

DISTILLATE CONDENSER

Elyria enamelled—3 in. diam. \times 10 ft.Later used $1\frac{1}{2}$ in. lead-coil condenser

HYDROCHLORIC ACID CONTAINER

25-gal. stoneware crock

HYDROGEN CHLORIDE GENERATOR

50-gal. jacketed Pfaudler kettle

Agitator—Speed 60 R. P. M.

STILL

50-gal. jacketed Pfaudler kettle

Oil container—50 gal. drum

Burner—1 in. gas line

Condenser—2 in series—13 in. diam.— $5\frac{1}{2}$ turns
of 1-in. lead pipe

This investigation was started at the American University Experiment Station of the Bureau of Mines and was continued under the Research Division of the Chemical Warfare Service.

SMALL SCALE MANUFACTURING SECTION
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MANUFACTURE OF ARSENIC TRICHLORIDE¹

By R. C. SMITH

Received January 4, 1919

Arsenic trichloride has occupied an important place as an intermediate in the manufacture of several toxic gases in connection with the Research Division, Chemical Warfare Service, at the American University Experiment Station, Washington, D. C. At first three general methods were considered for the preparation of this compound:

- 1—The action of dry chlorine gas on arsenic metal
- 2—The action of hydrochloric acid on arsenic trioxide
- 3—The action of sulfur monochloride on arsenic trioxide

This latter method was selected as the most practical because of the simplicity of the process, the small amount of apparatus required, the short time necessary to complete the operation, and the high yields of almost pure product.

The reaction employed in the manufacture is indicated below:



With the proper temperature control the reaction proceeds with no difficulty. It is necessary that the arsenic trioxide be as dry as possible. The commercial supplies of raw materials proved satisfactory.

The reaction was carried out in a 75-gal. unjacketed cast-iron kettle heated directly by a gas burner. Agitation was effected by means of a stirrer operated at 60 R. P. M. The bottom of the kettle was provided with a 2-in. outlet closed by a cap. The top was provided with a hand-hole for charging the solid material. A thermometer well was inserted for obtaining the temperature of the mixture. The vapor during the reaction and the distillation passed through a 2-in. opening in the cover connected to a T, the outlets of which led to the condensers. A sight glass and iron stop-cock were inserted between the reflux condenser and the kettle. A 2-in. iron gate-valve was inserted be-

tween the distillate condenser and the kettle. The upper end of the reflux was connected to the bottom of a 4-in. lead tower filled with stones, over which water was allowed to run; this served to absorb the sulfur dioxide formed in the reaction.

Forty-six pounds of arsenic trioxide were charged through the hand-hole, which was then closed. The kettle was heated until the temperature inside reached 95° to 100° C., at which temperature the sulfur monochloride starts to reflux. This usually took about 45 min. At intervals of 5 to 10 min. during this heating 200 to 300 cc. sulfur monochloride were added. The heat of reaction is very great and the addition of the sulfur monochloride greatly assisted in bringing up the temperature. The sulfur monochloride was run in by gravity from a 30-gal. iron drum mounted on a platform balance above the reaction kettle. This container held enough for one complete run and was filled from the supply drums by means of a small Roco pump. The sulfur monochloride could thus be weighed as it was added. A sight glass inserted in the line just before it entered the reaction kettle enabled us to estimate the rate of adding the sulfur chloride. Agitation was started as soon as the mixture was sufficiently fluid.

