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QUARTZ CRYSTAL AGING EFFECTS

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TABLE OF CONTENTS

(Continued)

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

Figure Page

LIST OF FIGURES (Continued)

LIST OF TABLES

I. PURPOSE

The purpose of this research was to reduce the aging and failure rates of quartz resonators, thereby increasing their reliability. The investigation examined the effects of various materials, fabrication techniques, and operating conditions on aging and reliability. In the first phase of the work the stabilities of resonators fabricated of natural, swept natural, cultured, and swept cultured quartz were examined; and the stabilities of resonators constructed of the various types of quartz and exposed to selected types of radiation, principally gamma, were determined.

In the second phase additional research on the aging of low-frequency resonators and on the aging of 3 MHz, 5 MHz, and 10 MHz AT-cut resonators was conducted. For the low frequency units, evaluations with regard to frequency stability were made for the effects of edge finish. The behavior of resonators plated for annular-field excitation was investigated and measurements of the reliability of 10 MHz resonators at 125 and 85°C were completed.

Methods of x-ray diffraction topography were applied for examination of the various units to correlate defect structure with aging, when feasible, and to aid in determining causes for failures or anomalous aging behavior.

II. SUMMARY

The purpose of this research is to reduce the aging and failure rates of quartz resonators, thereby increasing their reliability.

Aging measurements at 85°C of low frequency units ranging in frequency from 81.9 to 500 kHz and having edge finishes of "state-of-the-art", semi-polished, polished, and polished-plus-etched have been made for over 9000 hours. The aging of the groups was 0.36, 0.46, 0.51, and 0.35 ppm/week respectively indicating no improvement in aging as a result of edge polishing. The aging of resonators, of SL and CT-cuts and of 455 and 500 kHz frequency, exhibited no recognizable difference.

The average aging rate at 85°C of AT-cut 3 MHz resonators (123) was found to be 2.0 pp10^9/week over a 10,000 hour measurement period. Aluminum plated units averaged 1.2 pp10^9/week versus 2.3 pp10^9/week for gold plated ones. The average Q values were 1.2 and 0.75 x 10^6, respectively.

Annular field excitation of plano-convex 5 MHz units reduced the average aging rate to 1/10 that for the conventionally plated control specimens. Successful frequency adjustment of the annular plated elements was conducted by etching the quartz after the application of electrodes. Frequency spectrum analysis of the units indicated no additional responses as a result of annular field excitation. However, the fundamental response was attenuated about 25 db.

Aging studies of 10 MHz units at 125°C indicated that aging was holder dependent. Units in the HC-27/U holder were superior to those in the T-5$\frac{1}{2}$, indicating serious outgassing or gas pressure problems in the latter container.

X-ray diffraction SID studies of 5 MHz plano-convex and 5 MHz plane-parallel, beveled-edge units of $\frac{1}{2}$" diameter indicated that the oscillation of the former was confined to a central zone of 3/16" diameter whereas for the latter it spread over the entire plane-parallel zone (0.340"). Hence, the plano-convex units could be excited by an annulus external to the active zone but the others could not be so excited. The Q values for the plano-convex units were greater by a factor of about four.

III. FACTUAL DATA

A. INTRODUCTION

Aging studies of about 300 quartz resonators in the frequency range 81.9 kHz to 30.0 MHz* stored at 85°C have been made. Frequency measurements of one group of 10 MHz units stored at 125°C were performed.

The 3 MHz units with conventional electrodes and the 5 MHz units with both conventional and annular electrodes were mounted and sealed in HC-27/U glass holders. In addition, approximately 35 units were mounted in holders sealed by cold welding.

Frequency spectra and x-ray topographic analyses were made of units plated with conventional and with annular electrodes.

B. APPARATUS AND PROCEDURES

1. General

The equipment and procedures used for the resonator fabrication and the frequency measurements are described briefly in this section.

All equipment required for the conduct of this research has operated satisfactorily during the two year period covered by this report.

2. Vacuum Plating and Sealing Equipment

Two vacuum systems of conventional design were used. The base-plating system was operable in the 10^{-7} torr range. The evacuation, baking, and sealing system for units mounted in HC-27/U holders operated in the 10^{-6} torr range.

The diffusion pump of each system was cold-trapped using dry ice in acetone as the coolant mixture.

3. Base Plating

The base-plating chamber consisted of a Pyrex pipe cross having a 4-inch I.D. A chamber pressure of about 2 x 10^{-7} torr was obtained by a combination of diffusion pumping, evaporated titanium gettering, and by cryogenic pumping with a surface cooled by liquid nitrogen. An arrangement of heaters and filaments allowed the heating of the quartz wafers to temperatures up to 450°C and the simultaneous evaporation of electrodes onto each side.

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*Third overtone of 10 MHz fundamental units.

4. Sealing of the HC-27/U Glass Container

Typical sealing procedures and a functional sketch of the sealing chamber were presented in Technical Report ECOM-02251-3, November 1966.

5. System and Procedures for Sealing Cold Weld Crystal Containers in Vacuum

A cold-weld sealing system was designed, constructed, and placed in operation during the period of this work.

The principal components are: (1) a 10-ton hydraulic press with pneumatic controls, (2) a Pyrex-pipe vacuum chamber, and (3) a pair of cold-weld sealing die-sets, one for the HC-6 container and one for the E7-1 container. A vacuum system was utilized to evacuate the Pyrex pipe when required.

A sketch of the system is shown in Figure 1. Note that the Pyrex pipe is evacuated from a side port. The opposite port is used for loading. The oven, consisting primarily of a stainless steel cylinder with eight axially parallel tantalum strips attached to its inner walls, is raised and lowered by means of the hydraulic ram. The die is positioned in the center of the cross and rests on a $2\frac{1}{2}$ inch diameter, solid, stainless-steel cylinder supported by a suitable base. The strength provided in the base section allows the maximum press force to be exerted on the dies without pressure change within the evacuated chamber.

The system may be evacuated to the 10^{-5} torr pressure range and the loaded die baked for one hour or longer at 400°C with no observable deleterious effects.

Figure 2 is a photograph of the assembled system. The vacuum coupler is a flexible, stainless-steel pipe with flanges silver soldered to each end.

Containers for cold welding consist generally of two geometries. One is a cylindrical can and its accompanying base similar to the transistor container TO-5. However, it may be of various dimensions and materials. The second is a container and base generally patterned after the HC-6/U container except for wider flanges and differences of materials. The cylindrical container used here, the E7-1 (as designated by JEDEC*), has the cap and base made of Kovar with the flange zone at the mating faces clad with copper. The pins are sealed into the metal base with Corning No. 7052 glass beads and an inset portion of the entire base on its outer surface is a sealing glass. The HC-6/U type has a similarly constructed base, but the cap is made of nickel.

The HC-6/U cold weld container is available with an aluminum cap and a mating base. However, none of this latter type have been sealed here.

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*Joint Electronic Device Engineering Council

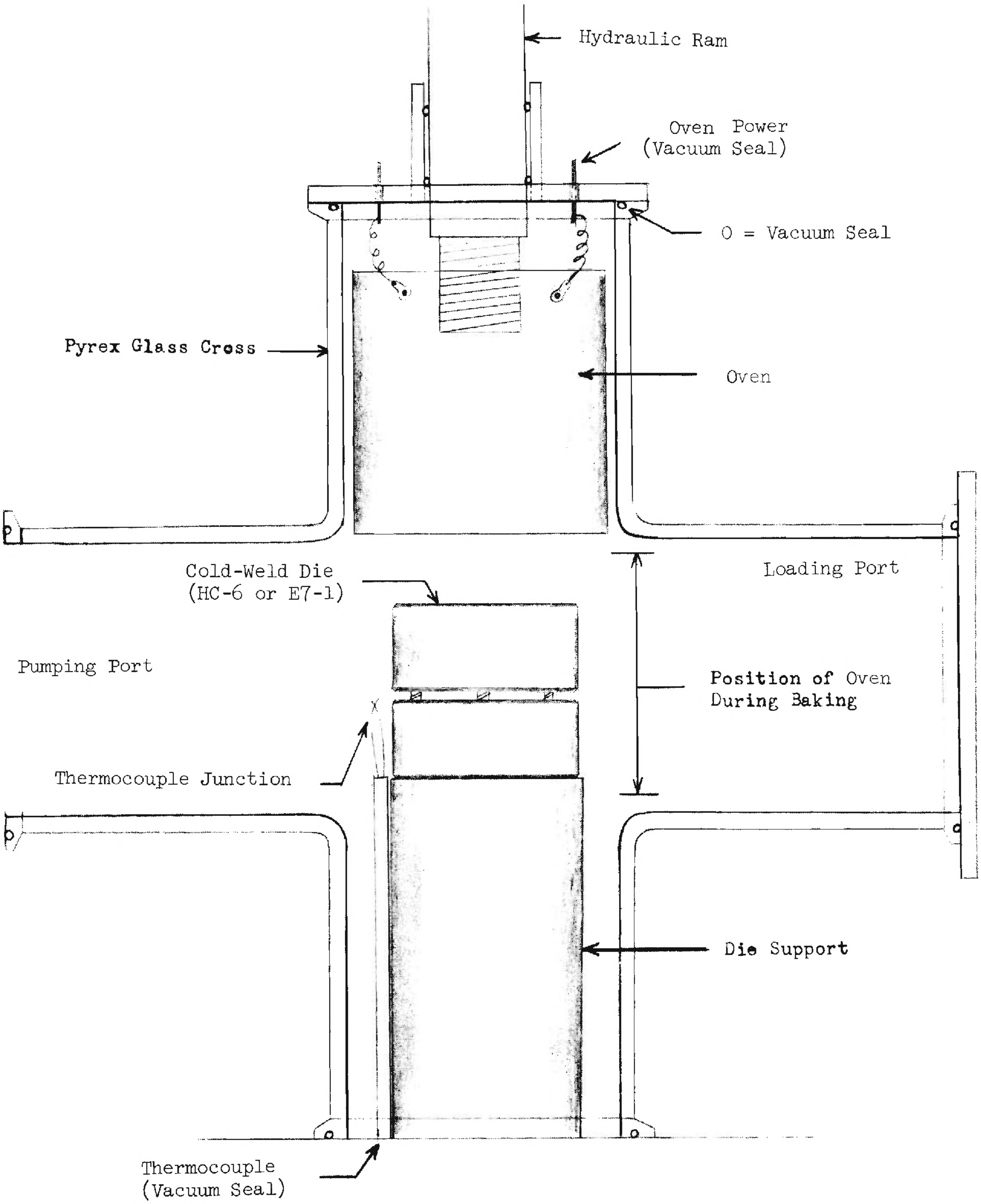

Figure 1. Drawing of cold-weld sealing system.

