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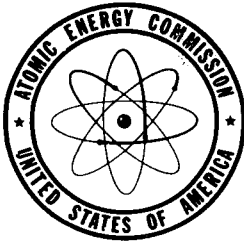
DOW-65

FLUORIMETRIC DETERMINATION OF URANIUM IN PHOSPHORIC ACID

By
M. D. Yeaman

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Dow Chemical Company

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ABSTRACT

/ A description is given of the method used at the Western Division of The Dow Chemical Company for the determination of uranium in phosphoric acid and other phosphatic materials. The extent of interference by cationic and anionic substances is reported, as are the effects of variation in technique and handling.

Detailed instructions, with drawings, for the construction of the modified fluorimeter used are included. Other equipment needed and the chemicals consumed by the method are tabulated. /end

CHEMISTRY

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THE FLUORIMETRIC DETERMINATION OF

URANIUM IN PHOSPHORIC ACID

Many investigators (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13) have studied the fluorescence of uranium in a fluoride flux and have developed or improved analytical procedures utilizing this phenomenon. The standard deviations associated with these procedures are all very nearly the same, roughly 5 per cent.

A number of elements contribute to this deviation by interfering with the uranium fluorescence in one of two ways. (1, 2, 3, 4, 5.) First, certain elements cause a decrease in the fluorescence and so are called quenchers. Second, other elements cause a shift in the fluorescent spectra, resulting, as the concentration of the interfering element is increased, in an increase in intensity followed by a decrease.(5) Quencher elements of which microgram quantities appreciably reduce uranium fluorescence are: Ag, Au, Co, Cr, Cu, Fe, Hg, Ir, Mn, Ni, Pb, Pt, Th, and Zn. Of these iron is the major quencher present in commercial phosphoric acid.

A theoretical treatment of quenching has been reported by Price, Ferretti and Schwartz (3), who found that quenching was dependent on the concentration of the quencher and not on the uranium to quencher ratio. By diluting the solution sufficiently, the effect of the quencher becomes negligible. However, in many cases the resulting concentration of uranium is so low that a very sensitive instrument is necessary to determine its fluorescence. Such instruments have been designed (3, 10, 14), and in most cases operate very well. Chance contamination is probably the largest source of eriatic results in this dilution procedure and great care must be taken to minimize this source of error.

Difficulties were encountered in the determination of uranium in crude phosphoric acid and other phosphatic material when the dilution technique was applied.(15) Accurate analyses were made but severe etching of the platinum dishes used decreased their reflectivity, made them difficult to clean and shortened their life. As a result an extration method was deemed necessary.

Quenching may also be avoided by a chemical separation of the uranium from the contaminants responsible for it. This separation can be accomplished by extracting the uranium as uranyl nitrate into an organic solvent.(1, 2, 7, 15, 16). Ethers, ketones, aldehydes, and esters, i.e., solvents containing oxygen atoms capable of electron donation, are quite selective for uranium. Uranyl nitrate is not at all soluble in solvents such as benzene, chloroform, etc.

Thorium, cerium (IV), and gold are also extracted to a greater or lesser degree depending upon the solvent, the HNO_3 concentration and the salting-out agent.

The extraction may be done in a continuous manner using diethyl ether (17), or batchwise. Continuous extraction is comparatively time-consuming and will not be discussed here. Batch extractions are found to be quantitative for many solvents in conjunction with one of several salting-out agents. Desirable solvents have favorable distribution coefficients, high flash and boiling points, and low viscosities. Ethyl acetate fulfills some of these requirements, especially that of low viscosity, and in addition has a low cost. On the other hand, dibutoxytetraethylene glycol (penta ether) has a high boiling point and a slightly more favorable distribution coefficient, especially from commercial phosphoric acid. Penta ether is used at this laboratory but the low cost of ethyl acetate may recommend it in other instances.

Description of the Method.

The procedure used at Dow utilizes the extraction of uranyl nitrate by penta ether prior to the formation of fluorescent uranyl fluoride. One analyst is able to complete 800 to 1000 determinations per month. Most of the samples analyzed are phosphoric acid solutions but many other liquids have been dealt with. The ordinary uranium concentrations are from about 0.1 to about 2000 mg. U_3O_8 per liter.

Since the procedure is applicable only to liquids, a method of attack on solids was necessary. Phosphate rock and many other ores are readily taken into solution by means of a hot nitric acid leach. Usually a 1 to 5 gram sample, depending on the estimated uranium content, is weighed and transferred to a 100 ml. beaker. About 5 to 10 ml. of concentrated HNO_3 are added and the mixture heated until no more brown fumes appear. Then 20 to 30 ml. of 1:1 HNO_3 are added and allowed to boil for 30 minutes. Upon cooling the liquid and residue are transferred to a volumetric flask and the volume is adjusted. Aliquots of this solution are then analyzed.

Twenty-four determinations on the liquid samples are then taken concurrently through the following procedure:

1. Aliquots containing about 50 micrograms of U_3O_8 are pipetted into 25 mm. x 100 mm. test tubes. (For samples of high uranium concentration, micropipettes may be used. This is as accurate as diluting the sample and considerably more convenient and rapid.) The volumes of the aliquots are then adjusted to

5 ml. with distilled water.

2. In phosphoric acid solutions the uranyl ion forms a phosphate complex that is not extracted by penta ether. In order to form uranyl nitrate, in addition to a very high nitrate concentration, an agent to complex the phosphate is required. Aluminum nitrate is very satisfactory for both these purposes. This salt melts at $73°$ C. so that it can be added as a liquid. It is made up beforehand by dissolving 3600 grams of $Al(NO_3)_3 \cdot 9H_2O$ in 600 ml. of water and 400 ml. of concentrated HNO_3 on a hot plate. The HNO_3 is added to prevent decomposition of the nitrate to the oxide. The hot salt solution is then transferred to a steam-jacketed dispenser (see Appendix II) that is maintained at $100°$ C. Sixteen ml. of the above solution are added to the 5 ml. containing the original aliquot, saturating it at room temperature.

3. When the solution is cool, 5 ml. of penta ether are added from a Machlette automatic pipette.

4. The two phases are intimately mixed by stirring, four at a time, for 1 minute or more. The special stirring apparatus used is equipped with glass, screw-type impellers. A fuller description of the apparatus is given in Appendix II. Occasionally emulsion formation is encountered and centrifuging is necessary. Hence, as a matter of routine procedure all samples are centrifuged after stirring. The glass stirrers are rinsed with water, then with acetone, and another set of four samples may then be stirred.

5. The aqueous (lower) phase is then removed and discarded by immersing a pipette to the bottom of the test tube and drawing the liquid out into a trap. The pipette is wiped off and rinsed with water and acetone.

6. The contaminants that may have been extracted into the penta ether are eliminated for the most part by one wash with an ammonium nitrate solution. Nine ml. of solution, containing 660 grams NH_4NO_3 and 66 ml. concentrated HNO_3 per liter, are added to each test tube and the mixture stirred and centrifuged as above. The aqueous layer is not removed this time.

7. A 0.5 ml. aliquot of the penta ether layer is then transferred to a small gold dish, a description of which is given in Appendix II. The pipette is then rinsed with acetone after each delivery. The choice of using a 0.5 ml. aliquot is a compromise between sensitivity and time of analysis. A large aliquot would result in greater sensitivity but would require correspondingly longer time in the subsequent penta ether evaporation step. The pipettes used at Dow are calibrated to deliver 0.500 ± 0.002 ml. of penta ether. "The exact volume delivered by the pipette is not

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critical so long as it is reproducible." Control samples subjected
to the same conditions are run with each set, hence differences
due to this source would not appear.

8. The gold dishes are then placed on a $\frac{1}{4}$ inch thick
asbestos pad on a hot plate. After 20 to 30 minutes the HNO_3
and much of the penta ether are evaporated. During this time
another set of determinations are run through steps No. 1 and
No. 2, above.

9. The dishes are then placed directly on the hot plate
to volatilize the NH_4NO_3 and burn off the remaining penta ether.

10. To each dish, 2.5 grams of a flux consisting of 9
per cent NaF and 91 per cent $NaKCO_3$ are added. A flux dispenser
either of the hypodermic type made from glass tubing with a close-
fitting glass rod as a plunger or a spoon-type dispenser may be
used for this purpose. Again, as with the aliquot taken of the
penta ether, the exact weight is not critical as long as it is
reproducible. A variation in weight from 2.4 to 2.6 grams results
in about $\pm$ 1.5 per cent error.

11. The gold dishes are then placed, six at a time into
a muffle furnace and maintained at a termperature of 815° C. for
1.5 minutes. They are removed and the molten flux is swirled
about the walls of the dish. They are then replaced into the
furnace for about one minute.

12. After cooling, the flux disc is removed from the
dish and placed in the fluorimeter where the intensity of its
fluorescence is measured relative to that of a glass phosphor.
The fluorescence is directly proportional to the amount of uran-
ium in the flux up to about 10 to 15 micrograms of U_3O_8 in the
2.5 grams of flux. The fluorescence is also directly proportional
to the intensity of the ultraviolet-light source. Since this may
fluctuate over a period of time it is advisable to record the in-
tensity of fluorescence of the glass phosphor periodically while
determining the fluorescence of the flux disc.

A complete description, with drawings, of the modified
model R fluorimeter used at Dow is given in Appendix I.

13. The uranium in the original aliquot taken from the
sample is calculated using the following formula:

$$U_3O_8 = FI_D/I_G$$

where the U_3O_8 is given in terms of micrograms of U_3O_8 in the orig-
inal aliquot. I_D is the galvanometer deflection due to the fluores-
cence of the flux disc, corrected by subtracting the blank reading.

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This blank reading is obtained by measuring the fluorescence of
a flux disc containing no uranium and should be determined when
each batch of flux is made. I_G is the deflection due to the
fluorescence of the glass phosphor. F is determined by running
known amounts of uranium through the analytical procedure, deter-
mining I_D and I_G and calculating F from the three known values.
The value of F is very nearly constant for a given fluorimeter
and a given analyst. Variations in technique as well as other
factors will show up in a different F.

Extent of Interference With the Method

As mentioned above, thorium, cerium (IV), and gold are
at least partially extracted into the penta ether. Two micrograms
of cerium (IV) or 15 micrograms of thorium will reduce the fluo-
rescence by 10 per cent.(1,2) Cerium (III) is not appreciably
extracted, however, and the addition of iron (II) prior to extract-
ing will eliminate its effect. When the ratio of thorium to uran-
ium is high a separation must be made prior to extraction. If the
separation can be effected by paper column chromatography (18) no
further purification is necessary.

Even though the distribution coefficient of iron into
penta ether, C (organic)/C (aqueous), is only of the order of
0.001, enough iron is carried through the procedure to cause
quenching if its concentration in the original sample is about
10 grams per liter. This quenching is eliminated by washing three
times with ammonium nitrate solution instead of once. (Step 6 in
the procedure.) Samples of known uranium concentration should be
subjected to the same treatment for control

Anionic interferences are more serious than cationic in
affecting the determination of uranium in phosphoric acid. Figure
1 shows the decrease in extraction of uranium into penta ether as
a function of phosphate concentration. For example, if a 5 ml.
aliquot of a solution containing 400 grams PO_4 per liter were
treated only about 78 per cent of the uranium would be extracted.
However, if a 1 ml. aliquot of the same solution were used, 98
per cent of the uranium would be extracted. For this reason when
the phosphate concentration is known to be high as in the case of
commercial phosphoric acid (40% H_3PO_4), this effect must be taken
into account in choosing the volume of the aliquot. If the aliquot
is chosen on the basis of uranium concentration the effect of phos-
phate concentration must be corrected for by an empirical factor.
A smaller aliquot may be taken at the expense of sensitivity. This
latter method is preferred in routine control work.