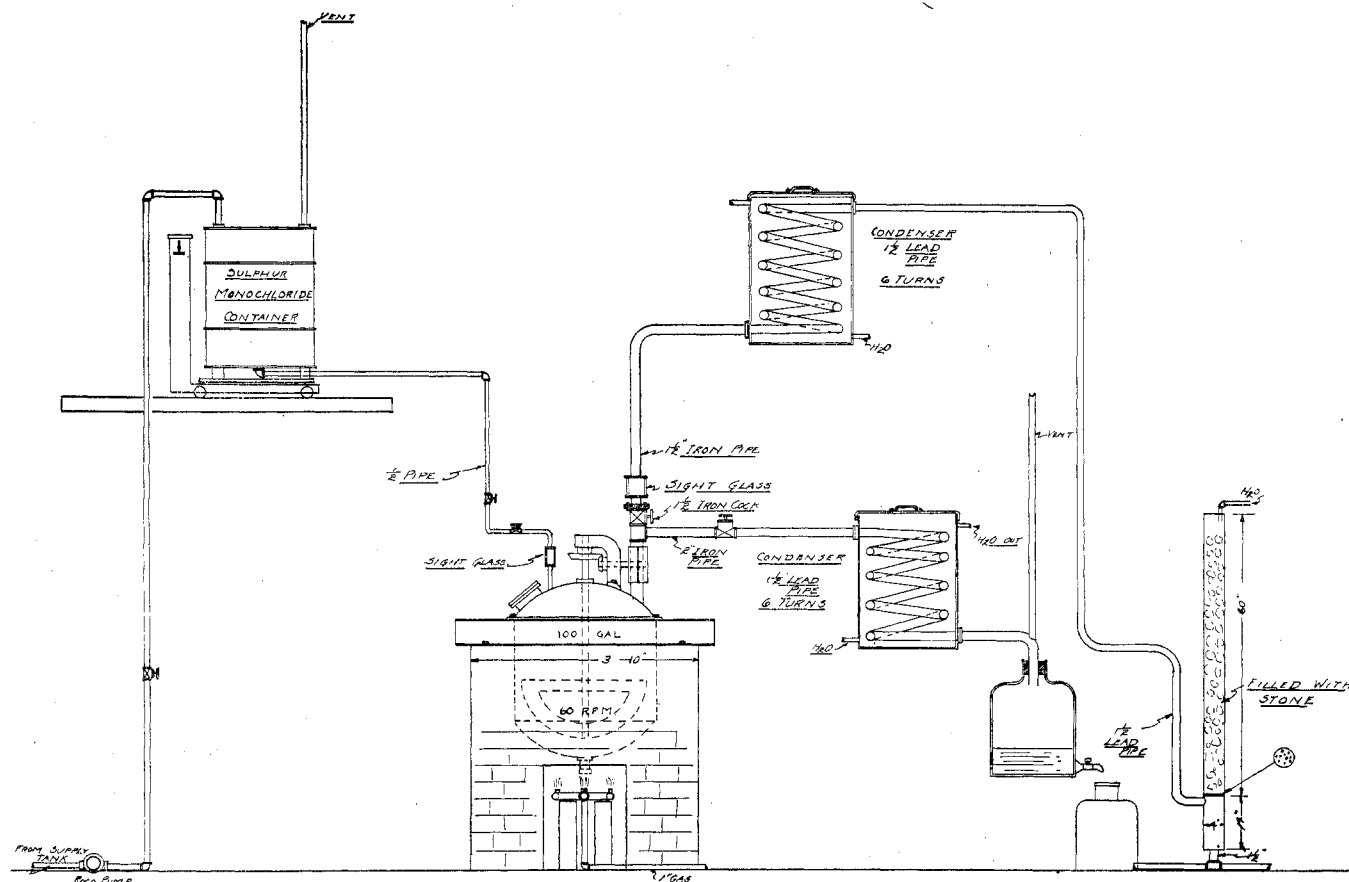
When the temperature of the mixture reached 95° to 100° C., the gas was turned off and the sulfur chloride allowed to run in at such rate as to produce a moderate refluxing. The temperature of the mixture rose to 120° to 125° C. The sulfur dioxide formed in the reaction passed up through the reflux condenser and was absorbed in the scrubber and carried away with the wash water.

The sulfur chloride was stopped when 89.5 lbs. had been added, and as soon as refluxing stopped the hand-hole was opened and 138 lbs. more arsenic trioxide added and the pot closed again. Heat was then applied to bring the temperature up to 95° to 100° C. and the sulfur chloride started again; 158.5 lbs. more sulfur chloride were added to complete the reaction. Care was taken to keep the arsenic trioxide in excess in order to prevent the product from being contaminated with sulfur chloride.

When the reaction was complete, heat was applied to the kettle, the reflux condenser cut off, the distillate condenser opened, and the distillation begun. The distillate was collected in a 10-liter aspirator bottle and drawn off into bottles or other containers. The first 25 to 50 lbs. arsenic trichloride was usually slightly colored and was saved to be redistilled. The remainder of the product was water white and averaged 99 per cent pure. The temperature of the mixture was 140° C. when the distillation began and did not rise until the product was nearly all distilled. Then the temperature gradually rose to 200° C., at which temperature the distillation was stopped. Above this temperature very little distillate comes over and it is yellow in color. The distillation required about 3 hrs. The average yield was 300 lbs. arsenic trichloride.

The residue in the kettle was discharged after cooling slightly, by unscrewing the cap on the bottom outlet. This residue consisted of molten sulfur containing a

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APPARATUS FOR MANUFACTURE OF ARSENIC TRICHLORIDE

trace of arsenic trioxide. If opened when too hot, the sulfur residue is liable to take fire.

The charge of arsenic trioxide was divided into two parts in order to use agitation during as much of the process as possible. The first charge required about $1\frac{1}{2}$ hrs. to complete and the second charge about 3 hrs. The total time of operation was between $7\frac{1}{2}$ and 8 hrs.

Based on the amount of sulfur chloride used the yield was 93 per cent of product averaging 99 per cent pure.

The first distillate which was always colored was decolorized by redistilling with a small amount of arsenic trioxide.

This investigation was started under the Bureau of Mines at the American University Experiment Station and was continued under the Research Division of the Chemical Warfare Service.

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ORIGINAL PAPERS

THE DETERMINATION OF CADMIUM BY THE HYDROGEN SULFIDE METHOD

By EDWARD SCHRAMM

Received August 12, 1918

I—INTRODUCTION

In the course of some coöperative work on the determination of small quantities of cadmium in brass it was found that varying results were obtained by several laboratories. A diversity of methods is in current use, most of which do not appear to have been tried out on materials of known composition.¹ The present work was accordingly undertaken with a view to developing a convenient and reliable procedure for this determination, and to ascertaining what degree of

¹ Two methods have been described in considerable detail in the second edition of Price and Meade, "Technical Analysis of Brass," pp. 229-233.

accuracy is to be expected. To accomplish these aims, analyses were made of brasses with cadmium additions and of salt mixtures of known composition. The hydrogen sulfide precipitation was chiefly employed for the necessary separations, and accordingly the work became primarily a study of the most suitable conditions for separating a small amount of cadmium from other metals by this method.

Structural brasses may contain, besides the principal constituents, copper and zinc, one per cent or more of tin, and varying quantities of lead, iron, manganese, arsenic, and other metals, which may have been added intentionally or introduced accidentally as impurities in the copper or zinc. Very little has been published on the determination of cadmium in brass, but its determination in spelter has been the subject of a