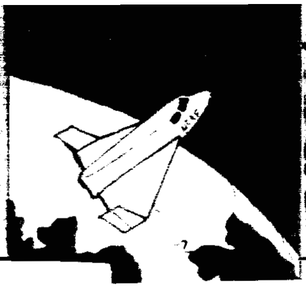

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(THRU)

1
(CODE)

11
(CATEGORY)

DM 64-411

BROMINE TRIFLUORIDE METHOD FOR OXYGEN IN LIQUID ALKALI METALS

CONTRACT NO.. NASw-882 & CONTROL NO. 10-2379

PERIOD COVERED: (Third Quarter) - July 1, 1964 to September 30, 1964

AUTHORS: H Kirtchik/SL Culp

Materials Development Laboratory Operation

Advanced Engine Technology Department

GENERAL ELECTRIC

CINCINNATI 15, OHIO

October 18, 1964

BROMINE TRIFLUORIDE METHOD FOR OXYGEN IN LIQUID ALKALI METALS

Third Quarterly Report
July 1, 1964 to September 30, 1964

H Kirtchik
SL Culp

Contract No. NASw-882
Control No. 10-2379

October 18, 1964

DM 64-411

Materials Development Laboratory Operation

SUBJECT: Third Quarterly Report
July 1, 1964 to September 30, 1964

CONTRACT NO.: NASw-882

CONTROL NO.: 10-2379

PREPARED FOR: Chief of Materials Research Program, Code RRM, Office of Advanced Research and Technology
NASA, Washington, D. C.

TITLE: BROMINE TRIFLUORIDE METHOD FOR OXYGEN IN LIQUID ALKALI METALS

AUTHORS: Hyman Kirtchik
Sigmond Culp

SUBMITTED BY: Materials Development Laboratory Operation
Advanced Engine & Technology Department
General Electric Company
Evendale, Ohio

SIGNATURES: H Kirtchik

Hyman Kirtchik, Manager
Analytical Chemistry Unit

WH Chang

W. H. Chang, Manager
Materials Applied Research

DATE: October 18, 1964

ABSTRACT

12418

This report describes the modified NASA extruder and other apparatus changes.

The exit double trap system was modified to a coil-type completely submersible in pentane slush. This allowed for better temperature control and resulted in acceptable blanks in the order of 5-20 micrograms of oxygen per hour with BrF_3 in the reaction cell.

Complete recoveries of $KBrO_3$ spikes were obtained only under certain specific conditions which apparently limited the solubility of oxygen in BrF_3.

I APPARATUS AND SYSTEM MODIFICATIONS

1. Modifications of the NASA extruder pertain to the cutter wire and waste boat vacuum manipulators, extruder rod feed-through, vacuum port and ionization gauge connections, and flange modifications to adapt the extruder to the two inch ball valve separating it from the reaction cell. The changes can be observed in Drawings 4012286-444 through -450.

Item 21 (Figure 5 in First Quarterly report) in these drawings is a modified Veeco #R505 bellows-sealed angle valve used to actuate the cutter wires or the waste boat without admitting air into the system. The actuating rods themselves are threaded to fit the screw holes formerly used to hold the valve seats in place. These seats are, of course, no longer required. The valve bodies have been bored out as shown in the drawings, and silver soldered to the end covers. The "O" ring is Viton elastomer in place of the normal rubber ring.

Item 31 is the vacuum feed-through for the extruder rod (Figure 6, First Quarterly report) and consists of two Consolidated Vacuum Corporation vacuum feed-throughs mounted end to end with a pump-out port between them. In order to utilize as much of the potassium sample as possible, a longer extruder rod was fabricated with two pin holes (see Part 33, Drawing #4012286-444). Thus, when rod actuator (#34) strikes the top of the vacuum feed-through, the first pin is removed, the actuator backed off, and the pin transferred to the second hold. In this manner, all but about 1/4 inch of potassium may be extruded.

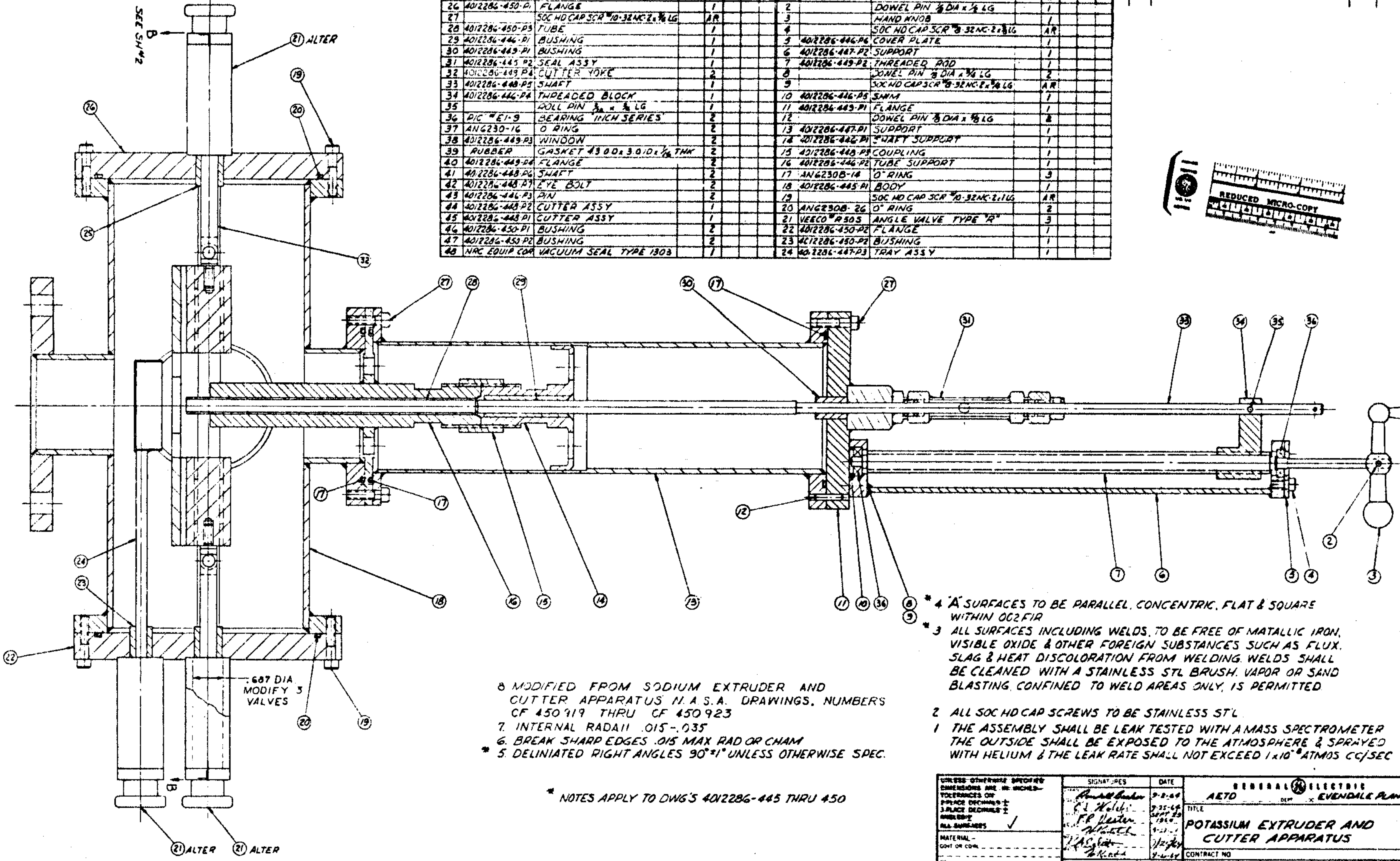
The remaining extruder modifications, such as the ionization gauge connector, flange connection to the ball valve, pump out port, etc., are self-evident from the drawings.

D 4012286-444

ITEM	IDENTIFICATION NO	DESCRIPTION OR NAME	ZONE	GROUP NO & QTY 1	2	3	4
25	4012286-450-P1	BUSHING		1			
26	4012286-450-P1	FLANGE		1			
27		SOC HD CAP SCR #10-32NC-2 x 5/8 LG		AR			
28	4012286-450-P3	TUBE		1			
29	4012286-446-P1	BUSHING		1			
30	4012286-449-P1	BUSHING		1			
31	4012286-445 P2	SEAL ASSY		1			
32	4012286-449 P4	CUTTER YOKE		2			
33	4012286-448-P5	SHAFT		1			
34	4012286-446-P4	THREADED BLOCK		1			
35		ROLL PIN 3/32 x 5/8 LG		1			
36	PIC #E1-9	BEARING INCH SERIES		2			
37	AN6230-16	O RING		2			
38	4012286-449-P3	WINDOW		2			
39	RUBBER	GASKET 4.3 O.D. x 3.0 I.D. x 1/16 THK		2			
40	4012286-449-P4	FLANGE		2			
41	4012286-448-P6	SHAFT		2			
42	4012286-448-P7	EYE BOLT		2			
43	4012286-446-P3	PIN		2			
44	4012286-448-P2	CUTTER ASSY		1			
45	4012286-448-P1	CUTTER ASSY		1			
46	4012286-450-P1	BUSHING		2			
47	4012286-450-P2	BUSHING		2			
48	NRC EQUIP COR	VACUUM SEAL TYPE 1303		1			

