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THE ELECTROLYTIC PREPARATION OF
SMALL QUANTITIES OF ALKALI METALS

By

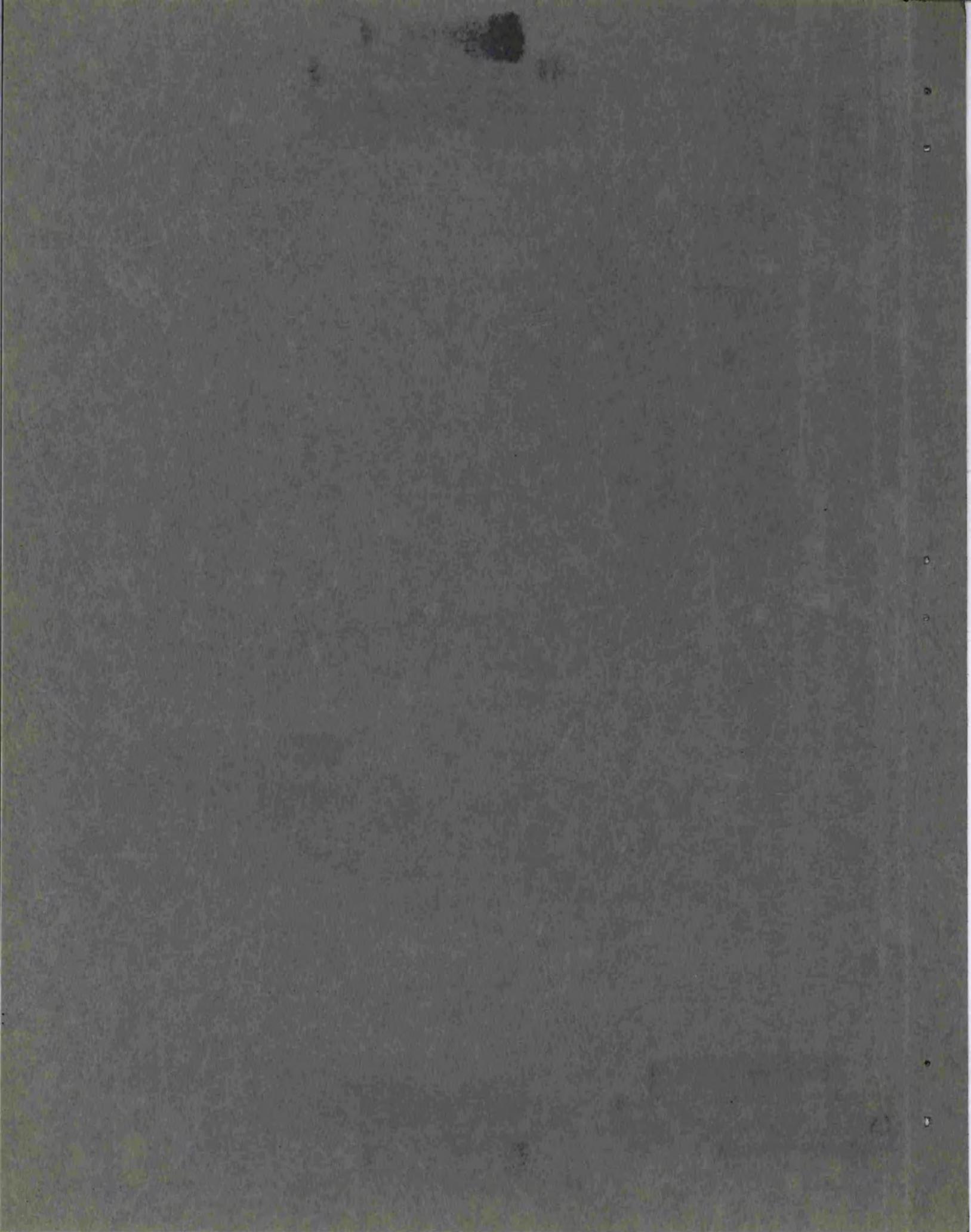
P. S. Baker
G. F. Wells
W. R. Rathkamp



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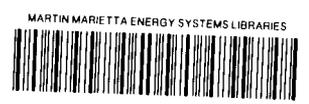
January 2, 1953

STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION
C. P. Keim, Director



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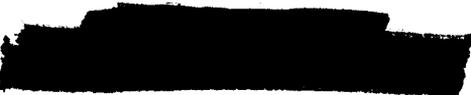
ABSTRACT

In the program of separating the isotopes of the alkali metals, it seemed desirable to develop a method for obtaining the metals in small quantities from their isotopic salts. The only methods available either involved large quantities of material or produced only thin layers of metal, neither of which was satisfactory for the purpose.