Sulfate concentrations greater than about 100 grams SO_4
per liter cause a precipitate upon the addition of the penta ether
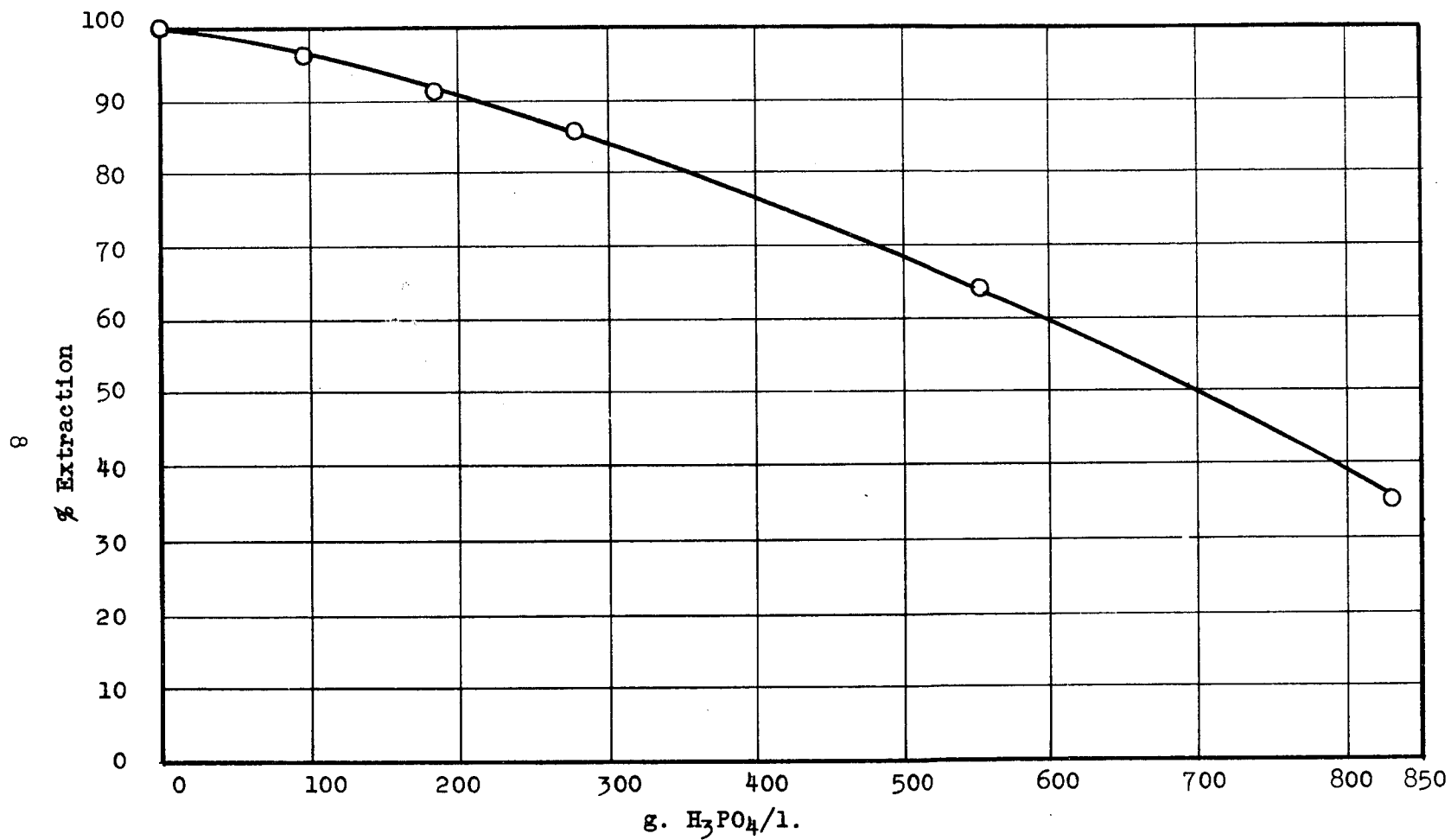to the sample saturated with aluminum nitrate. Some uranium is

Fig. 1--Effect of H_3PO_4 concentration on the extraction of uranium by penta ether.

occluded in this precipitate resulting in low and erratic results. Uranium may be separated from sulfate by an ammonium hydroxide precipitation. Aluminum is often used as a carrier for trace amounts of uranium in this precipitation. The hydroxide must be carbonate free to prevent the formation of the soluble uranyl carbonate complex. The precipitation may be performed in the 25 mm. x 100 mm. test tubes used in this method. After centrifuging the aqueous phase is decanted, the precipitate is dissolved in concentrated NO_3, and the solution is taken though the usual procedure. (In the case of high phosphate concentration this scheme is inapplicable.)

The distribution of uranyl nitrate between the penta ether and the saturated aluminum nitrate solution is 120:1. However, since the volume ratio is 1:4 for the organic:aqueous phases there is roughly a 3 per cent loss. The distribution between the penta ether and the ammonium nitrate wash solution is 33:1, the volumes being equal. These two factors, combined with an expansion of the organic phase, result in appreciably less than 1/10 of the uranium reporting in the 0.5 ml. aliquot from the penta ether. Empirically, this is 1/14.5 of the original amount. However, these losses are reproducible and are corrected for.

If the volume of aluminum nitrate solution per determination is plotted vs. the per cent extraction a maximum occurs at about 15.5 ml. for solutions containing no phosphate. (Figure 2.) A variation in volume from 15.3 to 17.6 ml. results in a deviation of about 1 per cent. At greatly increased phosphate concentrations a larger volume of aluminum nitrate solution is necessary to get maximum extraction. However, a 2 ml. volume range still has ± 1 per cent deviation. A volume of 16 ml. should be optimum for the majority of samples treated.

Stirring for one minute or greater seems to effect equilibrium between the two phases. When stirring was limited to 30 seconds, erratic results were noticed.

Cross contamination during the stirring and separating steps (steps 4 and 5 in the procedure) should be quite small since the original aliquoting results in uranium concentrations of equal order of magnitude in the test tubes.

Inhomogeneity of the flux may be responsible for some error. However, varying the time of mixing (by rolling) from six to eighty hours has not significantly lowered the standard error. Nor is this error appreciably lowered by fusion over a Meker burner as is done in other laboratories.

The sodium and potassium carbonates, and the sodium fluoride used in making up the flux contain a maximum of 0.001 per cent
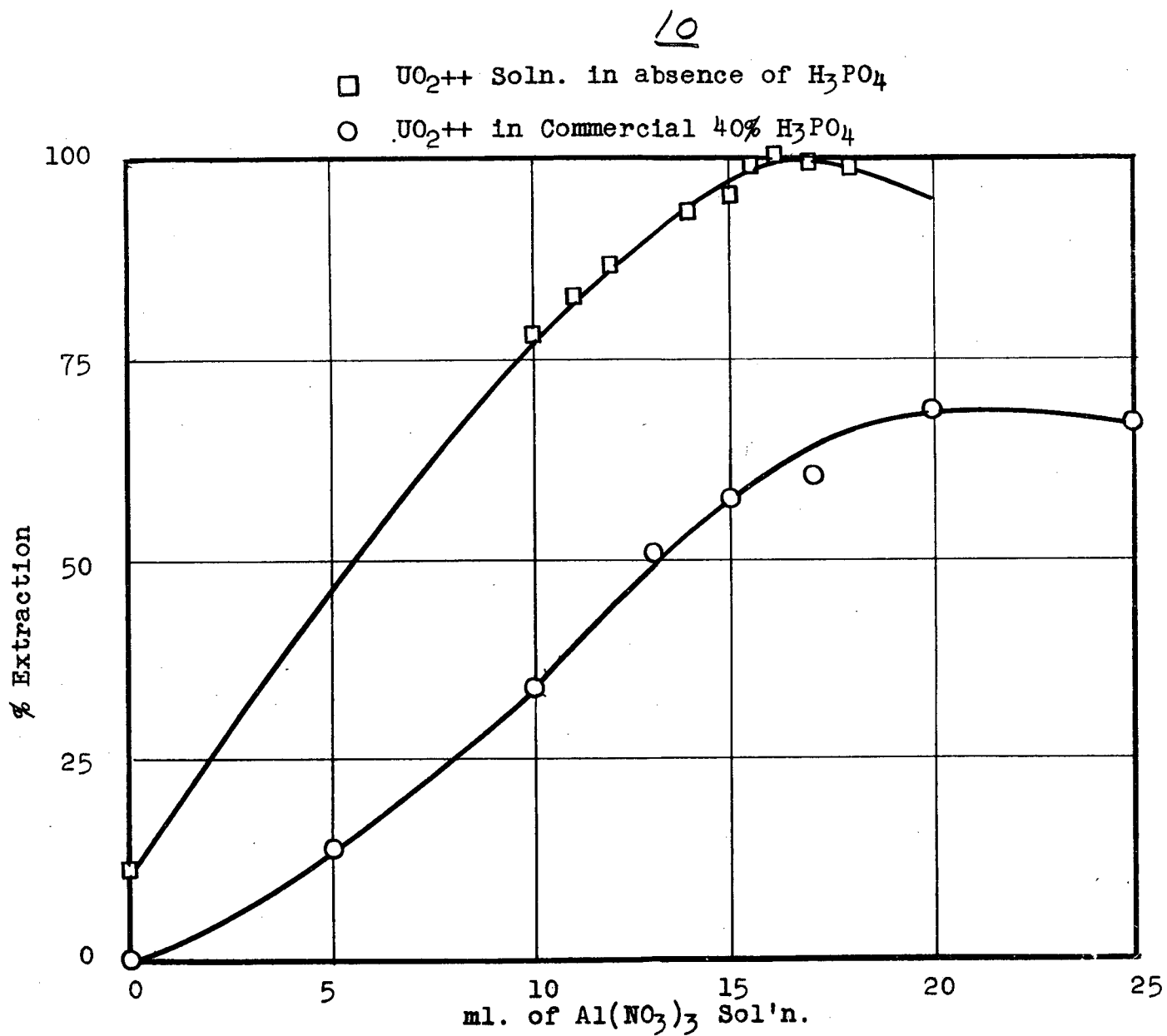
□ UO₂++ Soln. in absence of H₃PO₄

○ UO₂++ in Commercial 40% H₃PO₄

% Extraction

ml. of Al(NO₃)₃ Sol'n.

Fig. 2--Effect of Al(NO₃)₃ on the extraction of uranium by penta ether. , UO₂⁺⁺ solution in absence of H₃PO₄. , UO₂⁺⁺ in commercial 40% H₃PO₄.

Fe and 0.0005 per cent heavy metal impurities. If the maximum amounts are present 16 micrograms of heavy metals and 24 micrograms of iron would be present in the 2.5 grams of flux. This would, of course, result in appreciable quenching. The quenching due to lead, and many other elements, is reported as "variable quenching" (2) since multiple experiments gave inconsistent results for the quenching. This could be at least partly responsible for the high standard deviation.

If the swirling is efficient, errors due to local uranium concentration in the flux should be negligible.

Gold causes quenching; the higher the fusion temperature, the more gold that will dissolve in the flux. Likewise the longer the time of fusion the more gold that will dissolve until the equilibrium concentration is reached. A quantitative study of the solubility of gold in the flux has not been made. However, qualitatively it has been found that the longer the time of fusion and the higher the temperature, the more serious the quenching. At 815° C. or lower and with one to two minutes fusion time this effect is quite small.

The photovolt photoelectric photometer can easily be read to 0.5 division with a possible error of 0.5 to 5 per cent depending upon the absolute reading.

The manner in which the flux is cooled upon removal from the furnace affects the results slightly. The methods used to test this dependance were somewhat crude and only qualitative effects can be reported. The time of crystal formation evidently affects the fluorescence with the longer the time the greater the fluorescence in this range. As long as all the samples are treated similarly no serious errors should result.

The relationship between fluorescence and time of standing is quite interesting and as yet is unexplained. Taking the time of removal of the disc from the furnace as the reference point, there is an increase in the fluorescence with time which attains a maximum value, after about three hours. During the next three hours the fluorescence decreases, approaching a constant value. This phenomenon was studied by preparing, by the standard method, a number of discs of different intensities. When read on the fluorimeter, the maximum value was 6 to 8 per cent greater at three hours than the constant value reached after six hours. These flux discs were kept in a dessicator (over $Mg(ClO_4)_2$)when not being read. Discs which were not dessicated were subject to a larger deviation than the dessicated ones. If time were no object it would be advisable to wait until the following day before measuring the fluorescence of the discs. Where time is an important factor one must

assume that the same conditons prevail throughout the entire set
of samples and that the time error is corrected for by the known
samples run concurrently. Actually, duplicate samples run both
ways indicate that on waiting until the following day to determine
the fluorescence the standard error is appreciably less: 5 per cent
as compared to 7 per cent.

Increasing ambient temperature causes a decrease in the
fluorescence of the flux disc, and of the glass phosphor used as
a reference. The flux and the glass do not have the same tempera-
ture-fluorescence relationship, thus the ratio of their intensities
will not be constant. The glass being somewhat more affected, the
ratio is therefore an increasing function, increasing roughly 0.5
per cent per degree up to 27° C. and about 1 per cent per degree
above 27° C. This effect has no bearing where the samples and the
knowns are read at the same temperature.

BIBLIOGRAPHY

The references given are to documents that are not classified or that have been referred to in non-classified documents.