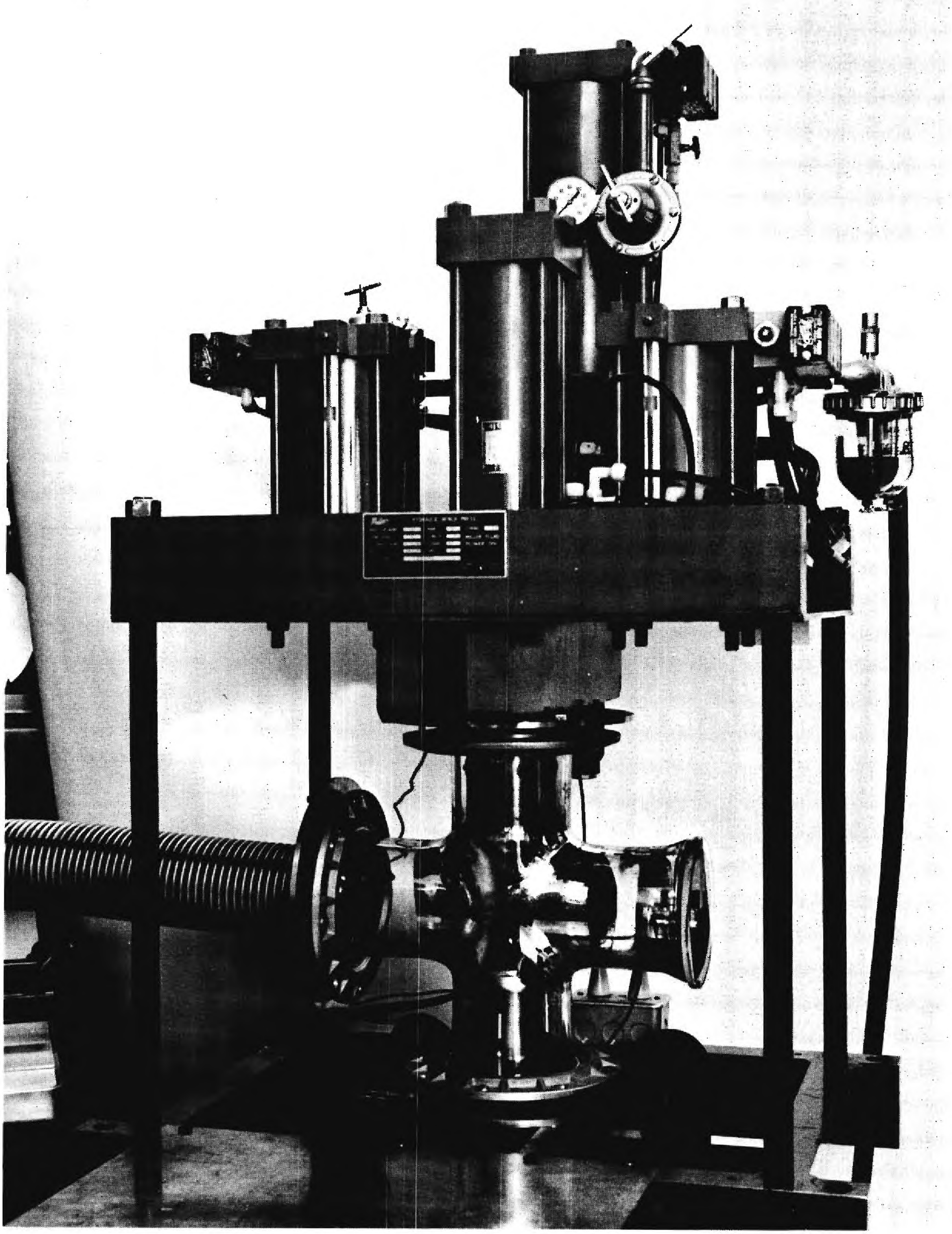

Figure 2. Cold-weld sealing system.

Information on the cold-weld sealing technique from a number of sources indicated that the mating flanges must be very clean for successful sealing. The cleaning method used here seems adequate and consists of: (1) dip the header and cover flanges in chromic acid (concentrated at room temperature), (2) rinse with distilled water, (3) rinse with reagent grade methanol, (4) dry with clean, warm air.

A number of HC-6 and E7-1 holders were welded by the cold weld method. Typical welded joints after cross-sectioning and polishing are shown in Figures 3A and 3B. The E7-1 holders, with the copper-clad Kovar mating surfaces produced welds of uniformly good quality when subjected to welding forces of 4 to 8 tons. The available HC-6 type holders with only the base mating surface copper-clad Kovar welded less well. The welds for the latter holders as shown in Figure 3B are distorted due to excessive compression of the softer header flange by the harder cap. Leak testing of a number of each type of holder indicated that the yield for the HC-6/U type holders would probably be low.

Although the hydraulic press utilized has a 10-ton capacity, studies here indicated that a force of 5 tons was adequate for successful sealing. The dies could be completely closed with about 2 tons of force.

6. Ultrasonic Bonding

The method used for the ultrasonic bonding of 3 and 5 MHz units was described in Technical Report ECOM-02251(E)-10, February 15, 1966. Recently the 20-watt bonder originally used was replaced with a 100 watt unit.* The additional power allows the bonding to the plating of thicker ribbons which will be needed for future work on shock and vibration resistant resonators.

7. Crystal Aging Ovens

At the start of the present research four ovens, of the "nested" design, providing space for 272 units were available. The solid-state control circuits for each oven were described in Technical Report ECOM-02251(E)-9, August 15, 1965. The ovens were housed in an enclosure which was held at 45°C ± 1°. Later an oven incorporating a large one-piece aluminum block heat stabilizer was built as described in Technical Report ECOM-02251(E)-10, February 15, 1966. This latter oven, which allowed insertion and extraction of individual resonators with little disturbance of adjacent units, was used for aging studies at 125°C as well as 85°C.

8. Frequency Measurements

With few exceptions, the frequencies of the resonators undergoing examination were measured by means of synthesizer-driven crystal-impedance bridges. The design of the three bridges used was covered in Technical Report ECOM-02251(E)-9.

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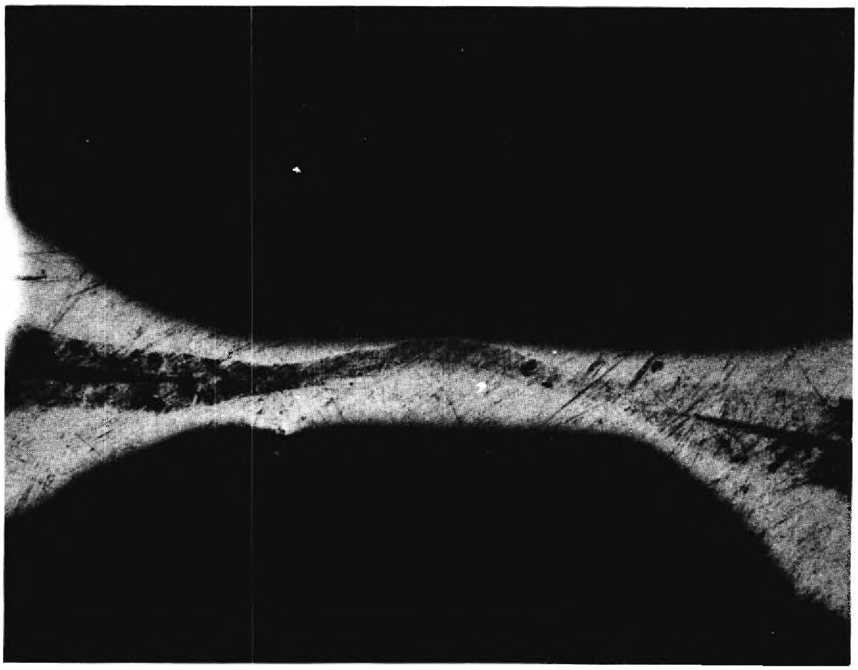
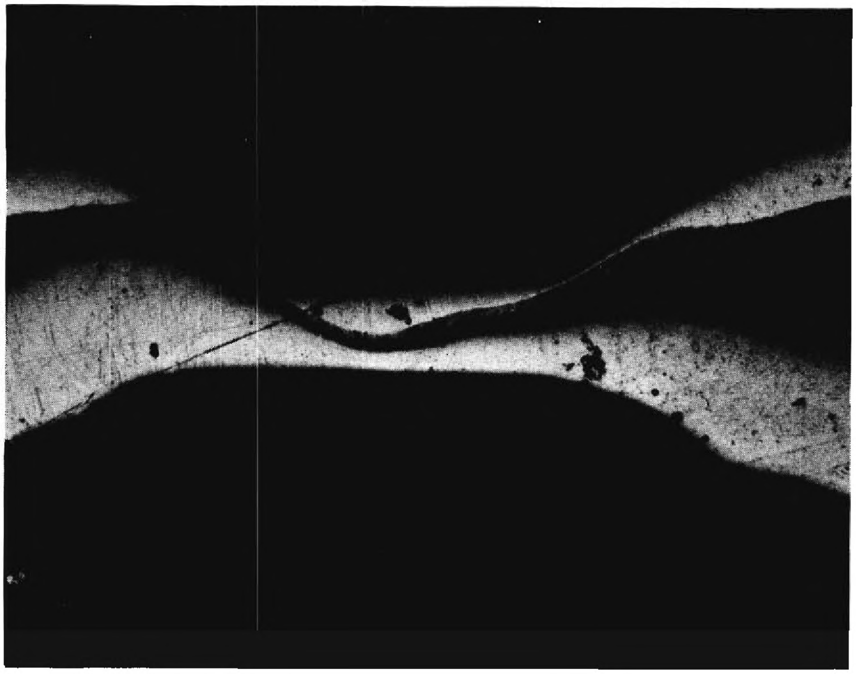
*Sonoweld Model No. W-1040-TSL.



A. E7-1 holder. copper clad kovar



B. Cold-weld holder equivalent to HC-6/u. copper clad kovar base, nickel cap.

Figure 3. Cross section of cold-weld seals made in air at room temperature.

The Hewlett-Packard Model 5100A-5110A synthesizer used to drive the bridges was stabilized by a 1 MHz signal obtained from a Manson Model RD-180-A crystal oscillator. The aging rate of the latter was + 1 x 10^{-11}/day. The frequency was offset +300 pp10^{10} from that of WWVL by comparing the house standard with WWVL using an RMS Model 18-20 1 VLF Receiver-Comparator.

9. Resonator Spectrum Analysis

The equipment used for spectrum analysis of 3 and 5 MHz resonators was described in Technical Report ECOM-02251(E)-3, November 1966. The system is typical of that used elsewhere except that the Hewlett-Packard frequency synthesizer was substituted for the usual sweep-frequency generator. The remote controlled search oscillator of the synthesizer was fed with a variable voltage obtained from a motor-driven potentiometer. Thus, clean R.F. signals were available and the bandwidth and sweep rate were easily controlled.

C. AGING STUDIES OF VARIOUS RESONATORS

1. Introduction

Aging data are reported on about 300 crystal units ranging in frequency from 81.9 kHz to 30.0 MHz. The aging of individual units of all frequencies is given in tables 1-A, 2-A, 3-A, 4-A and 5-A in the appendix.

Most of the studies were made at 85°C. However, the 10 MHz units subjected to aging at 85°C in previous work were aged 5000 hours at 125°C before continuing storage and measurement at 85°C for an additional period.

The principal variables investigated were: (1) the edge finish of center-mounted (L.F.) resonators, (2) the electrode metal for 3 MHz units, (3) annular excitation of 5 MHz units, (4) the aging temperature for 10 MHz units, and (5) the holder (HC-27/U vs. cold weld) for 3 and 5 MHz units.

2. Aging of Low Frequency Resonators at 85°C

a. General

Eighty-four resonators in the frequency range 81.9 kHz to 500 kHz were obtained from a commercial source. All of the units were mounted by use of leads soldered to the electrodes in the normal manner. The edge finishes of the quartz plates were varied to include 21 units with each of the following finishes: (1) state-of-the-art (SA), (2) semi-polished (SP), (3) optically polished (OP), and (4) optically polished and etched (OP+E).

