MONTHLY REPORT - CHEMICAL GROUP.

Sept. 1942

RECEIVED
LAWRENCE
BERKELEY LABORATORY
1982
LIBRARY AND
DOCUMENTS SECTION

For Reference

Not to be taken from this room

UCRL-LA-198
c.1

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

DECLASSIFIED

UNCLASSIFIED

REPORT NO. UCRL-LA-198

COPY NO. I

CLASSIFICATION:

[redacted]

N O T E

This is a cover sheet for a classified document. Transmittal of the document must be covered by a signed receipt. It must not be left unattended or where an unauthorized person may have access to it. When not in use, it must be stored in a locked file or safe. While ... ssion and until you have ... its transfer, it is your ... ation contained herein is

UCRL # 198 C.I

AUTHOR

Carter, Kamen and Larson

TITLE

Monthly Report - Chemical Group

Sept. 1942

... CONTAINED IN THIS ... THROUGH YOUR NEGLIGENCE.

Special Review of Declassified Reports

Authorized by USDOE JK Bratton

Unclassified TWX P182206Z May 79

CLASSIFICATION CANCELLED

FEB 7 1973

Per DOC

By Roger S Dildine FEB 7 1973

REPORT PROPERLY DECLASSIFIED

J. R. Stewart 8-30-79

Authorized Derivative Classifier Date

Marilyn J Pennington 10-23-79

By Date

UNCLASSIFIED

E.O.L. copy

UCRL NO 198

C.I

[redacted]

MONTHLY REPORT - CHEMICAL GROUP

UNCLASSIFIED

September-1942

I. Preparation of Tuballoy Halides.

Work early this month centered principally on the tetrabromide. Recently, however, it appears that the tetrabromide is not as suitable as the tetrachloride. Further work on the bromide is therefore dependent on additional tests on the hill.

Tuballoy tetrabromide is much more difficult to prepare than the tetrachloride, as shown by our experience, and as reported by the Bureau of Standards.

The only method found satisfactory is according to the reaction:

$$T_3O_8 \text{ (or } TO_2) + C + Br_2 \longrightarrow TBr_4 + (CO + CO_2 + COBr_2)$$

Our experiments (see Fig. 1) extended only to about 800°C. The experience of the Bureau of Standards is that a satisfactory rate is attained only at 1000°C. At 800°C, we made only 50-75 gm in 3 hours. The Bureau at 1000° was preparing a kilogram in 8 hours. It was found essential, in obtaining a reactive carbon-tuballoy oxide mixture, to proceed by charring a sugar-oxide mixture. Merely mixing carbon, even lamp-black, with the oxide, gave a charge reacting very slowly with bromine.

A number of improvements in the preparation of the bromide have been planned, including the possibility of conversion of the chloride to bromide. If further work on the hill indicates the bromide is desirable, these will be continued.

On the preparation of tuballoy tetra-chloride, much greater progress has been made. We now have several methods which can turn out a kilogram or

UNCLASSIFIED

[redacted]

SECRET UNCLASSIFIED

more per run. The principal problems in this line at present are: to determine the most satisfactory materials for constructing equipment, and to work out practical details for regular production. Short summaries of the various methods are given below.

Production from carbon-tuballoy oxide mixture and chlorine. (See Fig. 2)

This also is essentially a high temperature reaction, requiring temperatures above 800°C. It also requires preparation of the charge by charring a sugar-oxide mixture. The product, however, is very pure (99+%) and separated from the charge. One short run using small amounts gave 150 g of product.

Production of tuballoy tetrachloride from tuballoy oxide and sulphur mono chloride.

This method was used by the Bureau of Standards and by the commercial supplier. It proceeds according to the reaction:

$$T_3O_8 \text{ (or } TO_2) + S_2Cl_2 \longrightarrow TCl_4 + (SO_2 + S + \ldots)$$

(See Fig. 3)

As run by the Bureau of Standards, this was carried out at 1000°C. Our experiment was also done at this temperature, but it is probable it will go at considerably lower temperatures. One six-hour run by this method gave us 1675 grams of product, (1400 grams 96%+) from a 2000 gram charge of T_3O_8 in 5 hours. A principal difficulty is the removal of sulphur (or sulphur compounds) from the product.

Production of tuballoy tetrachloride from tuballoy oxide and carbon tetrachloride.

The upper temperature limit on this reaction is fixed by thermal decomposition of the carbon tetrachloride to carbon and chlorine at about 750°C. The reaction apparently proceeds in two or more ways, of which the first occurs at lower temperatures than the rest:

$$TO_2 + 2CCl_4 \longrightarrow TCl_4 + 2COCl_2$$

$$TO_2 + 2COCl_2 \longrightarrow TCl_4 + 2CO_2$$

UNCLASSIFIED

SECRET UNCLASSIFIED

Our first runs by this method were made at 650-700° C., after a short period above 750° had shown the production of considerable carbon. They gave more than a kilogram each of product analyzing 99.5% TCl_4. The product was the best looking of any yet made, and was chiefly in the form of long black lustrous crystals. A small amount (same purity) was in the form of a dense very dark green powder.