(1) C. J. Roddin, "Analytical Chemistry of the Manhattan Project"
     McGraw-Hill Book Co., 1950. Numerous references are included
     to work done in this field.
(2) C. F. Coleman, A. A. Smales, C. Feldman, W. Williams, T. W.
     Bartlett, H. Grotta, Report C-4.360.2, July, 1945.
(3) G. Price, R J. Ferretti, S. Schwartz, Report CC-2985, June,
     1945.
(4) W. F. Neuman, Report M-1730, July, 1945.
(5) K. P. Overton, A. F. Williams, F. H. Burstall, Report CRL-AE-
     78, April, 1951
(6) R. L. McCutchen, C. D. Susano, Report Y-414, May, 1949.
(7) W. R. Grimes, F. E. Clark, Report H-1.740.10, May, 1948.
(8) U. Koskela, D. Kaufman, Report MITG-A65, May, 1949.
(9) S. Jacobs, Report CRL-AE-54, April, 1950.
(10) J. C. Center, Report AECD-3006, September, 1948.
(11) F. S. Grimaldi, H. Levine, Report AECD-2824, January, 1948.
(12) F. S. Grimaldi, F. N. Ward, R. Kreher, Report AECD-2825,
     April, 1950.
(13) J. B. Zimmerman, Memorandum Series No. 11", Department of
     Mines and Technical Surveys, Mine Branch, Ottawa, Canada,
     June, 1951.
(14) O. Kaufman, M. Costello, U. Koskela, Report MITG-A70.
(15) J. M. Granfield, Report MITG-251, November, 1950.
(16) Irving, H. M. "Solvent Extraction and Inorganic Analysis."
     Quarterly Reviews, Volume V, No. 2, 1951.
(17) C. J. Rodden, "Manual of Analytical Methods for the Determina-
     tion of Uranium and Thorium in Their Ores." U. S. Govern-
     ment Printing Office, washington, 25, D. C.
(18) J. L. Beecher, Report C-4.381.4, February, 1946.
(19) T. V. Arden, Report CRL-AE-3.
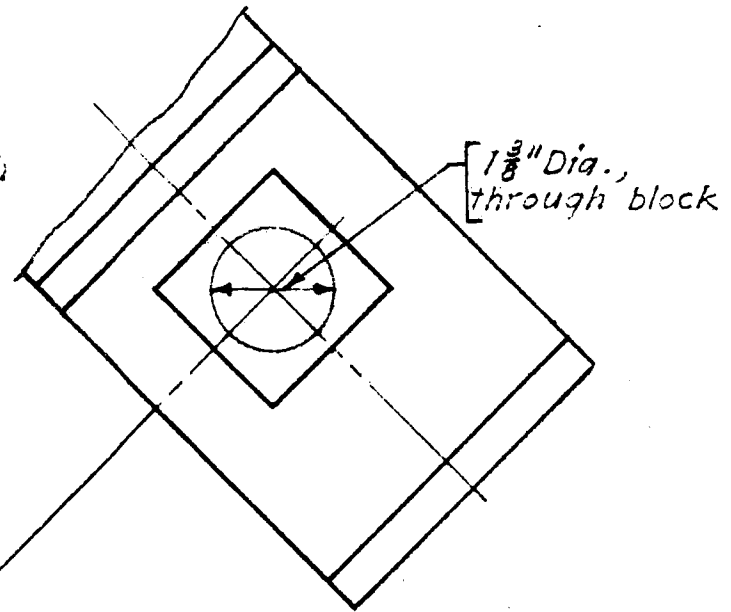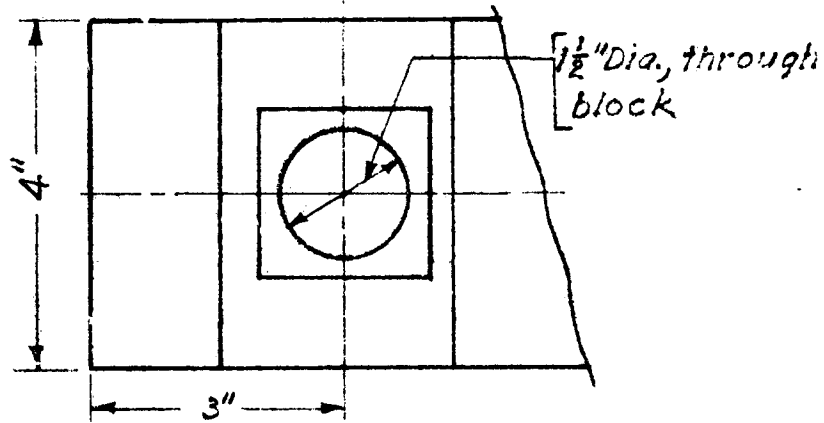
APPENDIX I

MODIFIED MODEL R FLUORIMETER

The fluorimeter used at Dow is a modification of the Model R (18) first constructed at Oak Ridge National Laboratory. The main modification was in the light source. Since the intensity of fluorescence is directly proportional to the intensity of the ultraviolet light source, more intense General Electric CH4 (spot) or EH4 (flood) lamps were substituted for the Hanovia lamp in the original Model R. A constant-voltage-supply transformer was also incorporated. With the above exceptions and some minor rearrangements, the design is that of the Model R and any Model R can be adapted to use the more intense CH4 or EH4 lamps.

Included in this Appendix are a list of the parts of the fluorimeter, drawings from which the parts may be made, and 2 views of an assembled fluorimeter.

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<u>COMPLETE PARTS LIST FOR MODIFIED</u>
<u>MODEL R FLUORIMETER</u>

Drawing No.	Quantity Required	Item	Material
I.	1	Center block	Wood
II	1	Slide	"
III	1	Photocell Holder	"
IV	1	Holder Support	"
V	1	Spring Guide	"
VI	1	Guide bar	"
VI'	1	" "	"
VII	1	End Bar	"
VIII	1	Slide cover	"
IX	1	Clip	Brass
X	1	Spring	Bronze or steel
XI	1	Base	Wood
XII	1	Transite base plate	Transite
XII'	1	Transite spacer	"
XIII	1	Shutter plate	Brass
XIII'	1	Screen plate	"
XIV	1	Brass Collar	"
XV	1	Transite Socket Support	Transite
XVI	1	Socket cap	Steel
XVII	1	Lamp Shield	"
	4	2 1/2" No. 8 R.H. Wood Screws	
	9	1 1/4" No. 6 R.H. " "	
	2	3/4" No.6 R.H. Wood Screws	
	3	1" No. 10 F.H. " "	
	8	1" No. 6 F.H. Wood Screws	
	6	1/2" No. 6 F.H. Wood Screws	
	8	6/32 x 1/2" R.H. Machine Screws	
	2	6/32 x 1/4" R.H. " "	
	7	8/32 x 1" R.H. " "	
	2	10/24 x 1/2" R.H. " "	
	2	1/4/20 x 1 1/2" R.H. " "	
	1	U.V. Filter, 2" x 2"	Glass
	1	Yellow Filter, 2" x 2"	"
	1	Blue Filter 2" x 2"	"
	1	Phosphor, 2" x 2"	"

     The filters and phosphor are Corning Cat. No's. 5874, 3486, 9780, 3750 respectively. (The U.V. Filter sets in the block (I) below the transite base plate (XII). The yellow and blue filters set in the block below the photocell holder (III).

|		
1	Photometer: Photovolt Model 512M, Photovolt Corp., New York City, New York	
1	U.V. Lamp: General Electric CH4 or EH4.	
1	Constant voltage transformer, Cat. No. 301883, Sola Electric Co. 4633 West 16th St., Chicago 50, Illinois.	

$1\frac{1}{2}$"Dia., through block

$1\frac{3}{8}$"Dia., through block

4"

3"

$3\frac{3}{4}$"

$2\frac{1}{4}$"

$1\frac{1}{2}$"

45°

$1\frac{1}{2}$"

$4\frac{1}{4}$"

2"

$\frac{1}{2}$"

1"

45°

2"

45°

$4\frac{1}{4}$"

$\frac{3}{8}$"

8"
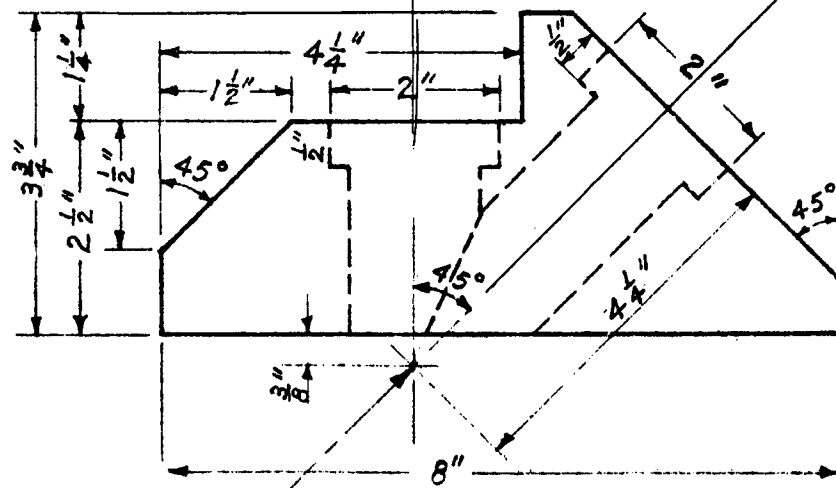
Wood
One piece
Paint flat block

1-CENTER BLOCK

Scale: $\frac{1}{2}$"=1"

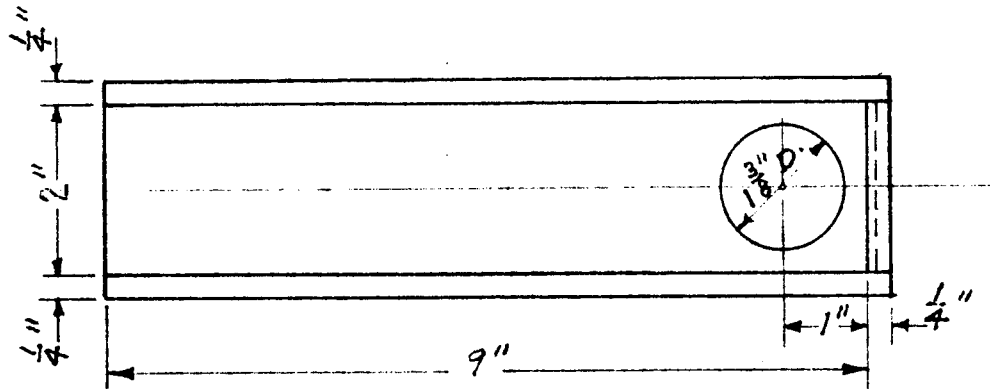Note: It is important center
lines of holes meet at this point

$\frac{3}{4}"$ Dia.

$4\frac{1}{2}"$

$\frac{3}{4}"$

$2"$

$\frac{1}{4}"$

$2"$

20"

$\frac{1}{2}"$ $\frac{1}{4}"$
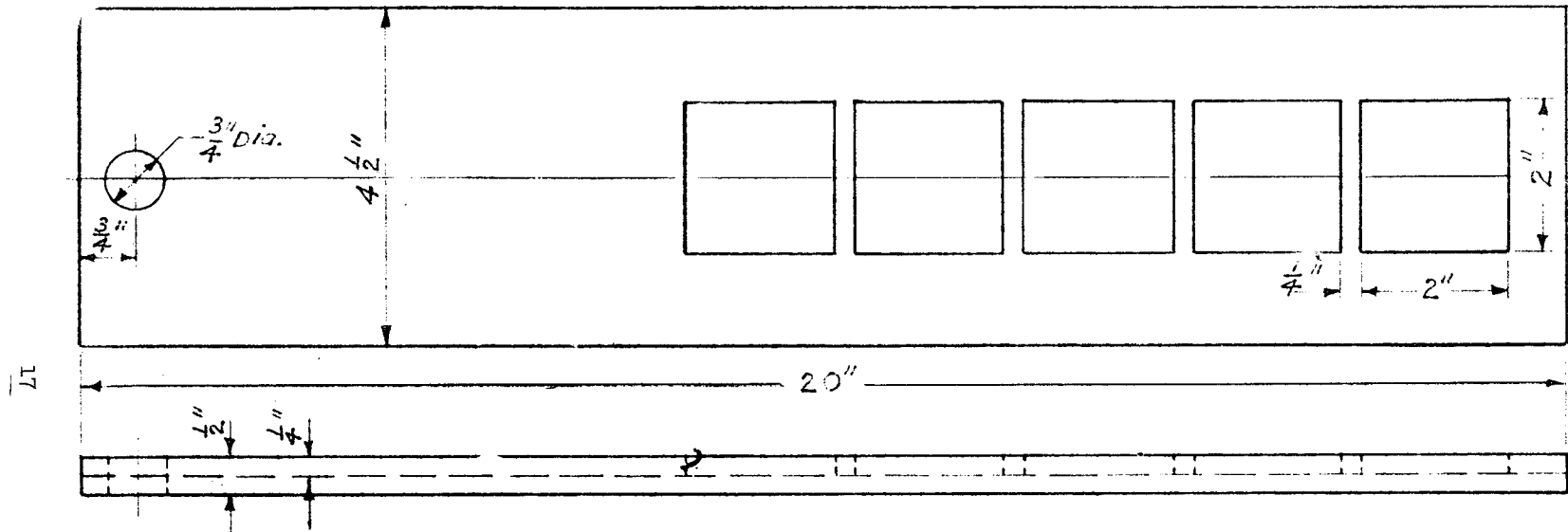
Glue together two layers of $\frac{1}{4}"$ plywood after cutting holes in upper piece.
One piece paint flat black.