ITEM	IDENTIFICATION NO	DESCRIPTION OR NAME	ZONE	GROUP NO & QTY 1	2	3	4
1		ASSY		X			
2		DOWEL PIN 1/8 DIA x 1/2 LG		1			
3		HAND KNOB		1			
4		SOC HD CAP SCR #8-32NC-2 x 3/8 LG		AR			
5	4012286-446-P6	COVER PLATE		1			
6	4012286-447-P2	SUPPORT		1			
7	4012286-449-P2	THREADED ROD		1			
8		DOWEL PIN 1/8 DIA x 3/4 LG		2			
9		SOC HD CAP SCR #8-32NC-2 x 3/4 LG		AR			
10	4012286-446-P5	SHIM		1			
11	4012286-449-P1	FLANGE		1			
12		DOWEL PIN 1/8 DIA x 5/8 LG		2			
13	4012286-447-P1	SUPPORT		1			
14	4012286-446-P1	SHAFT SUPPORT		1			
15	4012286-448-P3	COUPLING		1			
16	4012286-446-P2	TUBE SUPPORT		1			
17	AN6230B-14	"O" RING		3			
18	4012286-445-P1	BODY		1			
19		SOC HD CAP SCR #10-32NC-2 x 1 LG		AR			
20	AN6230B-26	"O" RING		2			
21	VEECO #R505	ANGLE VALVE TYPE "R"		3			
22	4012286-450-P2	FLANGE		1			
23	4012286-450-P2	BUSHING		1			
24	4012286-447-P3	TRAY ASSY		1			

REVISIONS



*4 "A" SURFACES TO BE PARALLEL, CONCENTRIC, FLAT & SQUARE WITHIN .002 FIR

*3 ALL SURFACES INCLUDING WELDS, TO BE FREE OF METALLIC IRON, VISIBLE OXIDE & OTHER FOREIGN SUBSTANCES SUCH AS FLUX, SLAG & HEAT DISCOLORATION FROM WELDING. WELDS SHALL BE CLEANED WITH A STAINLESS STL BRUSH. VAPOR OR SAND BLASTING, CONFINED TO WELD AREAS ONLY, IS PERMITTED

2 ALL SOC HD CAP SCREWS TO BE STAINLESS STL

1 THE ASSEMBLY SHALL BE LEAK TESTED WITH A MASS SPECTROMETER THE OUTSIDE SHALL BE EXPOSED TO THE ATMOSPHERE & SPRAYED WITH HELIUM & THE LEAK RATE SHALL NOT EXCEED 1×10^{-8} ATMOS CC/SEC

8 MODIFIED FROM SODIUM EXTRUDER AND CUTTER APPARATUS N.A.S.A. DRAWINGS, NUMBERS CF 450919 THRU CF 450923

7 INTERNAL RADII .015-.035

6 BREAK SHARP EDGES .015 MAX RAD OR CHAM

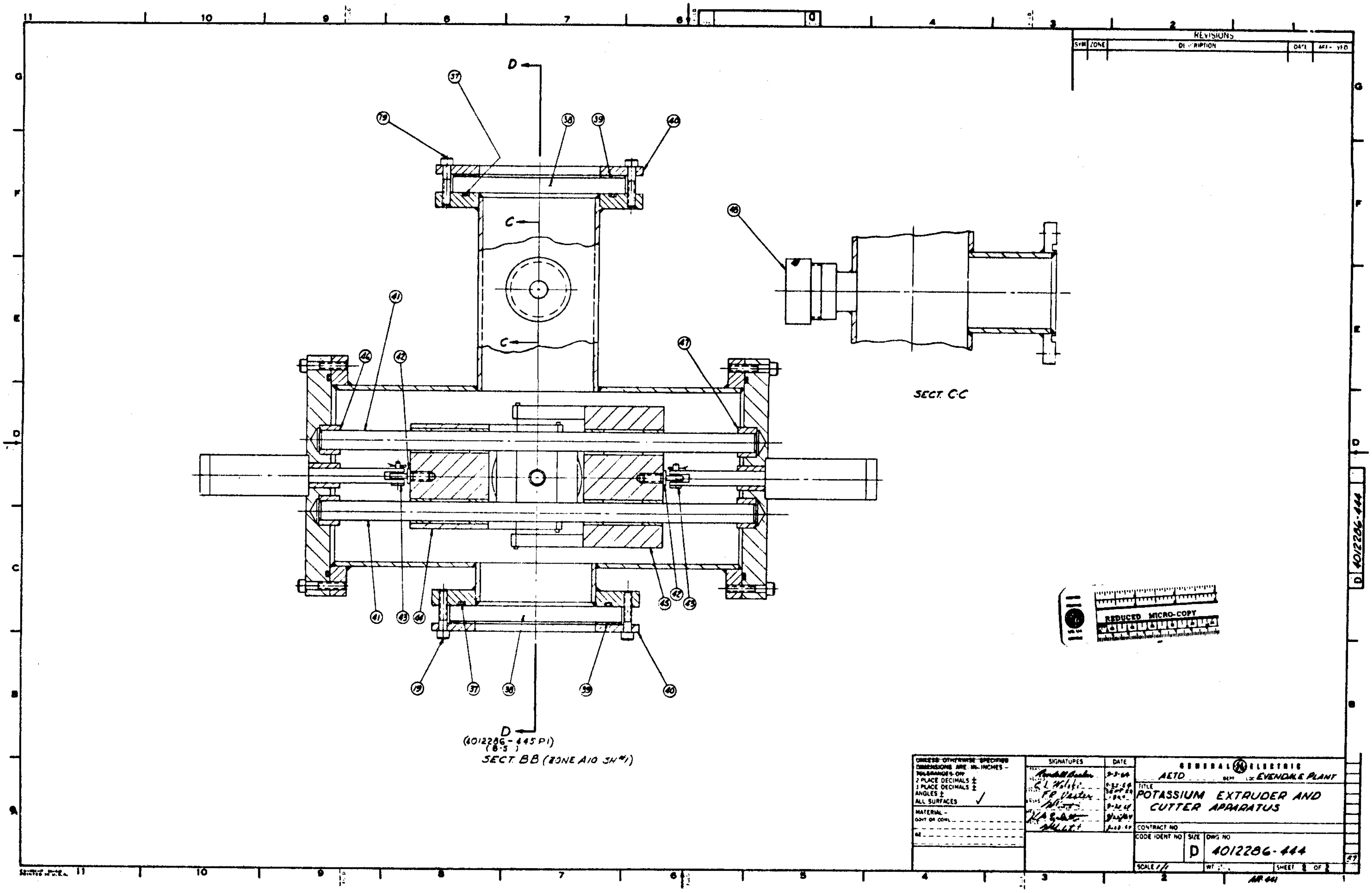
*5 DELINIATED RIGHT ANGLES 90° ± 1° UNLESS OTHERWISE SPEC.

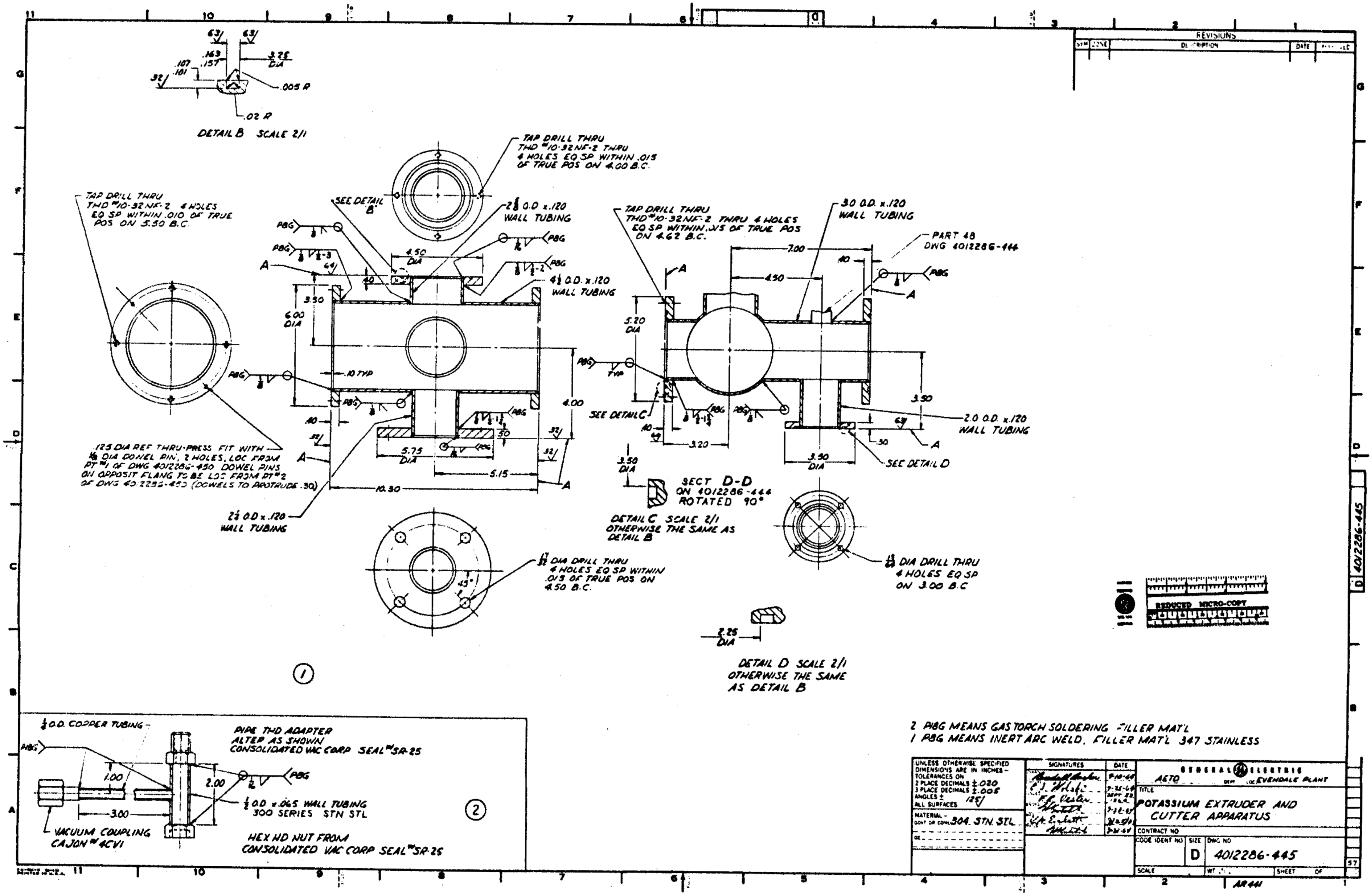
* NOTES APPLY TO DWG'S 4012286-445 THRU 450