Eight of the units of initially poor performance were removed from the oven for x-ray studies after 4 to 10 weeks of measurement. Three failed for unknown reasons. The remaining 73 units were continued on measurement for a period of over 9000 hours at 85°C.

b. Aging measurements

Aging data for these units were obtained and plotted for the period noted. Typical patterns of behavior for units of the various frequencies covered are shown in Figures 4,5,6,7, and 8. The data have been analyzed for frequency-change correlations with respect to resonator frequency category, edge finish, and cut of the quartz (SL or CT) and are summarized in the tables presented subsequently. It will be noted that the parameters for which comparisons are made are the aging rates per week during the first 30 days, during the last six months of operation, and for the total period of about 54 weeks.

Table 1 gives the aging summary with respect to frequency. The highest initial aging rate (for the first 30 day period), 14.4 ppm/wk, was obtained for the 250 kHz, DT-cut units. These units also had the highest total aging rate of 0.51 ppm/wk for the entire period of approximately 54 weeks. The 100 kHz, NT-cut units, however, had the highest average aging rate for the final six months (4368 hours).

TABLE 1

Aging Analysis of L.F. Units with Respect to Frequency

Frequency (kHz)	Number Units	Aging Rate 1st 30 days (ppm/wk)	Aging Rate Last 6 mos. (ppm/wk)	Aging Rate Total Period (ppm/wk)	Cut
81.9	12	7.7	0.19	0.36	NT
100	10	9.7	0.27	0.46	NT
250	12	14.4	0.17	0.51	DT
455	18	9.1	0.14	0.35	CT,SL
500	21	9.6	0.14	0.29	CT,SL

The average aging rates for all frequencies was less than 0.3 ppm/wk, well under the maximum acceptable rate of 1.0 ppm/wk for the last 6 months. An acceptably low aging rate is usually obtained for most units within a 60 day period of storage at 85°C.

The results of the aging analysis with respect to edge finish are shown in Table 2. These data display a surprising uniformity of the aging rates with respect to edge finish. The principal exceptions are the rates displayed for the units with the optically polished edges in the last two columns of the table, i.e., the rates for the last six months and for the total period. In addition, three units of this group were removed during the initial aging because of higher than normal aging rates, and thus were not included in the analysis.

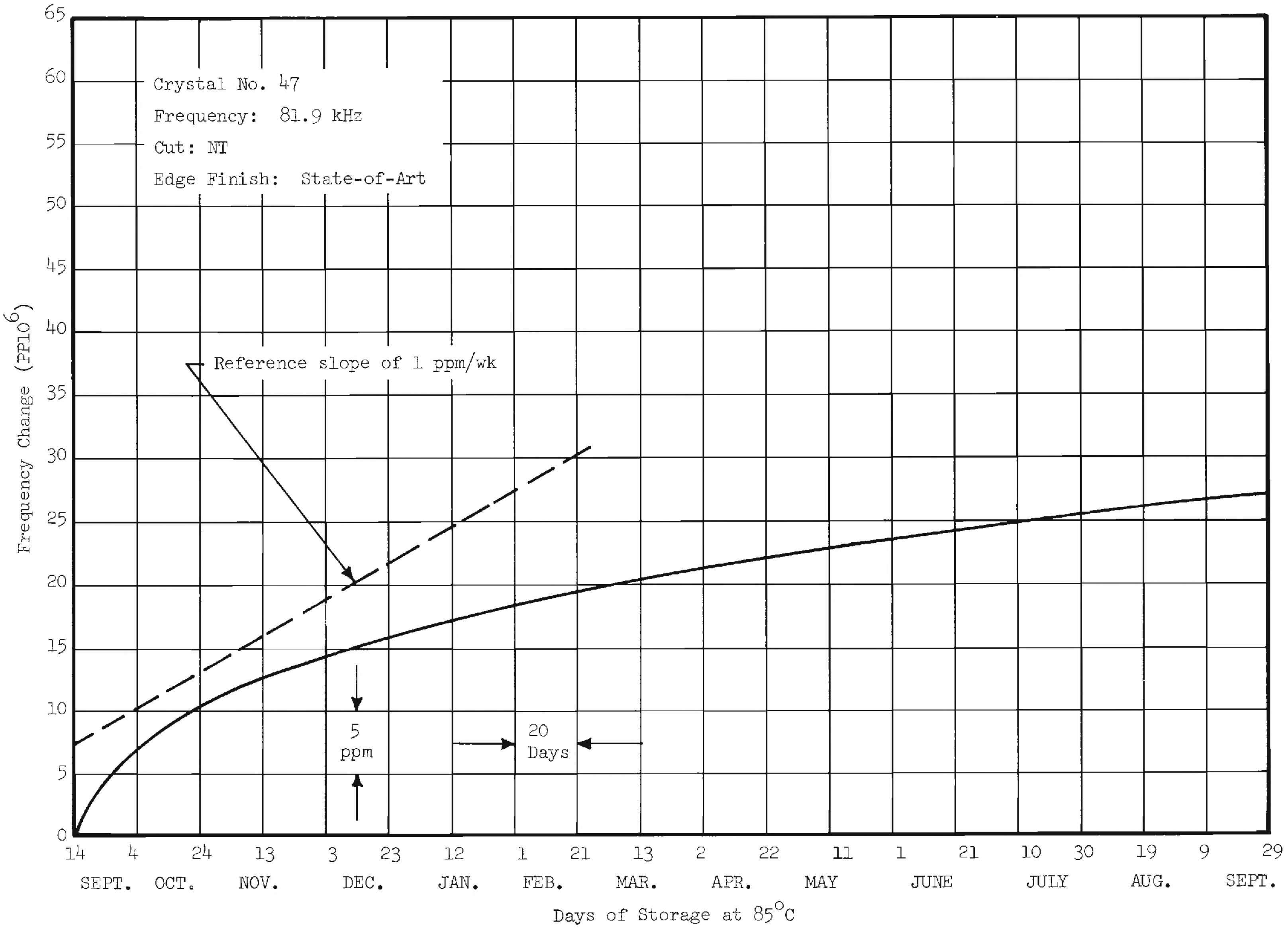


Figure 4. Aging data for 81.9 kHz unit No. 47.

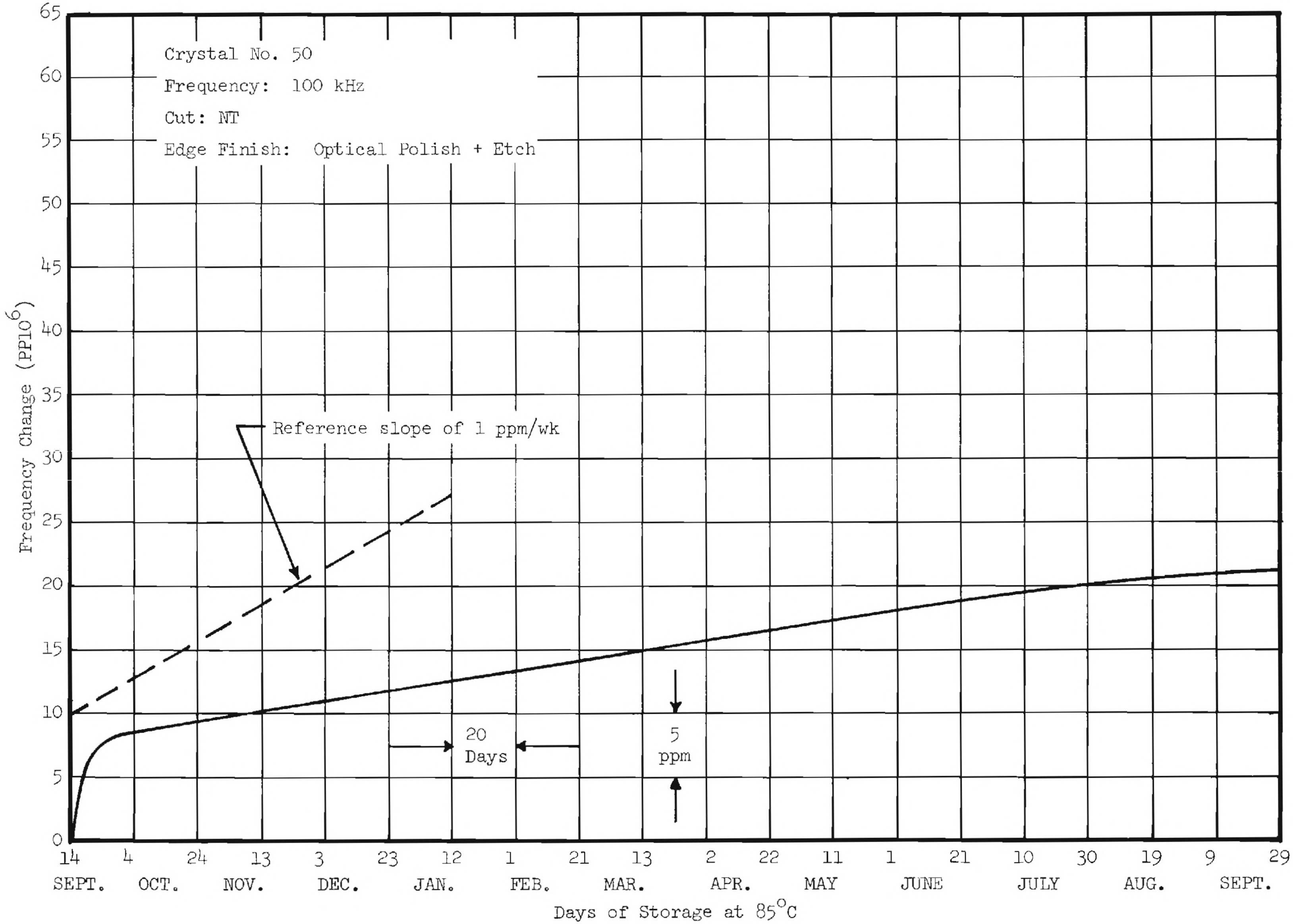


Figure 5. Aging data for 100 kHz unit No. 50.