II SLIDE

Scale: $\frac{1}{2}" = 1"$

$\frac{1}{4}''$

2''

$\frac{1}{4}''$

$\frac{3}{8}'' D.$

9''

1''

$\frac{1}{4}''$

1''

45°

$\frac{1}{4}''$
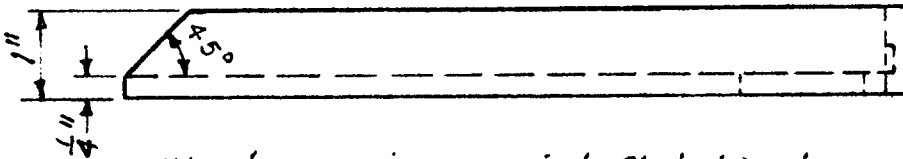
Wood-one piece, paint flat black.

III PHOTOCELL HOLDER

$2\frac{1}{2}''$

$2\frac{1}{2}''$

1''
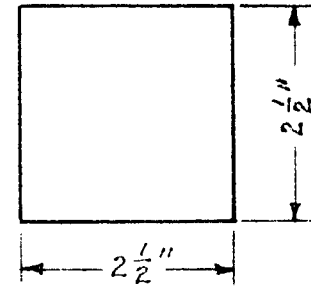
Wood-one piece,
paint flat black.

IV HOLDER SUPPORT

Scale: $\frac{1}{2}'' = 1''$

18"

30°

1"

1/8"

1/2"

V SPRING GUIDE

3/4"

9/16"

18"

VI GUIDE BAR

1"

9/16"

VI' GUIDE BAR

5 3/4"

1/2"

1/4"

9/16"

1 3/8"
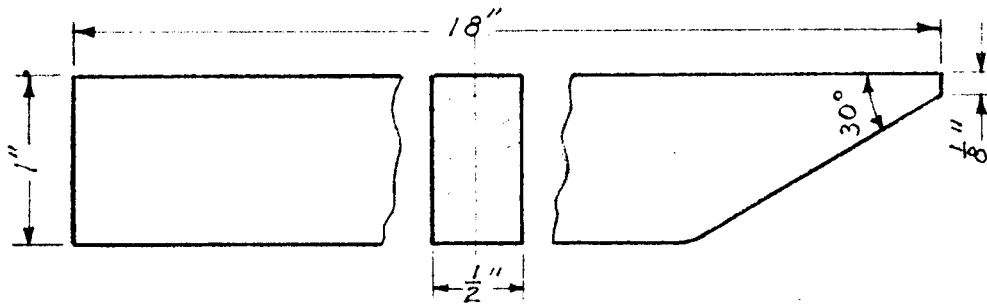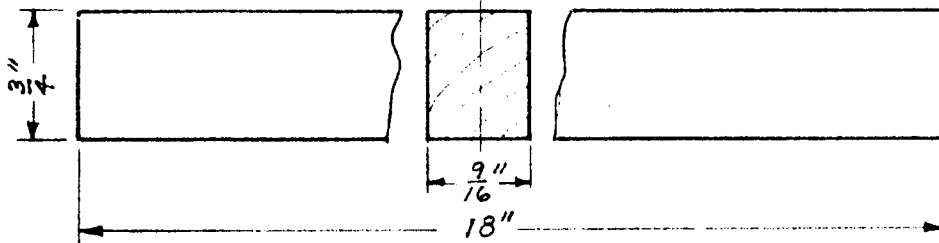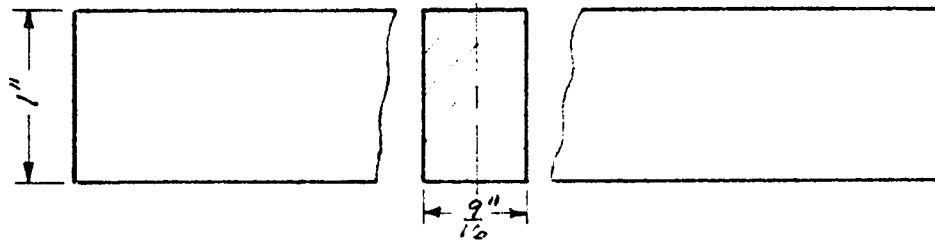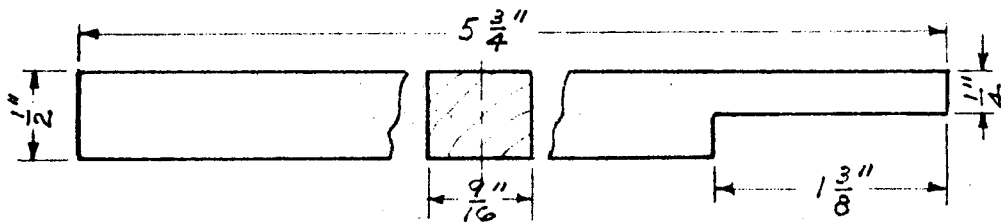
VII END BAR

Wood
One piece each
Paint flat black

Scale: 1"= 1"

Drill $1\frac{3}{8}"$Dia.

Cut back
$\frac{1}{8}"$ at bottom,
$\frac{3}{8}"$ at top.

3"

13"

$5\frac{3}{4}"$

$7\frac{1}{2}"$

$\frac{1}{4}"$
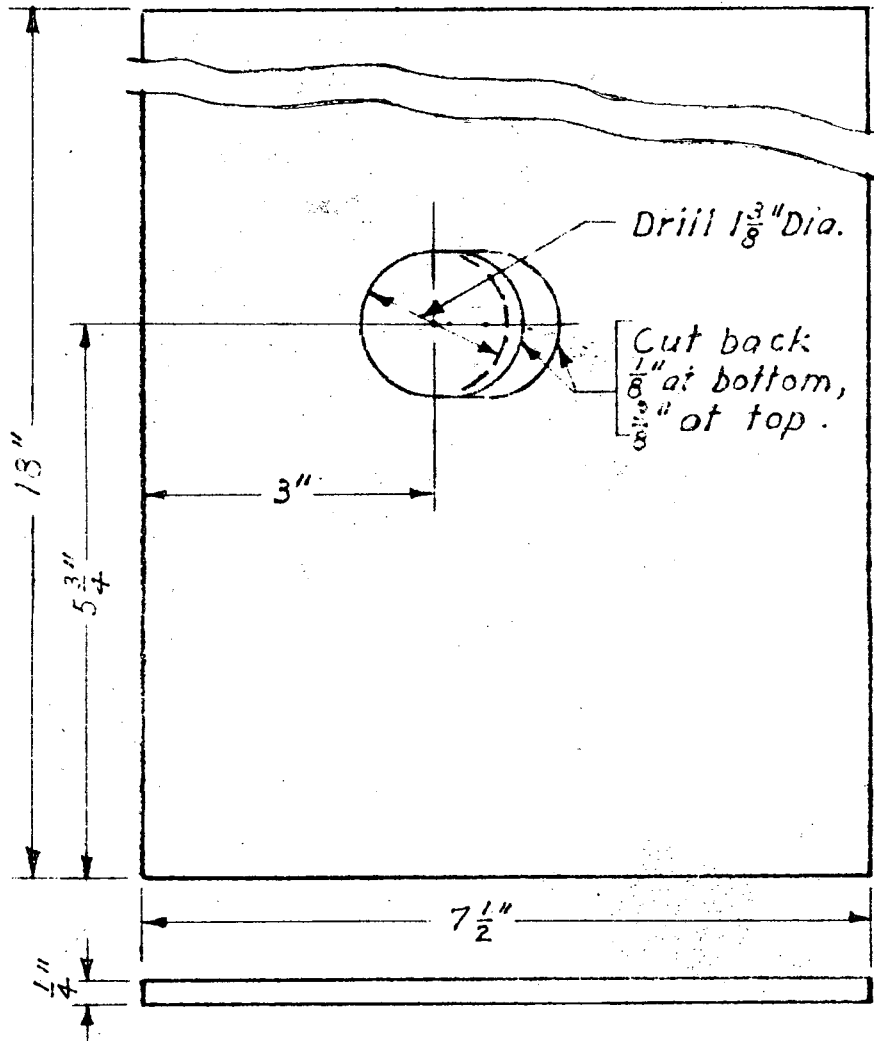
$\frac{1}{4}"$ Plywood, one piece.
Paint flat black.

VIII SLIDE COVER

Scale: $\frac{1}{2}" = 1"$

20

$\frac{1}{8}$" Bore

$\frac{3}{8}$"

$1\frac{3}{8}$"

$\frac{1}{4}$"

$\frac{1}{2}$"
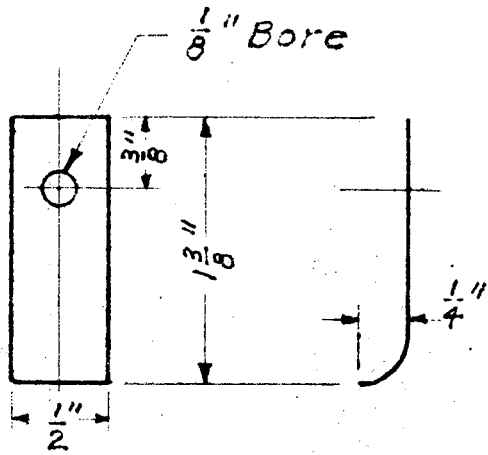
0.030" Brass - one piece.

IX CLIP

$\frac{1}{8}$" Bore

$3\frac{1}{2}$"

$\frac{7}{16}$"

$\frac{1}{2}$"
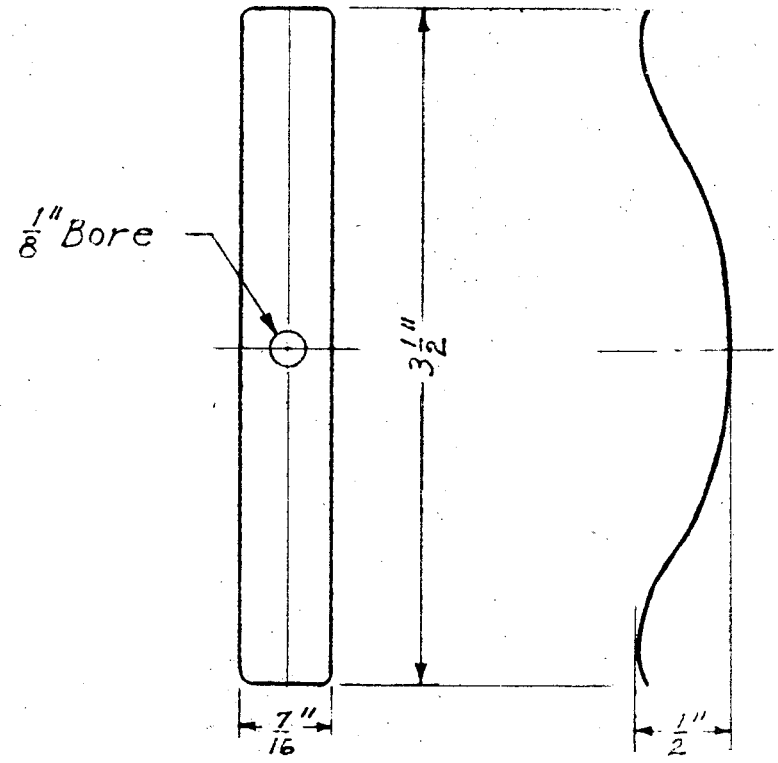
0.050 Bronze or spring steel - one piece.

X SPRING

Scale: 1"=1"

8 #6 FH Wood
screws (1")

Holes for 4 #8 RH
wood screws (21/2")
to attach Center
Block (1)

Holes for 9 #6
RH wood screws
(1¼") to attach
Slide Cover.