Several possibilities were considered, including chemical reduction as well as electrolysis of both aqueous and non-aqueous solutions of salts. The electrolysis of the fused chloride was finally adopted as most suitable.

Using readily available materials of construction, a cell was developed which permits the formation of more than one gram of lithium metal from as little as 10 cc (20 g) of the fused salt. The cell may also be used for semi-continuous production of larger amounts of metal. Total recovery of metal and salt from the cell is above 95% of the material charged to the cell.

A technique for removing the molten metal with a stainless steel pipet and a method for storing it in glass for extended periods of time were also worked out.





A CELL FOR THE PREPARATION OF SMALL QUANTITIES OF ALKALI METALS

P. S. Baker, G. F. Wells, and W. R. Rathkamp

Owing to the high costs and small yields of the methods currently available for isotopic separation,¹ the conversion of isotopes as compounds to the metals will necessarily be confined to a small scale. The work described here deals with the development of a miniature cell designed for the preparation of alkali metals from small amounts of their salts. The experiments were carried out primarily with lithium salts, although metallic potassium was also prepared in the same type of cell.

CHOICE OF METHOD

Lithium was chosen for the development work because it is one of the least reactive of the alkali metals and was expected to be safer. Also, of the three alkali elements that have more than single naturally-occurring nuclides (lithium, potassium, and rubidium) the lithium 6 isotope is more abundant than the 40 and 41 isotopes of potassium; and lithium is more important industrially than rubidium, so that the lithium isotopes might be expected to be separated first. It was hoped, in any case, that the method finally worked out for lithium would, without major changes, be suitable for the preparation of the other alkali metals.

From the standpoint of the efficient utilization of any isotopic salts which might become available, the essence of the problem seemed to lie in determining how small an apparatus could be made, yet permit preparation of suitable quantities of metal. It was felt that one-half to one gram of recovered metal should be enough to allow most desired measurements. Several methods were considered:

1. Electrolysis of solutions of salts in non-aqueous solvents such as ethylene diamine, pyridine or liquid ammonia.^{2,3,4} From the standpoint of hold-up, it was thought that solutions of salts certainly would be advisable since the concentrations of the solutions could be quite low and the volumes small. Some work was carried out electrolyzing solutions of lithium salts in pyridine, but in spite of reports to the contrary, considerable difficulty was experienced in obtaining deposits of appreciable thickness which remained shiny.
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There appeared to be a reaction of the metal with the pyridine. Furthermore, the problem of collecting a thin deposit of the metal from the electrode was difficult. It was anticipated that ethylene diamine would be quite similar to pyridine, but because of the hazardous nature of the material, it was not tried. Articles dealing with the use of liquid ammonia as a solvent from which to deposit alkali metals were promising, but the apparent difficulty in setting up a liquid ammonia electrolysis system led us first to consider other possible methods.

2. Chemical reduction.^{5,6} Chemical methods were investigated and some reactions were carried out using the oxide, fluoride, carbonate, hydroxide, and halides of lithium, with magnesium, calcium, carbon, iron, barium, and ferrosilicon as reducing agents. The results showed varying degrees of success, but the limiting size of reactor was larger than seemed desirable; it also seemed very probable that these methods could not be applied to those alkali metals more active than lithium.
3. Electrolysis from aqueous solutions with a mercury cathode.⁷ A few experiments were carried out using a rather concentrated solution of lithium bromide in water with a sintered-glass barrier and a mercury cathode. Although deposition appeared satisfactory in small amounts, it has been reported that the solubility of lithium in mercury is small⁸ and that the separation from an amalgam is difficult, owing to the great stability of some of the intermetallic compounds formed.⁹ Admittedly, these arguments might not hold for other metals.
4. Electrolysis of fused salts.^{10,11} The results of preliminary trials with fused salts showed sufficient promise of success that the work on the other methods was, for the time being at least, abandoned and efforts were directed toward the fused-salt method.

DEVELOPMENT OF THE CELL

In constructing a cell for the electrolysis of small amounts of salts, there were a number of factors to be considered:

1. As seen from Table 1, the volume of salt per gram of metal is rather small in all cases. It is most advantageous in the case of lithium, particularly with LiI. But since deposition of iodine seemed less desirable than formation of chlorine at the anode, the iodide was not used. And since there was no great advantage in using bromide rather than chloride, the latter was used in all cases.

