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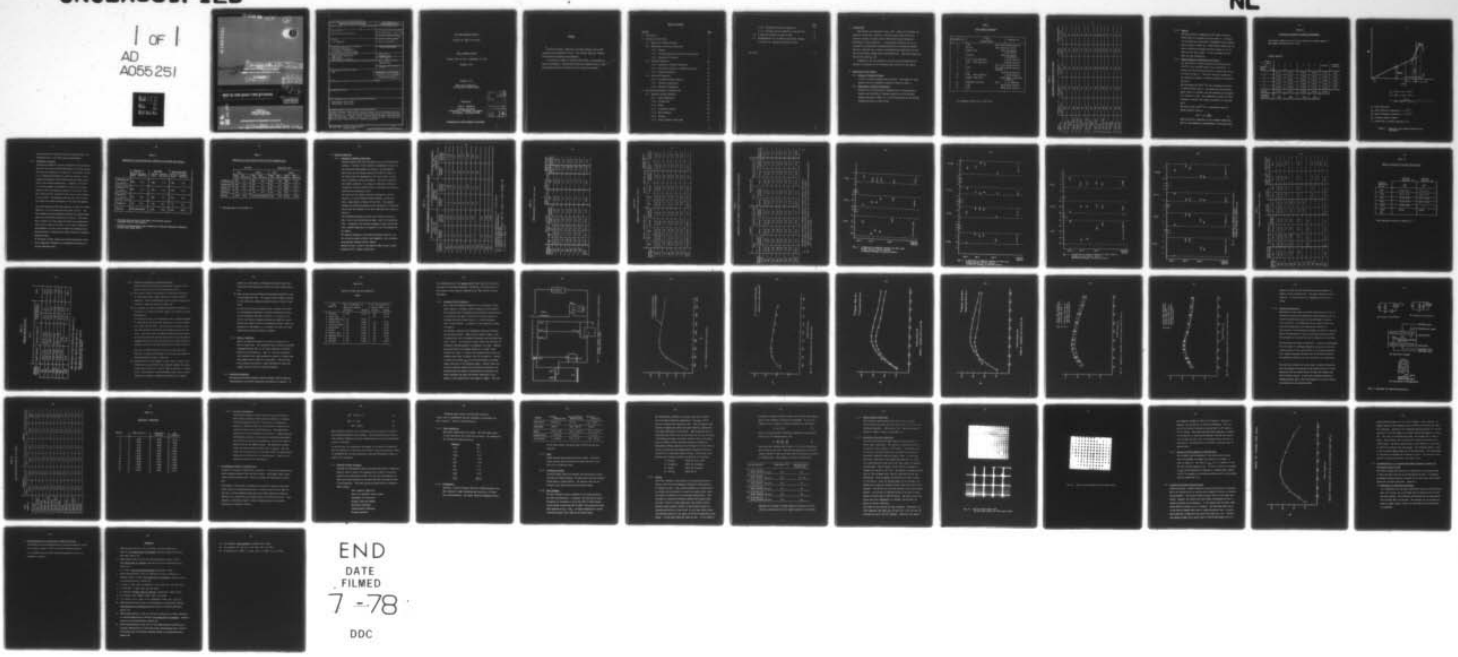

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UNIVERSITY OF CALIFORNIA · ENGINEERING · LOS ANGELES

(9) FINAL TECHNICAL REPORT, 25 Jun 75 – 24 Sep 77

(15) UNDER CONTRACT NO. DAAG 53-75-C-0222

P[redacted]: JUNE 25, 1975 TO SEPTEMBER 24, 1977)

(11) NOV[redacted]77

(12) 57 p.

(6)

MCP GLASS ANALYSIS STUDIES.

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Night Vision Laboratory
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California Science. Los Angeles
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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* MCP Glass Analysis Studies		5. TYPE OF REPORT & PERIOD COVERED Final, June 1975 - Sept. 1977 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J.D. Mackenzie		8. CONTRACT OR GRANT NUMBER(s) DAAG 53-75-C-0222 new
9. PERFORMING ORGANIZATION NAME AND ADDRESS Materials Department University of California Los Angeles, California 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Night Vision Laboratory DRSEL-NV-SD Fort Belvoir, VA 22060		12. REPORT DATE November 1977 13. NUMBER OF PAGES 59
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)* UNCLASSIFIED 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Req

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Microchannel Plate (MCP)
Microchannel Plate Glass

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Fourteen different commercially available glasses used in MCP production were analyzed in detail. The relevant physical, chemical and electrical properties were measured. An alternative method to fabricate MCP through a photosensitive glass was developed. Channel plates with hole diamteres down to 15μ were prepared and their secondary electron emissions measured.

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SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

MCP GLASS ANALYSIS STUDIES

Contract No. DAAG 53-75-C-0222

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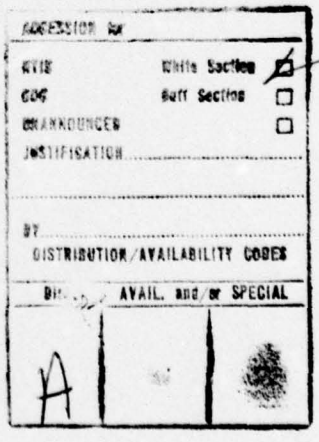

SUMMARY

Fourteen different commercially available glasses used in MCP production were analyzed in detail. The relevant physical, chemical and electrical properties were measured.

An alternative method to fabricate MCP through a photosensitive glass was developed. Channel plates with hole diameters down to 15μ were prepared and their secondary electron emissions measured.

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D

1. INTRODUCTION

This project was initiated in June, 1975. There were two major objectives and one minor objective. The first major objective was to evaluate a number of glasses used in MCP manufacturing through the measurement of many properties. A second major objective was to investigate the possibility of producing MCP's by an alternative method. The minor objective was to select a new industrial manufacturer for the type of lead glass tubings used in MCP manufacture. This minor objective was deleted in March, 1977.

A summary of the work performed to attain the above-mentioned objectives is presented in the following three sections of this report.

2. EVALUATION OF MCP GLASSES

2.1. Samples of Glasses Evaluated

A total of fourteen glasses were evaluated. The origins of these glasses and their designated numbers are shown in Table I.

2.2. Measurement of Physical Properties

Results for the strain point, annealing point, softening point, density and coefficient of thermal expansion for the fourteen samples are shown in Table II. A brief description of the various testing procedures is given below.

TABLE I

GLASS SAMPLES RECEIVED*

UCLA SAMPLE NO.	GLASS IDENTIFICATION		SUPPLIED BY
1	CGW	8161 (old)	Varian directly
2	Ni Tec	8161 (old)	John Rennie
3	Schott Clad	8531	John Rennie (ex Litton)
4	Philips	3502	John Rennie (ex Mullard)
5	Litton 8161 Substitute		Litton directly
6	CGW 8161 Substitute		Varian directly
7		8161 (old)	Varian directly
8	CGW	8161 (new) w/Alcarb	Varian directly
9	GE	821	Varian directly
10	CGW 8161 Substitute		Varian directly
11	Engrg. Glass Prod.	2364	Engrg. Glass Prod. directly
12	Hannibal Scientific	SG-16	J.D. Mackenzie
13	CGW	8164	Varian directly
14	CGW	8870	Varian directly

* All samples received are in tube form.

TABLE II

SOME PHYSICAL PROPERTIES OF MCP GLASSES

UCLA Sample No.	Strain Pt., °C ($\eta=10^{14.5}$ p.)	Annealing Pt., °C ($\eta=10^{13}$ p.)	Softening Pt., °C ($\eta=10^{7.6}$ p.)	Density gm/cm^3	Thermal Expansion ($/^oC \times 10^7$)
1 Old 8161	396	433	603	3.98	90
2 Ni Tec old 8161	406	440	598	3.99	90
3 Schott 8531	400	431	574	4.30	91
4 Philips 3502	384	425	625	3.33	95
5 Litton 8161 sub	402	437	601	3.98	90
6 CGW 8161 sub	399	435	607	3.98	89
7 Varian old 8161	398	434	602	3.97	88
8 8161 Alcarb	404	439	603	3.99	89
9 GE 821	403	437	595	4.03	89
10 CGW 8161 sub	402	436	597	3.99	89
11 EGP 2364	398	432	593	4.28	85
12 Hannibal SG-16	393	429	595	4.29	86
13 CGW 8164	420	456	630	3.60	82
14 CGW 8870	390	421	585	4.39	89

2.2.1. Density

The glass density is measured at 20°C using a bouyancy method based on Archimedes principle (Ref.1). An example of the statistical variation in independent density measurements is shown in Table III. These results showed that the density differences between different samples of the old 8161 are very small indeed. It can be assumed that the glass was well homogenized.

2.2.2. Thermal Expansion Coefficient and Viscosity

The coefficient of thermal expansion and annealing point ($\eta=10^{13}$p.) were obtained using a Leitz Dilatometer. A typical plot and the equations used to analyze the results are shown in Figure 1. The glass transition temperature, Tg, indicated in Figure 1 provides a measure of the annealing point.

The softening point ($\eta=10^{7.6}$p.) was determined according to ASTM standards (Ref.2). The method involves heating a glass fiber at a constant rate and observing its elongation as a function of time. The temperature at which the fiber elongates 0.5 mm per half minute represents the softening point.

The strain point ($\eta=10^{14.5}$p.) is determined using the Fulcher equation (Ref.3),

$$\log \eta = -A + \frac{B}{T-To} \qquad (1)$$

where A and B are constants, To is a constant temperature and T is the temperature corresponding to the strain point.

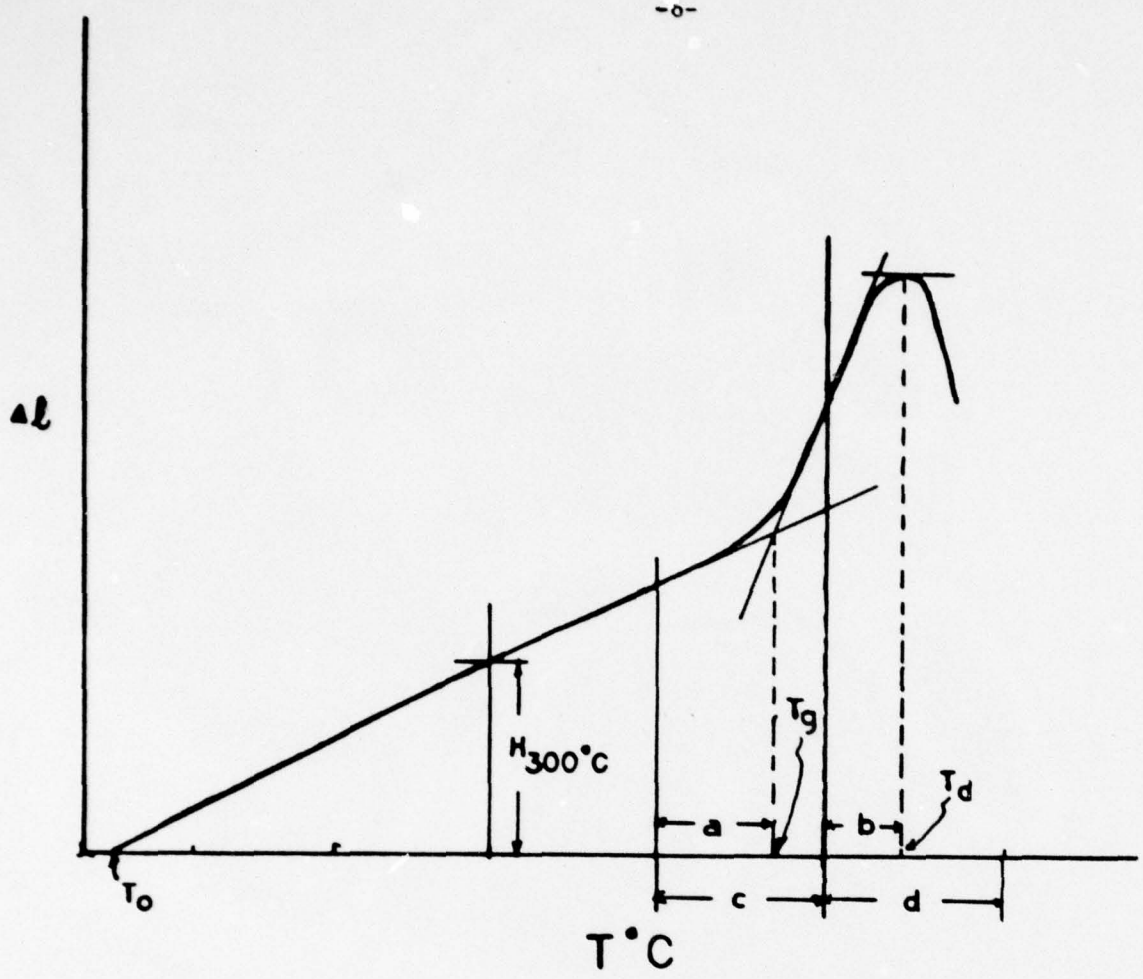
TABLE III

STATISTICAL VARIATION IN DENSITY MEASUREMENTS

Five density samples (a,b,c,d,e) were prepared from glass sample #1. Each sample was measured four times.