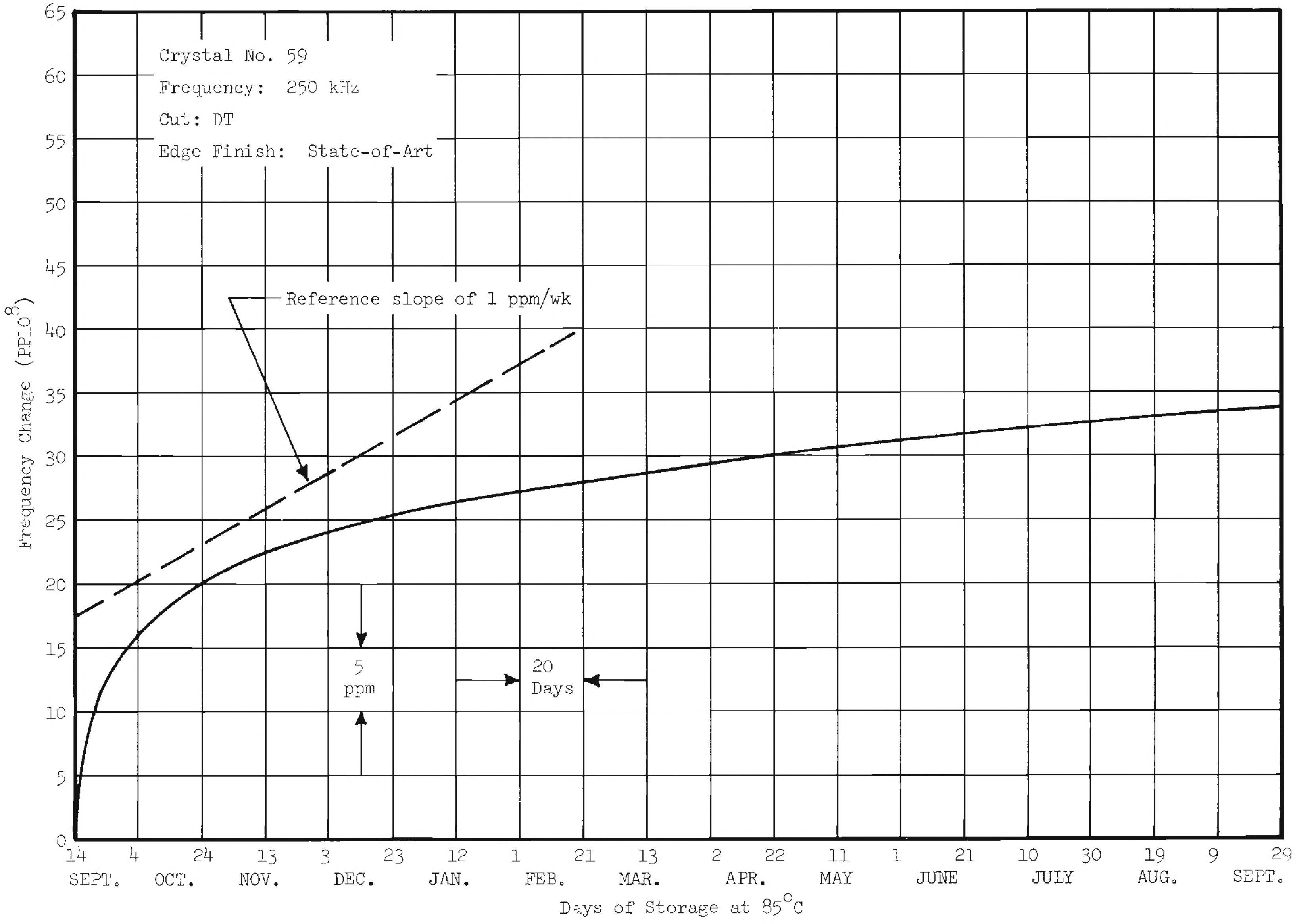


Figure 6. Aging data for 250 kHz unit No. 59.

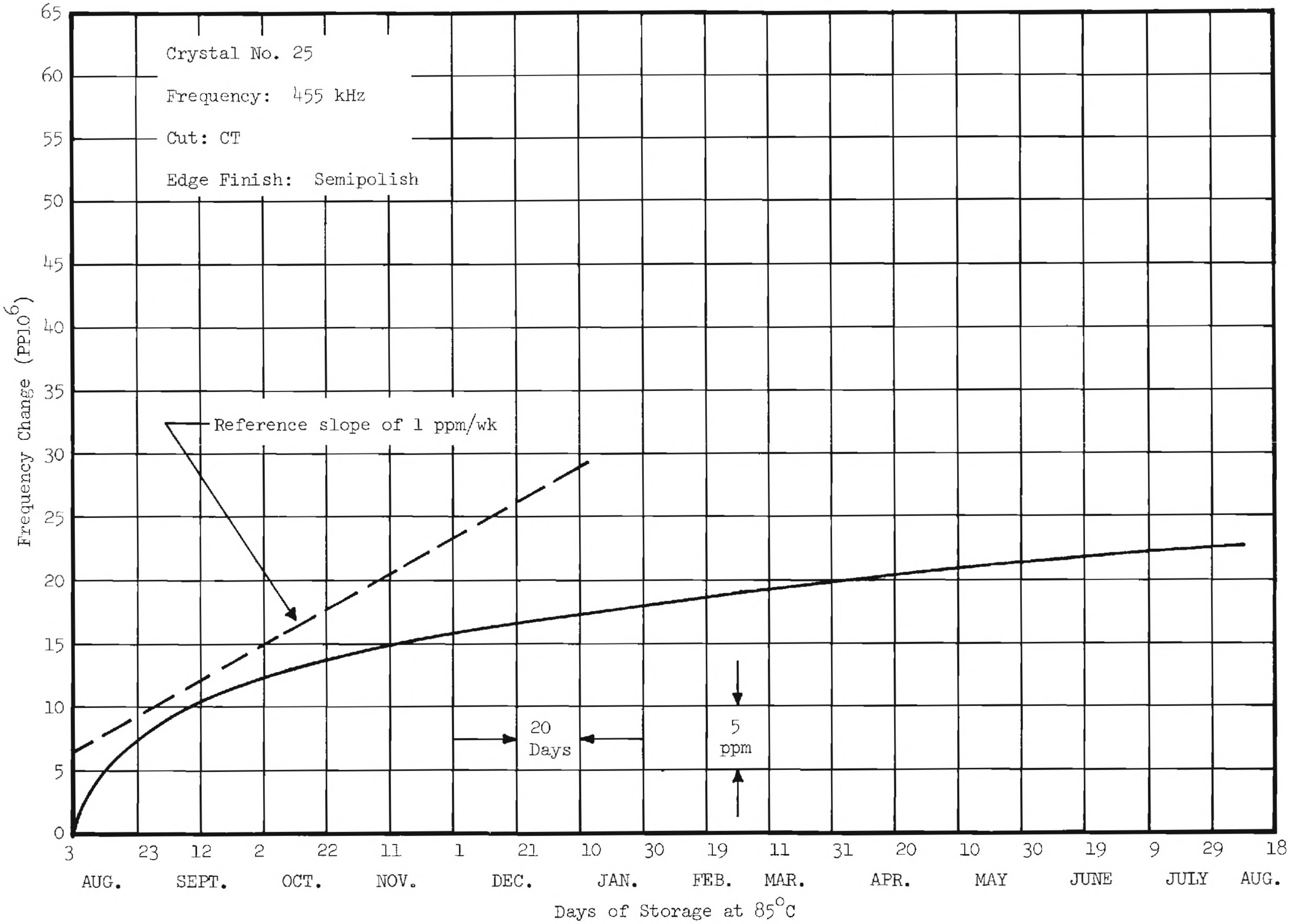


Figure 7. Aging data for 455 kHz unit No. 25.

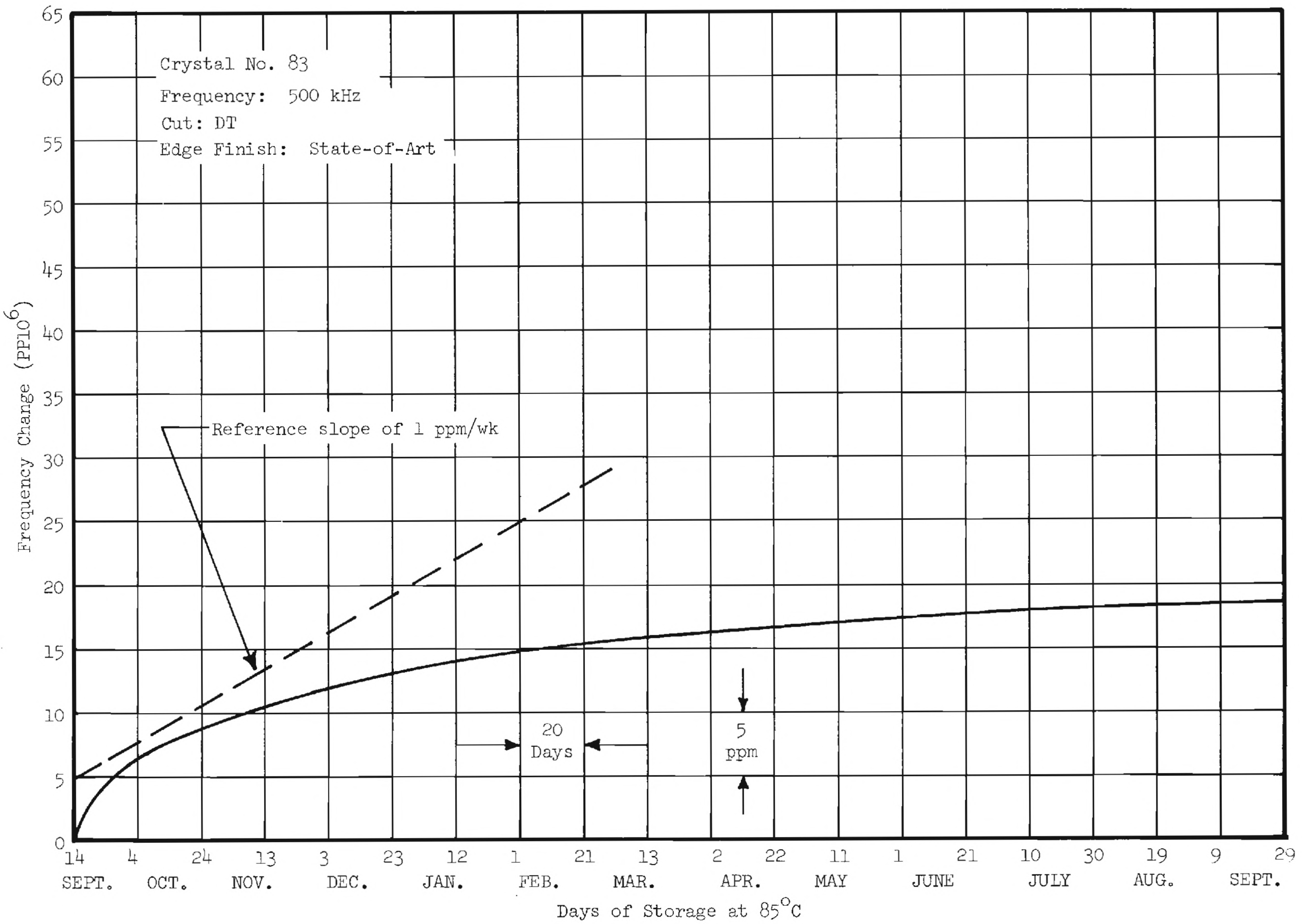


Figure 8. Aging data for 500 kHz unit No. 83.

TABLE 2

Aging Analysis of L.F. Units with Respect to Edge Finish

Edge Finish	Number Units	Aging Rate 1st 30 days (ppm/wk)	Aging Rate Last 6 mos. (ppm/wk)	Aging Rate Total Period (ppm/wk)
State-of-Art	20	9.1	0.13	0.37
Semi-Polish	17	11.2	0.16	0.36
Optically Polished	17	10.2	0.27	0.42
Optically Polished and Etched	19	9.5	0.14	0.37

Units in the 455 and 500 kHz frequency categories were fabricated using both SL and CT cuts of quartz. The data of Table 3 gives an aging summary based upon the particular cut used. Note that while the SL-cut gave the highest aging for the 455 kHz units during the last 6 month period it gave the lowest aging for the 500 kHz units for the same period.