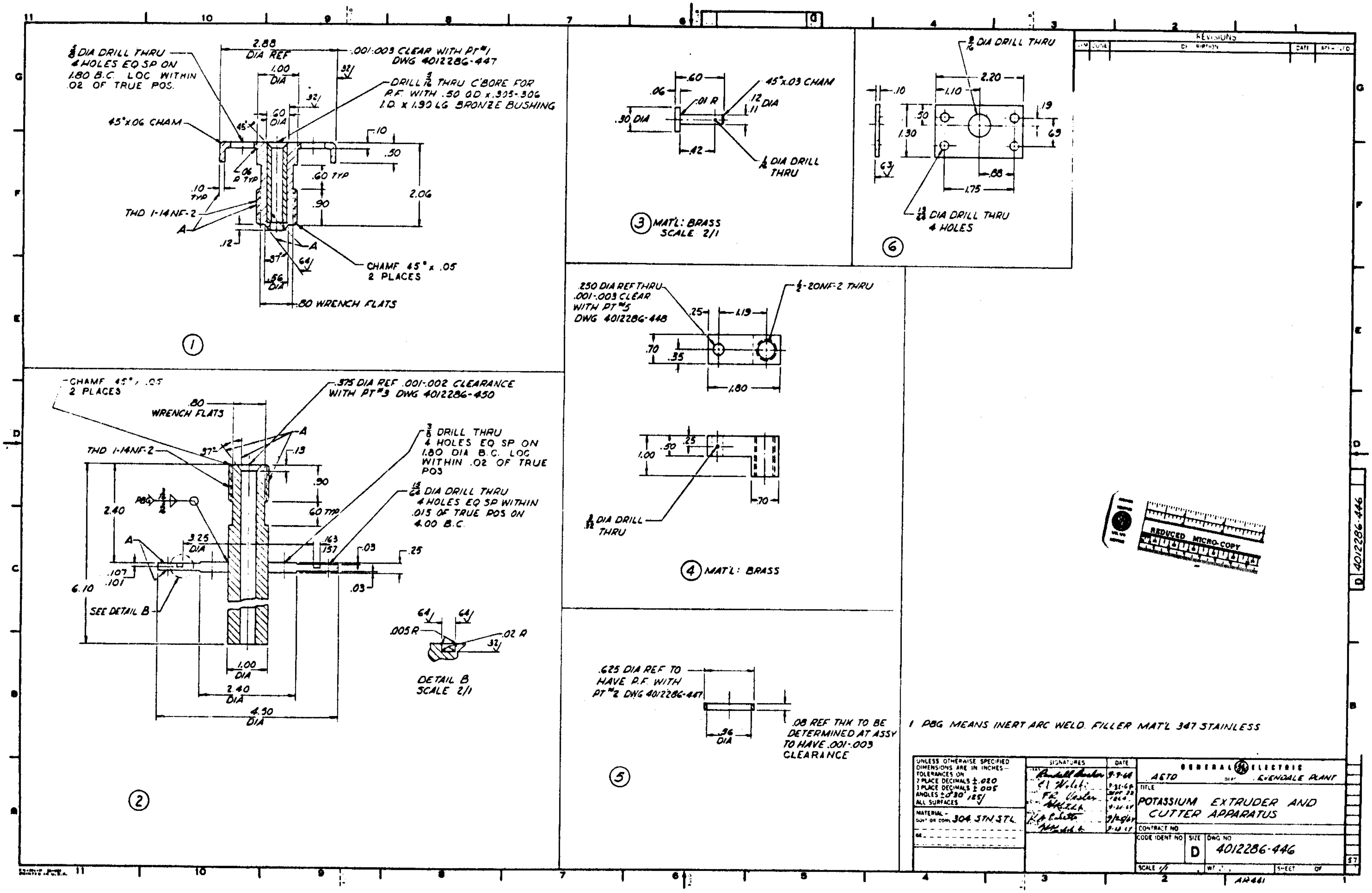
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES ON
2 PLACE DECIMALS ±
3 PLACE DECIMALS ±
ANGLES ±
ALL SURFACES ✓
MATERIAL -
CONT OR CONN
GI

SIGNATURES	DATE
Randall Becker	9-2-64
C. J. Walsh	9-25-64
F. R. Vester	SEPT 29 1964
	9-27-64
	9/29/64
	9-4-64

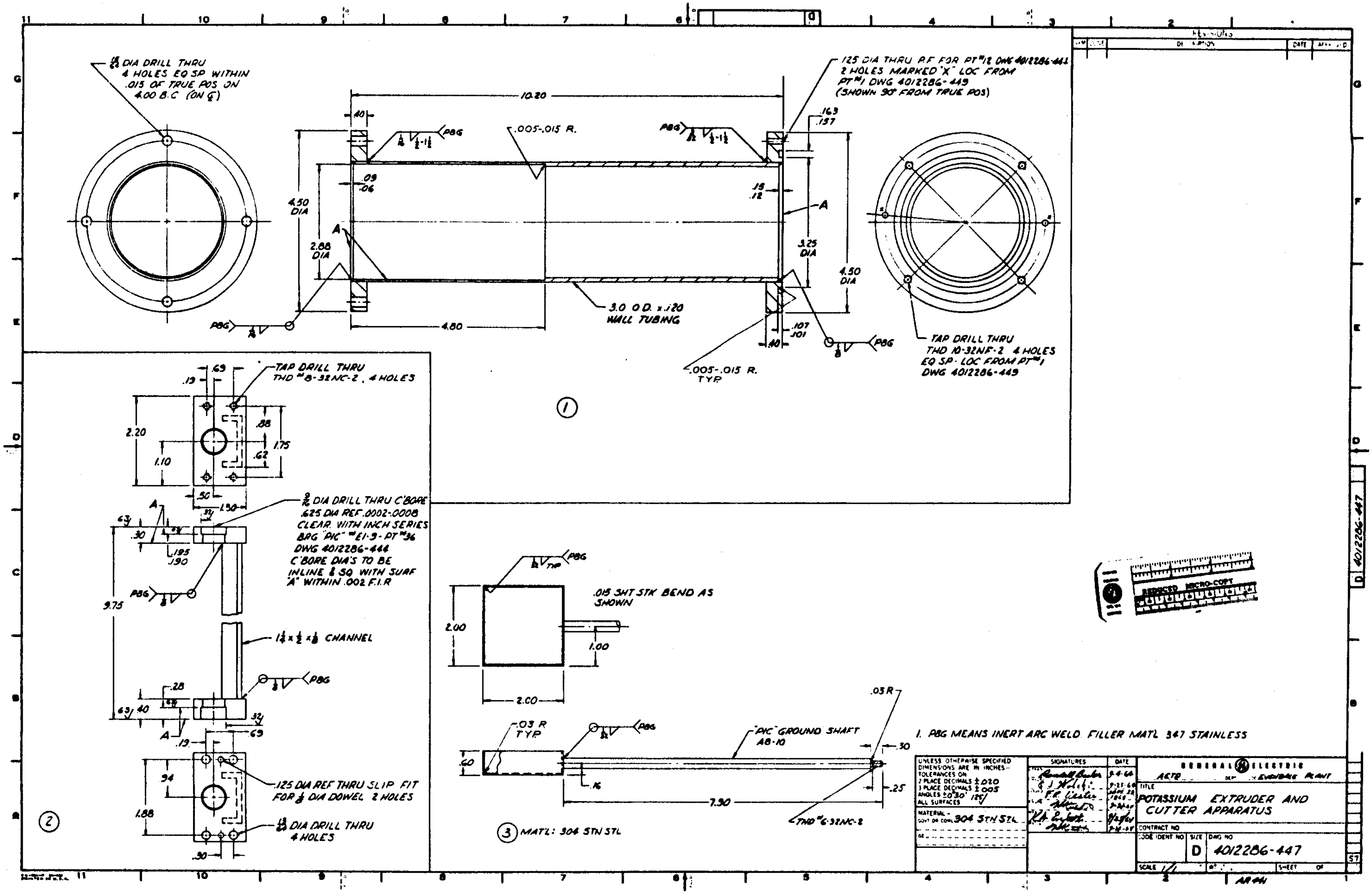
GENERAL ELECTRIC
AETD DEPT EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE D
DWG NO 4012286-444
SCALE 1/1
WT
SHEET 1 OF 2
57
AR441


D
37
38
39
40
79
C
C
41
42
43
44
45
47
48
19
SECT. C-C
D
(4012286-445 P1)
(B-5)
SECT. BB (ZONE A10 SH #1)
REVISIONS
SYM
ZONE
DESCRIPTION
DATE
APP-VED
4012286-444
REDUCED MICRO-COPY
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES –
TOLERANCES ON
2 PLACE DECIMALS ±
3 PLACE DECIMALS ±
ANGLES ±
ALL SURFACES ✓
MATERIAL –
GOVT OR COML
SIGNATURES
DATE
Randall Becker
C L Walsh
F R Vester
K A G
9-3-64
9-23-64
Sept 64
9-24-64
GENERAL ELECTRIC
AETD
DEPT
LOC EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND
CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE
D
DWG NO
4012286-444
SCALE 1/1
WT
SHEET 2 OF 2
AR 441