Density (gm/cm^3):

Measurement # / Density Sample	1	2	3	4	Average	Standard Deviation
a	3.9777	3.9735	3.9784	3.9769	3.9766	.0022
b	3.9763	3.9740	3.9778	3.9773	3.9764	.0017
c	3.9771	3.9732	3.9792	3.9778	3.9768	.0026
d	3.9761	3.9750	3.9787	3.9761	3.9765	.0016
e	3.9780	3.9753	3.9787	3.9757	3.9769	.0017
average	3.9770	3.9742	3.9786	3.9768	3.9767	
Standard Deviation	.0008	.0009	.0005	.0009		



$$T_g = 400°C + (a/c) \times 100°C$$

$$T_d = 500°C + (b/d) \times 100°C$$

$$\alpha = \frac{H_{300°C}}{800 \times (300°C - T_o°C) \times L_o} + 6.3 \times 10^{-7} \ (/°C)$$

T_o = Room temperature

T_g = glass transition temperature, $\eta = 10^{13p.}$

T_d = glass deformation temperature $\eta = 10^{11.4p.}$

L_o = original length of sample

α = coefficient of thermal expansion (/°C)

Figure 1. Expansion curve obtained directly from dilatometer.

This calculation is possible after the softening point and annealing point of the glass have been determined.

2.2.3. Discussion of Results

The physical properties tested at UCLA have also been determined for the various Corning MCP glasses by outside sources. This data was transmitted to UCLA by Mr. John Rennie (letter to J.D. Mackenzie September 30, 1975) and consists of the analyses performed by Corning Glass Works and Emhart Corporation Glass Testing Laboratories. A summary of the data for the 8161 glasses is presented in Table IV and clearly indicates that the properties listed for "old" 8161, "new" 8161 (w/Alcarb) and "substitute" 8161 are all quite similar to one another. The average values for each type of glass are within the standard deviation of the other two glasses.

These same properties have been measured at UCLA for old 8161 (UCLA No. 1,2,7) and substitute 8161 (UCLA 5,6,10). The UCLA average values and standard deviation are compared with those from the outside laboratories in Table V. The agreement is shown to be quite good and within the standard deviation for all cases of old 8161. In the case of substitute 8161 agreement is still close although the annealing point and coefficient of expansion are barely outside the standard deviation range.

On the basis of these results one could conclude that there is no significant difference in the physical properties of old and substitute 8161.

TABLE IV

COMPARISON OF SELECTED PHYSICAL PROPERTIES OF VARIOUS 8161 GLASSES

	Old 8161 +*		New 8161+		Substitute 8161+	
	Average Value	Standard Deviation	Average Value	Standard Deviation	Average Value	Standard Deviation
Softening Pt. (η-$10^{7.6}$p.)	598	3.5	598	1.3	599	1.5
Annealing Pt. (η-10^{13}p.)	437	2.1	439	1.8	439	1.2
Strain Pt. (η-$10^{14.5}$p.)	401	0.7	400	1.4	401	1.3
Expansion	90	0.3	90	0.7	91	1.1
Density	3.99 (Published)		3.99	0.01	3.99	0.01

+ The above date consists of the Emhart and Corning analyses (received from Mr. John Rennie).

* Includes Corning analysis from "Properties of Selected Commercial Glassew", Corning Glass Works (1971).

TABLE V

COMPARISON OF UCLA PHYSICAL DATA WITH OTHER LABORATORIES*

	Old 8161				Substitute 8161			
	UCLA		Other*		UCLA		Other*	
	Avg. Value	Std. Deviation	Avg. Value	Std. Deviation	Avg. Value	Std. Deviation	Avg. Value	Std. Deviation
Softening Pt.	601	2.7	598	3.5	602	5.0	599	1.5
Annealing Pt.	436	3.8	437	2.1	436	1.4	439	1.2
Strain Pt.	400	5.3	401	0.7	401	2.1	401	1.3
Expansion	89	1.2	90	0.3	89	0.6	91	1.1
Density	3.98	0.01	3.99 (Published)		3.98	0.01	3.99	0.01

* The above data is from Table IV.

2.3 Chemical Properties

2.3.1. Analysis of Chemical Composition

Chemical analyses have been performed on all of the MCP glasses received. (UCLA No. 10 was received to supplement UCLA No. 6). The laboratories performing the analysis, the experimental method used and the average variation are shown in Table VI. The laboratories are designated by the first letter of their name in subsequent tables and figures. The results shown for each sample represents the average of "duplicate analyses". In addition, results received from Mr. John Rennie have been included and are indicated as such.

The results of the chemical analyses performed on old 8161 (UCLA No. 1,2,7) and substitute 8161 (UCLA No. 5,6,10) are shown, respectively, in Tables VII and VIII. The combined average and standard deviations of the analyses for old and substitute 8161 are compared to the data supplied by Mr. Rennie in Table IX.

The individual analyses and their error limits are shown in Figs. 2 and 3 for old 8161 and in Figs. 4 and 5 for substitute 8161. In addition, the combined averages of these results and their standard deviations are compared to the data supplied by Mr. Rennie.

The chemical analyses of the other MCP glasses (UCLA No. 3,4, 8,9,11,12) are shown in Table X and compared to the corresponding analyses received from Mr. Rennie.

Results for Nos. 13 and 14 are shown in Table XI and a repeat analysis of No. 9 shown in Table XII.

TABLE VI

LABORATORIES PERFORMING ANALYSES AND THEIR ESTIMATED VARIATION

	(A) Analytical Research Lab., Inc. Monrovia, CA.		(C) Coors/Spectro-Chemical Laboratory Golden, Col.		(N) National Spectrographic Lab., Inc. Cleveland, Ohio	
Elements Determined	Analytical Methods*	Average Variation (wt. %)	Analytical Method*	Average Variation (wt. %)	Analytical Method*	Average Variation (wt. %)
PbO	G	±.10	G	±.08	G	±.25
SiO_2	G	±.08	G	±.07	G	±.25
K_2O	AA	±.12	AA	±.3†	AA	±.2
BaO	G	±.01	AA	±.2†	AA	±.15
Rb_2O	G	±.12	AA	±.2	AA	±.15
Na_2O	AA	±.04	AA	±.03†	AA	±.02††
Cs_2O	G	±.04	ES	±.1	AA	±.05
Bi_2O_3			G	±.1	AA	±.5
Al_2O_3	AA	±.05				
MgO	AA	±.005				
CaO	AA	±.005				

* G - Gravimetric (Wet analysis) Value of all 14 UCLA samples.
AA - Atomic absorption spectrophotometry
ES - Emission spectroscopy
† - UCLA No. 3 (BaO± .03, Na_2O ± .005), No. 4 (K_2O ± .4, BaO ± .01, Na_2O ± .2)
†† - UCLA no. 4 (Na_2O ± .2)

TABLE VII

CHEMICAL ANALYSES OF CGW - 8161 (old)

Elements Determined (wt.%)	UCLA No. 1 old 8161					UCLA No.2 NiTec old 8161	UCLA No.7 Varian old 8161	Combined Results (UCLA No. 1,2,7)	
	LAB A	LAB B	LAB N	Average Value	Standard Deviation	LAB C	LAB C	Average Value	Standard Deviation
PbO	50.03	48.09	50.48	49.53	1.26	48.66	48.38	49.13	1.06
SiO_2	38.30	38.94	39.56	38.93	0.63	38.92	39.52	39.05	0.52
K_2O	5.47	5.0	4.78	5.06	0.35	5.0	5.0	5.05	0.25
BaO	1.96	3.4	2.53	2.63	0.73	3.2	3.3	2.88	0.62
Rb_2O	2.60	3.3	2.11	2.67	0.60	3.3	3.2	2.90	0.53
Na_2O	0.65	0.34	0.27	0.42	0.20	0.25	0.31	0.36	0.16
Cs_2O	0.65	0.73	0.23	0.54	0.27	1.1	1.0	0.74	0.34
Total wt. %	99.66	99.8	99.96	99.81	0.15	100.43	100.71	100.11	0.44

TABLE VIII

CHEMICAL ANALYSES OF CGW-8161 (Subst.)

Elements Determined (wt. %)	UCLA No. 5 Litton 8161 sub.					UCLA No. 6 CGW 8161 sub.				COMBINED RESULTS UCLA No. 5,6	
	LAB A	LAB C	LAB N	Average	Standard Deviation	LAB C	LAB N	Average	Standard Deviation	Average Value	Standard Deviation
PbO	51.81	48.68	50.70	50.40	1.59	48.80	51.40	50.10	1.84	50.28	1.46
SiO_2	38.27	39.08	39.21	38.85	0.51	39.00	39.17	39.09	0.12	38.95	0.39
K_2O	6.02	5.2	5.38	5.53	0.43	5.3	5.18	5.24	0.08	5.42	0.35
BaO	0.69	3.3	1.97	1.99	1.31	3.3	1.77	2.54	1.08	2.21	1.11
Rb_2O	1.42	3.2	2.30	2.31	0.89	3.2	1.98	2.59	0.86	2.42	0.78
Na_2O	0.67	0.17	0.19	0.34	0.28	0.17	0.17	0.17	0.00	0.27	0.22
Cs_2O	0.70	1.1	0.22	0.67	0.44	0.90	0.21	0.56	0.49	0.63	0.40
Total wt.%	99.58	100.73	99.97	100.09	0.58	100.67	99.88	100.28	0.56	100.17	0.51

TABLE IX

COMPARISON OF THE CHEMICAL ANALYSES OF CGW-8161 (OLD AND SUBSTITUTE)

Elements Determined (wt.%)	Old 8161					Substitute 8161					Patent *** Composition
	UCLA		Other*	Selected Analyses**		UCLA		Other*	Selected Analyses**		
	Average	Standard Deviation		Average	Standard Deviation	Average	Standard Deviation		Average	Standard Deviation	
PbO	49.13	1.06	50.29	50.27	0.23	50.28	1.46	51.08	51.25	0.47	51.5
SiO_2	39.05	0.52	39.01	38.98	0.63	38.95	0.39	37.82	38.62	0.69	39
K_2O	5.05	0.25	5.60	5.28	0.44	5.42	0.35	5.73	5.58	0.37	5.1
BaO	2.88	0.62	1.88	2.12	0.35	2.21	1.11	1.76	1.83	0.12	1.8
Rb_2O	2.90	0.53	2.27	2.33	0.25	2.42	0.78	2.27	1.99	0.41	2.0
Na_2O	0.36	0.16	0.26	0.39	0.22	0.27	0.22	0.24	0.32	0.24	0.2
Cs_2O	0.74	0.34	0.42	0.43	0.21	0.63	0.40	0.47	0.39	0.23	0.2
Total wt. %	100.11	0.44	99.73	99.78	0.16	100.17	0.51	99.32	99.69	0.30	99.80

* The above data consists of Emhart analyses (received from Mr. John Rennie).

** Selected Analyses includes results from Lab A, Lab N and Emhart analyses.

*** "Glass Composition and Method of Makind It," R.H. Dalton and C.B. Hares (Corning Glass Works) U.S. 2,964,414, Dec. 13, 1960.

