient intrinsic brilliancy are: 1st, the electric arc or light; 2d, the magnesium ribbon light; 3d, the oxy-calcium light; 4th, the oxy-magnesium light; and 5th, the oxy-zirconium light. The first has greater brilliancy than any other in the list, but in addition to fifty or one hundred cups of a nitric acid or bichromate battery a good regulator is also necessary; this involves a very considerable expenditure of money, and even when this is made, the labor and trouble required to manage the battery, and the continued change in the part of the carbon electrodes between which the arc of light passes renders its use unsatisfactory.

The magnesium ribbon light has the great disadvantage of the emission of fumes of oxide, which coat the surface of the condensing lenses in spite of all attempts to dispose of it otherwise. The light also is not concentrated on a small fixed surface; but, is emitted from a varying length of ribbon.

The oxy-calcium light produced by projecting the flame of mixed oxygen and hydrogen gases upon a cylinder or pencil of calcium oxide is the one generally employed. It is fixed in

its position in the optical axis of the apparatus, it is thrown into operation with comparative facility when cylinders containing the compressed gases are available, and it has sufficient intrinsic brilliancy for the majority of experiments. The difficulties in the way of its use are however serious, and it is very desirable that they should be lessened. They arise chiefly from the volatility of the calcium oxide at the intensely high temperature employed. The volatilized material depositing on the condensing lenses prevents the passage of the luminous rays, and the cavity formed in the cylinder of lime at the spot where the flame impinges soon interferes with the brilliancy of the light; this necessitates a change in the position of the lime cylinder to present a new surface to the action of the flame, and this in its turn implies a distraction of the attention of the experimenter, which interferes seriously with the satisfactory management of his subject. Though the attempt is made to avoid this difficulty by clock work, or other mechanical contrivances, they are still unsatisfactory in their action. Another serious objection is the necessity of placing the cylinders in a closed vessel when not in use to protect them from the action of the air.

The oxy-magnesium light is similar to the preceding, differing only in the substitution of a cylinder or pencil of magnesium oxide for calcium oxide, and the light emitted is of equal brilliancy. Following the instructions given for the preparation of these cylinders, I have taken the greatest pains to procure samples of magnesium oxide of the utmost purity. I have also tried various methods for its preparation, among which the combustion of the metal in oxygen may be mentioned, but failure has thus far attended all efforts to make pencils or cylinders which could withstand the intense heat of the flame of the mixed oxygen and hydrogen gases without undergoing volatilization. The pencils obtained were fully equal in this respect to those of calcium oxide; but, I did not find any superiority that repaid the trouble of their preparation.

The oxy-zirconium light produced by the action of the flame of mixed oxygen and hydrogen gases on a cylinder of zirconium oxide meets all the requirements of the case in question. It has the intrinsic brilliancy, the invariable brilliancy, the fixity of position in the optical axis of the apparatus, and it does not volatilize under the heat employed. The condensing lenses remain free from deposit, and after the light is once adjusted the experimenter can carry on his demonstrations without the distraction of his attention that attends the use of the other lights. All that is necessary is according to the size of the reservoirs of compressed gas to open the cocks a little as the pressure diminishes. There is also no necessity to remove

the zirconium oxide pencil from its position, as is the case with the calcium oxide, it may on the contrary remain *in situ* for any length of time, and the apparatus is always ready for use whenever it is wanted.

Though the standard works on chemistry generally mention the light-emitting power of zirconium oxide under a high temperature, the only successful attempt that has been made to apply it practically that I am aware of was that of Tessié du Motay. Unsatisfactory references to his process for preparing zirconia cylinders are to be found in various chemical works and journals, the best that I have seen being that given on page 47 of "Crooke's Select Methods in Chemical Analysis." The careful reader of this and other articles on zirconia will be prepared to expect difficulties in the way of its preparation, and it is to the removal or lessening of these difficulties that I now propose to address myself by the minute relation of the process I have finally adopted after many weeks of experiment.

The subject naturally divides itself: 1st, into the preparation of zirconium oxide; and, 2d, the preparation of the cylinders or pencils.

#### *Preparation of zirconium oxide.*

The compound of zirconium used is that known as the zircon of North Carolina. It is essentially zirconium silicate, and the composition of this and other specimens of zircon will be found in Dana's Mineralogy. The difficulty in the operation consists in the complete removal of the silica and of the sodium compounds used in the disintegration of the mineral.

1st. Select the zircon crystals or fragments thereof of as light a color as possible, and carefully remove all attached foreign matter; provide about ten grams in weight.