In the two runs above, there was some difficulty in separating the product from the charge, because of the slow rate of distillation at 650°C. The attempt was therefore made to convert the oxide to the chloride in place, with no distillation at all, at a somewhat lower temperature, and to subsequently distill the product from the unreacted charge at a much higher temperature, in the absence of any carbon tetrachloride. A run was then made at 450°C, using 500 g of tuballoy oxide. After three hours, the run was stopped. The material in the tube appeared entirely converted to chloride, consequently, instead of distilling it off, it was removed for analysis. It should be mentioned that one of the principal obstacles to the preparation of a pure product is the difficulty of removing it from any surface on which it has condensed, or on which it has been melted. The adhesion is so great that the container is apt to be broken, and in any event the time consumed gives plenty of opportunity for hydrolysis by the moisture unavoidably present.

In the low-temperature run just described, however, the product was in the form of fine, separate crystals, with a small amount of unreacted oxide (in lumps) which could be completely removed from the tube by pouring it out. A material balance of the charge and product gave a value of 90% conversion to the chloride. The crystalline material analyzed 93% TCl_4; the small amount of lumps were 77% TCl_4.

UNCLASSIFIED

[redacted]

Preparation of tuballoy tetrachloride from tuballoy carbide and chlorine.

Some small-scale experiments on this preparation have been made. It appears that the carbide is completely converted to the chloride at low temperatures, (about 350°), leaving only a small residue of light carbon particles. Future work on this problem is planned as soon as more tuballoy carbide is available.

Summary of work on preparation of tuballoy chloride.

A number of methods of preparation have been developed, all of which proceed at a satisfactory rate and nearly to completion. Regular production of a satisfactory product depends on a number of factors, now being studied:

1. Materials to withstand the temperatures and corrosive conditions encountered. Some that are under investigation are: quartz, silicon carbide, porcelain, graphite, and pyrex.

2. Condenser materials not wet by TCl_4. Graphite is being investigated.

3. Satisfactory separation of charge and product. This can be done by distillation at a high temperature, or by a substantially complete conversion without distillation.

4. Choice of a one or two-step process. It is possible that satisfactory yields of 99+% material can be produced in one step. However, it may be simpler and faster to make 90% material and subsequently to purify it by distillation in vacuum.

Purification of tuballoy halides.

Work on this problem has been almost entirely confined to distillation methods. The vacuum still, which has been in use, has been redesigned to prevent any mixing of the crud and the distillate, and to provide a more satisfactory method of heating (see Fig. 4). Recent tests on the new still show it to be quite satisfactory. The new still will take a kilogram of charge,

and complete the distillation in less than 3 hours.

Another method of distillation is in a stream of nitrogen (see Fig. 5). This has the advantage of not requiring a vacuum vessel good at high temperatures, and of permitting condensation at higher temperatures to give larger crystals. Several runs made with small amounts have shown that this is a suitable method.

II Recovery of Unused Charge

Organization and Purposes

At the start of last month, it became evident that adequate procedures for efficient recovery of the source material would be required to make the general process feasible on a large scale. It was felt on grounds of economy that recovery of material both on the first (crude) run as well as the second (enrichment) run might also be desirable. The writer, at the request of Prof. Jenkins, then organized a crew including Mr. Schmidt, Mr. Kilner and himself for the purpose of investigating all types of recovery procedures which might be contemplated. This report chronicles the experiments performed and conclusions drawn to date.

Methods of Recovery

The procedures to be devised depend on the nature of the tuballoy deposit, the portion of the vacuum chamber from which the deposit is obtained, and the major contaminants introduced by the metals used in the construction of the apparatus. One may classify recovery procedures as follows:

1. Dry methods.
2. Wet methods.
3. Electrolytic methods.

Each of these has its special advantages and it has been the task of the Recovery Crew to determine the exact conditions under which each is feasible.

Experiments on Recovery from Copper and Iron using Wet Methods.