63/
63/
.163
.157
3.25 DIA
.107
.101
32/
.005 R
.02 R
DETAIL B SCALE 2/1
TAP DRILL THRU
THD #10-32NF-2 4 HOLES
EQ SP WITHIN .010 OF TRUE
POS ON 5.50 B.C.
TAP DRILL THRU
THD #10-32NF-2 THRU
4 HOLES EQ SP WITHIN .015
OF TRUE POS ON 4.00 B.C.
SEE DETAIL B
2⅜ O.D x .120
WALL TUBING
PBG
4.50 DIA
.40
3.50
6.00 DIA
A
64/
4½ O.D. x .120
WALL TUBING
.10 TYP
4.00
.40
32/
5.75 DIA
.50
5.15
10.30
A
.125 DIA REF THRU-PRESS FIT WITH
⅛ DIA DOWEL PIN, 2 HOLES, LOC FROM
PT #1 OF DWG 4012286-450 DOWEL PINS
ON OPPOSIT FLANG TO BE LOC FROM PT #2
OF DWG 4012286-450 (DOWELS TO PROTRUDE .50)
2⅜ O.D x .120
WALL TUBING
17/32 DIA DRILL THRU
4 HOLES EQ SP WITHIN
.015 OF TRUE POS ON
4.50 B.C.
45°
TAP DRILL THRU
THD #10-32NF-2 THRU 4 HOLES
EQ SP WITHIN .015 OF TRUE POS
ON 4.62 B.C.
3.0 O.D. x .120
WALL TUBING
PART 48
DWG 4012286-444
7.00
4.50
.40
5.20 DIA
TYP
SEE DETAIL C
3.20
3.50
2.0 O.D. x .120
WALL TUBING
3.50 DIA
.30
SEE DETAIL D
3.50 DIA
SECT D-D
ON 4012286-444
ROTATED 90°
DETAIL C SCALE 2/1
OTHERWISE THE SAME AS
DETAIL B
13/32 DIA DRILL THRU
4 HOLES EQ SP
ON 3.00 B.C
2.25 DIA
DETAIL D SCALE 2/1
OTHERWISE THE SAME
AS DETAIL B
①
¼ O.D. COPPER TUBING
PIPE THD ADAPTER
ALTER AS SHOWN
CONSOLIDATED VAC CORP SEAL™ SR-25
1.00
2.00
3.00
VACUUM COUPLING
CAJON # 4CV1
¼ O.D. x .065 WALL TUBING
300 SERIES STN STL
HEX HD NUT FROM
CONSOLIDATED VAC CORP SEAL™ SR-25
②
REVISIONS
SYM
ZONE
DESCRIPTION
DATE
2 PBG MEANS GAS TORCH SOLDERING FILLER MAT'L
1 PBG MEANS INERT ARC WELD, FILLER MAT'L 347 STAINLESS
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES -
TOLERANCES ON
2 PLACE DECIMALS ±.020
3 PLACE DECIMALS ±.005
ANGLES ±
ALL SURFACES 125/
MATERIAL - 304 STN STL
SIGNATURES
DATE
9-10-64
9-25-64
SEPT 22 1964
9-22-64
9-25-64
9-21-64
GENERAL ELECTRIC
AETD
EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND
CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE
D
DWG NO
4012286-445
SCALE
WT
SHEET
OF
57
AR441
D 4012286-445
REDUCED MICRO-COPY

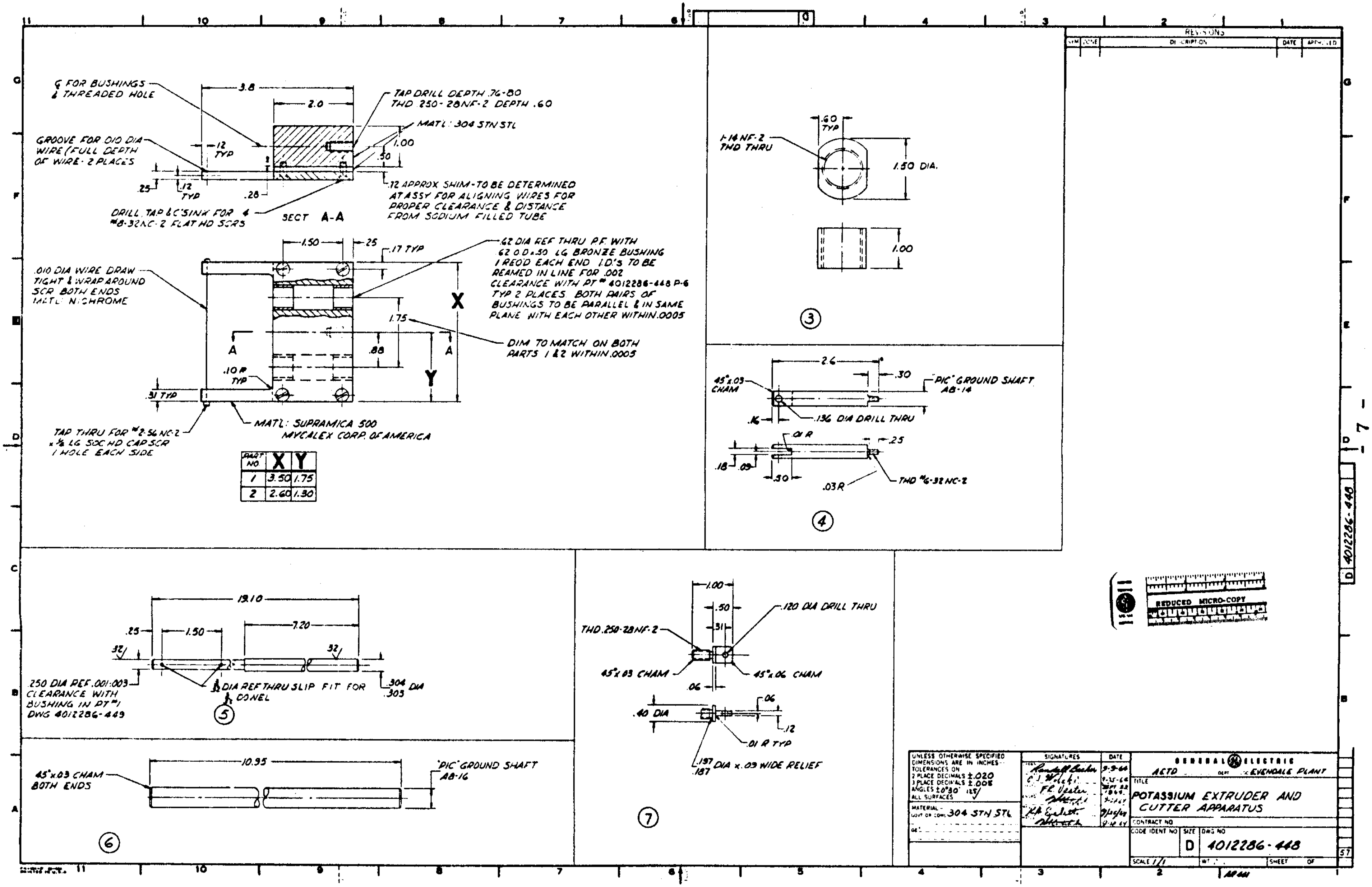


①
2.88 DIA REF
.001-.003 CLEAR WITH PT #1 DWG 4012286-447
1.00 DIA
32/
$\frac{3}{8}$ DIA DRILL THRU 4 HOLES EQ SP ON 1.80 B.C. LOC WITHIN .02 OF TRUE POS.
DRILL $\frac{3}{16}$ THRU C'BORE FOR P.F. WITH .50 OD x .305-.306 I.D. x 1.90 LG BRONZE BUSHING
.60 DIA
45°x.06 CHAM
45°
.06 R TYP
.10
.50
.60 TYP
2.06
.90
.10 TYP
THD 1-14NF-2
A
.12
37°
64/
.56 DIA
CHAMF 45° x .05 2 PLACES
.80 WRENCH FLATS
②
CHAMF 45° x .05 2 PLACES
.375 DIA REF .001-.002 CLEARANCE WITH PT #3 DWG 4012286-450
.80 WRENCH FLATS
THD 1-14NF-2
37°
A
.13
$\frac{3}{8}$ DRILL THRU 4 HOLES EQ SP ON 1.80 DIA B.C. LOC WITHIN .02 OF TRUE POS
.90
.60 TYP
$\frac{13}{64}$ DIA DRILL THRU 4 HOLES EQ SP WITHIN .015 OF TRUE POS ON 4.00 B.C.
2.40
PBG 1
3.25 DIA
.163
.157
.03
.25
.107
.101
6.10
SEE DETAIL B
.03
64/
.005 R
.02 R
32/
DETAIL B SCALE 2/1
1.00 DIA
2.40 DIA
4.50 DIA
③ MAT'L: BRASS SCALE 2/1
.60
.06
.01 R
45°x.03 CHAM
.12 DIA
.11
.30 DIA
.42
$\frac{1}{16}$ DIA DRILL THRU
④ MAT'L: BRASS
.250 DIA REF THRU .001-.003 CLEAR WITH PT #5 DWG 4012286-448
.25
1.19
$\frac{1}{2}$-20NF-2 THRU
.70
.35
1.80
1.00
.50
.25
.70
$\frac{1}{32}$ DIA DRILL THRU
⑤
.625 DIA REF TO HAVE P.F. WITH PT #2 DWG 4012286-447
.56 DIA
.08 REF THK TO BE DETERMINED AT ASSY TO HAVE .001-.003 CLEARANCE
⑥
$\frac{9}{16}$ DIA DRILL THRU
.10
2.20
1.10
.50
1.30
.19
.69
63/
.88
1.75
$\frac{13}{64}$ DIA DRILL THRU 4 HOLES
1 PBG MEANS INERT ARC WELD. FILLER MAT'L 347 STAINLESS
REVISIONS
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES— TOLERANCES ON 2 PLACE DECIMALS ±.020 3 PLACE DECIMALS ±.005 ANGLES ±0°30' 125/ ALL SURFACES
MATERIAL - 304 STN STL
SIGNATURES
DATE
9-9-68
9-21-68
9-21-68
9/12/68
9-12-68
GENERAL ELECTRIC
AETD
EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE D
DWG NO 4012286-446
SCALE 1/1
WT
SHEET OF
AR441
4012286-446
REDUCED MICRO-COPY