The use of other salts as additives to increase the volume, with the necessity of a distillation for purification, was ruled out as unsuitable for small quantities of metal where recovery of the distilled material might be difficult. ¹²

TABLE I ¹

<u>Salt²</u>	<u>Specific Gravity</u>	<u>Melting Point °C</u>	<u>Grams salt per gram of metal</u>	<u>cc salt per gram of metal</u>
LiCl	2.07	614	6.1	3.0
LiBr	3.64	547	12.5	3.4
LiI	4.06	446	19.3	4.8
KCl	1.99	790	1.9	1.0
KBr	2.75	730	3.0	1.1
KI	3.13	723	4.2	1.4
RbCl	2.76	715	1.4	0.5
RbBr	3.35	682	1.9	0.6
RbI	3.55	642	2.5	0.7

1. Data from Lange's Handbook of Chemistry, 8th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952.

2. Oxygen-containing compounds were not even considered for fused-salt electrolysis on account of the interfering side-reactions which occur.

2. In any batchwise electrolytic process, hold-up in the cell is considerable. Most commercial cells operate continuously so that this factor is relatively unimportant,¹¹ but where the raw material is to be limited, hold-up should be kept to a minimum.
3. The materials of construction should be such that they will retain the molten salt, yet not react appreciably with it or with the products of the electrolysis.
4. The minimum size of the cell would be limited by the fact that separate anode and cathode compartments are essential to prevent interaction of the products of electrolysis. Furthermore, the barriers in the usual industrial cells might no longer function efficiently in that capacity in very small cells where anode and cathode are in close proximity.

5. The actual dimensions would be determined also, to some extent, by the materials of construction which are available.

CELL PARTS

Of all the parts of the cell, the diaphragm seemed most critical. Stainless steel sheet and gauze, and inconel sheet and gauze were attacked by the chlorine evolved during the electrolysis. Calcium fluoride, porcelain, alumina, thoria, zirconia, beryllia, and magnesia were attacked to various degrees, either by the molten salt or by the metal formed during the reduction. Alundum was finally chosen, primarily because small thimbles were readily available in various sizes, whereas the magnesia and beryllia, which were slightly more resistant, would have required special fabrication.

For the cathode, stainless steel seemed to work best. The cathode diameter did not seem critical as long as the current was not too high.

For the anode, carbon or graphite was almost mandatory to prevent reaction with the chlorine. The decision to have the anode serve as the container was one of expediency, since it permitted a smaller cell than otherwise would have been possible. It did have the disadvantage, however, of absorbing a small amount of salt as the electrolysis proceeded.

To permit heating of the cell and to retain any salt which might soak through the anode, the graphite was inserted in a stainless steel container which, in turn, was wrapped with a calrod heater.

The connection from the power source to the anode actually was made through a clip lead fastened to a small piece of rod welded to the edge of the steel container. It had been found that connections directly to the graphite were short-lived, owing both to the corrosion of the clip lead by the escaping chlorine and to the oxidation and spalling of the graphite as a result of contact with the air.

FINAL CELL

The size of the final cell, representing what seemed to be the optimum conditions with respect to a number of factors, was governed by the experiences encountered in resolving the difficulties which arose during the investigation. When the cell dimensions were too small, the lithium metal came in contact with the alundum very shortly after electrolysis had begun, and remained there until removed, reacting slowly with the alundum throughout the entire period. Also, when the cell was small, the escaping

chlorine formed bubbles in the molten salt and carried the salt up between the graphite and alundum, depositing it as a solid around the top of the cell. The most serious difficulty, however, was what seemed to be the tendency of the chlorine gas to diffuse through the pores of the alundum, then to react with the metallic lithium in the cathode compartment. By enlarging the cell slightly, these difficulties were either alleviated or eliminated entirely.

The final cell is shown in Figure 1, and a smaller version (but with the same cross-sectional dimensions) in Figure 2. The materials of construction comprised a three-sixteenths inch stainless-steel cathode supported in a soapstone "yoke", * a 1-1/2" x 3" graphite crucible with 0.080" wall serving as combined anode and anode compartment, and a 1" x 2-7/8" alundum thimble** as a diaphragm and acting also as the cathode compartment.