The first experiment was performed with the 37" can. The purposes here were to ascertain how the tuballoy distributed itself under conditions of a cold arc source and how quantitatively the source material could be recovered using water and mechanical action (i.e. scrubbing). The geometry was as indicated diagrammatically below (Fig. 6). A "C" was constructed on a radius (inside) of 1' and with an aperture of 6"x 6". The inside of the "C" was lined with 1 mil Cu foil. Foils were placed immediately above and below the source shield to collect all material falling in the space between the shield and the "C". To ascertain how much tuballoy got past the "C" and distributed itself around the vacuum can, the liquid air trap was covered with foil also. No foils were used on the collector. A charge of 88.6 grams was placed in the reservoir. When the run was finished, the can was opened and the distribution first ascertained visually. It could be seen that practically all the material (approx. 99%) was collectible from the ion source and shield and the region between the shield and the "C". No more than approx. 0.2 grams of tuballoy was in the "C". The inside of the "C" showed no signs of heavy ion bombardment, a smooth, black coating of the tuballoy metal being found spread evenly throughout the whole inside of the "C". Less than 1/10 milligram of tuballoy deposited on the liquid air traps showing that the "C" collected all the tuballoy not remaining in the source region. The collector showed some pitting and a small deposit of tuballoy about equivalent to what was in the "C". Since all the material seemed to remain in the ion source region, the source, shield and slits were carefully cleaned with water and a brush. The recovery data is listed below:

Source and Shield -	63 grams
Slits	21 grams
Reservoir	6 grams
Total	90 (± 5) grams

It is seen that by this method, all the tuballoy regardless of its state of combination can be recovered from copper or brass by vigorous mechanical action and washing. It was noted that while little effort was required to remove the deposit from a graphite surface (slits), the coating on copper proved very tenacious. In a separate experiment pure tuballoy chloride was rubbed into copper and allowed to stand in air. Hydrolysis and reaction on the copper by the acid formed resulted in a closely adhering, chemically combined coating of the tuballoy chloride (probably as tuballyl chloride or oxide) with the copper. Only acid (approx. 6 N HCl) sufficed to remove this coat completely.

Since it appeared that copper might be the major contaminant and complication in the recovery of the tuballoy, methods for the separation of copper and tuballoy were investigated, keeping in mind that both large and small scale procedures might be needed.

The first type of procedure tried both for ascertaining possibilities for recovery as well as separation of tuballoy from copper was electrolysis. A preliminary experiment showed that to get high current efficiencies and smooth deposition of copper, a rotating electrode was required. The apparatus was built incorporating a large rotating copper cathode with variable speed of rotation and a sheet platinum anode. The protocol of a typical electrolysis run is given herewith:

Equipment: 1 Platinum Electrode (2" x 3")

1 Rotating Copper Electrode

(3.104 cm diameter, 6.3 cm long,

area = 0.6140 dm^2)

Reagent: Solution containing 1.13 mg tuballoy/cc and 40 mg copper/cc as chloride.

Electrolysis: 100 cc of solution adjusted to pH = 1 used.
Cathode rotated at 165 r.p.m.; current = 0.5 amperes
Voltage held below 2 volts.

The pH was measured with a glass electrode as the electrolysis proceeded and was used to determine how quickly the copper was being removed. The pH dropped from 1 to 0.15 in 2 hours and in 5 hours, practically all of the copper color in solution was discharged. No tuballoy plated out. Current-voltage curves for pure copper solutions when compared with solutions containing both tuballoy and copper in the proportion indicated above showed that practically none of the current was carried by the tuballoy. Only by running the voltage up above 4 volts could one obtain some tuballoy oxide deposit on the cathode and this went back into solution when the current was turned off. Analysis of the completed run above showed 97% recovery of the tuballoy in solution whereas all of the copper was plated out. Much data on the voltage-current relations for various Cu-T solutions were obtained.

It can be concluded that one may remove tuballoy incorporated with copper into solution by electrolysis and afterward plate out the copper without plating out the tuballoy (because of the high over-voltage required to bring down tuballoy as the oxide at the cathode).

The electrolytic setup was also found useful by the analysts for determination of the 4-valent tuballoy in the presence of the 6-valent form, as well as for a variety of other analyses and was turned over to them at the conclusion of these experiments.

Another method which suggested itself for use in separating tuballoy from copper was based on the selective absorption exhibited by activated alumina for metal ions. Chromatographic columns (i.e. long cylindrical tubes packed with alumina) were set up and the absorption characteristics of some laboratory alumina investigated. In the first experiment, alumina powder was slowly dropped through a long thin column of solution containing Cu and T, thus

SECRET

reversing the usual chromatographic procedure in which the solution is percolated through the alumina. (This procedure was suggested by an article in Science, Vol. 96, 212.) Due to the heterogeneity of the alumina particles, variable speeds of dropping were encountered and the method proved impractical. Hence, recourse was had to the usual procedure of packed columns. In another experiment, 5 cc of a solution containing 9.70 mg T/cc and 10.0 mg Cu/cc (pH = 2.95) were run slowly through a column of alumina packed into 3 mm glass tubing, using the vacuum of the water aspirator to pull the solution through the column. The tuballoy was completely absorbed as a green band on the alumina, the copper appearing below the tuballoy band as a blue coloration. It proved possible by washing the alumina column to completely wash out the copper band while leaving the tuballoy still absorbed on the alumina.