(VII)

(VI)

(VI')

(V)

(X)

(IX)

5½"

7½"

XI   BASE   Scale: ½"=1"

22
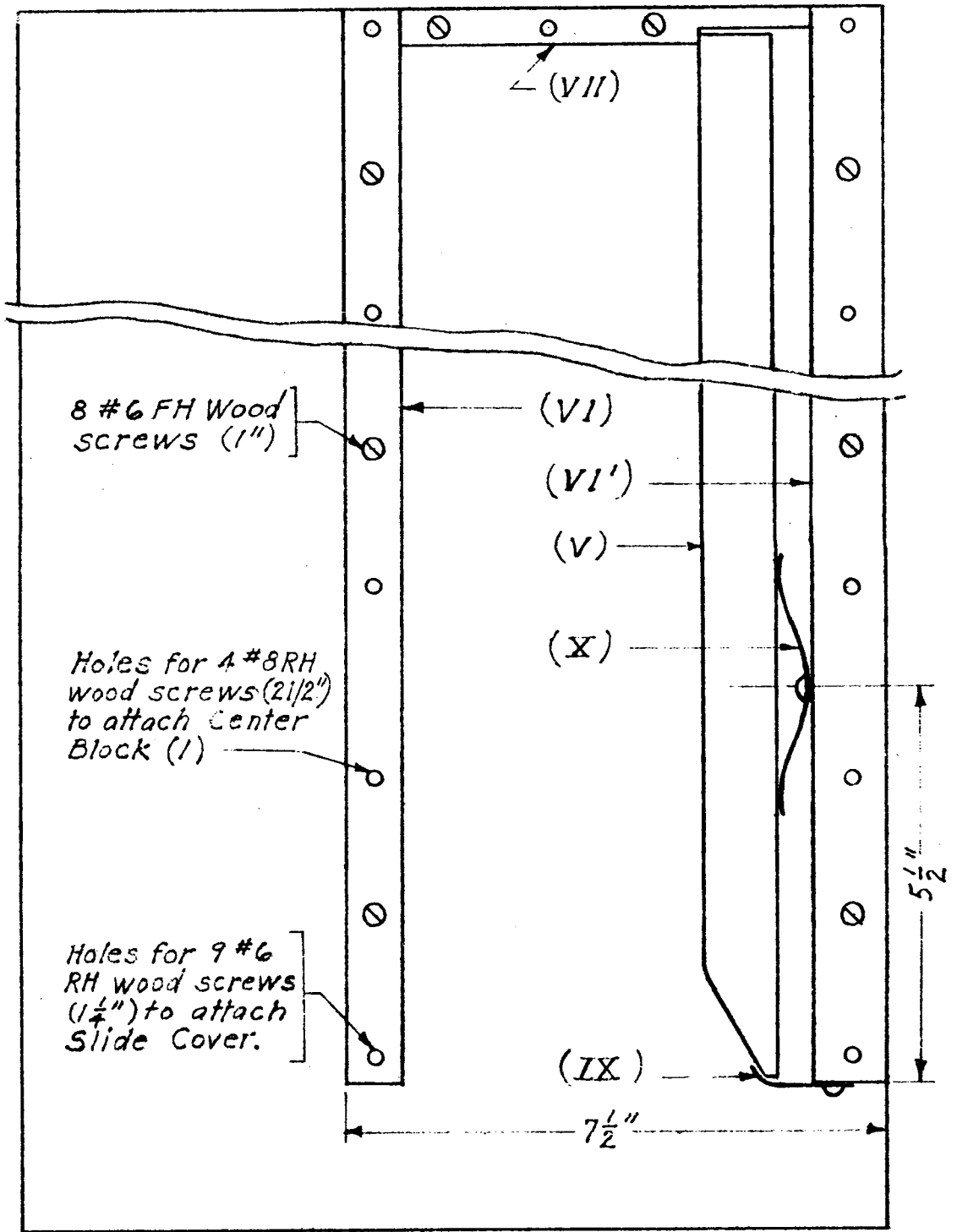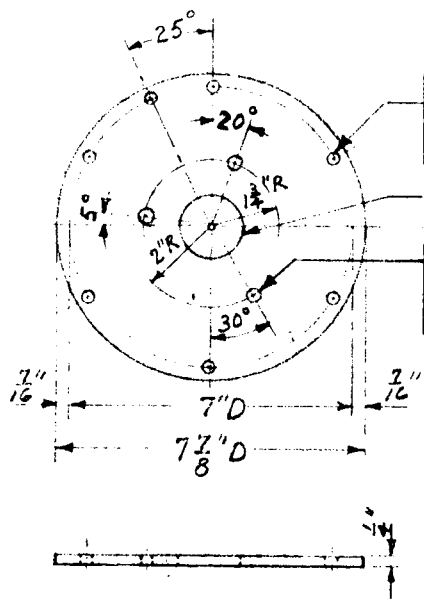
XII - TRANSITE BASE PLATE

25°
→ 20°
5°
2"R
1½"R
30°

7 Holes $\frac{3}{16}$" Dia for 8/32 × 1" RH Mach. screws.

1½" Dia hole

3 Holes $\frac{3}{16}$" Dia. for #10 × 1" FH. Wood screws.
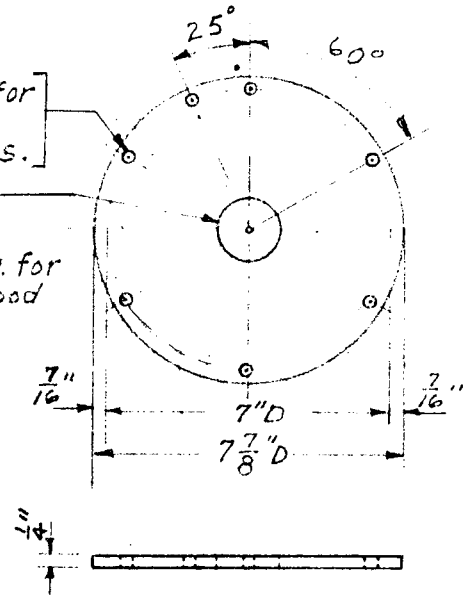
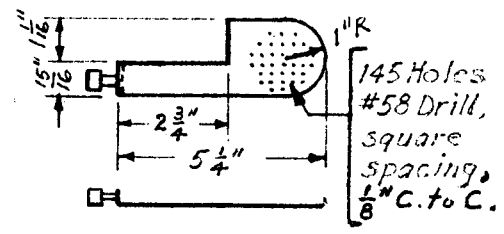$\frac{7}{16}$"   7"D $\frac{7}{16}$"

7$\frac{7}{8}$"D

$\frac{1}{4}$"

XII' - TRANSITE SPACER

25°   60°

$\frac{7}{16}$"   7"D $\frac{7}{16}$"

7$\frac{7}{8}$"D

$\frac{1}{4}$"

XIII - SHUTTER PLATE

25°
60°
30°
1"R
7$\frac{7}{8}$"D
$\frac{7}{16}$"

2$\frac{3}{4}$"
1"R
$\frac{15}{16}$"
5$\frac{1}{4}$"

Small drawer pull

$\frac{1}{16}$" Brass

XIII' - SCREEN PLATE

30°
1"R
7$\frac{7}{8}$"D
$\frac{7}{16}$"

$\frac{15}{16}$"
$\frac{1}{16}$"
2$\frac{3}{4}$"
5$\frac{1}{4}$"
1"R

145 Holes #58 Drill, square spacing, $\frac{1}{8}$" C. to C.

Scale: $\frac{1}{4}$" = 1"

23
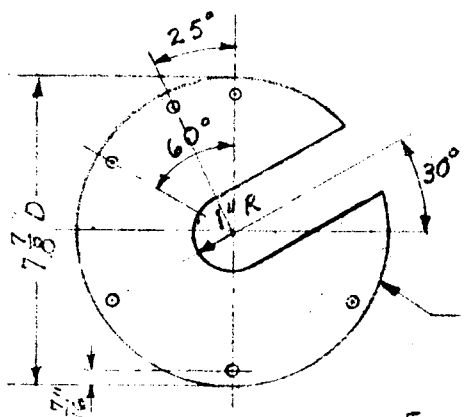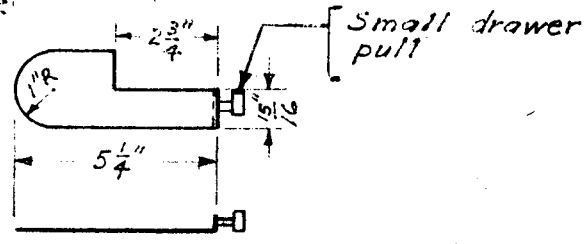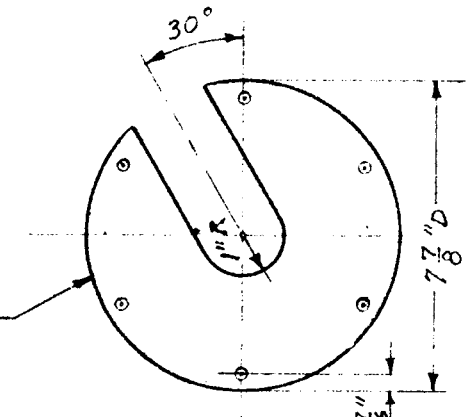
3 - 6/32" x ½" RH
Mach. screws

See Fig XII for
spacing of holes

35°

5½" D

35°

7" D

7 ⅞" D

¼"
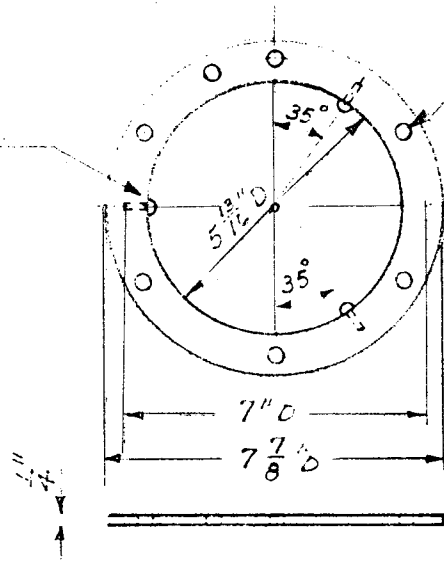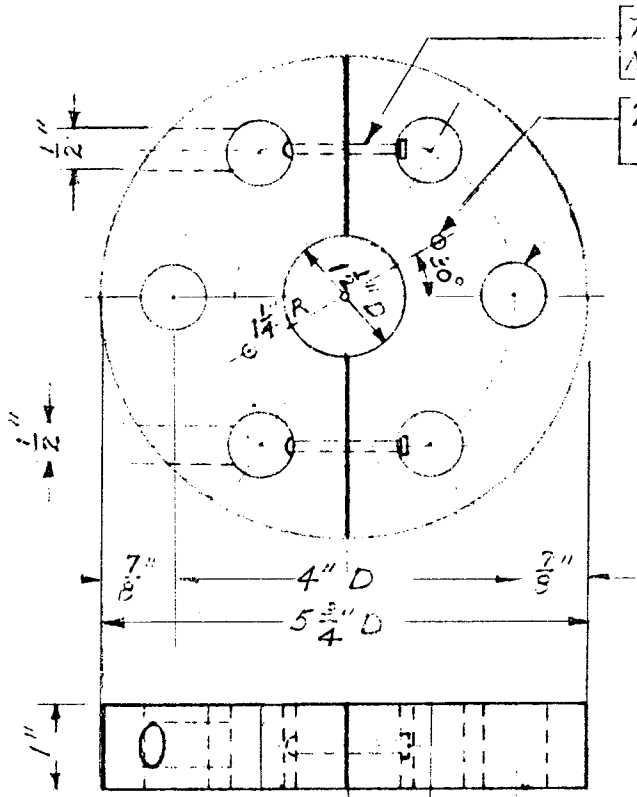
XIV - BRASS COLLAR

Scale ¼" = 1"

Two, ¼ - 20 x 1½" R.H.
Mach. screws.

2 Holes, threaded, for
10/24 x ½" RH Mach. screws.

6 - ¾" Holes equally spaced.