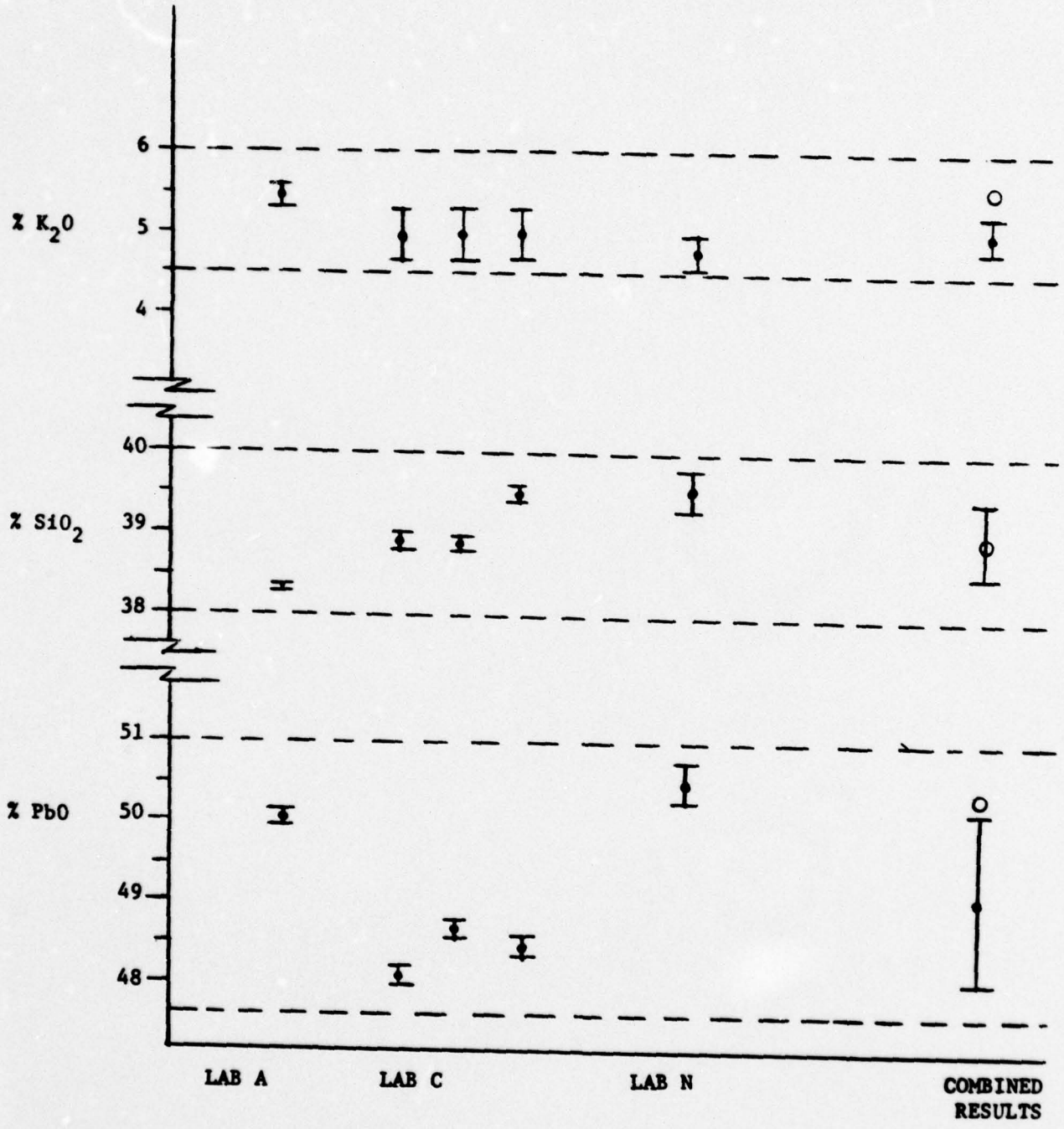


Fig. 2. A Comparison of Chemical Analyses for 8161 (old)
(O-Data received from Mr. Rennie)
●-Combined averages of analyzed results.

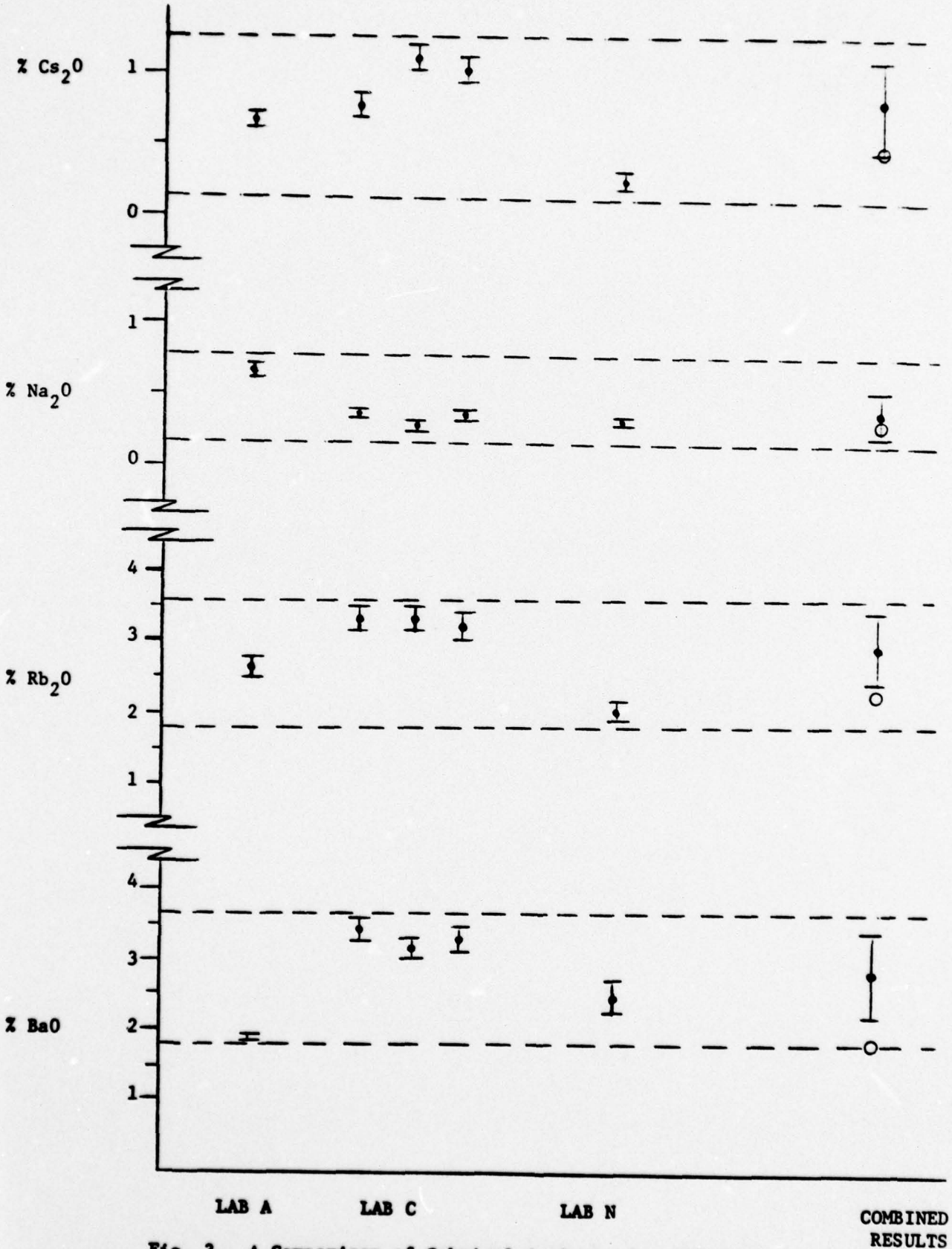


Fig. 3. A Comparison of Cehmical Analyses for 8161 (old)
(O-Data received from Mr. Rennie)
●-Combined averages of analyzed results.

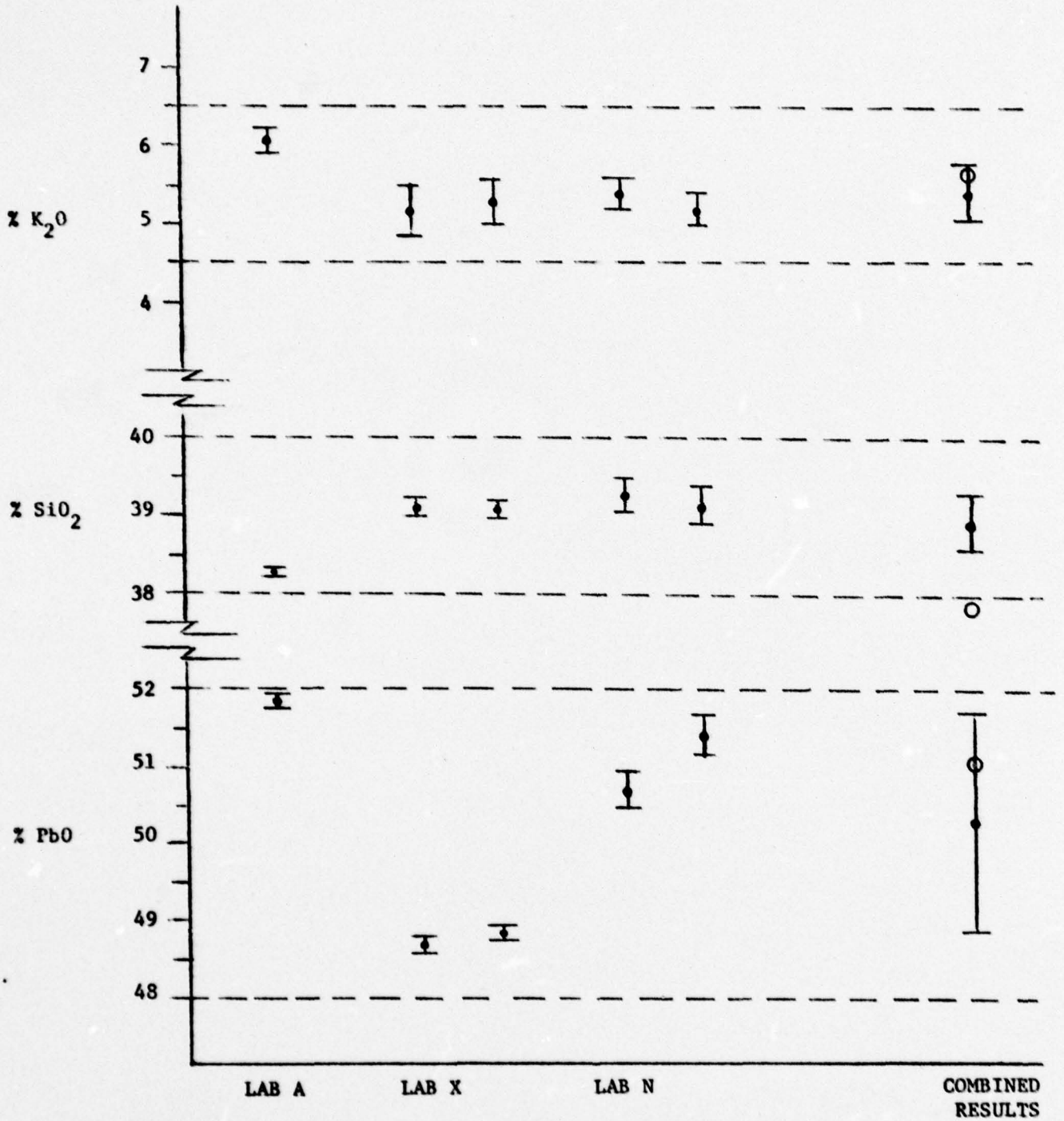


Fig. 4. A Comparison of Chemical Analyses for 8161 (Subst.)
(O-Data received from Mr. Rennie)
●-Combined averages of analyzed results.