TABLE 3

Aging Analysis of 455 and 500 kHz Units with Respect to Cut of Quartz

Frequency	Cut	Number Units	Aging Rate 1st 30 days (ppm/wk)	Aging Rate Last 6 mos. (ppm/wk)	Aging Rate Total Period (ppm/wk)
455	SL	9	12.3	0.165	0.37
455	CT	9	11.5	0.120	0.34
500	SL	11	11.7	0.114	0.28
500	CT	10	15.1	0.170	0.32

c. Comments

It is evident from the data presented that the edge-finish of the resonators examined played only a superficial part in determining the aging rates of the units. The behavior of units with optically polished edges implies that the strain introduced by polishing was greater than that introduced by "state-of-the-art" finishing; however, etching after polishing removed the strain and its undesirable effects.

Since the edge finish does play so small a part in determing the relatively high initial aging rate displayed by fow frequency resonators, the remaining factor of principal significance in contributing to the aging must be the mounting assembly and lead-attachment method. Examination of the effects of these elements on the aging of resonators are anticipated in the near future.

3. Aging of 3 MHz Resonators at 85°C

a. General

The technical specification for the current research required the fabrication of one hundred resonators of natural quartz of 3 MHz fundamental frequency. These resonators were to be sealed in evacuated HC-27/U holders* and to be mounted by thermocompression or ultrasonic bonding in order to eliminate solders and cements as contributors to aging mechanisms. The target aging rate initially was an acceptance requirement of less than 4 pp10^8 aging for the first 30 days and a maximum of 1 pp10^8/week thereafter. The acceptance requirement was subsequently modified by agreement with the contracting officer's technical representative to require that an aging rate of 1 pp10^8/week be realized by the end of the fourth week at 85°C. No limit was placed on the total aging for the initial four weeks.

b. Resonator fabrication

The fabrication details and procedures used in preparing these units were presented in Technical Report ECOM-02251(E)-3, November 1966. In addition a number of units were recently fabricated in a similar manner but sealed in cold-weld holders as described in Section III-B-5 of this report. Since a high bakeout temperature (450°C) was one feature of the requirements for the fabrication of these units, it was necessary to search for plating materials and a bonding method which would fulfill the requirements. Initial experiments eliminated silver as a plating material and placed gold in the doubtful category because of thin-film agglomeration effects on the quartz plate. For temperature related reasons also most bonding materials appeared undesirable. Ultrasonic bonding appeared to be a reasonable solution. A selection was thus made of aluminum as a plating material and of ultrasonic bonding as the lead attachment method; as a result, aluminum ribbon could be ultrasonically bonded directly to the plating in the absence of a reinforcing sub-plated zone. For comparison purposes 6 resonators plated with evaporated gold and 10 plated with sputtered gold were prepared in addition to the 106 aluminum plated ones. Ultrasonic bonding was used in all cases except for 5 units bonded with pyroceram and Ag cement.

c. Aging measurements (HC-27/U holders)

A total of 176 units were fabricated for this study (122 of which are still on measurement). The total number of hours at 85°C during which

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* A subsequent assignment by contract modification required a study of similar resonators sealed in evacuated, cold-welded holders.

frequency measurements were conducted range from 12,500 for the earlier fabricated units to 9300 for the more recently fabricated ones.

Aging data for typical resonators are depicted in Figures 9, 10 and 11. It will be noted that these units display precipitous aging changes of 15 to 25 pp10^8 during the first 30 days and thereafter follow a more gentle aging slope. The terminal aging rates approach a value of 1 pp10^9/week for the majority of the resonators.

The data obtained for the various resonators have been analyzed with respect primarily to plating material and processing. These include the plating categories of evaporated aluminum, evaporated gold, and sputtered gold. Other features of interest were effects of the vacuum within the container after sealing and of conditioning of the aluminum plated resonators before the aging measurements were begun.

For the purpose of this analysis the initial aging period for units to stabilize to the designated aging level of one pp10^8 per week was examined and compared. The results are reported in Table 4. A similar analysis for the behavior of the units during the remainder of the total aging period was prepared and is reported in Table 5.

The data of Table 4 display the average time for the 3 MHz units to reach an aging rate of 1 pp10^8/wk. These data clearly indicate, from the standpoint of the stabilization period, that resonators plated with properly applied evaporated aluminum electrodes, perform in a manner superior to those plated with gold electrodes. The resonators of poorest performance are those of group No. 14. These units were also aluminum plated. However, the HC-27/U container was not evacuated in the usual manner. Rather the cap was provided with pump-out tubulation (3 mm O.D. and 2 mm I.D.) through which the unit was evacuated subsequent to sealing of the base to the cap. The evacuation process was thus essentially the same as for the T-5½ holder. Table 4 also reveals that resonators coated with evaporated gold electrodes gave performance superior to those with sputtered gold electrodes.

TABLE 4

Average Stabilization Period of 3 MHz Units at 85°C

Plating	Number Units	Period (Days)	ΔF During Period (pp 10^8)	Remarks
Aluminum only	96	9.4	-6.0	Does not include Group 14
Aluminum Group 14	10	46.0	-23.3	Evacuated through tubulation attached to HC-27/U container
Gold Evap.	6	23.3	+5.7	
Gold Sputtered	10	27.3	+8.7	

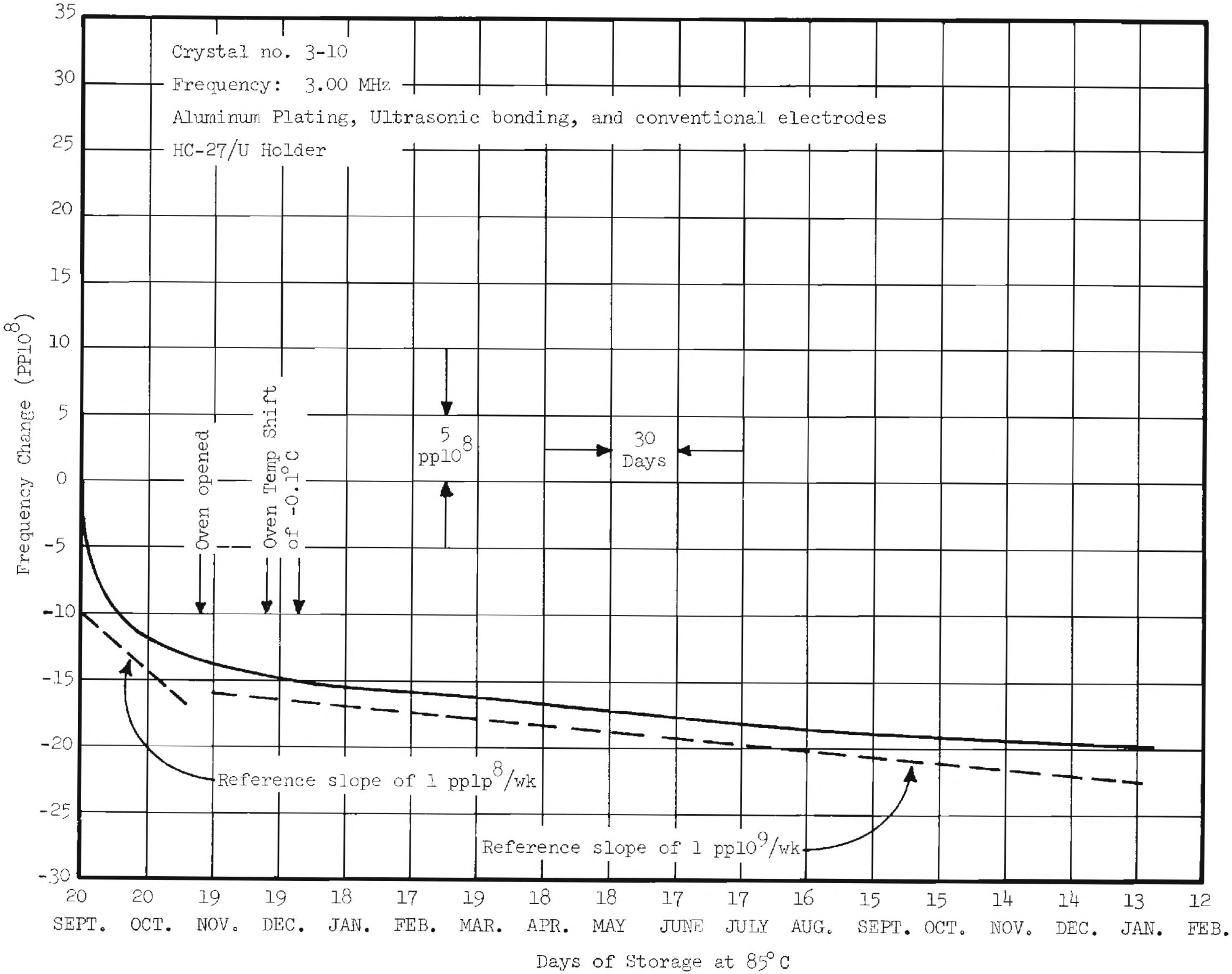

Figure 9. Aging data for aluminum plated 3 MHz unit No. 3-10.

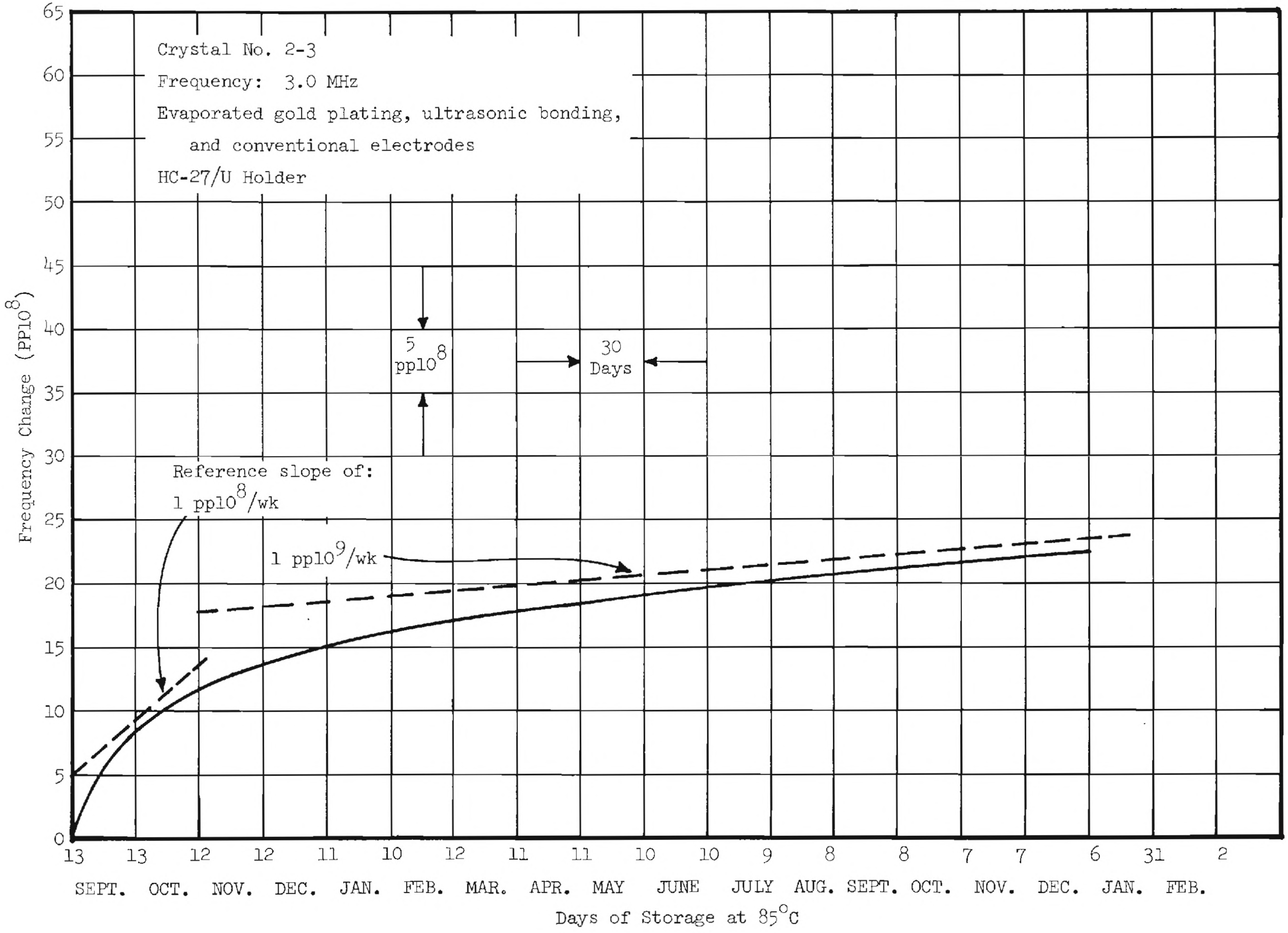

Figure 10. Aging data for evaporated gold plated 3 MHz unit No. 2-3.