½"
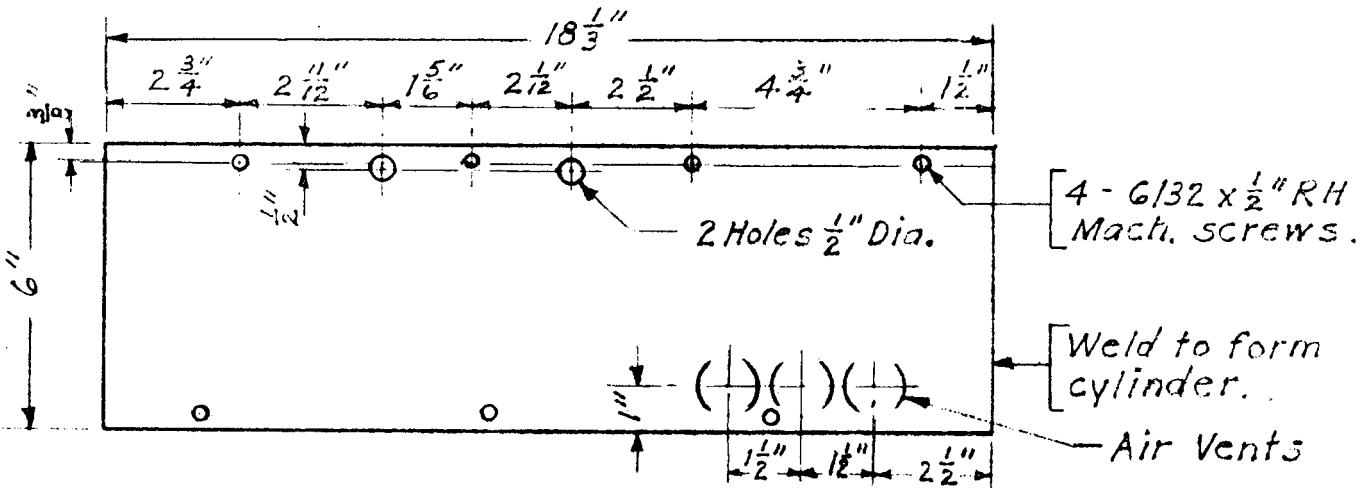
60°

R 1¼"

D

6 1¼"

½"

7/8"

4" D

7/8"

5 ¾" D

1"

Scale: ½" = 1"

XV - TRANSITE SOCKET SUPPORT

24

2 - 10/24 x $\frac{1}{2}$" RH
Mach. screws.

$\frac{7}{16}$" Dia. hole
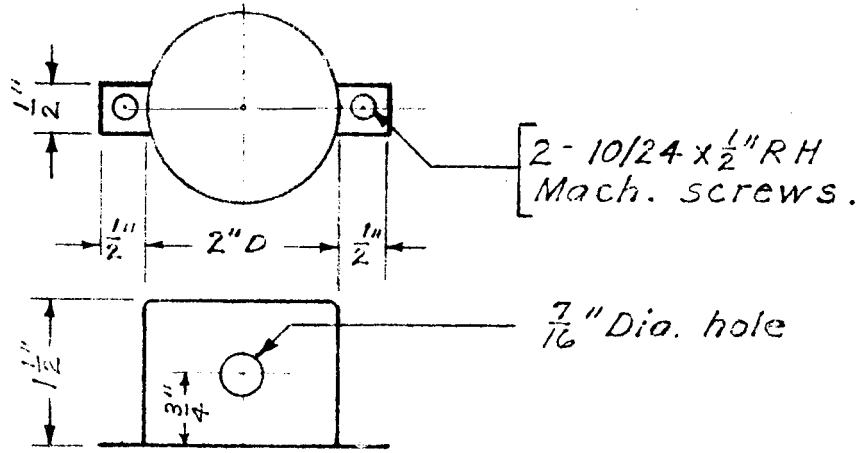
18 Guage Steel Plate

XVI - SOCKET CAP
Scale: $\frac{1}{2}$" = 1"

4 - 6/32 x $\frac{1}{2}$" RH
Mach. screws.

Weld to form cylinder.

Air Vents

2 Holes $\frac{1}{2}$" Dia.

18 Guage Steel Plate

XVII - LAMP SHIELD
Scale: $\frac{1}{4}$" = 1"

scale: $\frac{1}{2}'' = 1''$
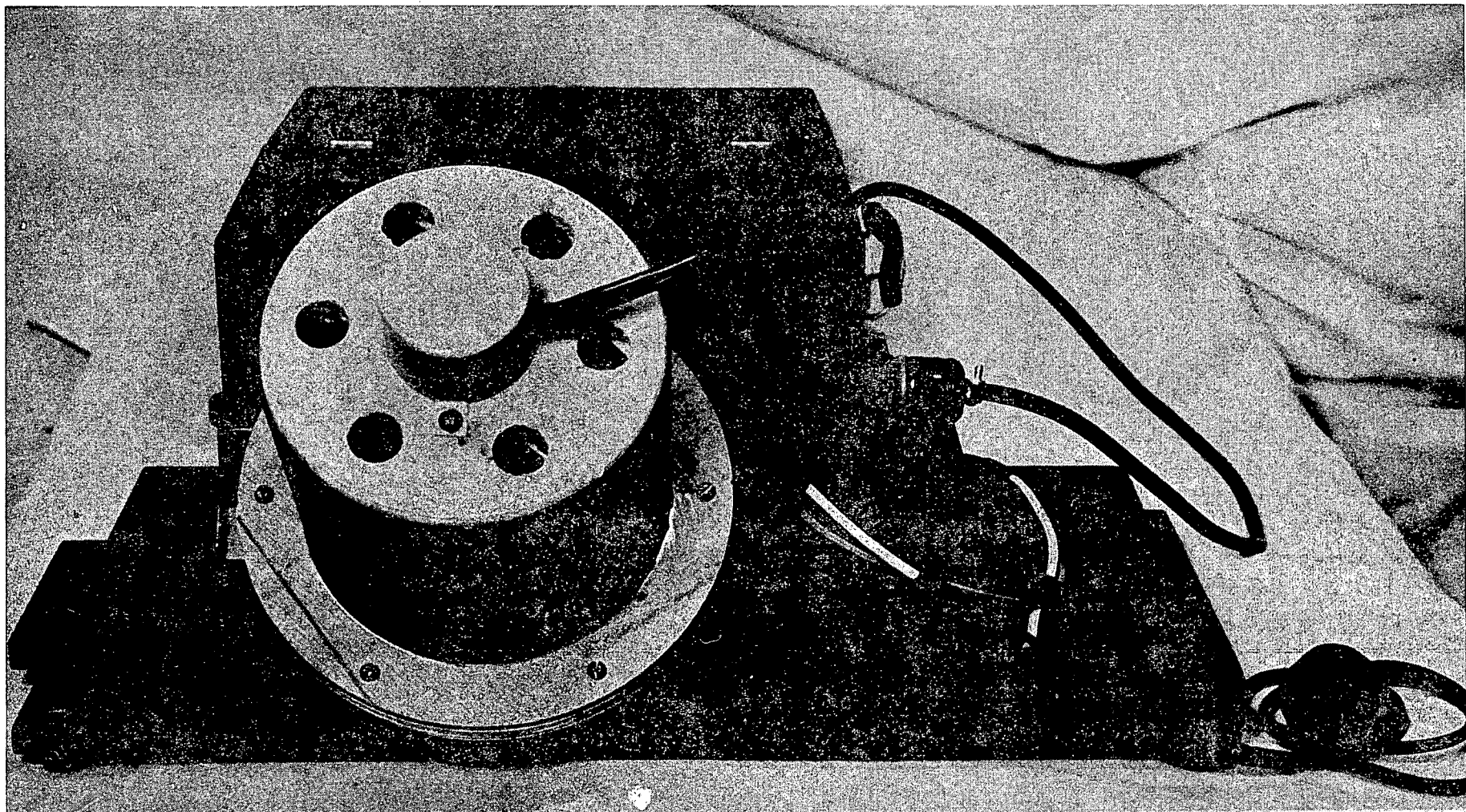
26

XV
XVI

XVIII

XIV

XIII'

XII'

XIII

XII
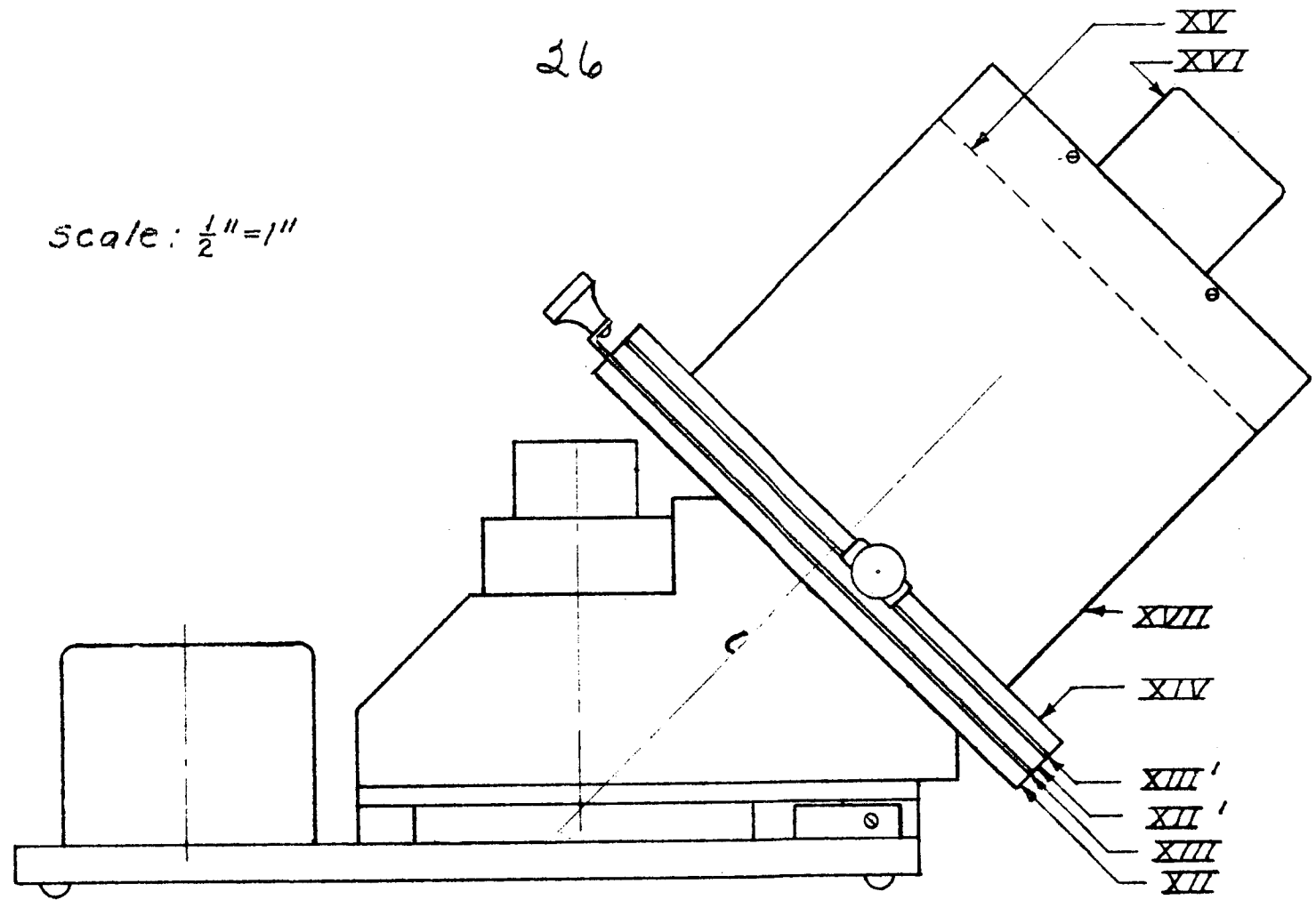
FLUORIMETER ASSEMBLED
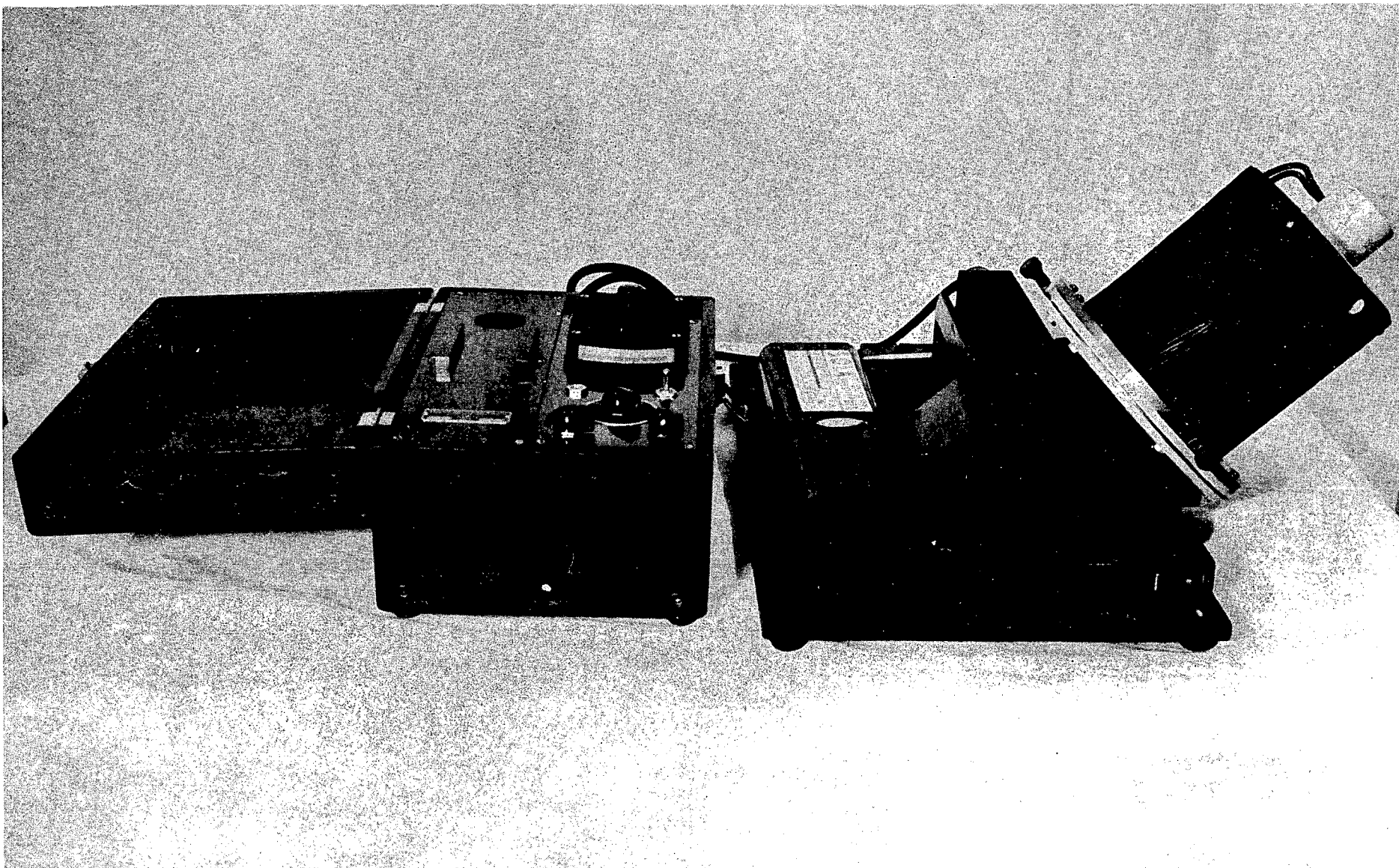
APPENDIX II