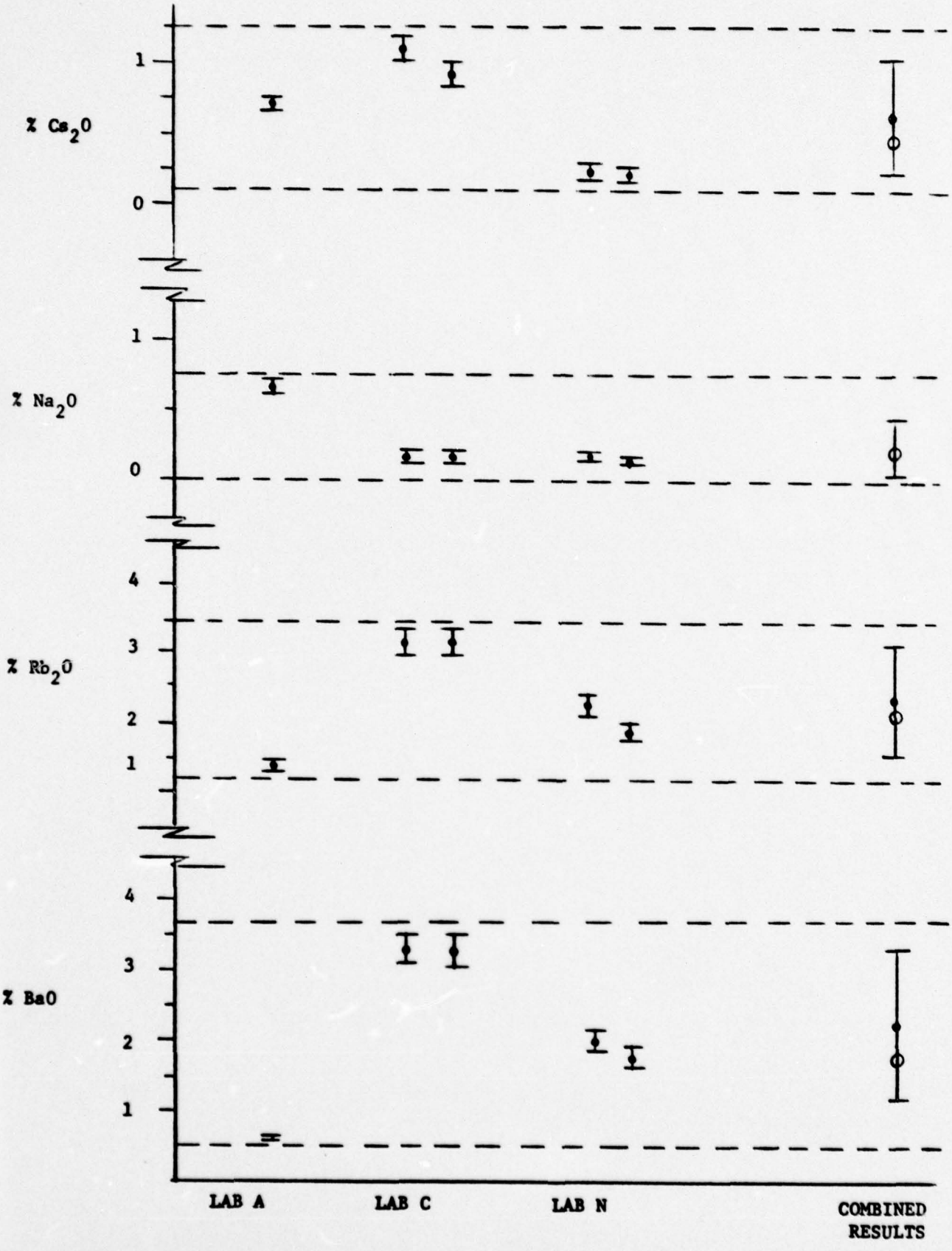


Fig. 5. A Comparison of Chemical Analyses for 8161 (Subst.)
(O-Data received from Mr. Rennie)
●-Combined averages of analyzed results.

TABLE X

CHEMICAL ANALYSES OF OTHER MCP GLASSES

Elements Determined (wt. %)	Schott 8531 (UCLA No.3)	Philips 3502 (UCLA No.4)				New 8161 (UCLA No.8)		GE-821 (UCLA No.9)		Engrg. Glass Prod. 2364 (UCLA No.11)	Hannibal Scientific SG-16 (UCLA No.12)
	LAB C	LAB C	LAB N	Average	Standard Deviation	LAB C	Other+	LAB A	Other+	LAB A	LAB A
PbO	58.77	27.01	27.68	27.35	0.47	48.68	51.86	54.50	53.99	57.60	57.5
SiO_2	34.50	49.02	49.80	49.41	0.55	38.76	37.51	36.73	37.66	35.84	35.7
K_2O	5.4	8.3	6.93	7.62	0.97	4.7	5.53	5.94	6.37	4.86	5.66
BaO	0.33	0.10	0.008	0.05	0.07	3.3	1.88				
Rb_2O						3.1	2.27				
Na_2O	0.05	4.5	4.52	4.51	0.01	0.72	0.24	0.47	0.56	0.23	0.30
Cs_2O						0.85	0.42				
Bi_2O_3		10.57	11.33	10.95	0.54						
Al_2O_3								2.32	1.59	1.11	0.27
MgO										0.21	0.02
CaO											0.06
Total wt.%	99.05	99.5	100.27	99.89	0.54	100.11	99.71	99.96	100.17	99.85	99.51

TABLE XI

CHEMICAL ANALYSES OF CGW-8164 AND CGW-8870

Elements Determined (wt.%)	CGW-8164 (UCLA No. 13) Lab* A	CGW-8870 (UCLA No. 14) Lab* A
PbO	44.8 ± 0.4	60.4 ± 0.3
SiO_2	45.9 ± 0.4	33.9 ± 0.3
K_2O	8.14± 0.08	5.37 ± 0.05
Na_2O	0.13± 0.01	0.17 ± 0.01
Bi_2O_3	0.98± 0.08	---
Total wt%	99.95	99.84

*See laboratory listings in Report No. 7.

TABLE XII

CHEMICAL ANALYSIS OF GE-821

Elements Determined (wt.%)	Lab* A				Other+
	Recent Analysis	Previous Analysis**	Average Value	Standard Deviation	
PbO	55.2 ± 0.2	54.50 ± 0.08	54.9	0.5	53.99
SiO_2	36.6 ± 0.2	36.73 ± 0.03	36.7	0.1	37.66
K_2O	6.04 ± 0.04	5.94 ± 0.02	5.99	0.07	6.37
Al_2O_3	1.32 ± 0.04	2.32 ± 0.01	1.82	0.70	1.59
Na_2O	0.59 ± 0.02	0.47 ± 0.00	0.53	0.08	0.56
BaO	0.20 ± 0.07	trace	0.10	0.14	--
Total wt.%	99.95	99.96	99.96	0.01	100.17

*See laboratory listing in Monthly Status Reports 4 or 5.

**See Table III, Monthly Status Report No. 6.

+The above data consists of Emhart analyses (received from Mr. John Rennie).

2.3.2. Discussion of Results of Chemical Analysis

Certain trends are evident in the chemical analyses, particularly those obtained for old and substitute 8161.

a] The chemical analyses performed by an individual laboratory on a particular glass sample shows some variation between samplings. This is demonstrated by the average variations obtained for "duplicate analyses" (Table VI).

b] In comparing the chemical analyses performed by different laboratories on a particular glass sample one observes certain discrepancies.

The results of Lab C are consistently lower in %PbO and higher in %BaO, $\%Rb_2O$, and $\%Cs_2O$ when compared to the other laboratories (Table VII and VIII). This difference probably results from the analytical techniques and standards used in the analysis. Since the values for %PbO and %BaO reported by Labs A and N (using different methods than Lab C) are in substantial agreement with the results received from Mr. Rennie (Selected Analysis, Table IX) one might questions the results of Lab C.

The value of %BaO received from Lab A for substitute 8161 (UCLA No. 5, Table VIII) appears to be low and was omitted in Selected Analyses columns of Table IX.

c] Some deviation is also apparent in the chemical analyses performed by the same laboratory on different samples of a particular type of glass (i.e. Lab N - %PbO in UCLA No. 5,6, Table VIII). This variation could presumably result from an actual difference in chemical composition between the two sample

glasses or, more likely, from human and inherent analytical errors since the difference is within the error limits (Table VI).

d] There is some variation between the analyses performed on both old and substitute 8161. The average values, however, generally fall within the combined standard deviation (Table VII and VIII).

In view of the results presented above it appears that there is no substantial difference in chemical composition between old and substitute 8161. This conclusion is reached on the basis of the numerous chemical analyses performed by several laboratories using a variety of experimental methods. When comparing all 14 MCP glasses, it is evident that there are large compositional variations among the samples.

2.3.3. Chemical Durability

Results on chemical durability in water and dilute HCℓ are shown in Table XIII. The techniques used are derived from ASTM recommended method (Ref. 4) for water durability and Shand's method for acid durability. (Ref. 3) The water durability tests indicated that these glasses are superior to common soda-lime glasses and are similar to pyrex glass. The acid durability results are similar to those published for high lead glasses and are inferior to soda-lime glasses.

2.4. Electrical Properties

The specific properties measured include secondary electron emission characteristics, electrical resistivity and dielectric constant. In

TABLE XIII

RESULTS OF WATER AND ACID DURABILITY

TESTS

UCLA Sample No.		ml.of 0.02N H_2SO_4 to Neutralize Extract (Trials)	Average	Wt. Loss (mg/cm^2) in 5% HCI, 100°C, 5 hr. (Trials)	Average
1	Old 8161	(11)	0.269	(8)	21.13
3	Schott 8531			(2)	67.79
5	Litton 8161 sub	(1)	0.324		
6	CGW 8161 sub	(3)	0.280	(3)	18.43
7	Varian old 8161	(3)	0.242	(3)	17.36
8	8161 Alcarb	(2)	0.315	(5)	19.25
9	GE 821	(5)	0.247	(5)	13.65
10	CGW 8161 sub	(1)	0.320	(4)	13.90
12	Hannibal SG-16	(3)	0.175	(3)	39.47
13	CGW 8164	(2)	0.265	(3)	2.33
14	CGW 8870	(4)	0.228	(3)	93.82

the following section, the reduced samples mentioned were prepared by treating in a controlled atmosphere (99.99% H_2, -75°F dew point) furnace using a firing schedule suggested by Mr. Emil Straka of Varian Associates.

2.4.1. Secondary Electron Emission

One of the most important properties in the analysis of MCP glass samples is secondary electron emission characteristics. The apparatus used in determining the secondary characteristics is essentially the same as that used in previous studies of secondary emission of glass (Ref. 5). A pulse technique (Ref. 6) was utilized. A schematic of the apparatus is shown in Figure 6.

The secondary apparatus was standardized using both platinum and soda-lime targets. These results, shown in Figure 7 and 8 respectively, are in substantial agreement with published work (Ref. 7 and 8). On the basis of these results the variation in secondary yield measurements is estimated to be ±10%. Measurements were made on all samples except No. 11 (Engr. Glass Products No. 2364). In general the secondary yield curves all resemble those shown in Figure 9 and 10 for glass No. 2 and No. 9 respectively, where δ_{max} for the reduced glass is somewhat higher than that of the unreduced sample. Despite large variations in chemical compositions and physical properties, the secondary electron emission characteristics, measured by the above techniques and under the present conditions, do not appear to vary significantly from sample to sample. This com-

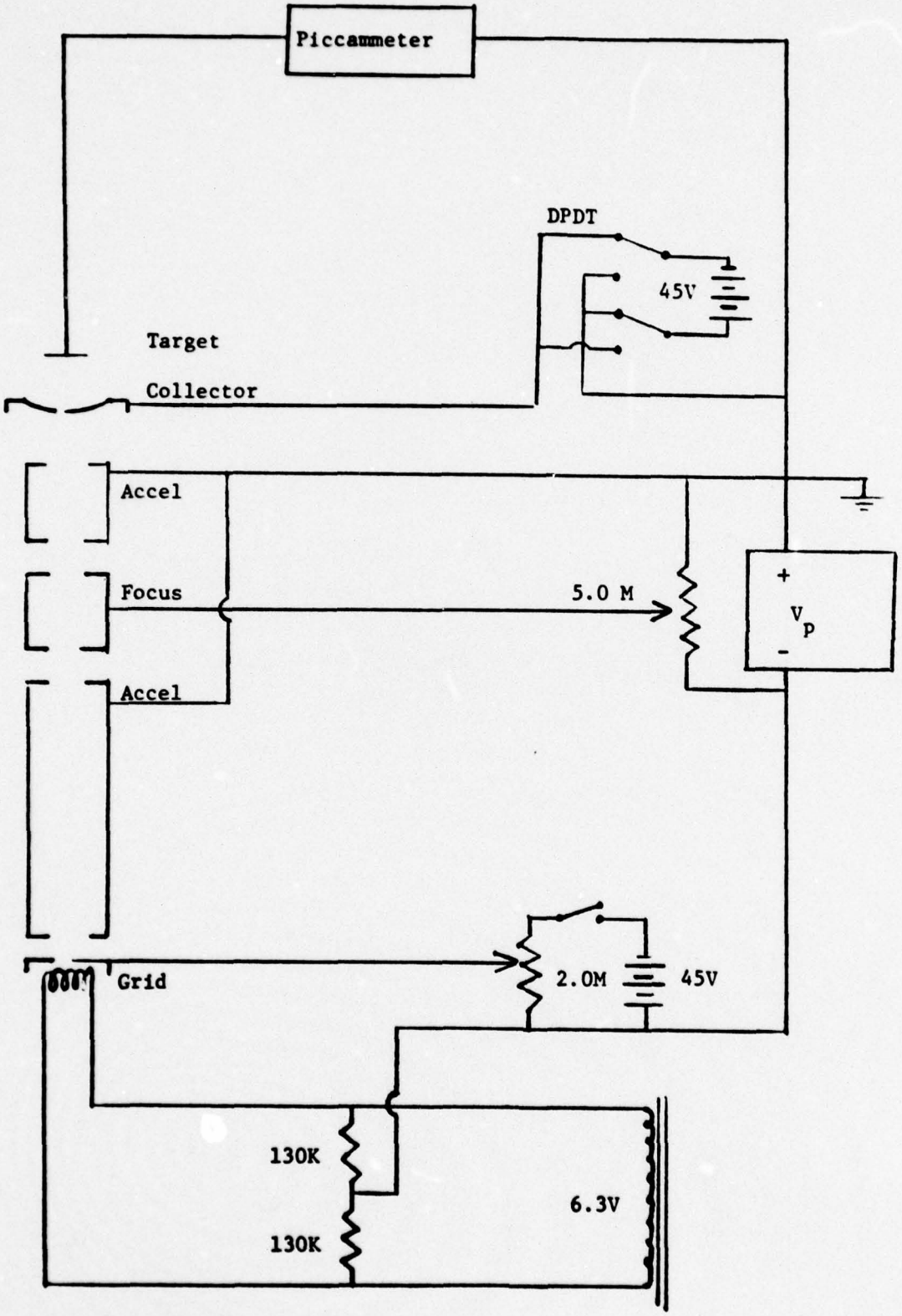


Fig. 6. Schematic Diagram (target bias method) of Apparatus for Measuring Secondary Electron Yields.