The experiment was repeated using larger tubes and with the object of obtaining quantitative data. It was found that one could effect 100% T recovery on the column while practically all the copper washed through. After the copper had been removed, the alumina was expelled from the tube and washed with I N HCl, whereupon all the T was dissolved off the alumina so that a complete separation of the T from the Cu was effected. The experiment was extended to iron and similar results obtained although separations were not as sharp as for the Cu-T couple. The iron is absorbed by the alumina first and then the tuballoy, so that by cutting the column into an iron and a tuballoy portion and eluting with acid, a separation is made. The effect of pH on these separations is being determined. In addition other absorbents, such as 8 - hydroxy quinoline, are being tried.

Attempts at separation by partition in organic solvents have yielded no simple process.

The chromatographic experiments have shown that addition of activated alumina to a solution containing Cu and T results in the quantitative removal

of the tuballoy by absorption. This is the basis for a simple recovery process for tuballoy in the presence of copper.

Further experimentation on separation of tuballoy from various metal ions have been postponed until a decision is reached on the nature of the metallic coating to be used in the vacuum chamber.

Experiments with Stainless Steel

The tenacity of the tuballoy deposit on copper requiring vigorous rubbing to remove the last traces of tuballoy from a copper surface together with the complications introduced by the large amount of copper ion mixed with the tuballoy have dictated the use of a more resistant and less reactive metal surface for the vacuum chamber and parts exposed to ion deposition. Hence, foils of stainless steel have been exposed to tuballoy ion currents in both the 37" outfit and Tank #1 on the hill. It is found, as expected, that little or no bonding occurs due to chemical reaction. Washing with hot water suffices to remove all but a negligible portion of the tuballoy from the stainless steel surface. What is left after washing with water is found to be mainly sputtered copper and this can be removed by dipping in 0.1 N HNO_3 which does not attack the stainless steel. Similar experiments are contemplated with monel metal. Much data on the composition and corrosiveness of stainless steels of various grades have been compiled and all the indications are it will be desirable to use stainless steel for all surfaces exposed to tuballoy or tuballoy chloride deposition.

Conclusions

Since the plan at present is to heat the entire ion source region so that practically all the tuballoy deposits in the "C" or vacuum chamber, it appears

SECRET

that the recovery can be made from stainless steel surfaces almost entirely. If care is taken to keep the deposit dry when opening the vacuum chamber to air, the tuballoy can for the most part be scraped out as the dry salt and perhaps recovered by a simple distillation. The ion source containing little of the tuballoy can be cleaned with acid or water and the tuballoy recovered, if desired, by the methods outlined in the preceeding pages. The tuballoy deposit not removed by scraping of the stainless steel can be cleaned off as often as necessary by a wet method, (either washing in water or dilute acid dip). A large air drying unit is now being obtained for further experiments on the removal of the tuballoy deposit in a dry condition. A few experiments with dry air in the 37" outfit have shown the desirability of such a unit.

It is considered that recoveries very close to 100% of the sputtered tuballoy can be made with the methods now at our deposal. This will be tested as soon as a model of the setup on the hill (R1) can be constructed for use in the 37" magnet.

III Analytical Methods

Organization activities of the Department consisted of assembling equipment, and reagents in such form as to facilitate making of rapid accurate analysis. All-glass delivery apparatus was assembled for common solutions to minimize concentration changes. All analytical equipment assembled in one place for the convenience of the analysts.

In addition to standard methods already in use, other methods were investigated. Volumetric tuballoy methods were checked and the silver reductor methods found satisfactory. For the present, however, the standard gravimetric methods have been retained as most convenient for routine analysis.

Micro methods for tuballoy were investigated. No present methods are satisfactory for our purposes. The polaograph method is being studied as a

SECRET

possible solution to the problem. Colorimetric methods will be used for some purposes. Precipitate volume methods show some promise as a result of preliminary experiments.

Routine activities consisted of quantitative and qualitative analysis on 31 samples from production and chemical groups.

Research work that is in progress or planned consist of the following investigations:

1. Polaographic analysis
2. Spectrophotometic methods for tuballoy
3. Precipitate volume methods for tuballoy
4. Micro-gravimetric analysis.

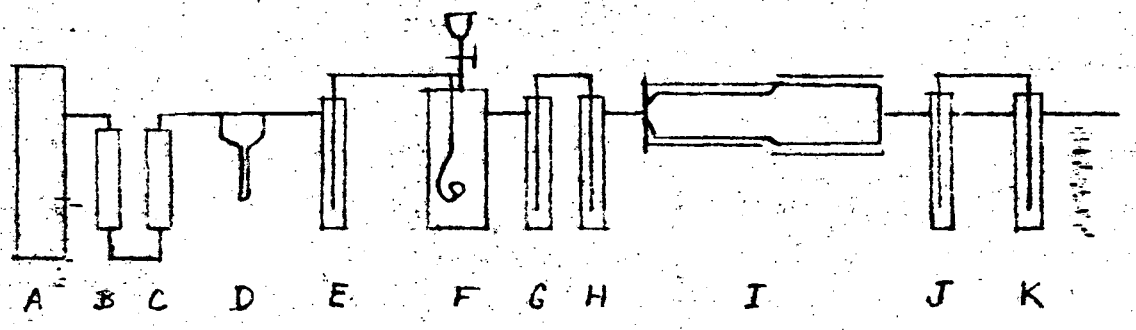
Submitted by J. M. Carter (Part I)