EQUIPMENT AND CHEMICALS REQUIRED

Equipment Needed

Pipettes. For each analyst the following pipettes are needed: one each, 5 ml., 2 ml., 1 ml., 1 ml. graduated, 0.2 ml. graduated, and one 0.050 ml. micropipette. For analyzing solutions containing 1 to 5 grams U_3O_8 per liter, micropipettes down to .1 microliter or less may be required. (Micro Chemicals Specialties Company, 1834 University Avenue, Berkeley, California, handles a large stock of micro equipment.)

Test Tubes. Forty-eight test tubes, 25 mm. x 100 mm. are needed for each analyst. It is convenient that they be numbered in sets of 24.

Gold dishes. Twenty-four gold dishes are needed for each analyst. The dimensions of the dishes, made of 99.99 per cent pure gold, used at this laboratory are shown in drawing XVIII. This dish will produce a flux disc that will fit the slide shown in the fluorimeter drawings. Western Gold and Platinum Company, 589 Bryant Street, San Francisco, California, have supplied the dishes used at Dow.

After each use, the gold dishes are heated in 1:4 HNO_3. Occasionally they must be remolded - a task easily accomplished by the analyst. After remolding the dishes are boiled in 1:1 HNO_3 for a few minutes to remove traces of Fe picked up from the mold.

Test Tube Racks. Racks for the 48 test tubes have been found convenient during pipetting, etc. They were constructed of sheet metal as shown in Drawing XIX and painted with acid-resistant paint.

Aluminum Nitrate Dispenser. This dispenser has been constructed at this laboratory according to Drawing XX. It has been found convenient although not essential. A simple apparatus for this purpose may be made from a two-neck round-bottom flask. A condenser should be fitted into one of the necks, the other neck being used for pipetting and aliquoting and closed off when not in use. A steam bath would keep this at the proper temperature.

Penta Ether Dispenser. A Machlette automatic pippette, 5 ml., has been used to deliver penta ether.

Stirring Assembly. A stirring unit capable of handling four samples simultaneously was designed at this laboratory and is shown in Drawing XXI. This unit is equipped with four variable speed stirrers (Eastern Industries, Model 1, available from many supply houses). Glass rod was used to make the screw-type stirrers. The test tubes are lifted to stirring position in racks similar to the larger ones mentioned above. Six of these racks are needed for each analyst.

Centrifuge. The centrifuge used at Dow is a Model CL clinical centrifuge, treated with acid resistant paint.

Separation Apparatus. Two suction flasks, connected in series as traps with suction provided by an aspirator are used with suction tubing and a pointed glass tube as a pipette to separate the aqueous $(Al(NO_3)_3)$ layer from the penta ether.

Hot Plates. Hot plates must be available. The electric ones used at Dow are multiple units, type 32, made by Heavy Duty Electric Company, Milwaukee, Wisconsin.

Flux Dispenser. A flux dispenser made of glass tubing with a solid glass plunger and calibrated to deliver 2.5 grams of flux has been found convenient. See Drawing XXII. A pan balance to weigh the flux or a spoon-type dispenser would also be satisfactory.

Dish Tongs. Tongs to hold the gold dishes while swirling were made by silver soldering nichrome wire to the tips of beaker tongs. The wire was shaped to fit the groove at the bottom of the dish. See Drawing XXII.

Muffle Furnace. A furnace capable of maintaining a temperature of 800° to 825° C. is required. One analyst can conveniently use 2 furnaces when fusing, but 4 analysts probably would require no more than 2, Furnace Type 11L, made by Western Gold and Platinum Company has been found to be particularly suited for this work. It is provided with a sliding tray that holds six gold dishes at a time. Spare elements and trays should be considered.

Fluorimeter. One fluorimeter (described in Appendix I) will serve for up to 5 analysts. Replacement parts needed are B batteries (Burgess M30) and 6-volt batteries (4F2H).

Chemicals Needed for 1000 Determinations.

$Al(NO_3)_3 \cdot 9H_2O$, C.P. granular	18	Kg.
Penta ether	5	l.
NH_4NO_3, C.P. granular	3.3	Kg.

Na$_2$CO$_3$, C.P. powder	1	Kg.
K$_2$CO$_3$, C.P. powder (Merck)	1.3	Kg.
NaF, C.P. powder	.275	Kg.
HNO$_3$, C.P. reagent	20	l.

The aluminum nitrate is dissolved in a weight ratio of Al(NO$_3$)$_3$·9H$_2$O:H$_2$O:concentrated HNO$_3$ = 18:3:2, and kept at an elevated temperature, about 100° C. The ammonium nitrate solution is made to contain 660 grams NH$_4$NO$_3$ and 66 ml. concentrated HNO$_3$ per liter of solution.

The flux is made to contain 9 per cent NaF, 39.5 per cent Na$_2$CO$_3$ and 51.5 per cent K$_2$CO$_3$ by weight. These powders are mixed by rolling in a glass carboy for about 24 hours.

Ninety per cent of the nitric acid reported above is used in cleaning the gold dishes.

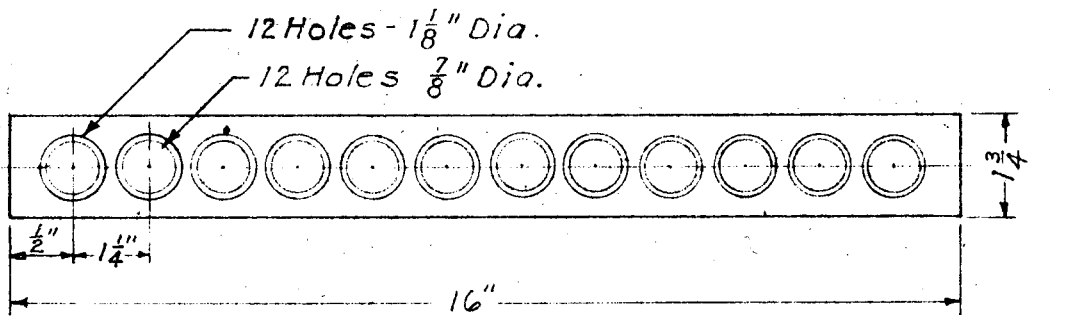The above chemicals do not include those needed to dissolve solid samples.
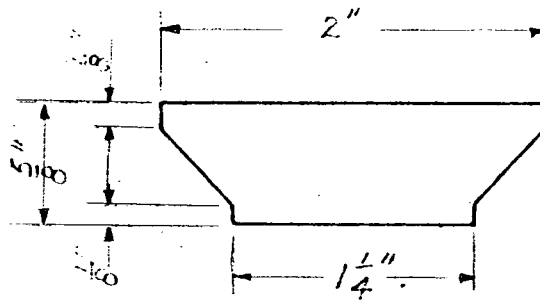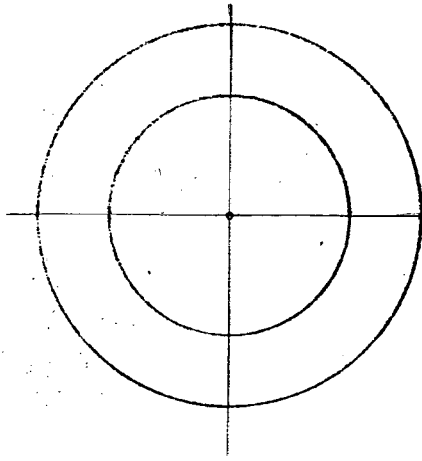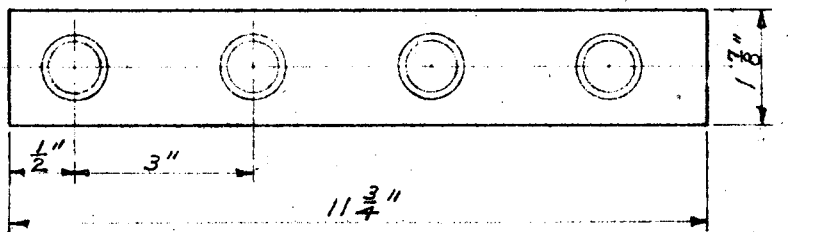
.025" Thick

GOLD DISH

Scale: Actual Size

XVIII

12 Holes - $1\frac{1}{8}$" Dia.

12 Holes $\frac{7}{8}$" Dia.

$1\frac{3}{4}$"

$\frac{1}{2}$" $1\frac{1}{4}$"

16"

$3\frac{5}{8}$"

$\frac{3}{4}$"

$1\frac{3}{8}$"

$\frac{1}{16}$" Thk. Steel

LARGE TEST TUBE RACK
Scale: $\frac{3}{8}$" = 1"

$1\frac{7}{8}$"

$\frac{1}{2}$" 3"

$11\frac{3}{4}$"

$3\frac{7}{8}$"

$\frac{3}{4}$"

$\frac{1}{16}$" Thk. Steel

SMALL TEST TUBE RACK
Scale: $\frac{3}{8}$" = 1"

XIX

33

$\mathbf{F}\ \dfrac{55}{50}$

Steam

51 mm. Glass Tubing

60 mm. Glass Tubing

12 ℓ. Flask

5 ℓ. Flask

Asbestos Lined Iron Collar For Support

70 mm. Pyrex Tube

20 mm Glass Tubing.