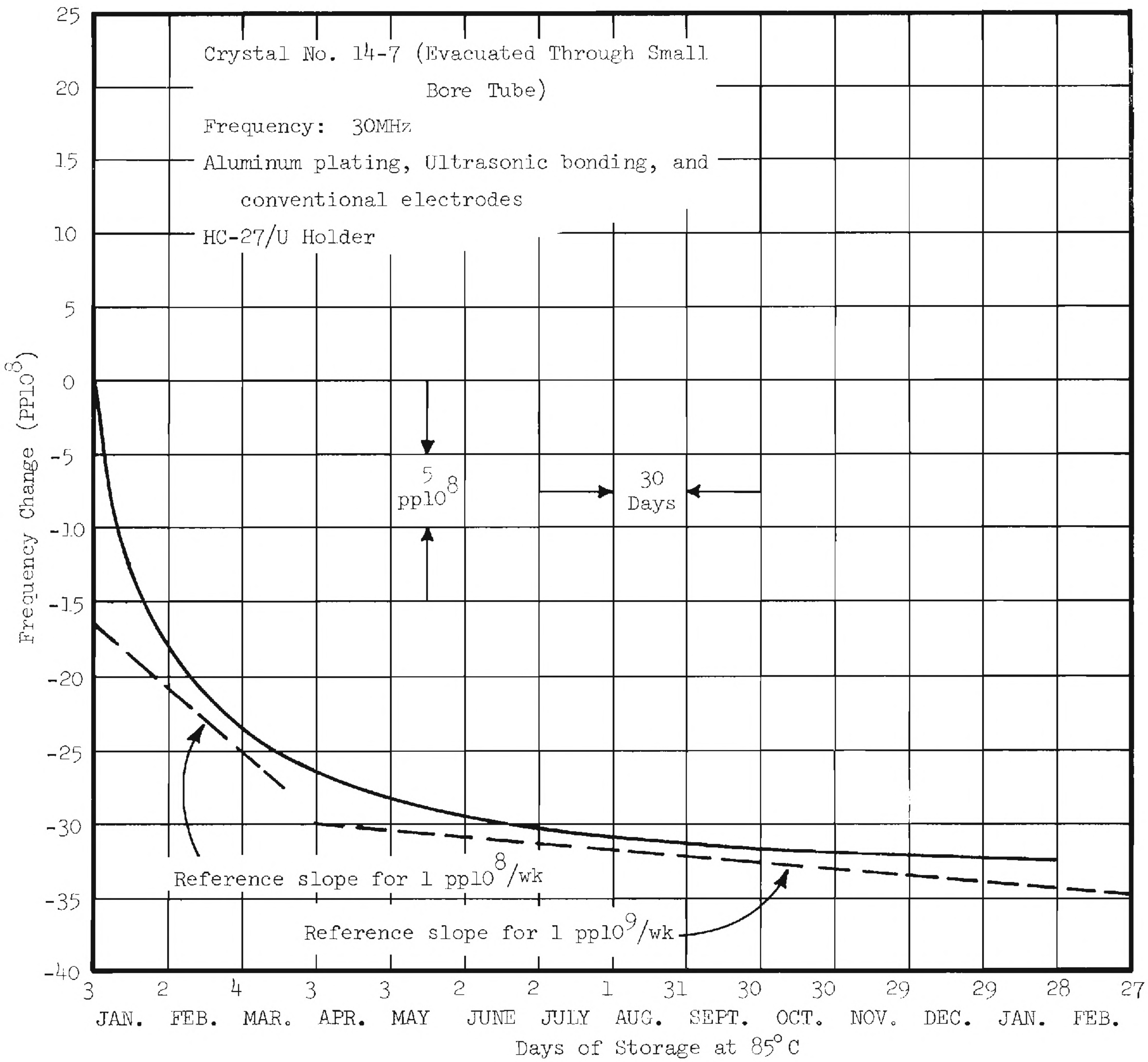

Figure 11. Aging data for aluminum plated 3 MHz unit No. 14-7. Evacuated through small-bore glass tube.

The aging rates of crystal resonators following the stabilization period are of prime importance in frequency control applications. Table 5 presents the total average aging rates and the aging rates during the last six months of operation of the resonators for the 3 MHz units under discussion.

The aluminum plated resonators performed in a manner superior to gold plated ones. Note also that during the final 6 months the resonators of the poorly-evacuated, aluminum-plated group 14 aged at the same rate as the evaporated gold plated units.

TABLE 5

Average Post-Stabilization Aging Rates of 3 MHz Units at 85°C

Plating	Number Units	Aging Rate During Total Period ($pp10^8$/wk)	Aging Rate During Final 6 mo. Period ($pp10^8$/wk)	Remarks
Aluminum only	96	-0.120	-0.047	Excluding group 14
Aluminum Group 14	10	-0.250	-0.098	Evacuated through tubulation
Gold Evaporated	6	+0.190	+0.095	
Gold Sputtered	10	+0.260	+0.120	

An effort was made to decrease the initial stabilization period of aluminum plated resonators by preaging. After the holder had been sealed a number of units were stored at temperatures above the aging temperature of 85°C for various periods. The results of these experiments are given in Table 6.

TABLE 6

Aging Performance of Preaged 3 MHz Units

Preaging			Stabilization Period		Aging Rate	Aging Rate
Time (Hrs)	Temp (°C)	Number Units	Days	ΔF/F ($pp10^8$)	Total Period ($pp10^8$/wk)	Final 6 months ($pp10^8$/wk)
16	170	7	18.0	-5.7	-0.240	-0.049
120 (ave)	100	28	1.7	-0.7	-0.150	-0.087

Table 6 indicates that preaging overnight (16 hours) at 170°C degrades the resonator performance. However, preaging for about 5 days at 100 °C gave considerable relief from the initial rapid negative aging of the untreated aluminum plated units. The frequency change resulting from 5 days storage at 100°C was about -5 ppm. Figure 12 illustrates aging data of a typical preaged unit. Note that the aging rate was less than 1 $pp10^8$/week initially and was less than 1 $pp10^9$/week for the last 4 months.

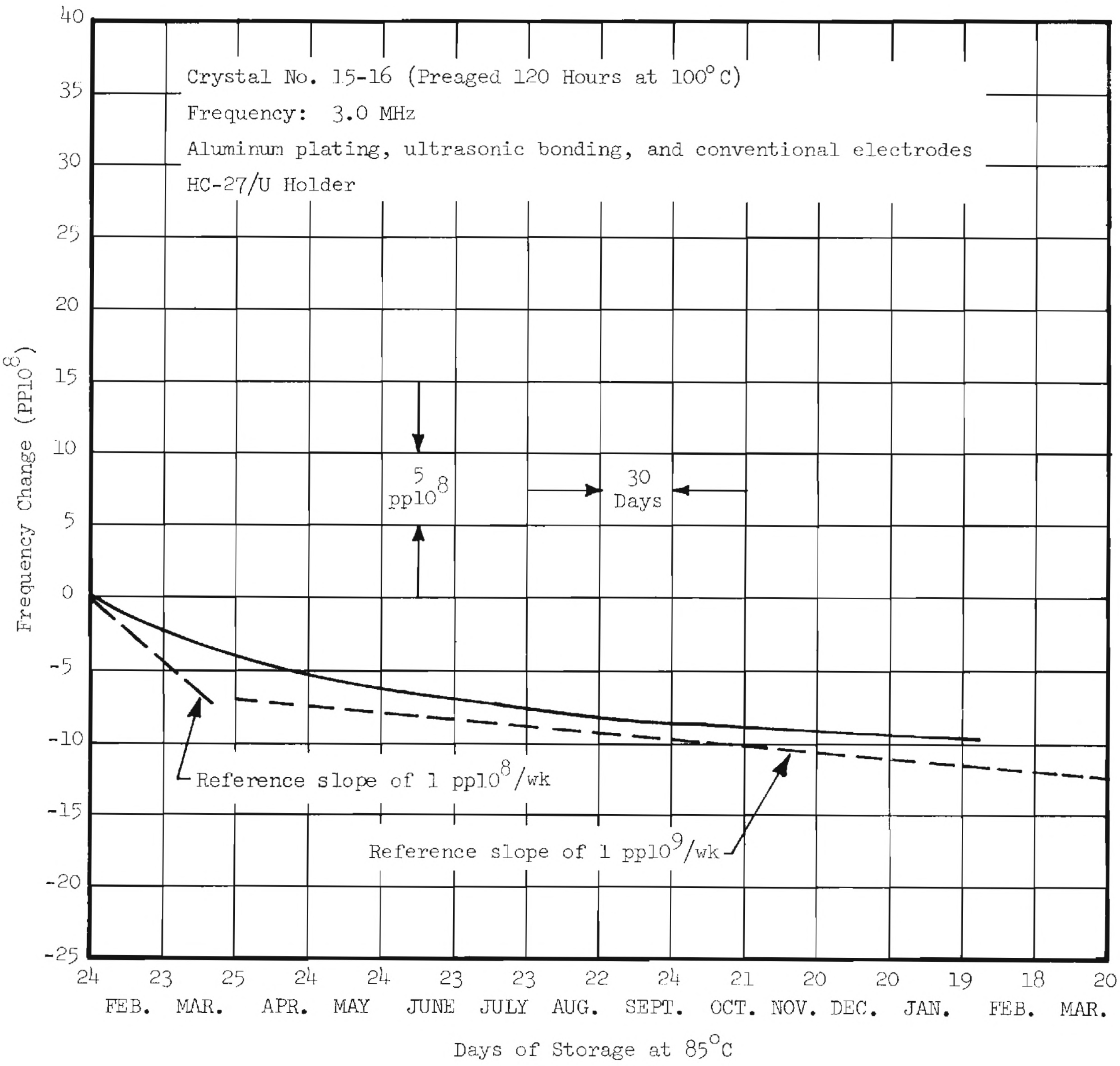

Figure 12. Aging data for aluminum plated 3 MHz unit No. 15-16. Preaged 120 hours at 100° C.