1. PBG MEANS INERT ARC WELD FILLER MATL 347 STAINLESS

UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES— TOLERANCES ON 2 PLACE DECIMALS ± .020 3 PLACE DECIMALS ± .005 ANGLES ± 0°30' ALL SURFACES 125	SIGNATURES	DATE	GENERAL ELECTRIC ACTP DEPT EVENDALE PLANT
MATERIAL— 304 STN STL			TITLE POTASSIUM EXTRUDER AND CUTTER APPARATUS
			CONTRACT NO
			CODE IDENT NO · SIZE D · DWG NO 4012286-447
			SCALE 1/1 · SHEET OF



PART NO	X	Y
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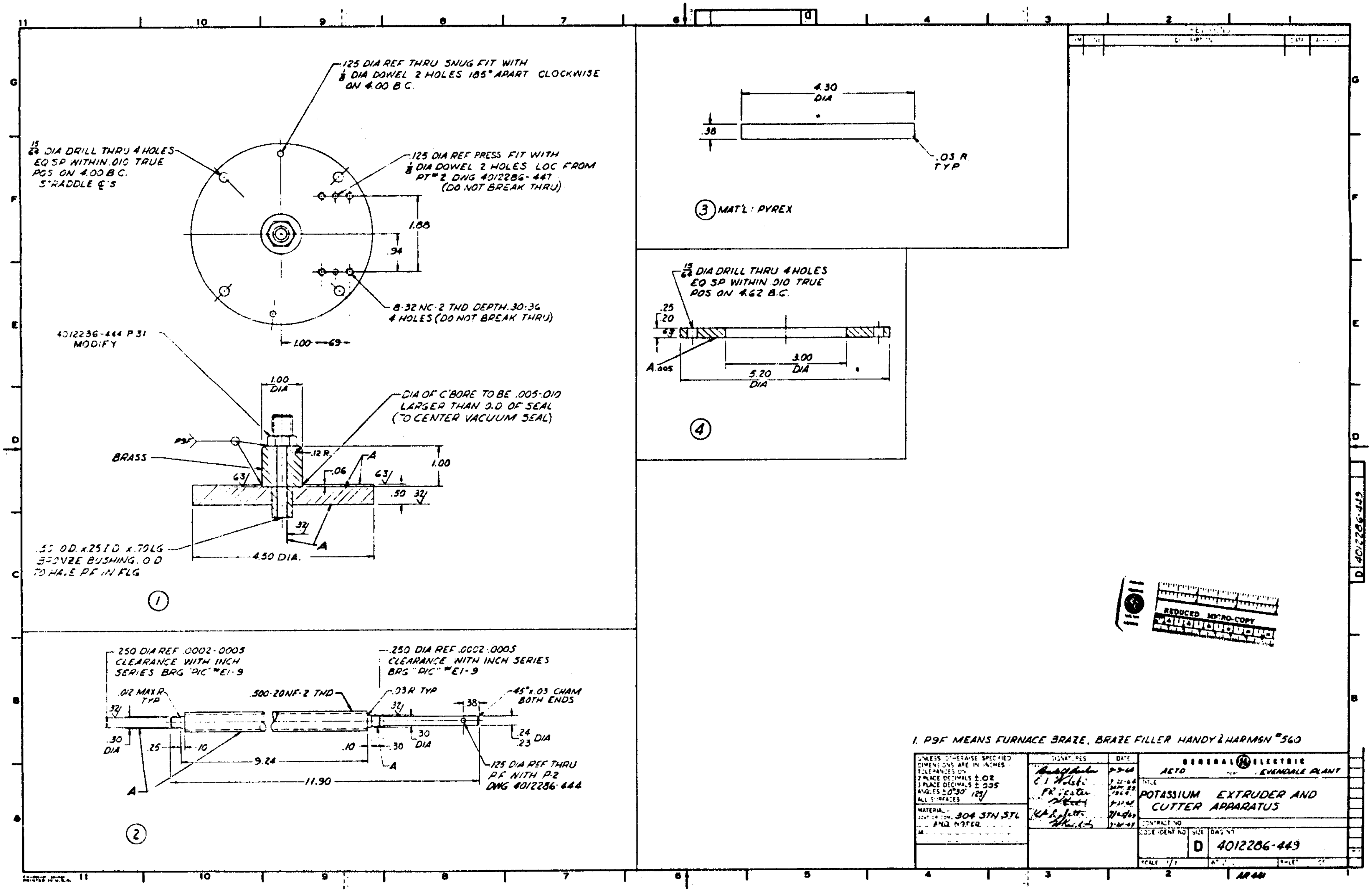
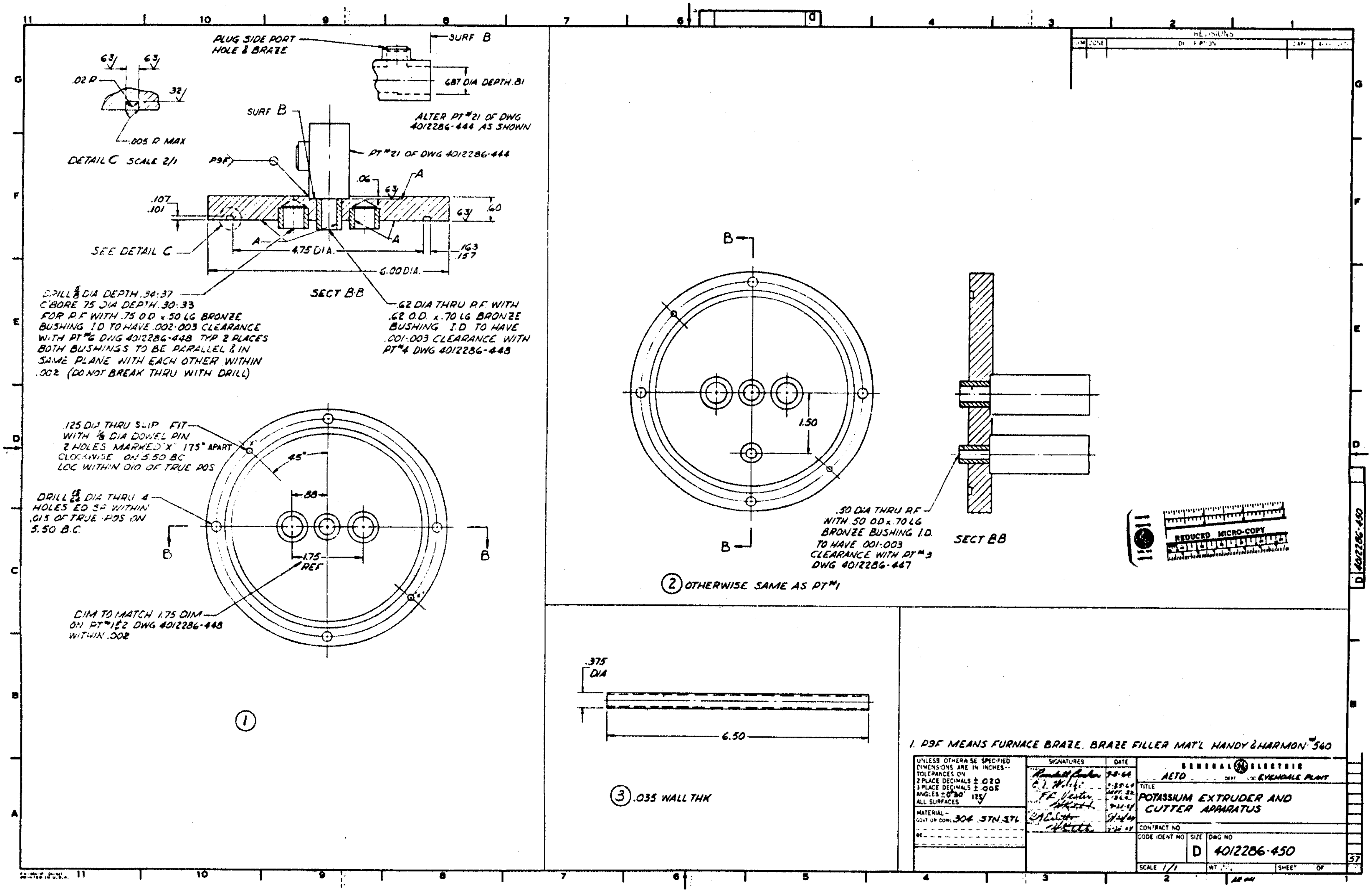
2	2.60	1.30