50 ml Burette

3 mm., 3 Way Stop Cock

Steam
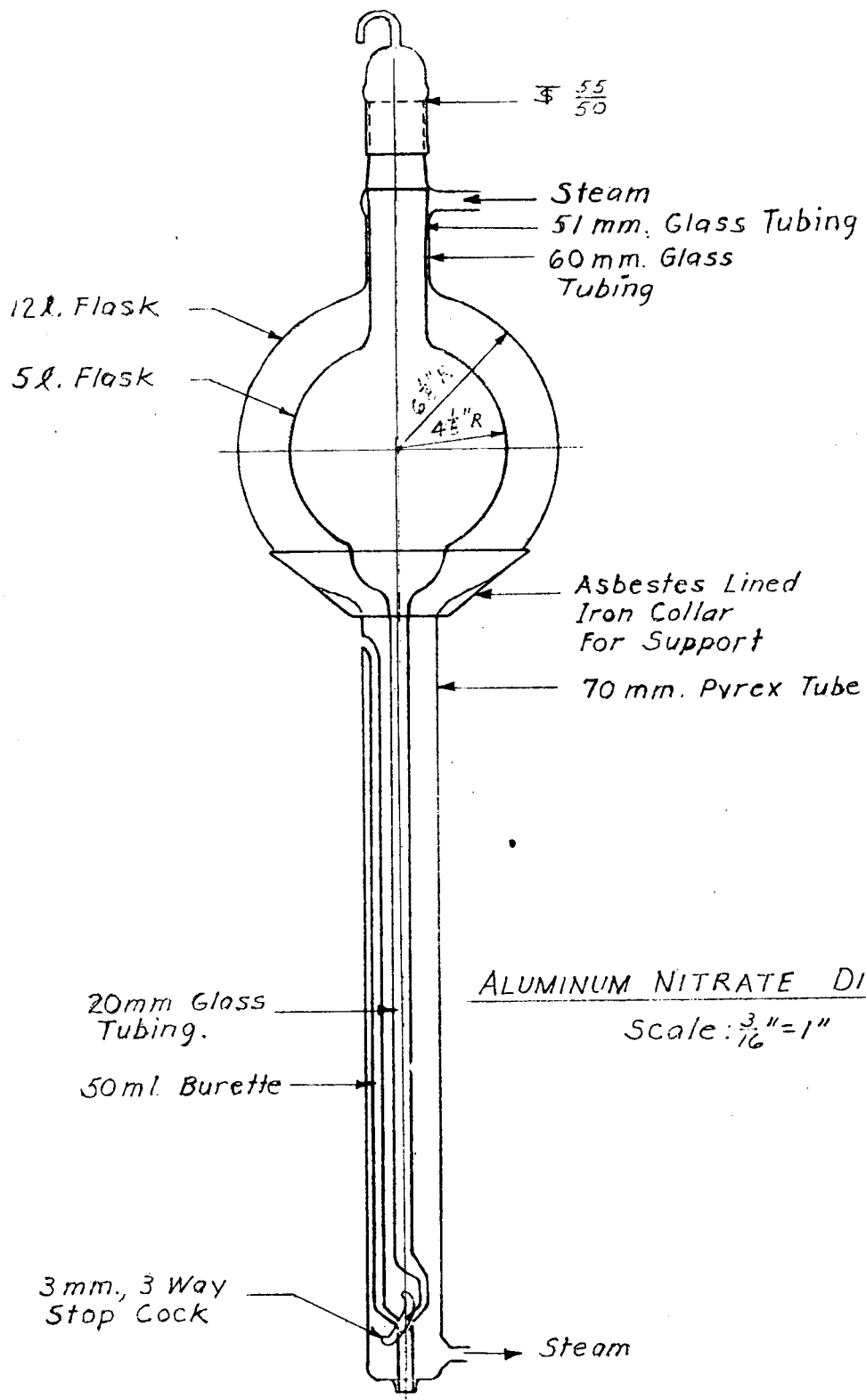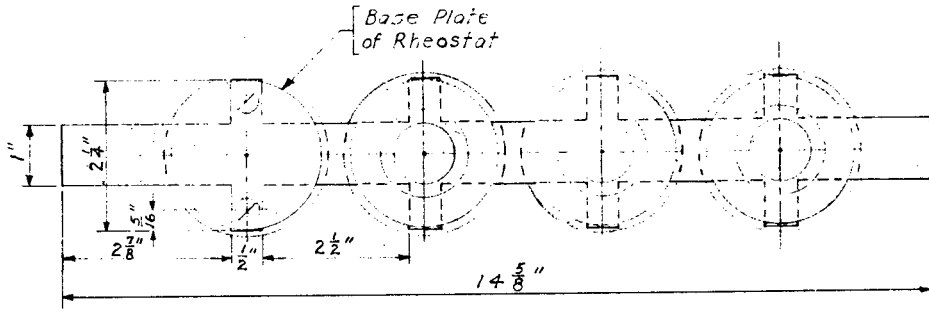
ALUMINUM NITRATE DISPENSER

Scale: $\frac{3}{16}$" = 1"

34

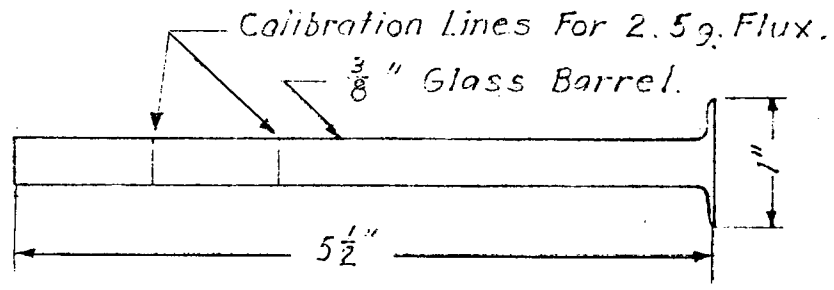Base Plate
of Rheostat

$1''$

$2\frac{1}{4}''$

$\frac{5}{16}''$

$2\frac{7}{8}''$

$\frac{1}{2}''$

$2\frac{1}{2}''$

$14\frac{5}{8}''$

TOP VIEW

$\frac{5}{8}''$ $2\frac{1}{2}''$ $3''$ $3''$ $3''$ $2''$ $\frac{1}{2}''$

— St. Stl.

$\frac{3}{8}''$

$5\frac{1}{2}''$

$12\frac{1}{8}''$

$14\frac{7}{8}''$

Glass Rod

$\frac{3}{8}''$Dia. Stainless Steel

St. Stl. $\frac{3}{4}''$ Dia.

Stainless Steel $\frac{1}{16}''$ thk.

$2\frac{5}{8}''$

$2\frac{1}{2}''$

$\frac{1}{4}''$

$\frac{1}{2}''$

$8'' \times 16\frac{1}{2}'' \times \frac{5}{8}''$ Wood Base

FRONT VIEW
Scale: $\frac{1}{2}''=1''$

XXI

Calibration Lines For 2.5g. Flux.

$\frac{3}{8}$" Glass Barrel.

1"

5$\frac{1}{2}$"

$\frac{11}{32}$" Glass Plunger

$\frac{3}{4}$"

6$\frac{5}{8}$"
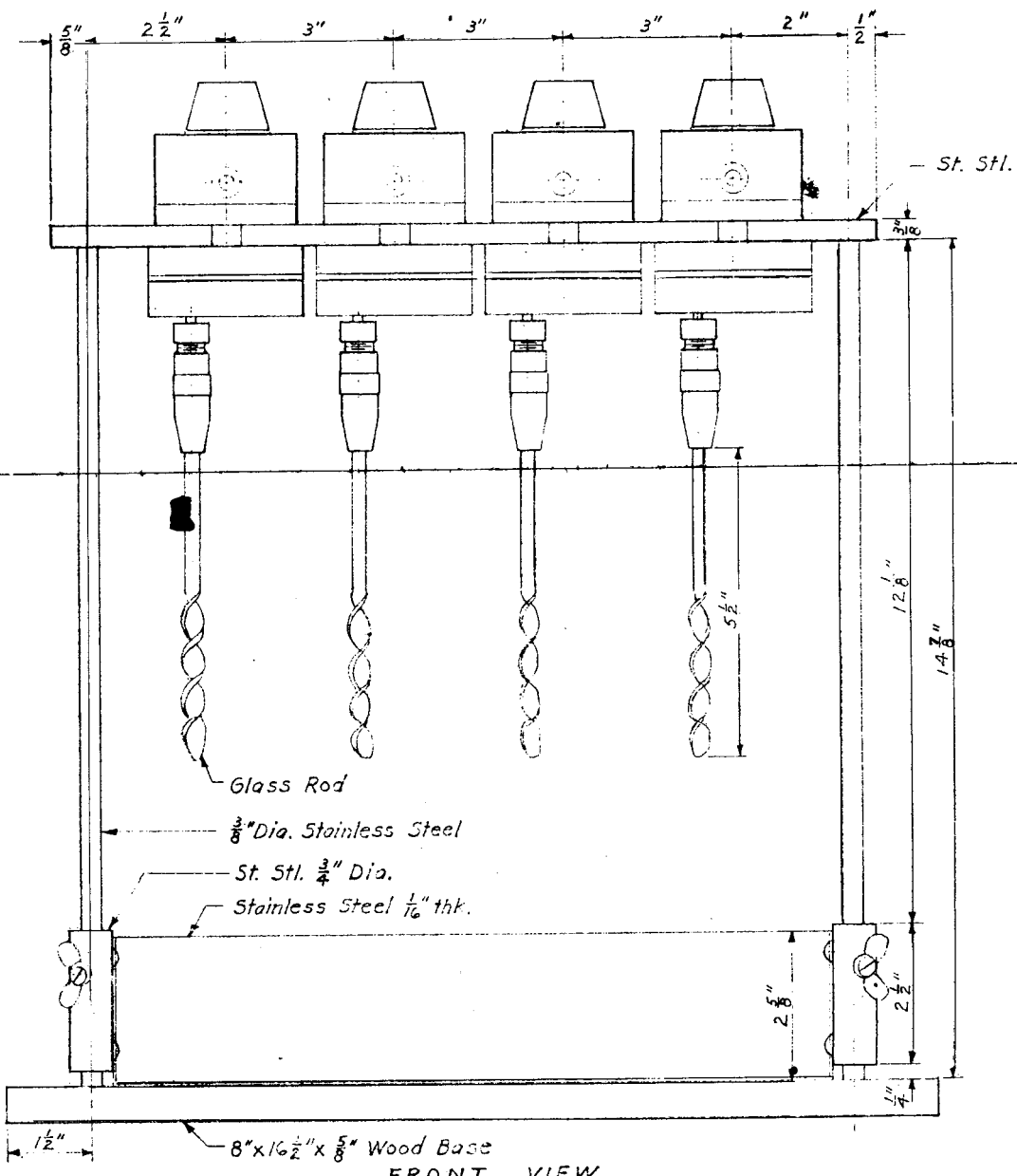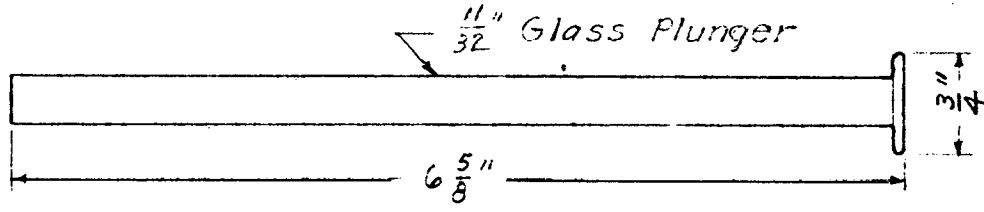
FLUX DISPENSER
Scale. $\frac{3}{4}$"=1"

Silver Soldered.

B.&S. No. 12 Nichrome Wire.

Standard Beaker Tongs

1$\frac{1}{2}$" $\frac{1}{2}$"   5"   2$\frac{3}{4}$"   2"

11$\frac{3}{4}$"
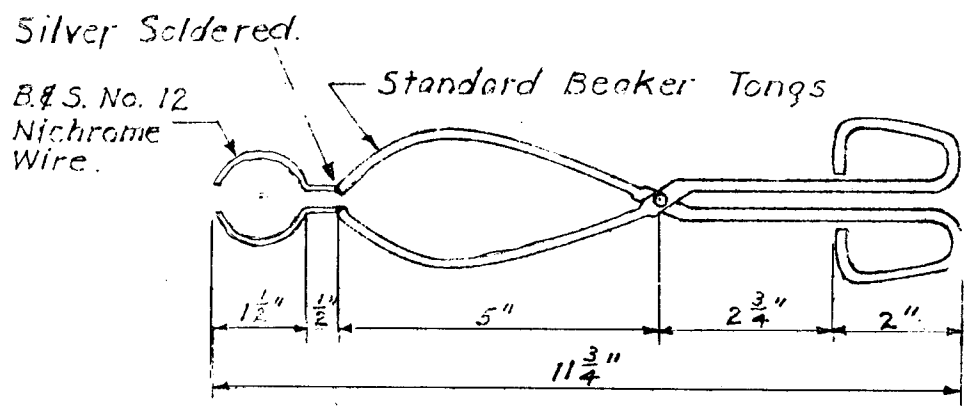
TONGS
Scale $\frac{3}{8}$"=1"

XXII

END OF DOCUMENT