

NOTES

A Note on the Preparation of Iodine Trichloride.—The authors were confronted recently with the problem of preparing two kilograms of iodine trichloride, sealed in glass ampoules in 50-g. quantities. Trial of the most promising methods suggested in the literature showed them to be unsuited for the preparation of a definite quantity of this relatively unstable material *in place* in glass tubes. The following very satisfactory method was worked out, and is described here because of the great economy of time and material which it effected.

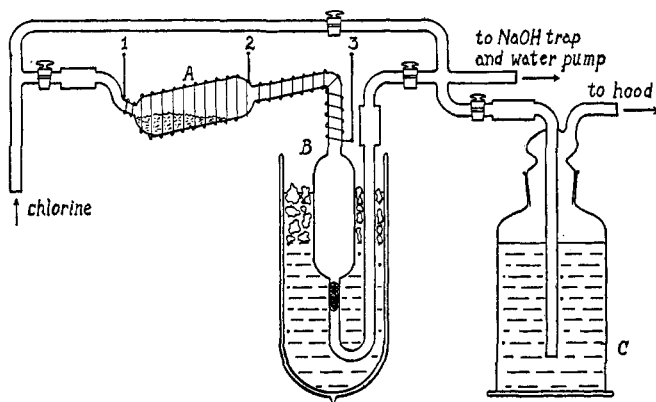


Fig. 1.—Apparatus for making iodine trichloride.

A slight excess of iodine was placed as shown in tube A, Fig. 1, before A and B were sealed together. The tubes were then placed in the system and B was immersed in ice water to a point 2 cm. from the bottom. The connecting tube between points 2 and 3 was heated electrically to about 100° to prevent deposition of the trichloride. Chlorine was then allowed to flow through the system at the rate of 80–90 cc. per minute until the iodine appeared to be completely liquefied owing to the formation of the monochloride. Some trichloride was also formed and was deposited mainly in the lower end of B on the loose plug of glass wool, thus helping to prevent the loss of the larger quantity of trichloride which came over later. The electrical heating was then extended to include A and was adjusted so as to keep the liquid monochloride *just below* its boiling point (100°). The ice water-bath around B was raised to a point 1 cm. from the top of this tube for the remainder of the run. The rate of flow of chlorine was increased to about 170 cc. per minute. At the conclusion of a run the system was partially evacuated, the tubes were disconnected at the rubber joints, which were closed with screw clamps, and B was carefully sealed off at a convenient place at each end.

It was found that a rate of flow of chlorine faster than that stipulated

or especially a temperature high enough to boil the liquid in A resulted in a too rapid deposition of the trichloride in B, with consequent plugging of this tube. The size of the tubing employed in construction of the apparatus was also found to be important. If B was less than 3 cm. in diameter or less than 9 cm. long, the deposit of trichloride invariably plugged up the tube so as to stop the flow of chlorine, thus forcing the system apart at one of the rubber connections, or at best nearly doubling the time required for a run owing to the decreased rate of sublimation of the trichloride. The tubing connecting A and B was 1 cm. in diameter, and the rest of the system was constructed of 8-mm. tubing, pyrex glass being used throughout. It was also found that if the final position of the cooling bath around B was higher than that indicated, plugging of the trichloride was likely to result.

Under the above conditions a dense core of iodine trichloride, light orange in color and containing only traces of monochloride, was formed in B, leaving no residue in A and resulting in only a slight loss of product beyond the glass wool in B. Small amounts of the trichloride were decomposed to the monochloride in the final sealing-off process. To produce 50 g. of product, 27.2 g. of iodine is required; 30-g. samples of iodine were used, yielding slightly more than 52 g. of product. The time required was slightly more than two hours per sample, including the necessary glass-blowing.

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The Analysis of Dilute Iodine Solutions.—The investigation of a reaction system comprising iodine, iodate ion and hydrogen peroxide required the accurate determination of the rate of disappearance of iodine when the amount initially present in a sample was less than 3 mg. From time to time the iodine was extracted with about 25 cc. of carbon tetrachloride, enough of the aqueous solution being taken to supply iodine equivalent to 1 to 5 cc. of 0.004 *N* sodium thiosulfate. The details of the method which enabled satisfactory determination of iodine even at concentrations below 10^{-5} *M* in the aqueous solution are as follows.

The carbon tetrachloride containing the iodine is transferred to a 500-cc. glass-stoppered flask containing approximately 50 cc. of a 1% potassium iodide solution, made sufficiently acid (about 0.001 *N*) to neutralize any basic substance added as preservative to the sodium thiosulfate solution. Freshly prepared 0.004 *N* thiosulfate is then run in until the carbon tetrachloride layer is practically colorless after shaking; 5 cc. of starch solution is then added, and the end-point taken as the mid-point of the drop which

causes the last trace of bluish color to disappear from the carbon tetrachloride layer.

On moderate shaking after the addition of the starch, the carbon tetrachloride layer remains in small bubbles of which the surface is blue even when the aqueous layer has been rendered entirely colorless in the approach to the end-point. Since the starch tends to remain in the water layer while the iodine tends to become concentrated in the carbon tetrachloride, conditions in the interface between the two layers are particularly favorable for the formation of the blue starch-iodine compound. With practice, the drop of thiosulfate which causes the removal of the last trace of this color can be easily observed—the more so since the carbon tetrachloride layer on shaking often assumes a slight yellow tinge when all of the iodine has gone. This combination of the starch and carbon tetrachloride end-points is advantageous since it permits concentration of the iodine, which the starch end-point does not, and since, in the presence of the I^- essential to satisfactory titration of iodine with sodium thiosulfate, it is more sensitive than is the carbon tetrachloride end-point alone.

Under the most favorable conditions $4(10^{-5})$ g. of iodine in 40 cc. of aqueous solution, corresponding to a concentration of $4 \times 10^{-6} M$, could be detected by the above method; the starch solution when used alone permitted the detection of iodine in a $2 \times 10^{-6} M$ solution, a value for the sensitiveness which agrees with earlier results obtained by Dr. H. E. Miller of this Laboratory. The starch solution was prepared by a method similar to that of Mutnianski,¹ recently described by Kolthoff,² except that potato instead of "soluble" starch was used. When potato starch is used, the solution must be boiled for a short time after the starch is added. Decantation after allowing suspended matter to settle insures a clear solution.

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¹ Mutnianski, *Z. anal. Chem.*, **36**, 220 (1897).

² Kolthoff, "Volumetric Analysis," Vol. II (1929), pp. 349 *et seq.* The sensitiveness for "soluble" starch under the best conditions is given on p. 350 as 1 to $2 \times 10^{-5} N$, *i. e.*, 5 to $10 \times 10^{-6} M I_2$.