CELL OPERATION

After introducing the salt into the cell and raising the temperature to the melting point the cathode was inserted and current turned on. In a few seconds the cathode became coated with a shiny deposit of metallic lithium. As electrolysis continued, the deposit of lithium increased in size and soon was in the form of a large drop or pool surrounding the cathode. When the cathode was removed, the drop could be observed floating on top of the fused salt. The drop remained as a perfectly shiny globule, although apparently exposed to the air. The explanation seems to lie in the presence of a thin layer of molten salt over the surface of the metal,¹³ and the combination of this with the protection afforded by the slow escape of lithium chloride vapor was sufficient to prevent oxidation.

If electrolysis was carried out over an extended period of time, a small amount of lithium chloride eventually seeped through the graphite container. This allowed some electrolysis at the surface of the stainless steel container and the consequent attack of the metal by the chlorine.

With the particular type of cell described, the usual charge was 35-40 grams of reagent grade lithium chloride, though as little as 20 grams and as much as 55 grams could be charged. It was found that the time of operation could be extended and the total amount of recovered metal increased

* The decision to insert the cathode at the top was reached after many unsuccessful attempts to introduce it through the bottom by use of a Kovar seal. (The molten salt gradually worked into the seal, and electrolysis took place there.)

** Norton RA 360, No. 5163.



FIGURE I. ELECTROLYTIC CELL



FIGURE 2. SMALL CELL

by adding more salt to the cell as the salt level decreased. The yield immediately available as metal was in the order of 40% based on the salt charged. Continued operation (at decreased efficiency) increased this somewhat. By extracting the contents of the cell with water and dilute HCl and then treating with appropriate reagents, it was possible to recover the remaining LiCl. Total recovery including metal and salt, was 95% of the original charge.

REMOVAL OF LITHIUM FROM THE CELL

Removal of the lithium metal was carried out by use of a stainless steel pipet, coated on the inside with a thin layer of oil (Figure 3). A technique was developed in which the molten metal was drawn into the pipet until salt started to enter the tip. At this time the salt solidified, thereby plugging the pipet tip and retaining the lithium metal. It was now possible to extrude the metal quite readily by means of a plunger. The metal could then be coated with oil or simply allowed to nitride in air to form a protective coating of its own. The former method was found to be the more satisfactory.

On numerous occasions, several of these extruded pieces were melted together in mineral oil, then pipetted into glass tubing to give pieces weighing several grams. In some cases the glass tubes were sealed off and in others the pieces of metal were removed into containers filled with oil (Figure 4). Both types of containers kept the lithium shiny for many months.