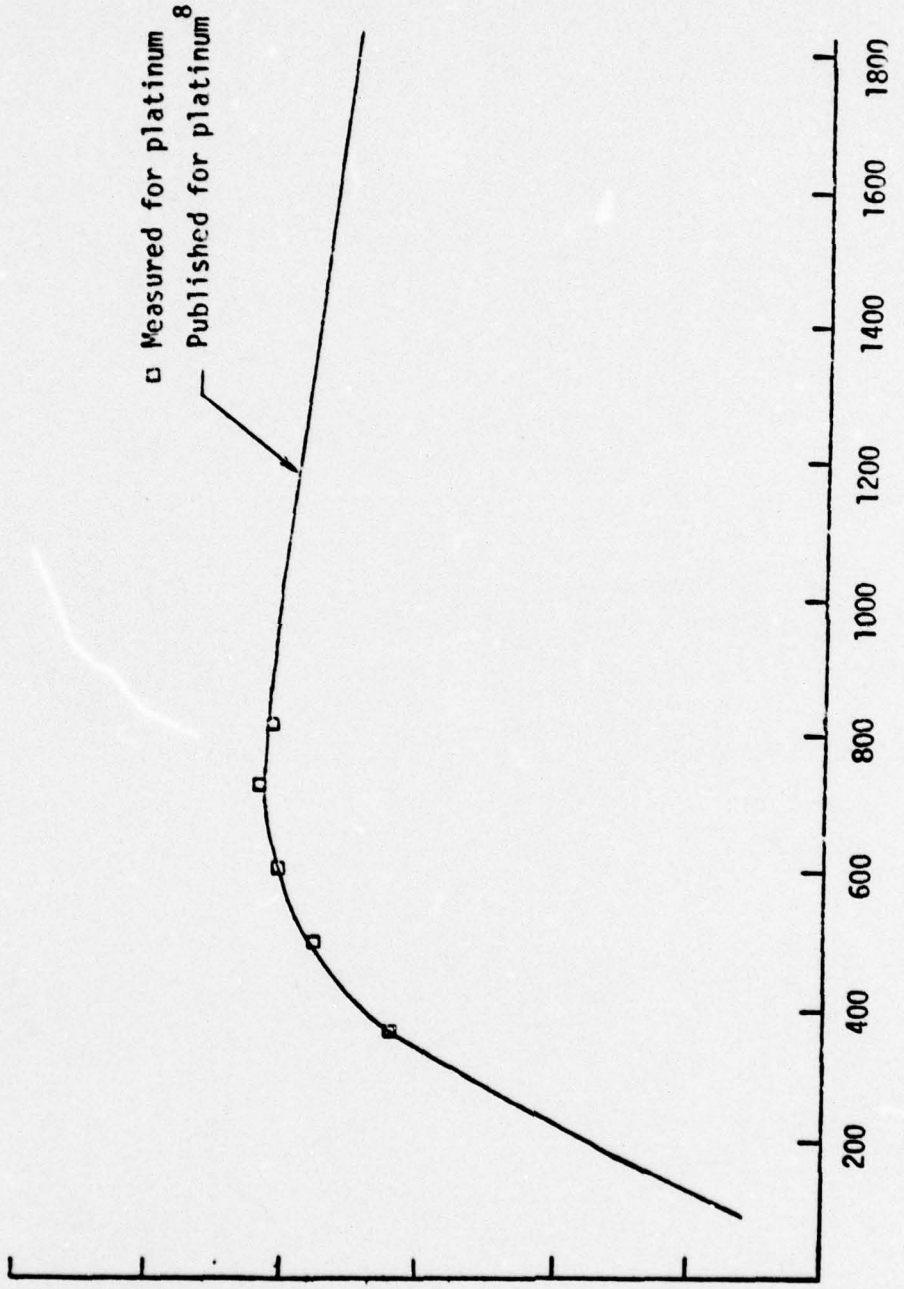


Fig. 7. Standardization results for platinum.

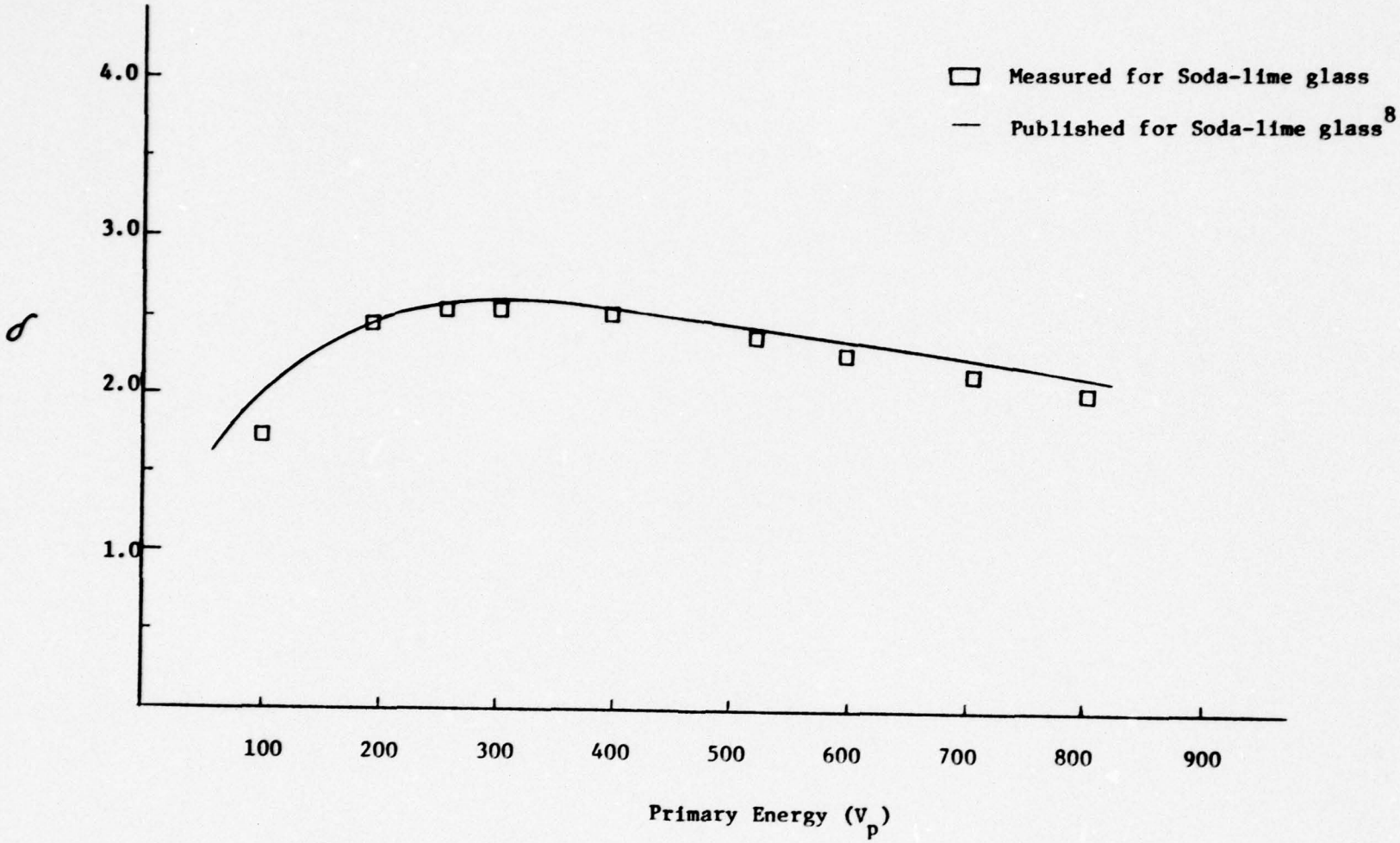


Fig. 8. Standardization Results for Soda-lime glass.