2d. Reduce five or six grams to powder in a steel mortar; or, by first heating to bright redness and chilling in water while very hot the same may be done in a porcelain mortar. Remove any mica or other foreign matter that may appear.

3d. Complete the pulverization in an agate mortar, introducing small quantities at a time, and reduce to an impalpable powder. The final yield of zirconia depends on the thoroughness with which this is done.

4th. Weigh out two grams of the fine zircon powder and mix it intimately in a mortar with ten grams of dry sodium carbonate, place the mixture in a covered platinum crucible of twenty cubic centimeters capacity.

5th. Place the crucible over a strong Bunsen flame; the burner should be at least fifteen millimeters in diameter: in about twenty minutes the mass in the crucible will have shrunk to one-third of its original volume if the heat is sufficient. To secure uniformity in temperature of the crucible

I have employed the following device. The platinum crucible being placed in a triangle of platinum wire supported on the ring of a retort stand, a graphite crucible having a diameter of five centimeters was taken and an opening fifteen to twenty millimeters in diameter made in its bottom. It was then placed mouth downward over the platinum crucible, with its mouth at the level of the bottom of the latter, and resting on the same support. A brass or iron tube two and a half centimeters in diameter and six to eight decimeters in length was placed vertically over the bottom of the graphite crucible, resting on it and enclosing the opening previously made therein. A furnace was thus constructed, the long tube being the chimney, giving a good draught, and the graphite crucible the body which confined the flame to the surface of the enclosed platinum crucible and heated it equally.

6th. The shrinkage of the mass having been satisfactorily accomplished it is to be fused; for this purpose a powerful gas blowpipe flame urged by a foot bellows answers very well. In place of the ordinary blowpipe flame I have used a modification contrived by my assistant, Mr. Ivin Sickels. It consists of a large Bunsen burner two centimeters in diameter, the upper opening is closed by a cap through which seven small tubes pass, each having a diameter of two and a half millimeters. The lower openings of the burners are also closed except one through which a tube passes and communicates with a foot bellows. Coal gas being turned into the burner, ignited, and the bellows thrown into action, seven clean sharp pointed blowpipe flames are produced which give a very intense heat.

The mass in the platinum crucible having been fused and the fusion continued until it begins to assume a pasty state, it is again liquified according to the plan of Berzelius by the addition of caustic soda about equal in weight to that of zircon. The heat being again applied the disintegration of the silicate continues, and if necessary a second addition of caustic soda may be made.

7th. The contents of the platinum crucible having cooled, separate them therefrom, and place in a beaker, add two hundred cubic centimeters of distilled water; any portions of the fused material that adhere to the walls or cover of the crucible are also to be removed by a jet of distilled water and added to the contents of the beaker. An occasional stirring will promote the disintegration of the mass, which is completed in the course of a couple of hours, silicate of sodium, the excess of sodium carbonate and soda dissolving, and leaving a white powder, which according to Dr. Melliss is composed of zirconium oxide, silicium anhydride, and sodium oxide, together with any zircon that may have escaped disintegration.

The contents of the beaker are thoroughly stirred and set aside for twenty-four hours to settle. The clear supernatant fluid is decanted, another two hundred cubic centimeters of distilled water added, the mixture stirred and set aside for twenty-four hours or longer, and when the precipitate has settled the liquid is decanted and the beaker with its contents set on the water bath to dry.

8th. Pulverize the dried material in the beaker with a glass rod, add twenty cubic centimeters of pure hydrochloric acid (Merck's), cover the beaker with a large watch glass and set on the water bath; when the acid has dissolved as much as it will take up, it is to be decanted while hot into a shallow evaporating dish of about five hundred cubic centimeters capacity. A second dose of twenty cubic centimeters of hydrochloric acid is added to the contents of the beaker, and when all lumps are broken down the mixture is transferred to the evaporating dish, a little hydrochloric acid being used to complete the transference.

9th. For the final separation of the silica the contents of the dish are evaporated to dryness on the water bath, and the heat continued until they cease to emit acid fumes, a little distilled water is then added and thoroughly incorporated with the residue by stirring. The mixture is again evaporated to dryness at 212° F. The second drying being completed, about two hundred cubic centimeters of distilled water are added, and when all the soluble material is taken up the mixture is transferred to a filter. On the filter there remains silica and undecomposed zircon. In the filtrate there are zirconium chloride, sodium chloride and iron chloride.