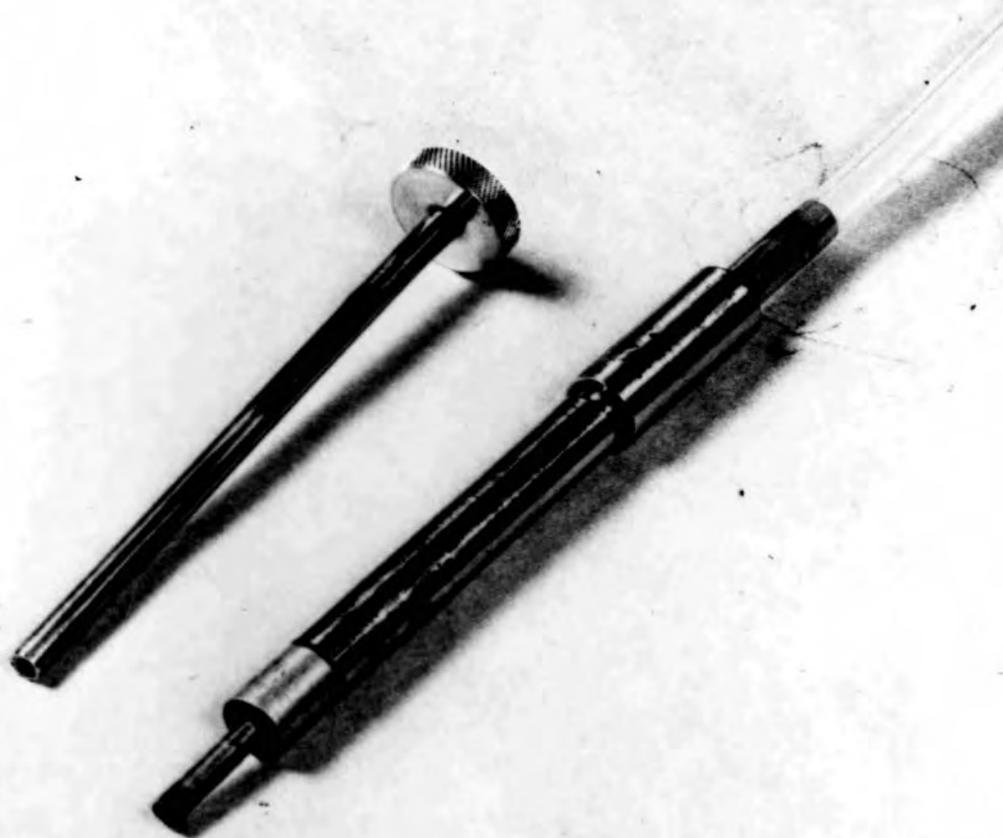


FIGURE 3. PIPET AND EXTRUDER

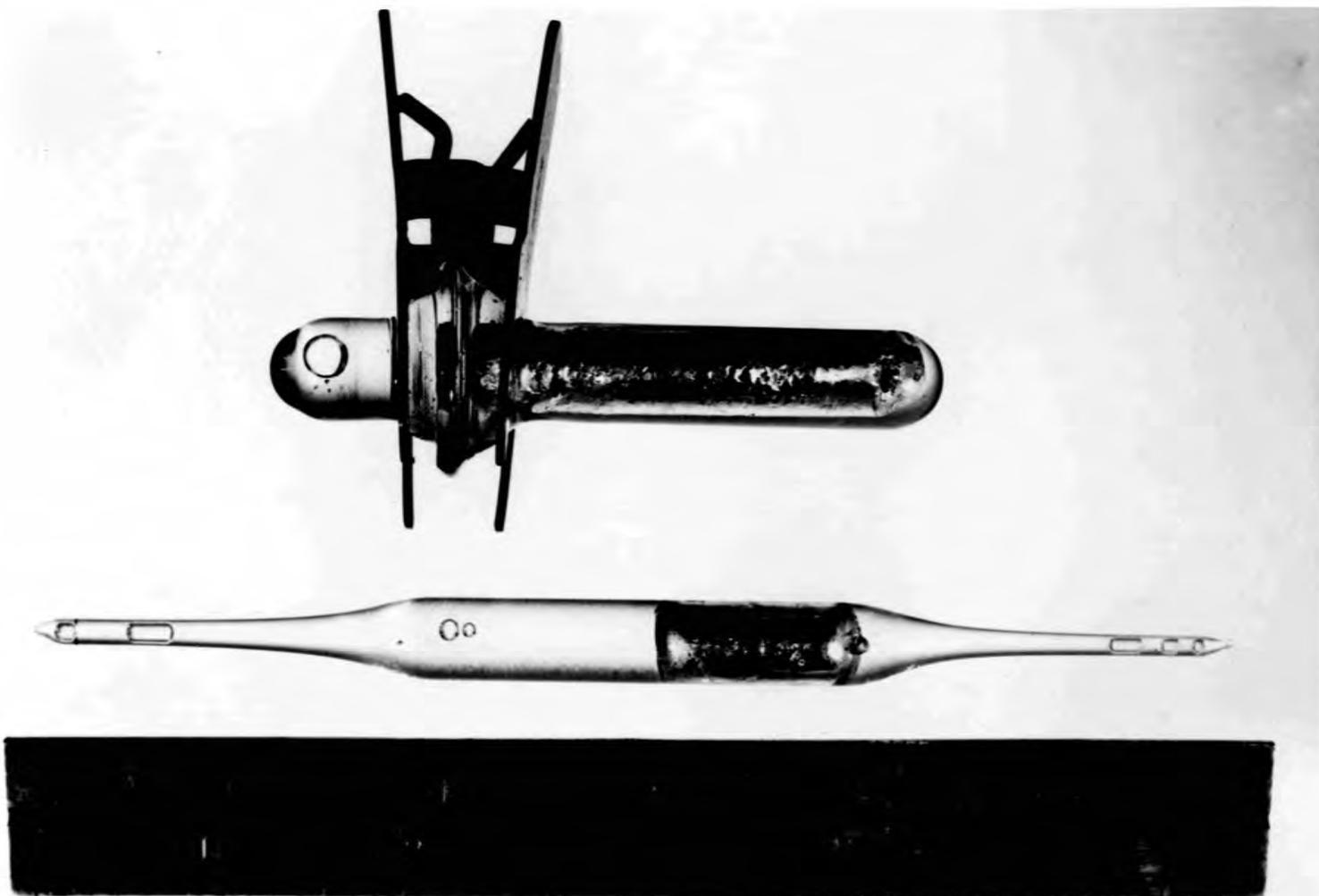


FIGURE 4. METAL SAMPLES IN GLASS & OIL

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