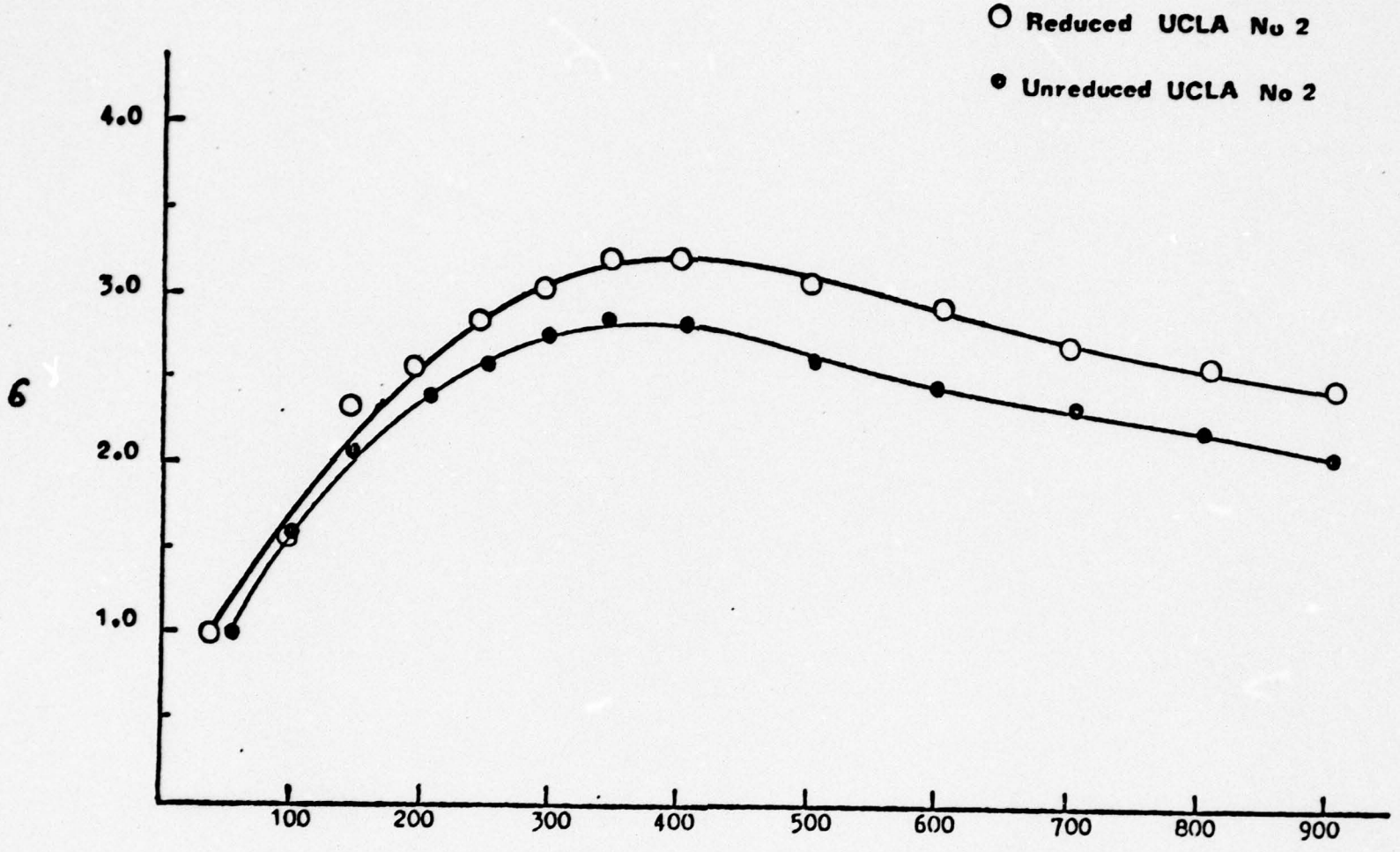


FIGURE 9. Secondary yield of old 8161

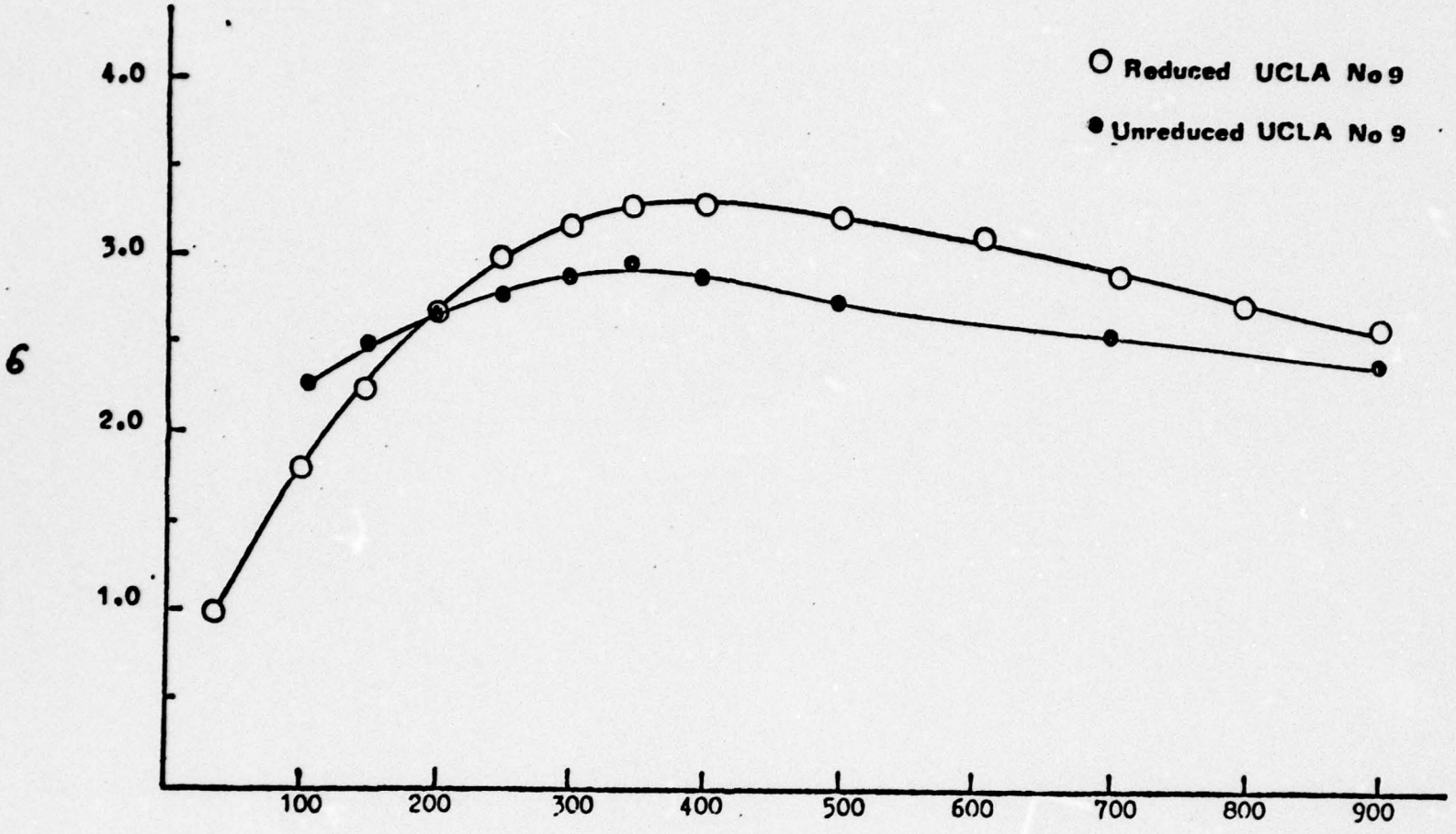


FIGURE 10. Secondary yield of GE No. 821

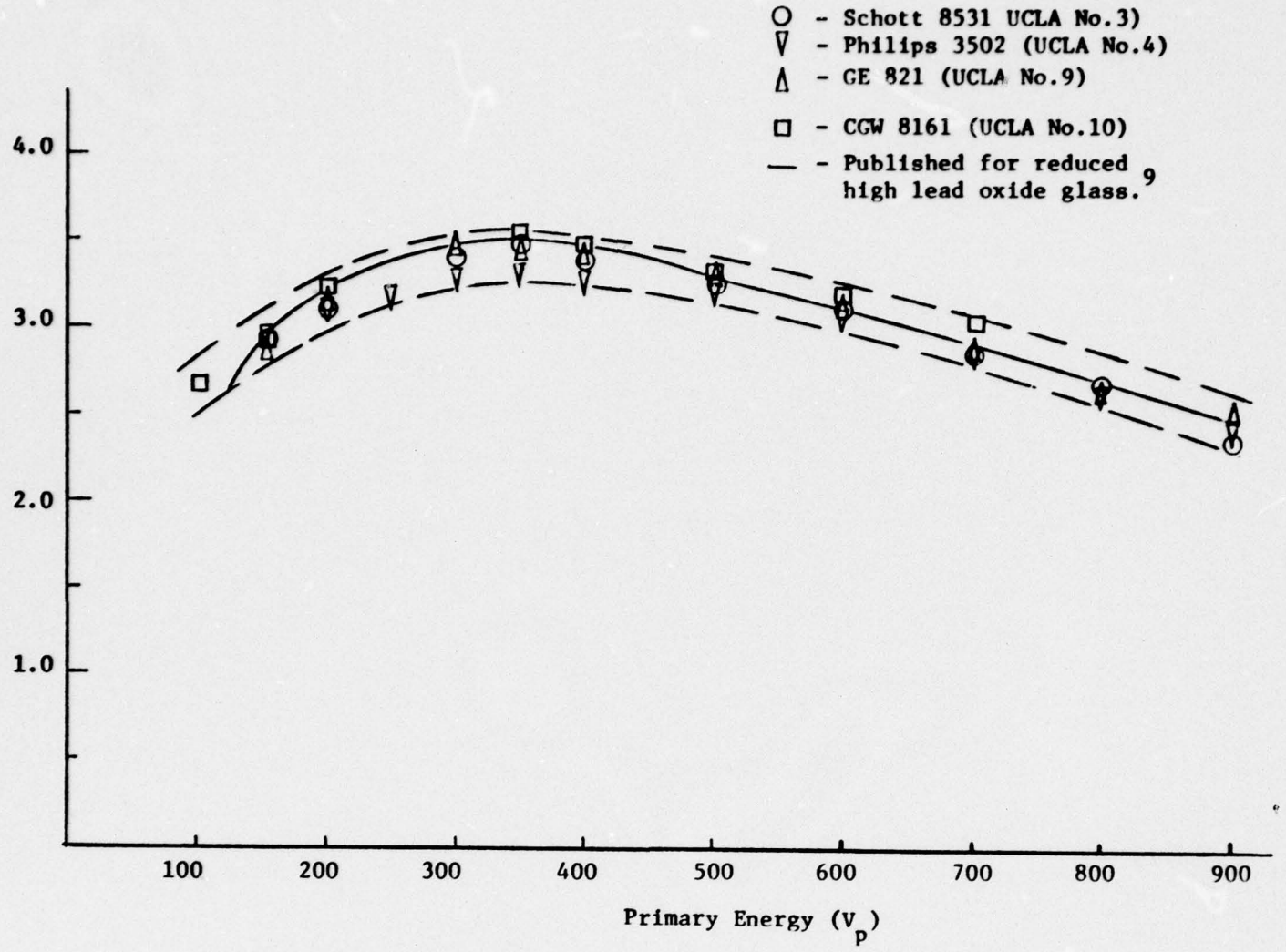


Fig. 11. Comparison of Secondary Yields for several Reduced Glasses.

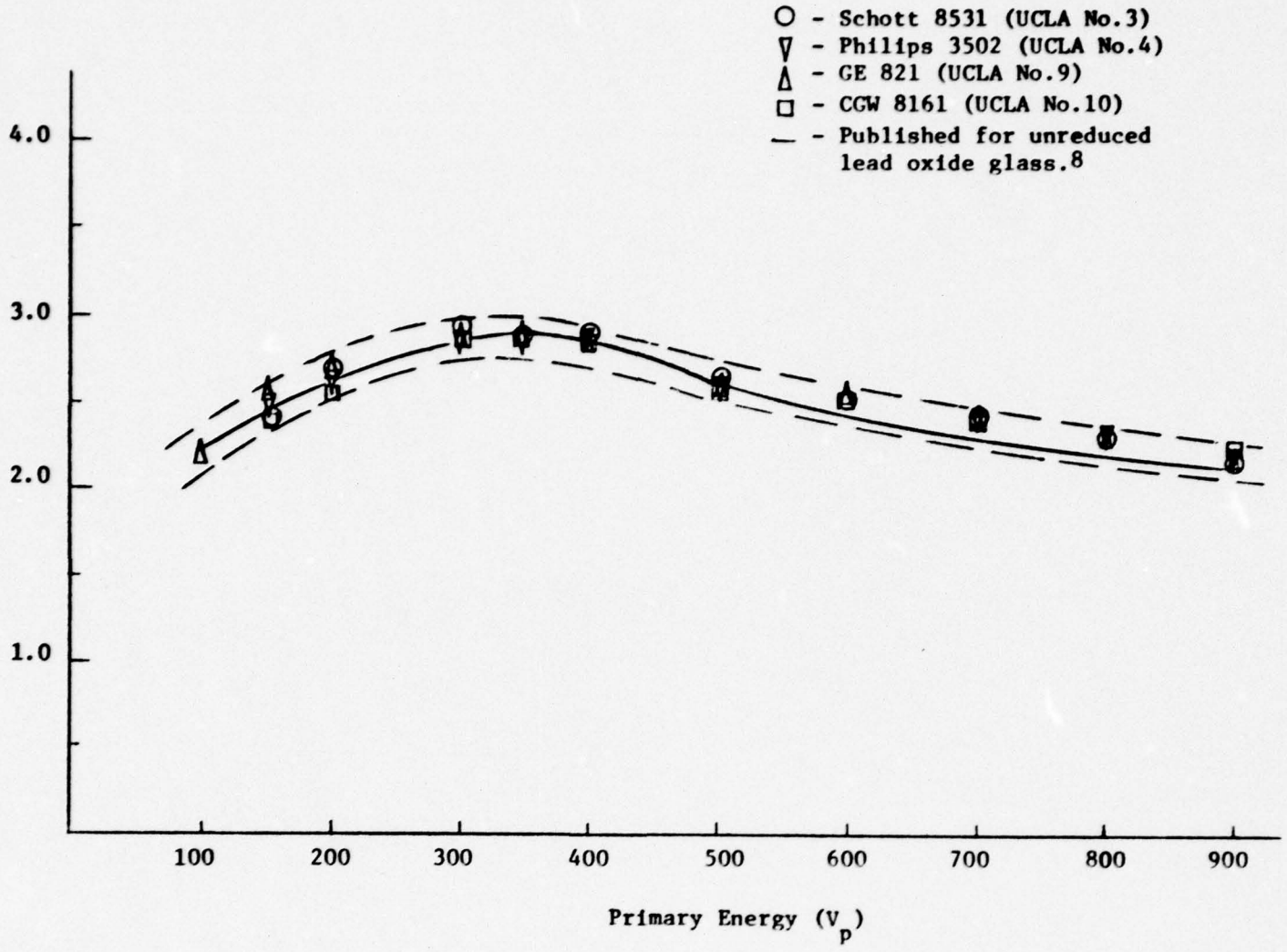


Fig. 12. Comparison of Secondary YIelds for several Unreduced Glasses.

