NOTE ON THE RECOVERY OF ARSENIC.

By Albert B. Prescott.

A few years ago I gave a report of some results as to the limits of recovery in a few chemical separations,* arsenic being one of the bodies under trial. It was one of the purposes of that report to show that there are limits to the extent of recovery in good chemical separations. In respect to arsenic, as As_2O_3, it was found that "the loss in separating from an avoirdupois pound of tissue substances, is, in round terms, about a thousand times the quantity needed for identification." This quantity, the least capable of sure identification by every good operator in every trial, was placed at 0.0000025 gram (a quarter of a hundredth of a milligram.). In the analyses from which these results were drawn, three several methods of concentration of the arsenic were used, in comparison with each other, but in all of them the final estimation was by weight of the elemental arsenic reduced from hydrogen arsenide, in the mirror by Marsh's method. When the arsenic was taken in a pure aqueous solution of standard strength, the recovery was very close. This method—the Berzelius-Marsh method—has lately been very carefully examined by Charles R. Sanger,† and reported with a very full history of this plan of analysis from its earliest literature. Having used the mirror method of estimating arsenic for a good many years, and directed its quantitative use by students, I desired to make a note upon certain features of the operation.

(1.) In all cases let the further end of the reduction tube be

* "Control Analyses and Limits of Recovery," 1885: *Proc. Am. Assoc. Adv. Sci.*, **34**, 109; *Chem. News*, **53**, 78. *Citing* Holthœffer and Prescott, Contributions Chem. Lab. Univ., Mich., 1883, II., 87. Also, Hubbard, *Ibid*, 1882, I., 12.

† "The Quantitative Determination of Arsenic by the Berzelius-Marsh Process, especially as applied to the Analyses of Wall Papers and Fabrics." 1891: *Am. Chem. Jour.*, **13**, 431.

bent vertically downward and carried into solution of silver nitrate, through which the gas is to bubble from the beginning to the end of the operation. This gives the best possible security against incomplete reduction of the arsenic from the gas at any period of its flow. And it gives a convenient indication of the rate of flow of the gas. The test of the flame of the escaping gas, for spots upon cold porcelain, is necessarily a brief and fitful test, incapable of that uninterrupted control required for close results whether quantitative or qualitative. The silver solution test is a severe one, and a dark stain of the end of the delivery tube after the gas has passed for one to two hours is not an indication of waste of arsenic. The organic dust of the air upon the surface of the silver solution, with the action of the light, is usually sufficient to give a perceptible silver stain after an hour or two. Special precaution of seclusion, and of freedom from laboratory vapors, can be taken if necessary. The test, however, with reasonable interpretation, is an effectual one, and, what is necessary in the quantitative operation, it excludes hydrogen sulphide, as well as the arsenide, in the gas beyond the seat of the mirror. To draw out the reduction tube for delivery into the silver solution, draw a second time, so as to have two narrowed portions of considerable length almost continuous with each other. Cut the tube at the extremity of the further narrowed portion, and then bend at right angles between the two narrowed portions. The delivery end will then be so light as hardly to need support for itself, but it is well to provide a rest at the bend.

(2.) The reduction tube is heated best through a wrap of copper gauze. This should be four to five inches long, wide enough to fully enclose the tube, and bound snugly and evenly with a wire from the edge of the gauze. The wrap should reach to the narrowed part if the narrowing be gradual, or to seven or eight millimeters from the narrowed part if that be sudden. In fact, however, the wrap should be adjusted after the mirror begins to form, so as to place the mirror at the right part of the narrowed tube, in proportion to the depth of the mirror. A heavy mirror may need to be carried back to the full width of the tube. The wrap serves a double purpose. It equalizes the temperature around the tube

and from one end of the heated portion to the other, and this is the greater advantage. It is a mechanical support, and this is desirable for even good hard glass in a two hours' heating. If the reduction tube be as wide as many advise, the wrap should be longer. I prefer a reduction tube of not over about six millimeters internal diameter, requiring not so high a heat for reduction. Then a single bunsen burner with bat-wing top is sufficient for supplying the heat.

I may mention other particulars, admitting of different personal preference. For a drying tube I use calcium chloride as surely neutral in reaction as though it were in a carbon and hydrogen estimation. I prefer the zinc to be coarsely granulated and previously prepared with a very slight charge, a mere trace, of platinum deposit. I do not use a generator distinct from the reduction flask. The arsenical solution is introduced from a graduated tube or a weighed container, through a valved thistle tube dipping into the generating liquid, and at the end washed down with water, and, from time to time, enough dilute acid is added to keep the gas going through the silver solution at an even and not too rapid rate. The reduction tube is not heated until the air is well out of the apparatus, avoiding water of combustion, and the arsenical liquid is introduced from half an hour to an hour and a half after the beginning of the operation, according to what is in hand. At the end of the operation, the gas is continued through the silver solution for as much as a quarter of an hour after flame has been removed and the reduction tube become cold. Undoubtedly arsenic is liable to be deposited in some state upon the zinc while the reduction is going on rapidly, but that the arsenic is continuously carried out in gas until it has been all removed is evidenced by the results.

UNIVERSITY OF MICHIGAN, August, 1892.