10th. The next step is the separation of the zirconium chloride from the iron chloride, and as completely as possible from the sodium chloride. This I have accomplished as follows. The filtrate being made up to five hundred cubic centimeters with distilled water, washed sulphurous acid gas is passed through the fluid as long as a precipitate forms, or until the contents of the flask smell strongly of sulphurous acid. The mixture is then boiled as long as it emits any odor of sulphurous acid, the loss of liquid being made up from time to time by the addition of distilled water. The precipitate of zirconium sulphite is allowed to settle for a day or two and is then collected on a filter, where it must drain for a day, the funnel being covered with a sheet of paper. As it is impossible to wash the precipitate properly on the filter, it must be carefully transferred therefrom to a beaker while it is still moist by means of a glass rod and jet of distilled water from a washing bottle. The lumps being completely broken up the contents of the beaker are again made up to five hundred cubic centimeters with dis-

tilled water well stirred, and when the precipitate has settled it is collected on a filter as before and allowed to drain as long as it will yield any fluid.

11th. The precipitate obtained above is dissolved in as little pure hydrochloric acid as possible, the solution diluted with distilled water to five hundred cubic centimeters and heated to boiling for some time. Ammonia is added to the hot solution, when the zirconium oxide is thrown down and is to be collected on a filter, washed with hot water and allowed to dry at the temperature of the air, the yellowish or whitish lumps resulting are pulverized in an agate mortar, when a white powder is obtained. The quantities I have given in the various operations detailed above apply to two grams of the powdered zircon. For the preparation of a zirconia cylinder of sufficient size the product obtained from four grams of zircon is required, the quantities may be doubled throughout; but, it is better to make two fusions of two grams each and double the quantities given in the latter part of the description.

I have also tried the separation of zirconium chloride from iron chloride by hydrochloric acid; but, though I worked at a temperature of 32° F., the yield was very small and therefore unsatisfactory. In the process by hyposulphite of soda I found it very difficult to get rid of the soda. The process of disintegrating the zircon by chlorine at a high temperature also failed to give satisfactory results in my hands, and I find that Dr. Melliss records the same experience.

#### *Preparation of the Cylinders.*

The zirconium oxide powder obtained in the manner described above is to be heated in a platinum crucible and kept at a bright red for five or six hours; it will under these circumstances shrink considerably in volume. I have sometimes in addition submitted the powder to the heat of the oxy-hydrogen flame with advantage, spreading it out for this purpose on a piece of platinum foil supported on a slab of iron, and directing the flame on the powder. The operator should wear smoked spectacles. The powdered oxide thus condensed by heat is then moistened with just enough water to give it a tendency to form small lumps. In this condition it is placed in a cylindrical mould and submitted to severe pressure by a piston fitting closely to the cavity of the cylinder, both of which should be properly oiled. The size of the pencils I have prepared is about six millimeters in diameter and one centimeter in length. When in use they are mounted so as to present one end to the action of the oxy-hydrogen flame, when a brilliant circular spot of light is formed admirably adapted for all kinds of optical experiments.

The cylinder in which the pencils have been compressed is about two centimeters in diameter and four centimeters in length; the cavity running centrally through it is six millimeters in diameter, the piston rod fits closely, and both it and the cylinder are of hardened steel; the source of compression is a small hydraulic press, and the pressure employed is about two tons. The pencil is forced from the cylinder after compression by the press itself, and is very hard. It is allowed to dry slowly and is then ready for use. When first heated the temperature is gradually increased until at last the full force of the oxy-hydrogen jet is employed. In case the pencil chips or loses any part of its substance the portions are to be preserved and ground up with old pencils in an agate mortar mingled with a little fresh zirconia powder and compressed in the cylinder. The pencils thus obtained from portions of older ones are generally superior to those made entirely from fresh oxide.

In the process of Tessié du Motay certain agglutinant materials are employed in preparing the pencils; but these reduce the brilliancy of the light considerably. With care in the management of the pencils the use of agglutinants may be avoided, and though they may be necessary in the case of pencils to be handled by an ordinary peripatetic calcium light manipulator they are not only unnecessary in the hands of a lecturer; but, are also detrimental exactly in the proportion in which they reduce the brilliancy of the light.

If the zirconium oxide is free from silica there is no evidence of fusion on the extremity of the pencil, though it may have been submitted to the action of the flame for a full hour. If on the contrary silica is present the spot on which the flame impinges becomes glazed, giving evidence of fusion, and the brilliancy of the light decreases greatly. The pencils made from the zirconia prepared in the manner related above have been tested alongside of those made from zirconia prepared by Merck, which is stated to be pure, and is sold at the rate of one dollar per gram. Whatever the process may be that is used in its preparation it does not give a product as free from iron and silica as the one which I have described, nor does it possess the same illuminating power.

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