.125 DIA REF THRU SNUG FIT WITH 1/8 DIA DOWEL 2 HOLES 185° APART CLOCKWISE ON 4.00 B.C.
15/64 DIA DRILL THRU 4 HOLES EQ SP WITHIN .010 TRUE POS ON 4.00 B.C. STRADDLE ℄'S
.125 DIA REF PRESS FIT WITH 1/8 DIA DOWEL 2 HOLES LOC FROM PT #2 DWG 4012286-447 (DO NOT BREAK THRU)
1.88
.94
8-32 NC-2 THD DEPTH .30-.36 4 HOLES (DO NOT BREAK THRU)
1.00
.69
4012236-444 P31 MODIFY
1.00 DIA
DIA OF C'BORE TO BE .005-.010 LARGER THAN O.D OF SEAL (TO CENTER VACUUM SEAL)
P9F
BRASS
.12 R
.06
A
63
1.00
.50
32
.50 OD x .25 I.D x .70 LG BRONZE BUSHING. O.D TO HAVE PF IN FLG
4.50 DIA.
①
.250 DIA REF .0002-.0005 CLEARANCE WITH INCH SERIES BRG "PIC" #E1-9
.250 DIA REF .0002-.0005 CLEARANCE WITH INCH SERIES BRG "PIC" #E1-9
.012 MAX R TYP
.500-20NF-2 THD
.03R TYP
.38
45° x .03 CHAM BOTH ENDS
.30 DIA
.25
.10
9.24
.10
.30
.30 DIA
.24
.23 DIA
.125 DIA REF THRU PF WITH P-2 DWG 4012286-444
11.90
A
②
4.30 DIA
.38
.03 R TYP
③ MAT'L: PYREX
15/64 DIA DRILL THRU 4 HOLES EQ SP WITHIN .010 TRUE POS ON 4.62 B.C.
.25
.20
.63
A .005
3.00 DIA
5.20 DIA
④
1. P9F MEANS FURNACE BRAZE, BRAZE FILLER HANDY & HARMSN #560
UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES
TOLERANCES ON
2 PLACE DECIMALS ±.02
3 PLACE DECIMALS ±.005
ANGLES ±0°30'
ALL SURFACES 125
MATERIAL 304 STN STL AND NOTED
SIGNATURES
DATE
C. J. Wolski
9-3-64
9-21-64
SEPT 29 1964
7-21-64
GENERAL ELECTRIC
AETO
EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE D
DWG NO 4012286-449
SCALE 1/1
SHEET
D 4012286-449
REDUCED MICRO-COPY
AR 441


PLUG SIDE PORT HOLE & BRAZE
SURF B
.687 DIA DEPTH .81
ALTER PT #21 OF DWG 4012286-444 AS SHOWN
PT #21 OF DWG 4012286-444
63
32
.02 R
.005 R MAX
DETAIL C SCALE 2/1
SURF B
P9F
.06
A
.107
.101
.60
SEE DETAIL C
4.75 DIA.
.163
.157
6.00 DIA.
SECT B-B
DRILL 5/8 DIA DEPTH .34-.37
C'BORE .75 DIA DEPTH .30-.33
FOR P.F WITH .75 O.D x .50 LG BRONZE
BUSHING I.D TO HAVE .002-.003 CLEARANCE
WITH PT #6 DWG 4012286-448 TYP 2 PLACES
BOTH BUSHINGS TO BE PARALLEL & IN
SAME PLANE WITH EACH OTHER WITHIN
.002 (DO NOT BREAK THRU WITH DRILL)
.62 DIA THRU P.F. WITH
.62 O.D. x .70 LG BRONZE
BUSHING I.D TO HAVE
.001-.003 CLEARANCE WITH
PT #4 DWG 4012286-448
.125 DIA THRU SLIP FIT
WITH 1/8 DIA DOWEL PIN
2 HOLES MARKED "X" 175° APART
CLOCKWISE ON 5.50 BC
LOC WITHIN .010 OF TRUE POS
45°
.88
DRILL 13/64 DIA THRU 4
HOLES EQ SP WITHIN
.015 OF TRUE POS ON
5.50 B.C.
B
1.75 REF
DIM TO MATCH 1.75 DIM
ON PT #1 & 2 DWG 4012286-448
WITHIN .002
①
B
1.50
.50 DIA THRU P.F.
WITH .50 O.D x .70 LG
BRONZE BUSHING I.D.
TO HAVE .001-.003
CLEARANCE WITH PT #3
DWG 4012286-447
SECT BB
② OTHERWISE SAME AS PT #1
.375 DIA
6.50
③ .035 WALL THK
REDUCED MICRO-COPY
1. P9F MEANS FURNACE BRAZE. BRAZE FILLER MAT'L HANDY & HARMON #560
UNLESS OTHERWISE SPECIFIED
DIMENSIONS ARE IN INCHES
TOLERANCES ON
2 PLACE DECIMALS ± .020
3 PLACE DECIMALS ± .005
ANGLES ± 0°30'
ALL SURFACES 125
MATERIAL - GOVT OR COML 304 STN. STL.
SIGNATURES
DATE
Randall Fowler 9-8-64
C. L. Welsh 9-25-64
F. E. Vester Sept. 28, 1964
9-21-64
9-24-64
9-28-64
GENERAL ELECTRIC
AETO DEPT LOC EVENDALE PLANT
TITLE
POTASSIUM EXTRUDER AND CUTTER APPARATUS
CONTRACT NO
CODE IDENT NO
SIZE D
DWG NO 4012286-450
SCALE 1/1
WT
SHEET OF
57
D 4012286-450
REVISIONS

2. Modifications of the analytical apparatus are shown in Figure 1. Minor changes involving the addition of a compound pressure gauge in the helium manifold, and the elimination of the CaF_2 trap in the rough vacuum system are shown here.

The only major modifications involve the effluent cold traps preceding connection to the Brady apparatus. During initial shakedown runs, high blanks on the order of 70 to 250 micrograms per hour were experienced. It was thought that this might be due to the BrF_3 or various impurities contained therein passing through the traps. Accordingly, copper mesh was placed in the annular space within the traps (see Figure 4, First Quarterly report) in an attempt to improve their efficiency. By this means, the blank rate was reduced to about 40 micrograms per hour--a still unacceptable level. In addition, it was difficult to control the temperature of the original traps in spite of the application of urethane foam insulation to the external surfaces of the trap. Also, at low temperatures (-135°C) and at positive pressures of helium, the elastometer "O" rings (both Viton and Teflon were tried) occasionally developed leaks due to their contraction.

All of these difficulties were corrected by replacing these traps with new ones constructed simply of 3/8" Monel tubing. In order to prevent plugging due to frozen BrF_3 carried over from the reaction cell, the first trap contains an initial section of one inch O.D. Monel tubing where the bulk of the impurities are frozen out. The 3/8" tubing leading from this section is welded to it about one inch from the bottom. Both traps are immersed in pentane slush (-130°C) contained in Dewar flasks; thus temperature control is excellent and oxygen liquefaction is prevented. The entire trap assembly is shown in Figure 2. With these traps blanks in the order of 5-20 micrograms per hour can be maintained.

3. Temperature measurements in the reaction cell were made with a copper-constantan thermocouple and a direct reading Sim-ply-trol Indicating Pyrometer having a special scale reading from -220°C to + 40°C.

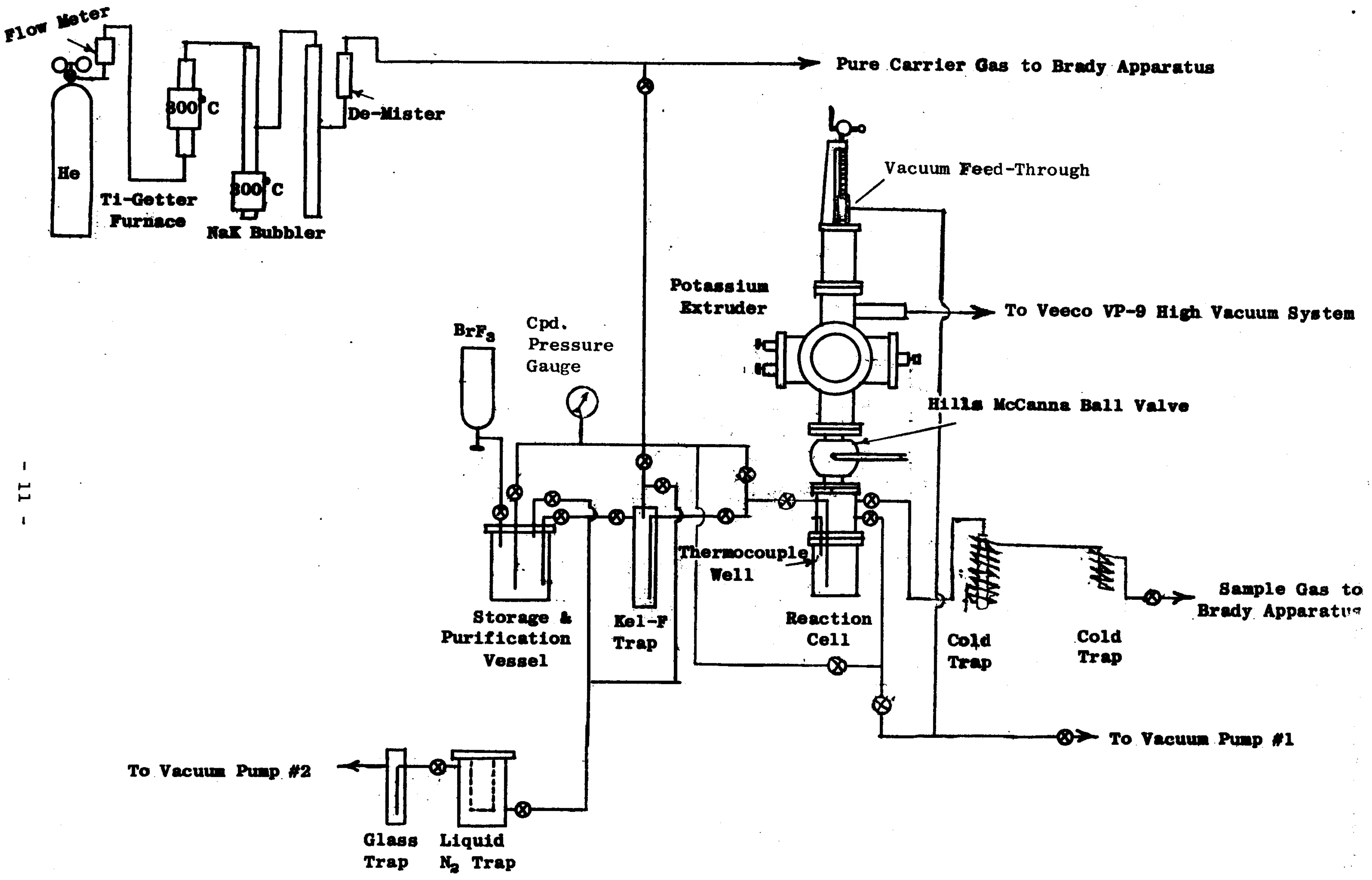


FIGURE 1 Modified System Design for BrF_3 Determination of Oxygen in Alkali Metals