M. D. Kamen (Part II)

H. E. Larson Part III)

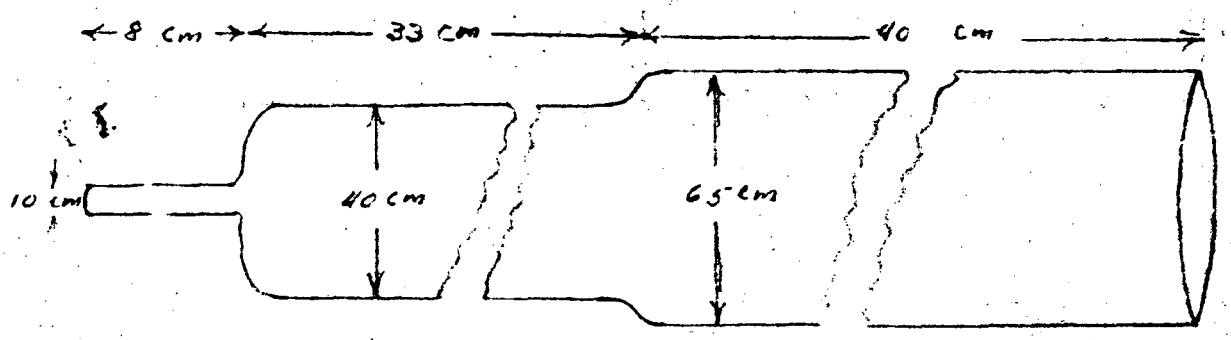
Fig 1

Apparatus for Preparation of $TiBr_4$



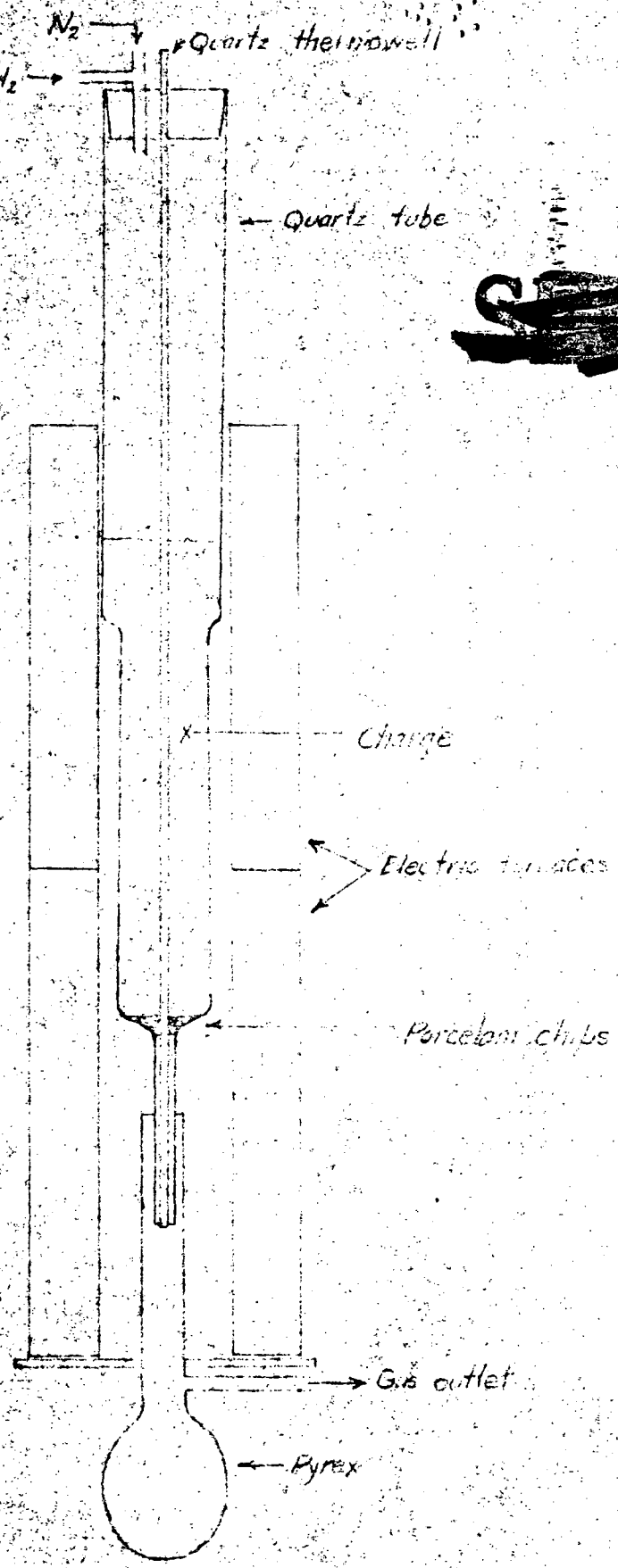
A N_2 tank
B $CaCl_2$ drying tube
C P_2O_5 drying tube
D Flow meter
E Trap
F Br_2 container
G Trap
H Conc. H_2SO_4 drying tube
I Quartz tube and ovens
J Trap
K NaOH soln. to remove Br_2