The average Q for all units was 1.04 x 10^6. The aluminum plated units averaged 1.10 x 10^6 and the gold plated ones 0.72 x 10^6. The lower value obtained for the latter units was apparently due in part to partial agglomeration of the gold films during baking and sealing of the HC-27/U holders.

d. Aging measurements at 85°C (cold-weld holders)

Nineteen units having conventional evaporated-aluminum electrodes were fabricated for sealing in cold-weld holders. The holders used were types HC-6 and E7-1. The sealing system has been described previously in Section II-B-5. The sealing operation was to load the holder into the proper die-set, evacuate, bake* for sixty minutes at temperatures ranging from 250 to 400°C, and then to seal at the baking temperature.

The aging for each unit during about 1000 hours of storage is given in Table 7. The aging rates of three units never decreased to ± 1 pp10^8/week. One unit (No. 16-7) was known to have a large leak and aged at a rate of -34.1 pp10^8/week. The others (Nos. 16-4 and 16-10) may have very small leaks. Unit 16-5 was erratic and the aging could not be determined.

Considering the fifteen units which achieved an aging rate of ± 1 pp10^8/wk or less: (1) seven aged less than 1 pp10^8/week from the initial measurement, (2) the average stabilization period to reach an aging rate of ± 1 pp10^8/week was 10.5 days, (3) the average ΔF during the stabilization period was -9.7 pp10^8, and (4) the average aging rate after the stabilization period was 0.58 pp10^8/week.

Typical aging data for a very good unit (No. 17-1) is shown in Figure 13. Figure 14 shows the data for a typical unit (No. 16-9).

e. Comments (cold-weld units)

Due to short aging period for the units sealed in cold-welded holders, a direct comparison of long-term aging with similar units in glass holders (HC-27/U) has little significance. The average stabilization period for units in glass holders was 9.4 days and during which time the frequency changed -6.0 pp10^8. These values compare fairly well with those given above for units in cold-welded holders.

There was no apparent improvement in aging rate obtained by the use of higher bake-out temperatures. This action may have been due to the inability of the small, 2-inch diffusion pump to handle the gas load at the higher temperatures. The dies (especially the set for HC-6 type holders) did not appear to operate properly at the higher bake-out temperature. The envelopes showed evidence of expansion and buckling at the higher temperatures and the base of the HC-6/U type exhibited metal flow and glass cracking above 300°C.

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*Two units (16-8 and 17-7) were evacuated but not baked.

TABLE 7

AGING DATA FOR ALUMINUM-PLATED 3MHz UNITS IN COLD-WELD HOLDERS

		Vacuum Bake		Stabilization Period *		Aging After Stabilization**		
Unit	Holder Type	Time (Min.)	Temp. (°C)	Time (Days)	ΔF ($pp10^8$)	Time (Hours)	Rate ($pp10^8$/week)	Remarks
16-1	HC-6	60	250	11	- 7.0	864	-0.58	
16-2	E7-1	60	250	0	0	1128	+0.62	Initial Aging < 1 $pp10^8$/wk
16-3	E7-1	60	250	0	0	960	+0.093	Initial Aging < 1 $pp10^8$/wk
16-4	E7-1	60	300	-	-	960	-4.40	Has not stabilized
16-5	HC-6	60	300	-	-	-	-	Erratic
16-6	E7-1	60	350	25	-14.0	360	-0.93	
16-7	HC-6	60	350	-	-	960	-34.10	Has not stabilized Definite Leaker
16-8	HC-6	(No Bake)		0	0	960	+0.42	Initial Aging < 1 $pp10^8$/wk
16-9	E7-1	60	350	11	- 8.8	736	-0.60	
16-10	E7-1	60	350	-	-	960	-6.20	Has not stabilized
16-11	E7-1	60	350	25	- 9.5	360	-0.65	
17-1	HC-6	60	250	0	0	1128	-0.37	Initial Aging < 1 $pp10^8$/wk
17-2	HC-6	60	300	0	0	960	-0.42	Initial Aging < 1 $pp10^8$/wk
17-3	E7-1	60	300	0	0	960	-0.18	
17-4	E7-1	60	350	25	- 9.6	360	-0.89	
17-5	E7-1	60	400	25	-23.3	360	-1.00	
17-6	E7-1	60	400	18	-17.0	528	-0.73	High Rs
17-7	E7-1	(No Bake)		0	0	792	+0.21	Erratic Initial Aging < 1 $pp10^8$/wk
17-8	E7-1	60	100	18	- 7.9	360	+0.93	

*Time (Days) at 85°C for unit to reach an aging rate of ± 1 $pp10^8$/week and the total ΔF during that time.

**Aging subsequent to the stabilization period except as noted in remarks column.

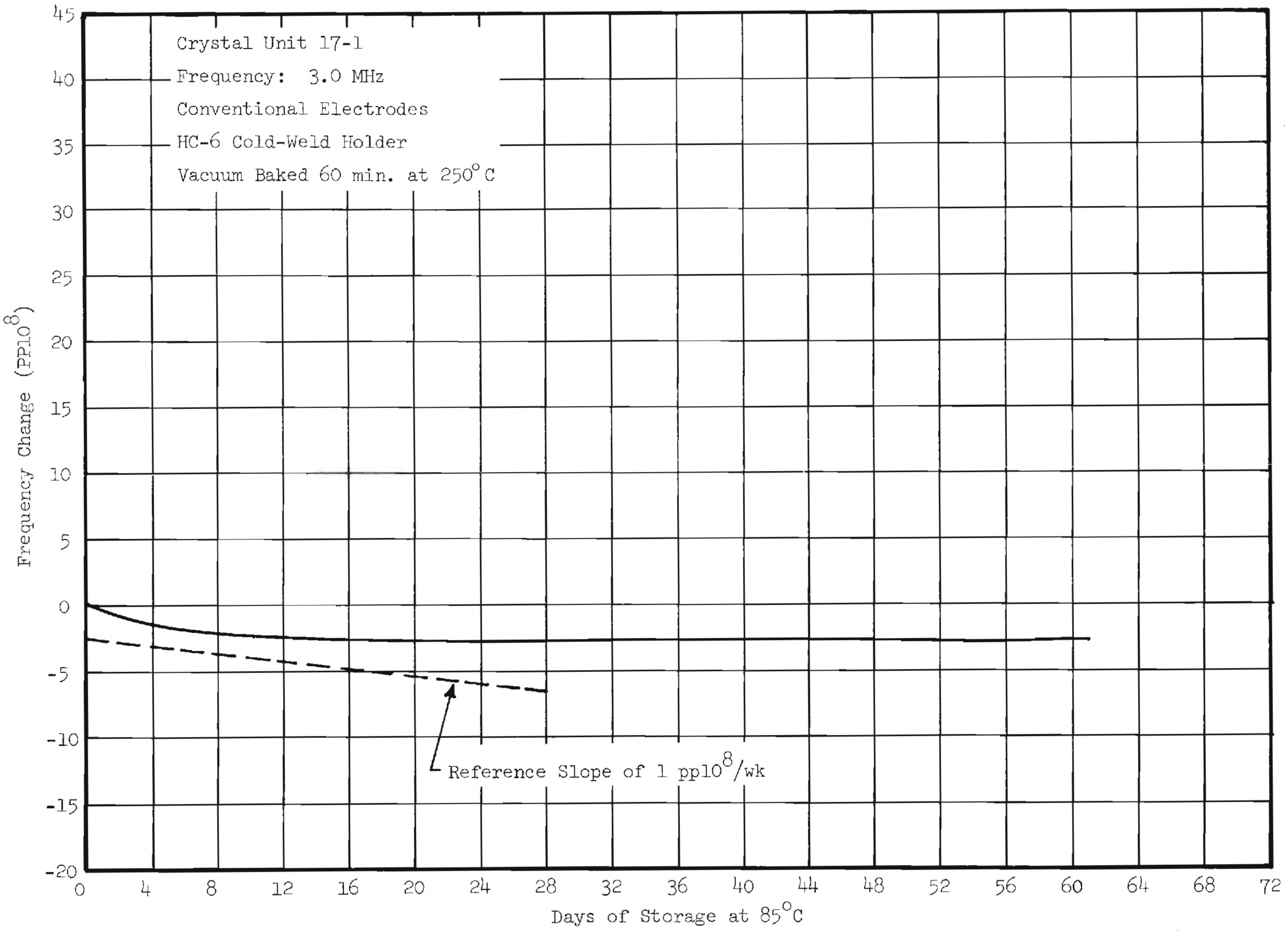

Figure 13. Aging data for aluminum plated 3 MHz unit No. 17-1.
HC-6 type cold-weld holder.

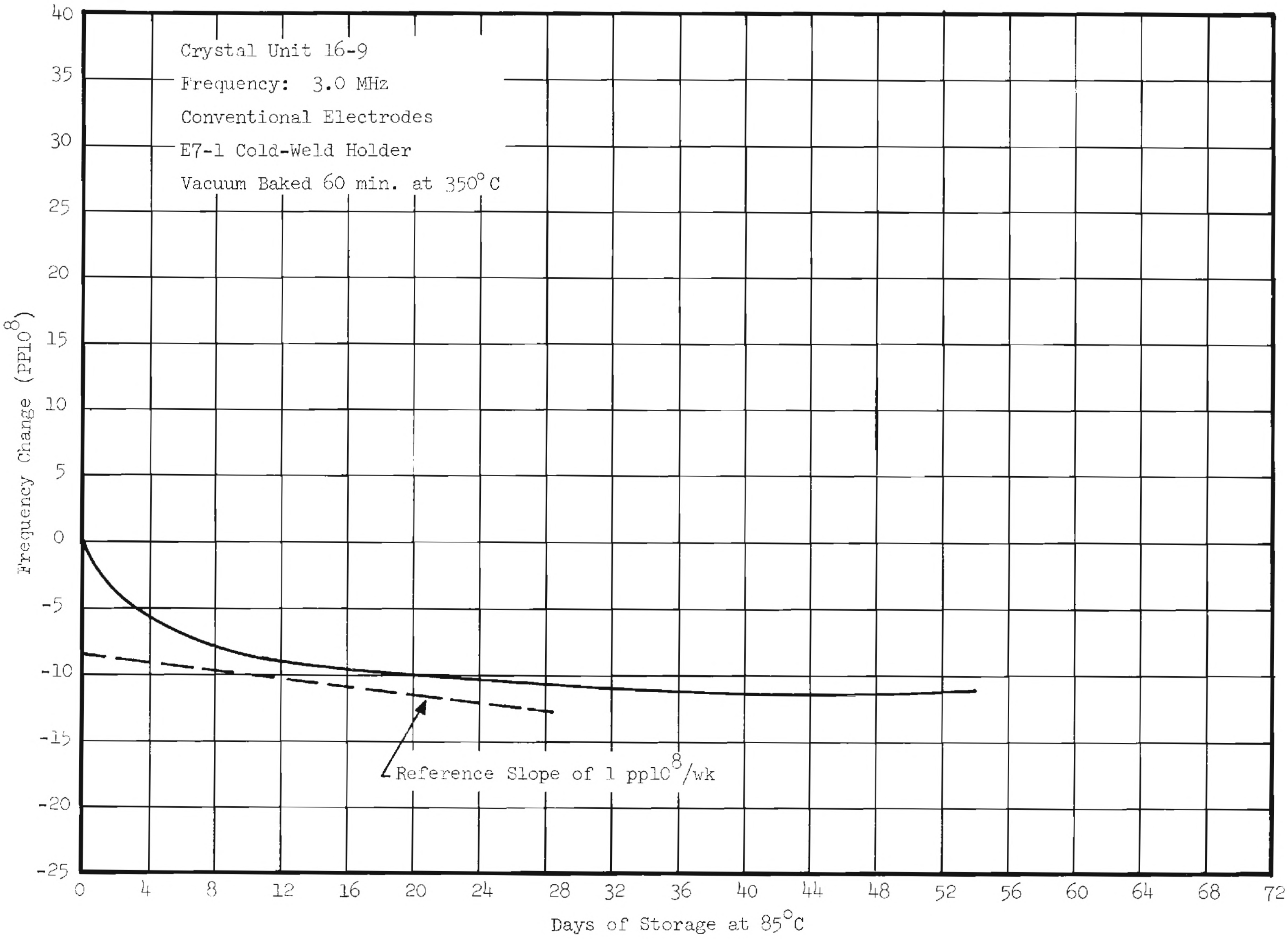

Figure 14. Aging data for aluminum plated 3 MHz unit No. 16-9. E7-1 type cold-weld holder.