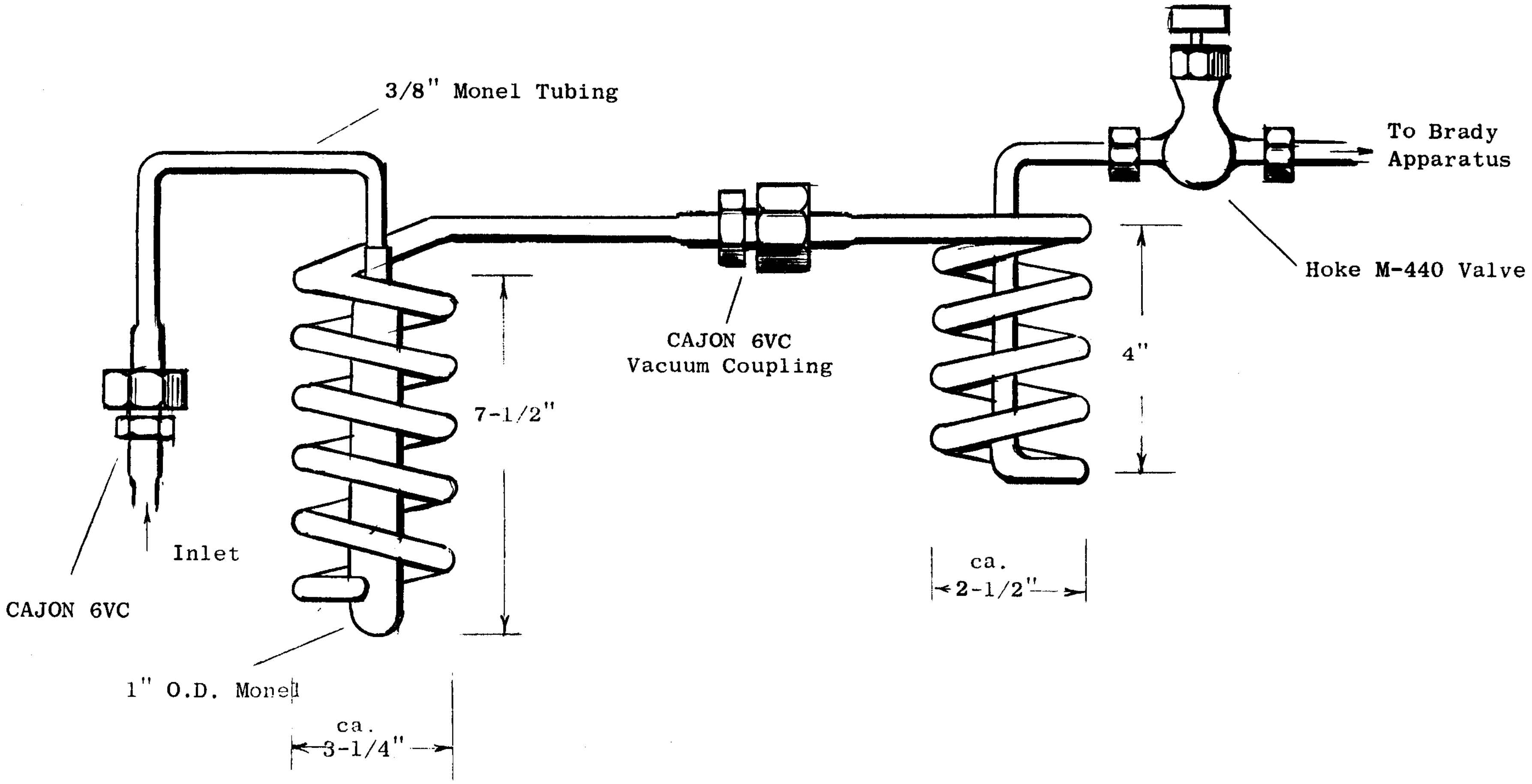


FIGURE 2 Revised Double Trap Assembly

II PROCEDURE FOR ANALYSIS OF $KBrO_3$ STANDARDS

In order to determine the overall accuracy of the entire apparatus, a series of potassium bromate standards containing various amounts of oxygen were analyzed. The standards were prepared by dissolving 1.7397 g. of dried reagent grade $KBrO_3$ (assay: 99.8% $KBrO_3$) in water and diluting to one liter in a volumetric flask. One micro-liter of this solution then contained 0.5 micrograms of oxygen in the form of bromate.

Aliquots of this solution containing the requisite amount of oxygen were then measured into previously prepared copper foil boats by means of a syringe microburet. The instrument used was manufactured by the Micro Metric Instrument Company and was designated Model No. SB2. Using a syringe, No. S1/4LT calibrated to deliver 0.200 microliters per division of micrometer dial, one small division of the dial was equivalent to 0.1 microgram of oxygen. Since the micrometer has one hundred small divisions per revolution, samples equivalent to ten micrograms of oxygen could be dispensed with good accuracy. The smallest samples used contained five micrograms oxygen--equivalent to one half revolution.

After dispensing the $KBrO_3$ solution into the copper boats, the solution was evaporated to dryness under infrared lamps and the samples were then baked for one hour at 120°C in a drying oven.

The procedure used for the analysis of these standard samples is as follows:

1. Remove the top portion of the extruder containing the potassium tube and substitute for it a circular 3/8" thick glass plate to seal the opening (see Drawing #4012286-444). With Pt-tipped tongs, place a copper boat containing the proper amount of dried $KBrO_3$ on top of the closed ball of the Hills-McCanna ball valve. Replace the glass port cover and rough down the extruder with the mechanical pump of the Veeco vacuum system. After the pressure in the extruder drops below 80 microns, switch over to the diffusion pump.

2. While the extruder is pumping down to 10^{-6} mm Hg, chill the cold traps of the rough vacuum system with liquid nitrogen. After the traps are cold, slowly open the valve between the monel and the glass traps. If the system has been pumped out previously, the pressure at the pump inlet should not exceed about 200 microns. The liquid nitrogen level in the monel trap should be maintained at not more than one or two inches while pumping. Excess liquid nitrogen is not necessary to trap out BrF_3 or other condensable vapors and will only chill the trap flange to the point where the Viton "O" ring will no longer be able to maintain an effective seal.

3. At this point, all analytical system valves (excluding vacuum system and helium purification system) should be closed, including the valve connecting the analytical system to the Brady apparatus. After the rough vacuum system has attained a pressure of about 6 microns, slowly open the vacuum valve to the reaction cell. The valve should be opened so that the vacuum pump gurgles slightly. Opening the valve too far or too rapidly may cause BrF_3 to be carried through the Monel freeze trap. Should this happen, yellow solid BrF_3 will appear frozen out in the glass cold trap. The valve connecting the two traps must then be closed and the glass trap disconnected, thawed, washed out, and dried before proceeding further.

   While the reaction cell is being pumped out, the valve connecting the reaction cell and the effluent cold traps may be opened and the cold traps pumped out simultaneously. After the mechanical pump has quieted down, open the valve to the vacuum system fully. When the pressure drops to about 6 microns, chill the reaction cell sufficiently to freeze the BrF_3 and continue cooling to about -10°C before removing the liquid nitrogen Dewar flask. While the BrF_3 in the reaction cell is still frozen, open the valve at the exit end of the second effluent cold trap, thus permitting the line connecting the analytical system and the Brady apparatus to be evacuated. Before doing so, make certain the valve at the entrance of the Brady apparatus is closed lest solution from the Brady be drawn back into the reaction cell.

At this point, the helium manifold may also be pumped out by first closing the valve connecting it to the pure helium supply line and then opening the reaction cell helium inlet valve. There are actually two helium inlets; one leading to a dip leg extending to the bottom of the reaction cell and another permitting helium to pass over the BrF_3, (see Drawing #4012286-182 in Second Quarterly report). Since the former will be plugged with frozen BrF_3 at this point, the other must be used to pump out the manifold. After pumping out the manifold, close the valve and refill the manifold with pure helium.

4. After the reaction cell and effluent cold traps have been pumped down to about 6 microns, fill the Dewar flasks surrounding the effluent cold traps with pentane slush. After the traps have cooled to below -120°C, close the valve to the rough vacuum system and the valve between the roughing cold traps. Open the helium inlet to the reaction cell. The compound pressure gauge in the helium manifold (see Figure 1) will indicate a vacuum of about 20 to 25 inches of mercury. Admit pure helium into the entire system by slowly opening the valve connecting the manifold to the helium supply system. Regulate the flow by observing the manifold pressure gauge and the flowmeter on the helium tank regulator. Do not exceed about 1.2 cubic feet per hour. After pressurizing to a positive pressure of about 3 to 5 pounds per square inch, open the valve all the way.