Quartz Tube



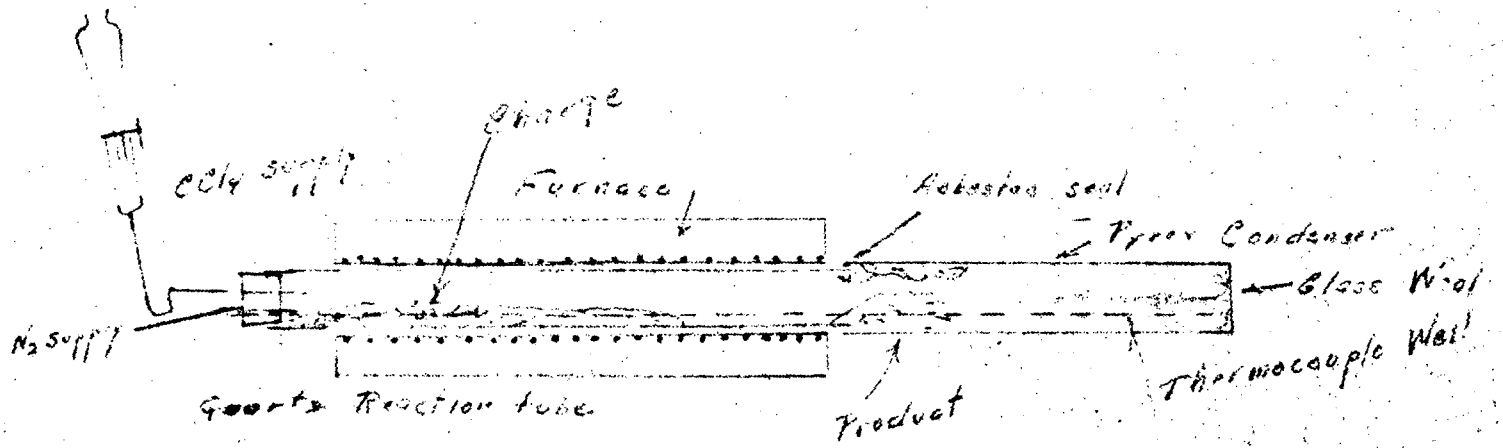
[redacted]

Fig. 2



[redacted]