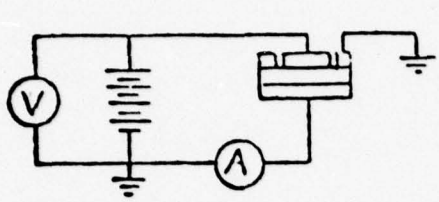
parison is shown for both reduced and unreduced samples in Figures 11 and 12 respectively. The small variations are unexpected. At present there is no explanation for this behavior.

2.4.2. Electrical Resistivity

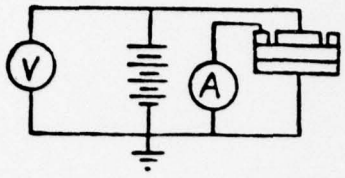
Measurement of the volume and surface resistivities of all unreduced and reduced glass samples has been performed in air at elevated temperatures using a direct measurement technique (Ref. 10 and 11). The measuring circuit, sample holder, and electrode configuration are illustrated in Figure 13.
The surfaces of the resistivity specimens are ground to approximately 240 mesh finish to ensure uniformity between specimens. The specimens are typically 25.4 mm in diameter and 2 mm thick.

All the results are shown in Table XIV. A series of measurements were also made in a nitrogen atmosphere to check for any deleterious effects of air, particularly on the reduced resistivities. Results obtained indicated that the difference between the resistivity values in air and nitrogen is not significant.

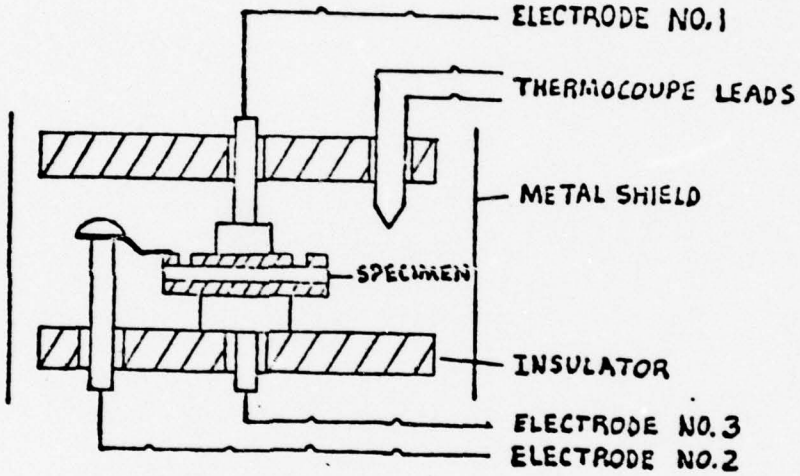
The electrical resistivity results shown in Table XIV indicate that the reduced and unreduced volume resistivities of old and substitute 8161 are substantially the same, and compare well with literature values. In the case of surface resistivity (reduced glasses only), there also appears to be little difference between old and substitute 8161.



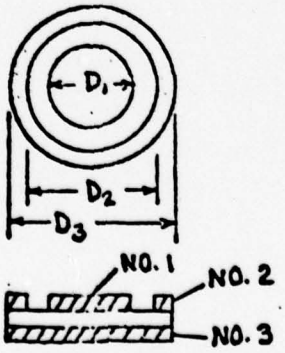
a) volume resistance



b) surface resistance



b) specimen holder



c) electrode configuration

Fig. 13. Apparatus for measuring resistance.

TABLE XIV

ELECTRICAL RESISTIVITIES OF MCP GLASSES

UCLA Sample No.	Unreduced		Reduced			
	Log_{10} of Volume Resistivity		Log_{10} of Volume Resistivity		Log_{10} of Surface Resistivity	
	250°C	350°C	250°C	350°C	250°C	350°C
1 Old 8161	11.7	9.8	11.4	9.6	12.2	10.7
2 NiTec old 8161	11.8	9.8	11.4	9.6	11.9	10.4
3 Schott 8531	11.2	9.3	11.1	9.1	11.7	9.7
4 Philips 3502	10.0	8.2	9.8	7.9	9.9	8.4
5 Litton 8161 sub	11.8	9.7	11.6	9.7	11.9	10.4
6 CGW 8161 sub	11.8	9.9	11.5	9.5	11.9	10.3
7 Varian old 8161	11.8	9.8	11.5	9.7	11.9	10.4
8 8161 Alcarb	11.8	9.9	11.6	9.7	11.7	10.0
9 GE 821	11.6	9.4	11.3	9.3	11.4	9.7
10 CGW 8161 sub	11.7	9.8	11.5	9.6	12.0	10.5
11 EGP 2364	11.2	9.3	11.2	9.3	11.5	9.6
12 Hannibal SG-16	11.3	9.4	11.2	9.3	11.5	9.7
13 CGW 8164	11.2	9.3	11.2	9.3	12.1	9.8
14 CGW 8870	11.2	9.2	11.2	9.2	11.7	9.3

TABLE XV

DIELECTRIC PROPERTIES

UCLA No.	Power Factor %	Dielectric Constant	Loss Factor %
1	0.06	8.59	0.52
2	0.08	8.59	0.69
3	0.12	9.88	1.19
4	0.04	7.79	0.31
6	~ 0.06	8.35	~ 0.50
7	~ 0.06	8.55	~ 0.51
8	~ 0.06	8.57	~ 0.51
9	~ 0.06	9.21	~ 0.55
10	0.09	8.47	0.76
12	~ 0.06	9.89	~ 0.59
13	~ 0.06	7.68	~ 0.46
14	~ 0.06	9.49	~ 0.57

2.4.3. Dielectric Properties

The dielectric properties have been measured using a General Radio Company impedance bridge (Model No.1608-A) in accordance with ASTM Standards (Ref.12). The dielectric samples were ground to a 000 mesh finish and ultrasonically cleaned in acetome before deposition of gold electrodes. The samples were typically 25.4 mm in diameter and 2 mm thick. A three electrode configuration, similar to that used in resistivity measurements was used for the dielectric measurements. Results are shown in Table XV for all the samples tested. The dielectric constant values are fairly normal for these type of glasses. The loss factor and the power factor of the Schott 8531 are significantly higher than the results for the other glasses. There is no explanation at present for this behavior.

3. AN ALTERNATIVE METHOD TO FABRICATE MCP

A number of alternative methods were considered. Of these the photosensitive glass technique appears to hold the best promise. Accordingly, after consultation with NVL personnel, this method was adopted for experimental development.

This method of fabrication is based upon the selective exposure with ultraviolet light of a photosensitive glass to create nucleation sites (Ref.13). Typically a lithia-aluminosilicate glass with minor additions of metallic chlorides (e.g. AgCl) and cerium oxide (CeO_2) is utilized (Ref.13-15). Upon exposure to ultraviolet light or similar radiation metallic particles (colloids) are formed as follows:

$$Ce^{3+} \xrightarrow{h\nu} Ce^{4+} + e^{-} \quad (1)$$

$$Ag^{+} + e^{-} \rightarrow Ag^{\circ} \quad (2)$$

$$nAg^{\circ} \rightarrow (Ag^{\circ})n \quad (3)$$

These metallic particles act as nucleating sites for selective crystallization during subsequent heat treatment. The crystallized regions have a lower chemical durability than the original glass and can be preferentially etched to form holes.

In this section, the progressive development of the method is summarized. Then the conditions to fabricate the best MCP to date are presented. Finally recommendations are made regarding an advanced experimental program to perfect this new method.

3.1. Important Process Variables

Although the photosensitive glass method has been used to "chemically machine" holes in glass, the technique was not known to have been applied to the fabrication of MCP. Not only are the channels very small and closely spaced, but the glass must have the required electrical properties. Thus many process variables must be considered. These include:

- Glass chemical composition
- Type of UV radiation, lamp vs laser
- Wavelength of UV radiation
- Exposure times and dosages
- Nucleation conditions
- Crystallization conditions
- Etching conditions

Rendering glass surface electronically conductive

A great deal of experimental work was performed to investigate the above variables. These are described below.

3.1.1. Glass composition

Many glass compositions were tested. The final glass composition selected for this study was as follows. The composition was obtained by chemical analysis.

Component	wt%
SiO_2	78.4
Li_2O	10.1
Al_2O_3	3.95
K_2O	3.42
Na_2O	3.49
ZnO	0.6
CeO_2	< .01
Ag_2O	0.07
Total	100.04

3.1.2. UV Radiation

Initially, a mercury UV-lamp, 200 watts, 3200Å wavelength, was used. Because of light scattering and refraction, UV lasers were used afterwards. The lasers tested are summarized below:

Company	Liconix Mountain View	Spectra Physics Mountain View	Molectron Sunnyvale
Laser Source	He-Cd (cw)	Ar (cw)	N_2 - (pulse)
wavelength	3250 Å	3511, 3634 Å	3371 Å
power	1.8 or 7 mw	0.02 - 0.16 mw	0.5 - 2.75 w
exposing time	1 - 600 sec	1 - 30 sec	1 - 10 sec
total energy	2 - 1000 mj	0.01 - 5 mj	300 - 10^4 mj

Of the three tested, the He-Cd laser (3250 Å) was the most effective.

3.1.3. Masks

Single aperture metal grids were first tested. Eventually, copper screens used in electron microscopy with hole sizes from 12.5μ to 180μ were used.

3.1.4. Irradiation Process

A special sample holder was designed and constructed on which the mask was clampled against the glass sample and this assembly placed behind a camera shutter. The exposure time was controlled by the shutter which faces the He-Cd laser.

3.1.5. Heat Treatment

The heat treatment process consisted of two steps-nucleation and then crystallization. In general, for this type of glass, nucleation is considered to occur from 350° to 550°C whereas crystal growth occurs from 550° to 600°C. The crystalline phase which appears is $Li_2O \cdot SiO_2$. At higher temperatures, another crystalline phase, $Li_2O \cdot 2SiO_2$ is the stable phase.

The optimum heat treatment process must take into consideration the glass-transition temperature of the glass (433°C) and the nucleation rate and growth rate. This is because rapid heating to temperatures above the glass transition temperature will cause deformation of the sample. Thus nucleation must be controlled such that it will be sufficient and yet not too rapid. As nucleation proceeds, the glass "stiffens" and so the temperature is raised to above the glass-transition temperature. Differential Thermal Analysis gives information on temperature of on-set of nucleation and maximum growth temperature and X-ray identifies the crystalline phases forming. From DTA and X-ray analyses the following sequence was selected to be optimum:

a) Heating - 150°C per hr to 530°C

b) Nucleation - 530°C for 30 minutes

c) Growth - 560°C for 40 minutes

d) Cooling - 200°C per hr

3.1.6. Etching

After heat treatment, that portion of the glass which was exposed to the UV has now undergone substantial crystallization. It consists of $Li_2O \cdot SiO_2$ crystals embedded in a glassy matrix. An etchant must be selected to attack this glass-crystal composite phase in preference to the unexposed glassy phase. Thus although the solubility difference between the original glass and $Li_2O \cdot SiO_2$ is of prime importance, the overall etching process is more complex. Further, as the etchant attacks the crystallized portion to form a hole, it will also slowly attack the unexposed portion of the glass. As the hole progressively gets deeper it will very slowly get wider as well. In the design of

the MCP of a certain D/d ratio, where d is the final hole diameter and D is the thickness, this must be considered. If d_o is the diameter of the originally crystallized portion of the sample,

$$d = d_o + D/x \tag{1}$$

where x is the solubility differential between the crystallized portion and the unexposed glass, and

$$x = \frac{\partial D}{\partial t} \Big/ \frac{\partial d}{\partial t} = \frac{\partial D}{\partial d} \tag{2}$$

Many acids were evaluated and finally a 4 wt% HF in H_2O solution was selected as the acid. This acid was mixed with a variety of organic liquids to form the etchant solution and tested at different temperatures. Some examples of these are shown below:

Etching Solutions	Temperature (°C)	Solubility Ratio Crystal/Glass
(1) 4% HF (80 w/o) Methyl alcohol (20 w/o)	0°C	50
(2) 4% HF (80 w/o) Ethyl alcohol (20 w/o)	0°C	42 - 46
(3) 4% HF (80 w/o) Butyl alcohol (20 w/o)	0°C	54
(4) 4% HF (80 w/o) Benzyl alcohol (20 w/o)	0°C	58
(5) 4% HF (80 w/o) Methyl acetate (20 w/o)	0°C	56
(6) 4% HF (80 w/o) Propyl acetate (20 w/o)	0°C	62

Equipment was designed to permit magnetic stirring to give an efficient etching rate with the samples mounted in the etchant.