5. The operation of the Brady apparatus is exactly the same as outlined in the Brady calibration procedure contained in the Second Quarterly report. During the preceding steps, pure helium from the NaK bubbler should be flowing through the apparatus and the flow rate, solution level, spectrophotometer and recorder adjusted in accordance with this procedure.

   Close the valve supplying pure helium to the Brady and open the valve supplying gas from the analytical system. Adjust the flow rate to the proper level (about 70 mm on the flowmeter). Warm the reaction cell with warm water to thaw the BrF_3. After the temperature exceeds 25°C, close the reaction cell helium inlet and open the inlet leading to the dip leg so that helium bubbles through the BrF_3.

Observe the blank rate on the recorder for about 30 minutes. The blank rate should level off to some constant value yielding a trace which is a straight line corresponding to about 10-15 micrograms of oxygen per hour.

6. After an acceptable blank has been obtained, again chill the cold traps in the rough vacuum system with liquid nitrogen. Close the valves connecting the Brady and the analytical system, the reaction cell and the effluent cold traps, and the helium inlet to the reaction cell.

   Employing the same procedure as outlined in Step 2, pump out the reaction cell but do not pump out the effluent cold traps. After pumping out the cell, chill it with liquid nitrogen to about -90°C. Partially open the ball valve connecting the cell and the extruder and close the valves of the rough pumping system. Open the ball valve all the way, permitting the sample to fall into the reaction cell; then close the ball valve. Pressurize the reaction cell with pure helium as outlined in Step 4 and open the valve to the effluent traps. While the steps set forth in this paragraph are being carried out, helium from the purification system can be bubbling through the Brady; during this time, the trace on the recorder should indicate no discernible blank. Again, stop the flow of pure helium to the Brady and open the valve connecting it to the analytical system. After 20-30 minutes, examine the recorder trace; meanwhile, maintaining the reaction cell at about -180°C with liquid nitrogen. The blank rate should be about the same as before.

7. After establishing the blank rate, close the helium inlet to the reaction cell. Remove the liquid nitrogen Dewar and substitute for it one containing warm water. As the pressure in the cell increases, the flow rate may be maintained by adjusting the needle valve on the flowmeter. After the

cell temperature reaches about 30°C, remove the warm water Dewar. When the pressure in the cell drops below the normal operating pressure, as evidenced by a flowmeter reading of about 60 or less, open the helium inlet to the dip leg.

After about 10 minutes, the absorbance of the Brady solution should begin to decrease. Complete removal of oxygen from the reaction cell requires about 45 minues. When the chart recorder trace assumes a slope identical to that obtained prior to warming the reaction cell, recovery can be considered complete.

8. Measure the displacement of the chart recorder trace (i.e., the difference in absorbance) and substract from 1.000. Read the corresponding amount of oxygen from the calibration curve.

III PRELIMINARY RESULTS OF ANALYSIS OF $KBrO_3$ STANDARDS

A total of twenty $KBrO_3$ standards containing known amounts of oxygen have been analyzed and the results are listed in Table I. The results are numbered consecutively in the order in which they were run.

Essentially complete recovery was only obtained under certain specific conditions, the limitations of which have not yet been fully determined. Samples 1 through 6 involved small samples of $KBrO_3$ not exceeding 25 micrograms of oxygen. Aliquots of standard $KBrO_3$ solution containing these equivalent amounts of oxygen, when dispensed into .001" copper foil cups did not cover the bottom of the cup. Since it was feared the cups might float in the BrF_3 they were slotted along the sides after drying. This could be done without loss of sample since the $KBrO_3$ was dried on the bottom of the cups only.

With samples containing the equivalent of 50 micrograms of oxygen or more, however, the cups could not be slotted because the dried $KBrO_3$ was deposited on the sides as well as the bottom of the cups. It was observed that Samples 7 and 8 floated in the $KBrO_3$ and contained no visible BrF_3. Sample 9 inadvertantly landed upon a previously dropped boat and it also contained no BrF_3. Low results on these three samples were, therefore, attributed to lack of reagent.

In the case of the first six samples for which satisfactory results were obtained, the reaction cell contained about 30 ml of BrF_3. All six sample cups landed in an upright position on the frozen BrF_3 (as verified through the glass cover-plate) and when the cell was thawed they were approximately 3/4 full with BrF_3.

Beginning with Sample 9, the configuration of the copper boats was changed from a cup shape to a flat rectangular piece of .008" copper with turned up corners to facilitate handling. Before running Sample 10, the reaction cell was cleaned out and 75 ml of fresh BrF_3 added. From this point on, the samples were completely submerged in BrF_3 and essentially dissolved in the entire volume of BrF_3. The only exception being Sample 16 which was added after almost all the BrF_3 had been evaporated out of the cell. Samples 10 through 14, which had all been completely submerged yielded low results.

Since satisfactory results had only been obtained when the sample had dissolved in a limited amount of BrF_3 contained in the copper cup, it was surmised that the incomplete recovery was perhaps due to excessive solubility of the liberated oxygen in BrF_3.

In an effort to decrease the solubility, the reaction cell was warmed to 40-50°C after sample introduction and following helium pressurization. Sample 15 was the first to be run in this manner and yielded 90.8% oxygen recovery. It is estimated that the cell contained about 20 ml of BrF_3 during this run. During the following analysis (Number 16 mentioned above) it was noted that almost all of the BrF_3 had been evaporated out of the cell, and this sample may not have come in contact with sufficient reagent. An additional 50 ml of BrF_3 was then added to the reaction cell and the remaining samples run. All subsequent results were low.

Sample Number 20 (containing 100 micrograms oxygen) was again run in a cup-shaped .001" boat but with a small pin hole placed in the bottom after the sample had been dried. It was hoped that only a limited amount of BrF_3 would enter the cup, thus limiting the solubility effect. After analysis, however, the cup was found to have submerged completely. Even so, the recovery (45.4%) was higher than that of any other 100 microgram sample.

If, as is suspected, low recoveries are to the solubility of oxygen in BrF_3, the following measures may prove to be corrective:

1. Limiting the amount of BrF_3 in the reaction cell to about 20 ml.

2. Further increasing the temperature of the cell to about 70°C (literature establishes precedence for this).

3. Reacting the sample under vacuum.

4. Adding SbF_5 to the BrF_3 in the reaction vessel, thus forming $BrF_2 \cdot SbF_6$ which is purported to be more reactive than BrF_3 alone to oxides.

TABLE 1

RESULTS OF ANALYSIS OF $KBrO_3$ STANDARDS

Date Run	No.	Calculated O_2 Content (μg)	O_2 Found (μg)	% Recovery	Blank Rate (μg/Hr)	Flow Rate (cc/Min)	Remarks
9-29	1	25	23.7	94.8	17.6	108	(1)
9-29	2	25	24.3	97.2	10.9	108	(1)
10-1	3	10	9.8	98.0	12.3	203	(1)
10-2	4	10	11.1	111	20.4	108	(1)
10-2	5	5	3.8	76.0	28.7	203	(1)
10-5	6	5	9.5	190	14.6	108	(1)
10-6	7	50	26.3	52.6	11.8	108	(2)
10-6	8	100	30.3	30.3	16.9	108	(2)
10-7	9	50	21.3	42.6	9.4	108	(3)
10-9	10	50	14.6	29.2	54.5	108	(4)
10-12	11	100	20.6	20.6	48.8	108	(4)
10-14	12	5	5.1	102	22.7	108	(4)
10-14	13	5	8.6	172	17.3	108	(4)
10-15	14	50	26.3	52.6	12.2	108	(5)
10-16	15	50	45.4	90.8	25.2	108	(5)

(1) Samples in .001" Cu foil cups with slotted sides. Approximately 30 ml BrF_3 in cell. Cups were about 3/4 full of BrF_3.

(2) Same as (1), but cups not slotted ($KBrO_3$ on sides as well as bottom). Cups floated in BrF_3.

(3) Dropped on top of previous boat. (.008" Cu sheet boat).

(4) Used new boats of flat .008" Cu sheet. Cell cleaned out (10-8-64) and refilled with $\approx$ 75 ml BrF_3.

(5) Procedure change beginning here: After dropping sample and admitting He, warm cell to 40-50°C.

TABLE 1

(Continued)

Date Run	No.	Calculated O_2 Content (μg)	O_2 Found (μg)	% Recovery	Blank Rate (μg/Hr)	Flow Rate (cc/Min)	Remarks
10-19	16	100	32.3	32.3	-	203	(6)
10-20	17	25	62.8	251	16.8	108	(6)
10-20	18	50	32.9	78.4	43.4	108	(6)
10-22	19	50	24.8	49.7	10.2	108	(6)
10-23	20	100	42.8	42.8	5.3	108	(7)

(6) BrF_3 level low; <u>boats exposed</u>. Add ≈ 50 ml BrF_3 .

(7) Sample in .001" Cu foil boat with pin hole in bottom--submerged completely.

IV WORK PLANNED FOR FOURTH QUARTER

1. Investigate means of obtaining complete recovery from $KBrO_3$ samples as outlined in Section 3.

2. Investigate the effects of carbonate additions to BrF_3 and measurement of the oxygen recovery therefrom.

3. Analysis of potassium samples previously analyzed by mercury amalgamation. Samples on hand include NASA samples in the range of 10 and 80 ppm, and GE samples containing about 45 ppm of oxygen.