Apparatus for prep. of $TiCl_4$



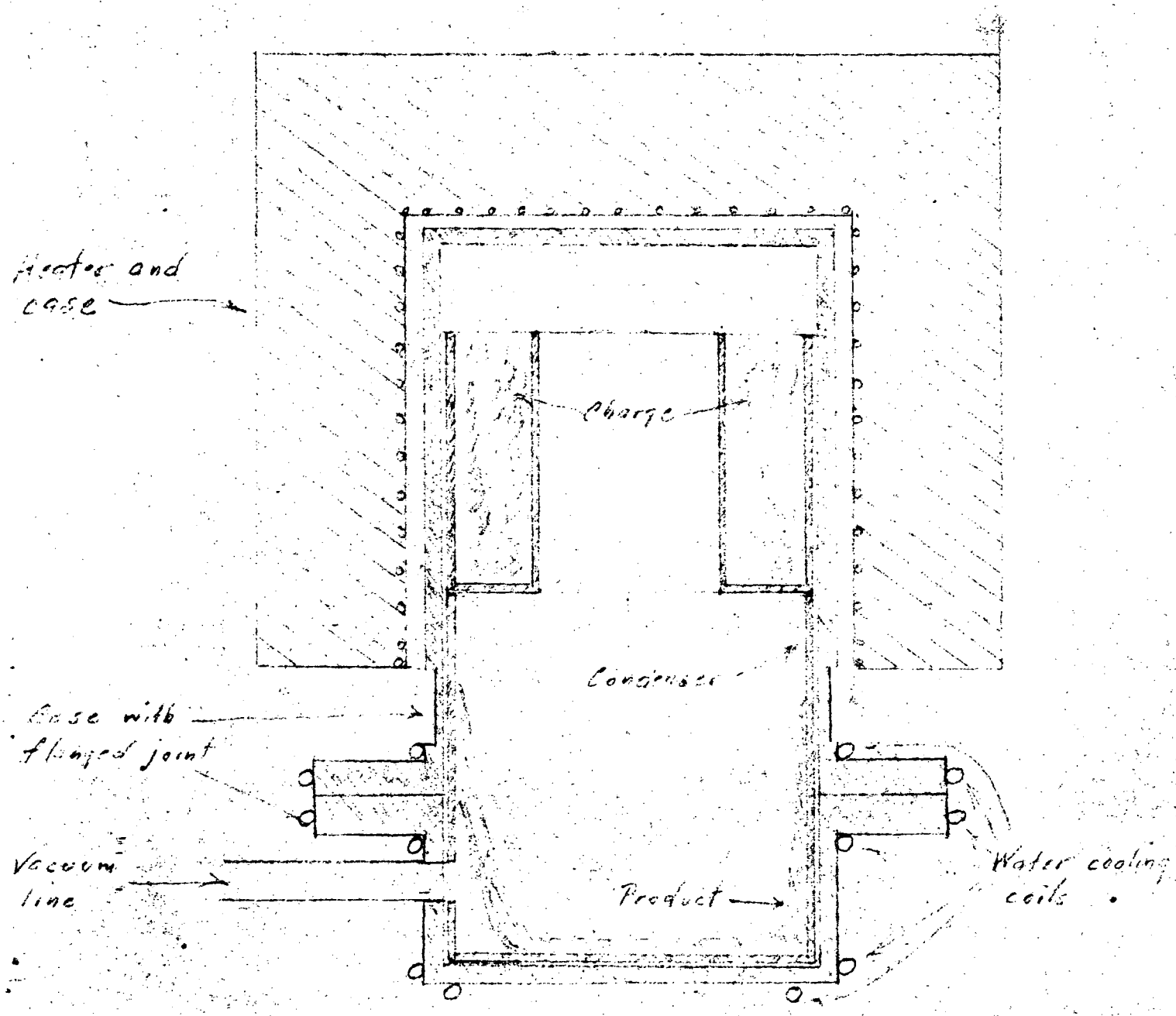
For the reaction using S_2Cl_2, the only changes were substitution of S_2Cl_2 for CCl_4 in the dropping funnel, and Cl_2 for N_2 in the gas inlet