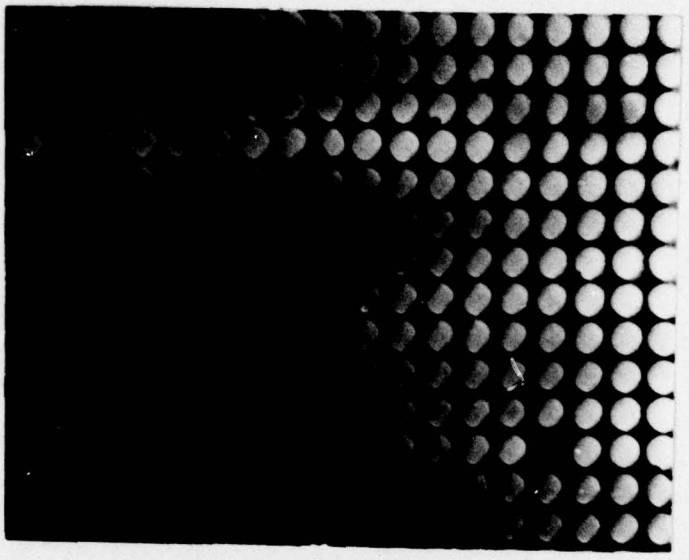
3.1.7. Typical Channel Plates Made

With the use of masks having hole size of 12.5μ, the best channel plates were made with final hole sizes of 15μ, the plate thickness being 480μ. (D/d ratio of 32). Typical photomicrographs are shown in Figure 14 and Figure 15.

3.1.8. Sub-Surface Electronic Conduction

The type of photosensitive glass used in these experiments is fairly highly insulating. The electrical volume resistivity of the glass at 25°C is about 3×10^{12} ohm-cm. Such glasses will not be useful as MCP's unless they can permit some degree of electronic conduction under an electric field. To introduce electronic conductivity, the glasses were immersed in a fused salt containing either Ag^+ ions or Cu^+ ions, after the channels had been made. The Li^+ and/or the Na^+ ions in the glass exchanged with the Ag^+ or Cu^+ ions. The degree of exchange and the depth of the exchanged layer could be controlled by time and temperature. After exchange, the resistivity at 25°C is about 8 x 10" ohm-cm. After the desired degree of ion exchange, the samples were cleaned in distilled water, dried and then fired in hydrogen. The Ag^+ and Cu^+ ions were reduced to the atomic states similar to the process of hydrogen-firing of the lead silicate glasses currently used in MCP production. The atomic silver and copper then form "aggregates" or "islands" and provided the needed electronic conduction.

This phase of the work has not been completed. Preliminary results suggested that $AgNO_3$ was the best salt to use and that Ag^+ exchange was better than Cu^+ exchange. Typically, the samples



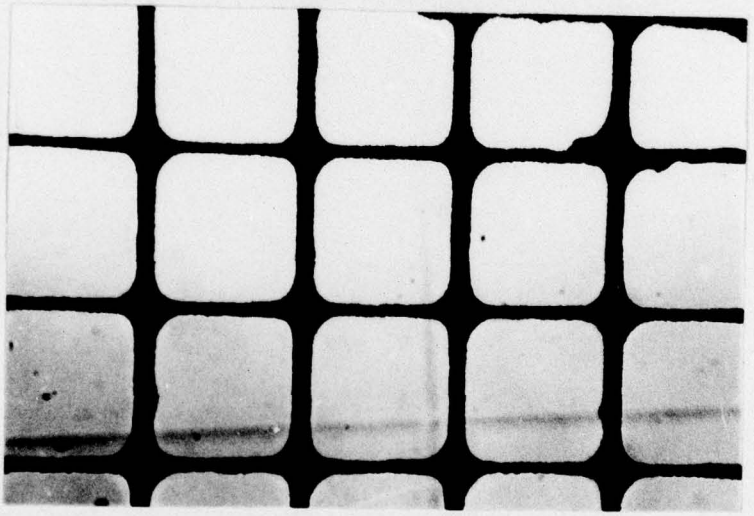


Fig. 14. Typical etched sample with
(a) 40μ round holes; (b) 225μ square holes

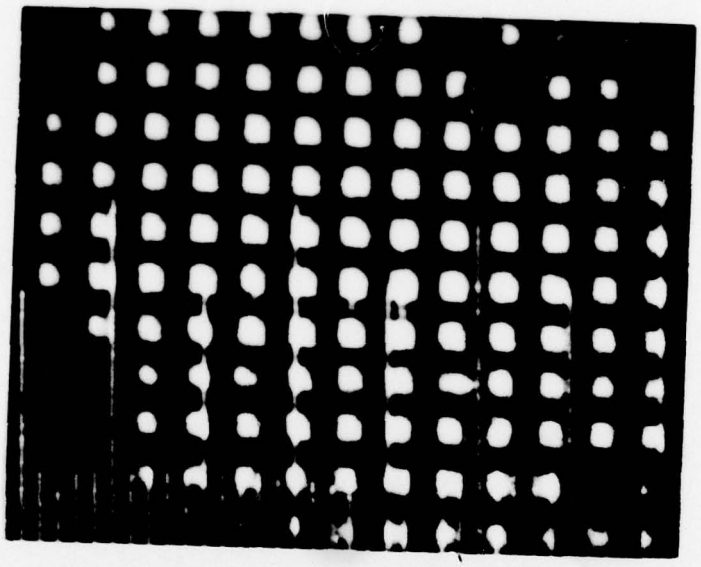


Fig. 15. Typical etched sample with 15μ square holes.

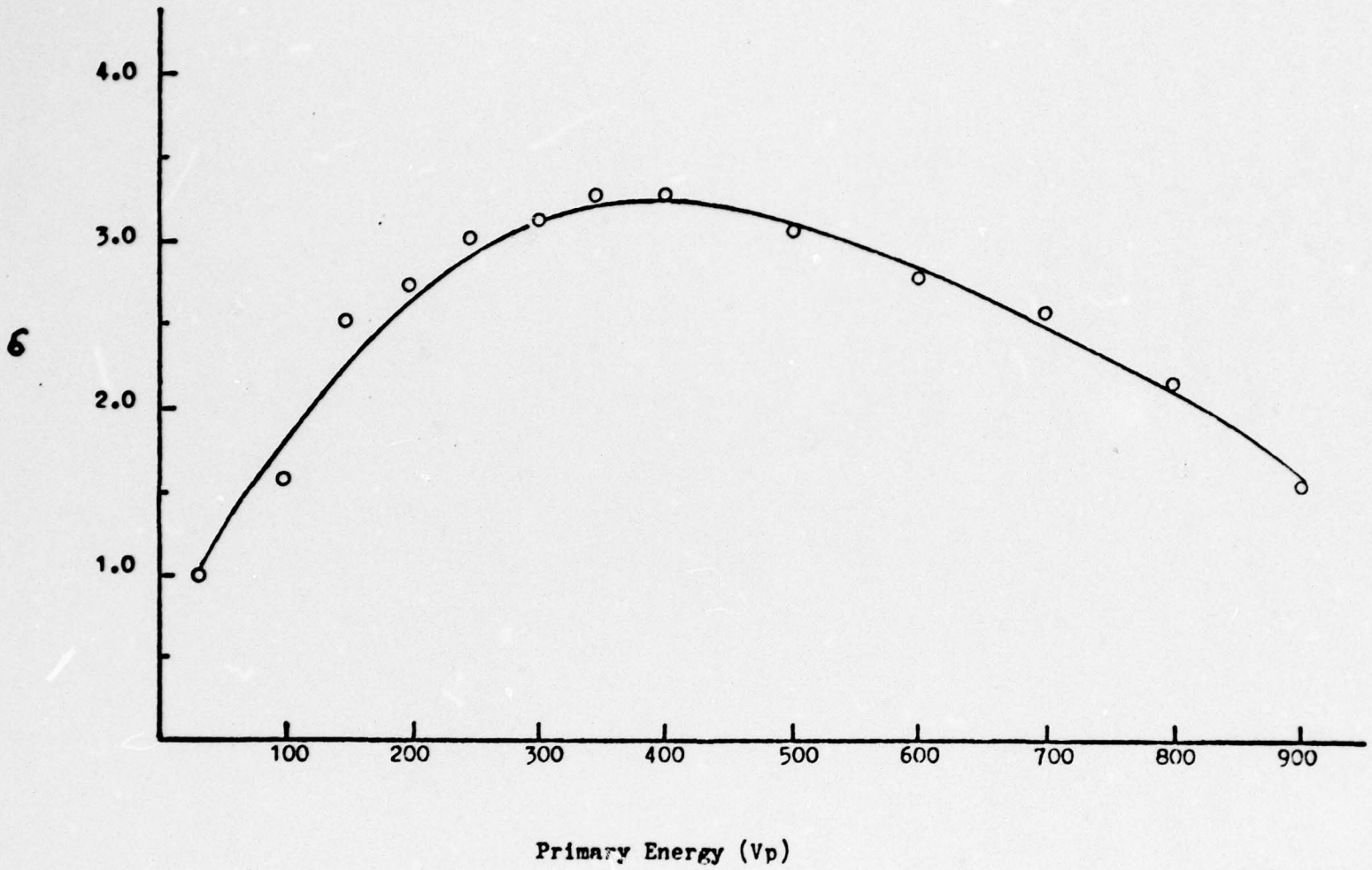
were immersed in $AgNO_3$ at 330°C for 10 minutes. Reduction in hydrogen was carried out at 425°C for 30 minutes. After reduction the surface resistivity carries from 4 x 10" ohm-cm to 8 x 10" ohm-cm. This small variation after reduction is similar to the behavior of lead silicate glasses. Although the resistivity is high, the dark color of the glasses after reduction is indicative of the possibility of electronic conduction under an applied field.

3.1.9. Secondary Electron Emission of New MCP Glass

The secondary electron emission of the photosensitive glass, after ion-exchange with $AgNO_3$ and reduction in hydrogen, is shown in Figure 16. The value of δ_{max} of 3.3 is similar to that for lead silicate glasses in use. It is not certain at the moment if δ_{max} can be significantly improved by changing glass compositions or by changing the processing variables such as ion-exchange time and temperature, etc.

3.2. A Tentative Alternate Process for MCP

Details governing a complex industrial manufacturing process to fabricate MCP's can obviously only be obtained after exhaustive efforts in research and development. The current research project has not really been completed. However, the results have been highly encouraging and hence a tentative process can be presented. It is proposed that the glass composition shown in Section 3.1.1. be adopted. The bulk glass made can be in the form of stamped thin discs or large cylindrical rods. A special metal mask must be made with the correct hole size (e.g. 7μ). Irradiation should be made with a He-Cd laser of 3250 Å wave-length for ¼ to 1



(Fig.16) Secondary yield of the ion exchanged sample ($AgNO_3$)

second delivering about 0.5 to 1.0 mj of energy. After exposure, the samples should be heat-treated in air at 530°C for 30 minutes and 560°C for 40 minutes. Thereafter the irradiated discs are etched in a stirred solution of 4% HF (80 weight %) in propyl acetate (20 weight %) at about 0°C. For a disc of thickness about 500μ, the etching time is about 3 hours. After etching, the acid solution is removed by washing in distilled water. The dried channel plate is then immersed in fused $AgnO_3$ at 330°C for 10 minutes for ion-exchange. The exchanged sample is then cooled and excess $AgNO_3$ washed off in distilled water. The dried sample is then fired in hydrogen for 30 minutes at 425°C. The process is completed by putting electrodes on the channel plate.

3.3. Recommendations for an Advanced Development Program to Perfect the Alternative Method for MCP.

The present program has resulted in a tentatively new proposed method to fabricate MCP's with the use of photosensitive glass. An advanced development program should be initiated as the next phase. This program should have two main objectives. These are:

a) Optimization of Materials and Process.

It is improbable that the glass composition selected, the heat-treatment, the etching, the ion-exchange and the reduction are the optimum ones possible. Both materials and process must be optimized so that the best MCP's can be made. The economics of the process and steps to impose quality control for each phase of the process must be considered.

b) Actual Production of a Limited No. of MCP's for Testing.

In parallel with the optimization step, the second objective should be to produce a number of MCP's for actual testing in devices.

It is estimated that the above advanced program will take 12 to 18 months to complete.

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