Fig 4

Improved Vacuum Still for TCA

UNCLASSIFIED

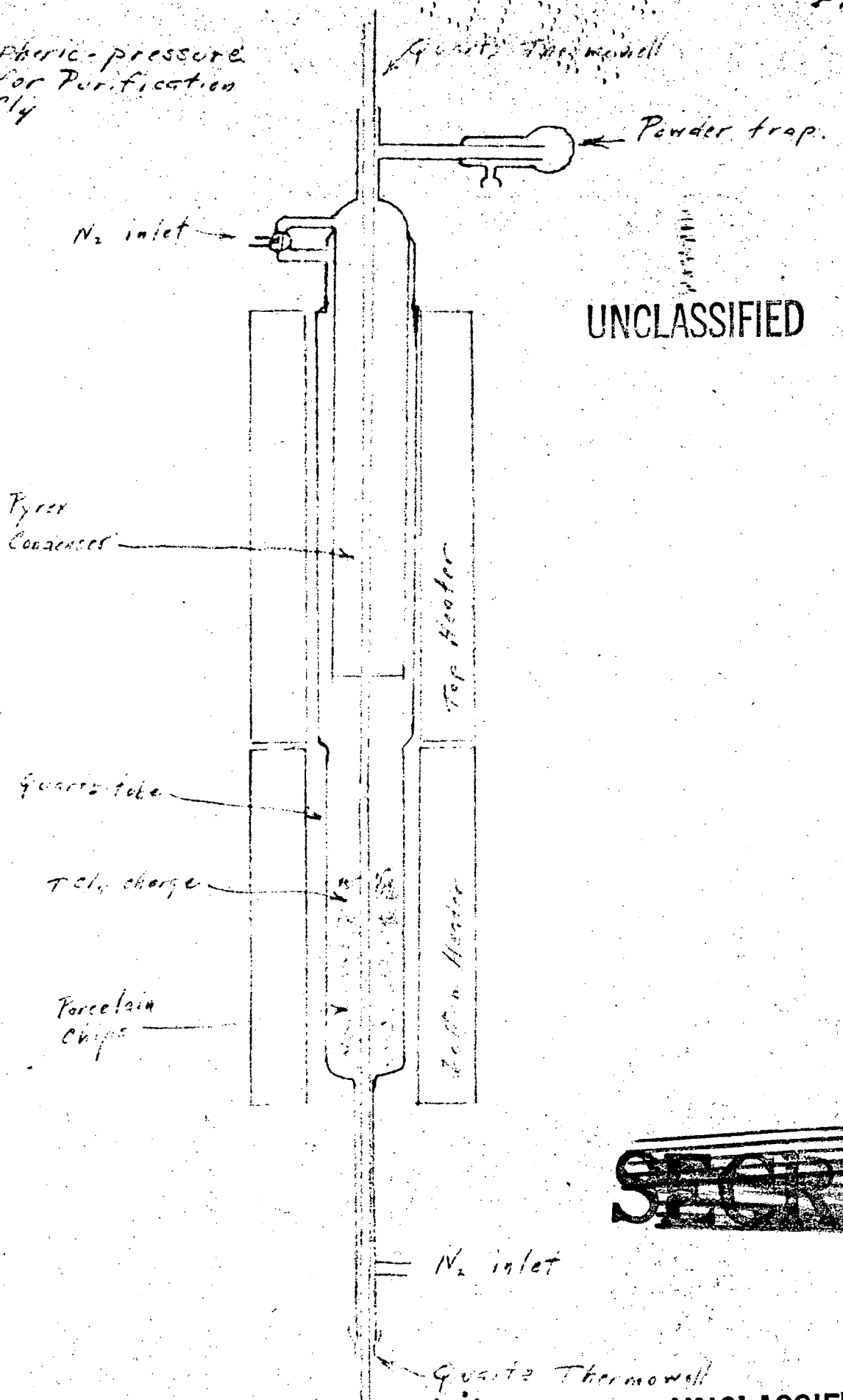
~~SECRET~~



UNCLASSIFIED

Fig 5

Atmospheric-pressure Still for Purification of TCl_4



UNCLASSIFIED

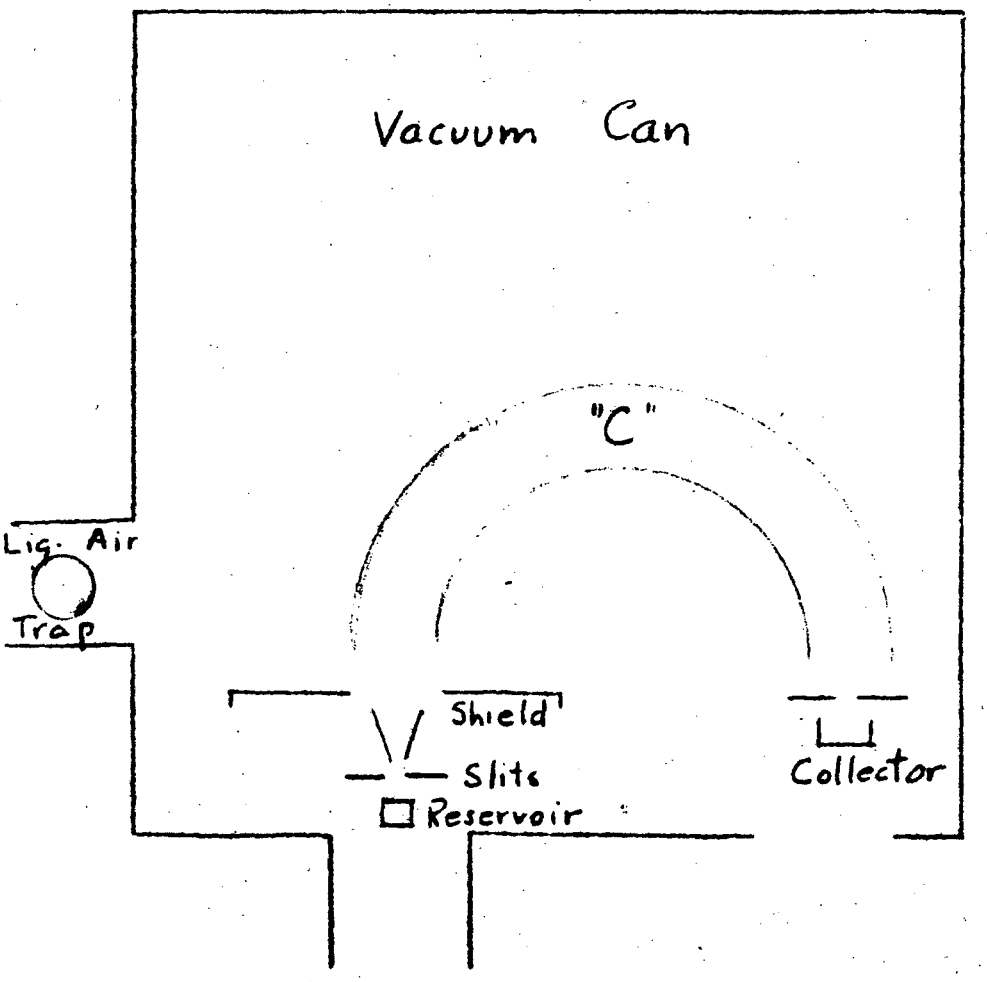
SECRET

UNCLASSIFIED

UNCLASSIFIED

Fig. 6.

[redacted]



UNCLASSIFIED