4. Aging of 5 MHz Resonators with Annular Electrodes at 85°C

a. General

Included in the initial requirements of the current research was a study of ultrasonically-bonded 5 MHz resonators having electrodes designed for composite field excitation.[1,2] An evaluation of oscillation patterns, impedance levels, and Q values by x-ray topographic techniques and by electrical measurements of units having parallel, composite, or annular field excitation was made. The results indicated the latter was the preferred method of excitation for small diameter 5 MHz resonators. Arrangements were made with the technical representative of the sponsor to utilize annular-field excitation in lieu of composite field excitation for the units to be fabricated and measured.

b. Resonator fabrication

The preparation of quartz resonators with annular electrodes was described in Technical Report ECOM-02251(E)-10, February 1966. The fabrication details (plating, sealing, etc.) were given in Technical Report ECOM-02251-3, November 1966. Units recently prepared for sealing in cold-welded holders were fabricated in a similar manner. The dimensions of the electrode annuli adopted for the standard aging comparisons were 9/32 inch O.D. and 7/32 inch I.D.*

c. Aging measurement (HC-27/U holders)

Twenty three units, six of which had conventional electrodes, were fabricated for this study. Both perpendicular and annular excitation were used; the aging data obtained have been analyzed on the basis of the excitation method in order to compare more readily the good and bad features of the respective methods. Aging data for typical resonators of each type are displayed in Figures 15, 16 and 17. Table 8 gives the average stabilization period required to reach an aging rate of 1 pp10^8/week and the total frequency change occurring during the stabilization period.

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[1] W. Ianouchevesky, The Stability and Q Factors of Quartz Crystals Excited by the Parallel Field Technique, Final Report Contract No. DA-91-591-EUC-1752, 1 May 1961 - 30 April 1963.

[2] W. Ianouchevesky, The Stability and Q Factors of Quartz Crystals Excited by the Parallel Field Technique, Final Report Contract No. DA-91-591-EUC-2962, 1 June 1963 - 31 May 1964.

*X-ray diffraction analysis revealed the oscillation to be confined to a central area of the quartz 3/16 inch in diameter for units of 2.5 diopter, plano-convex configuration.

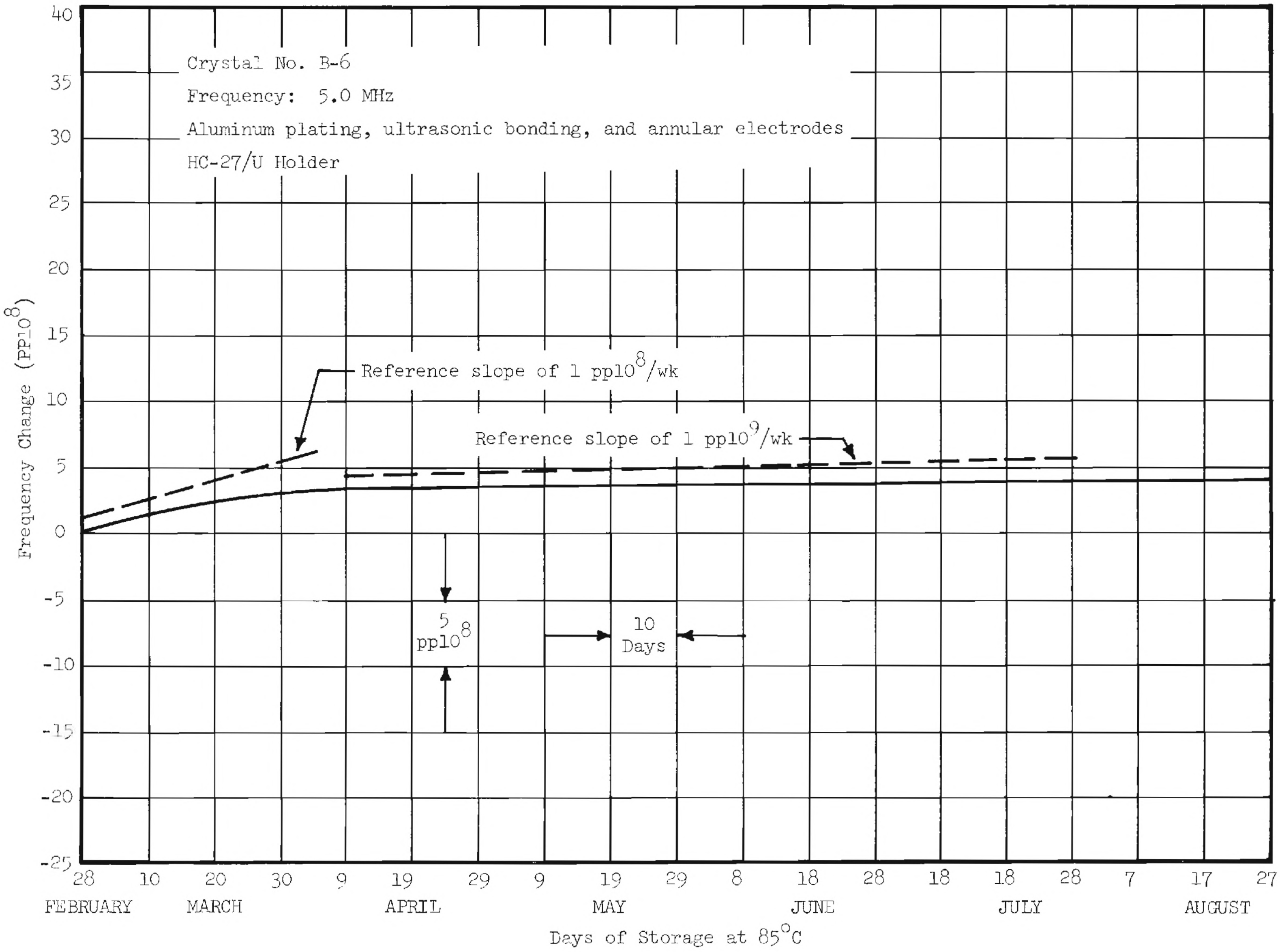

Figure 15. Aging data for 5 MHz unit No. B-6. Annular electrodes 9/32" O.D., 7/32" I.D.

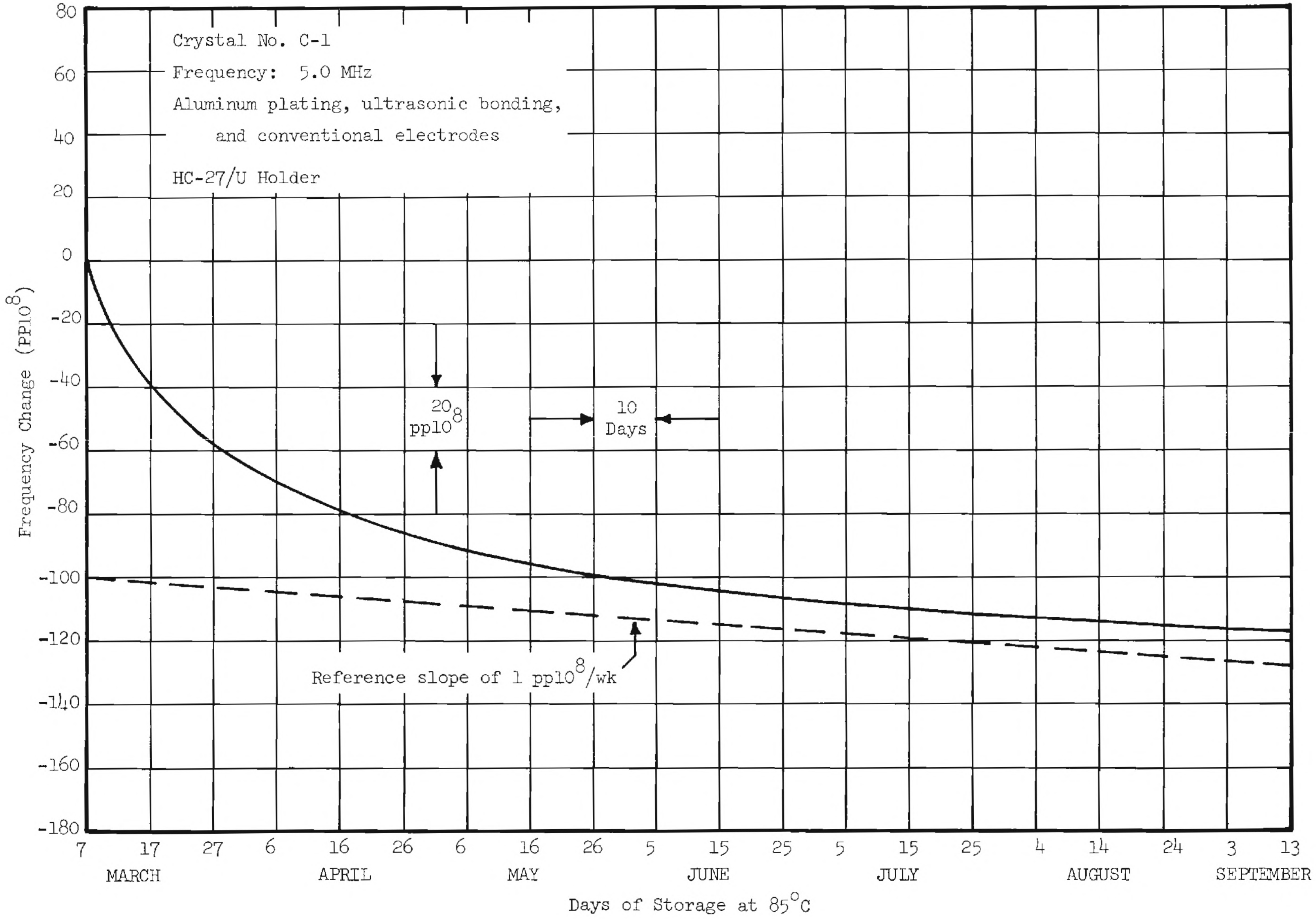

Figure 16. Aging data for aluminum plated 5 MHz unit No. C-1. Conventional electrodes.

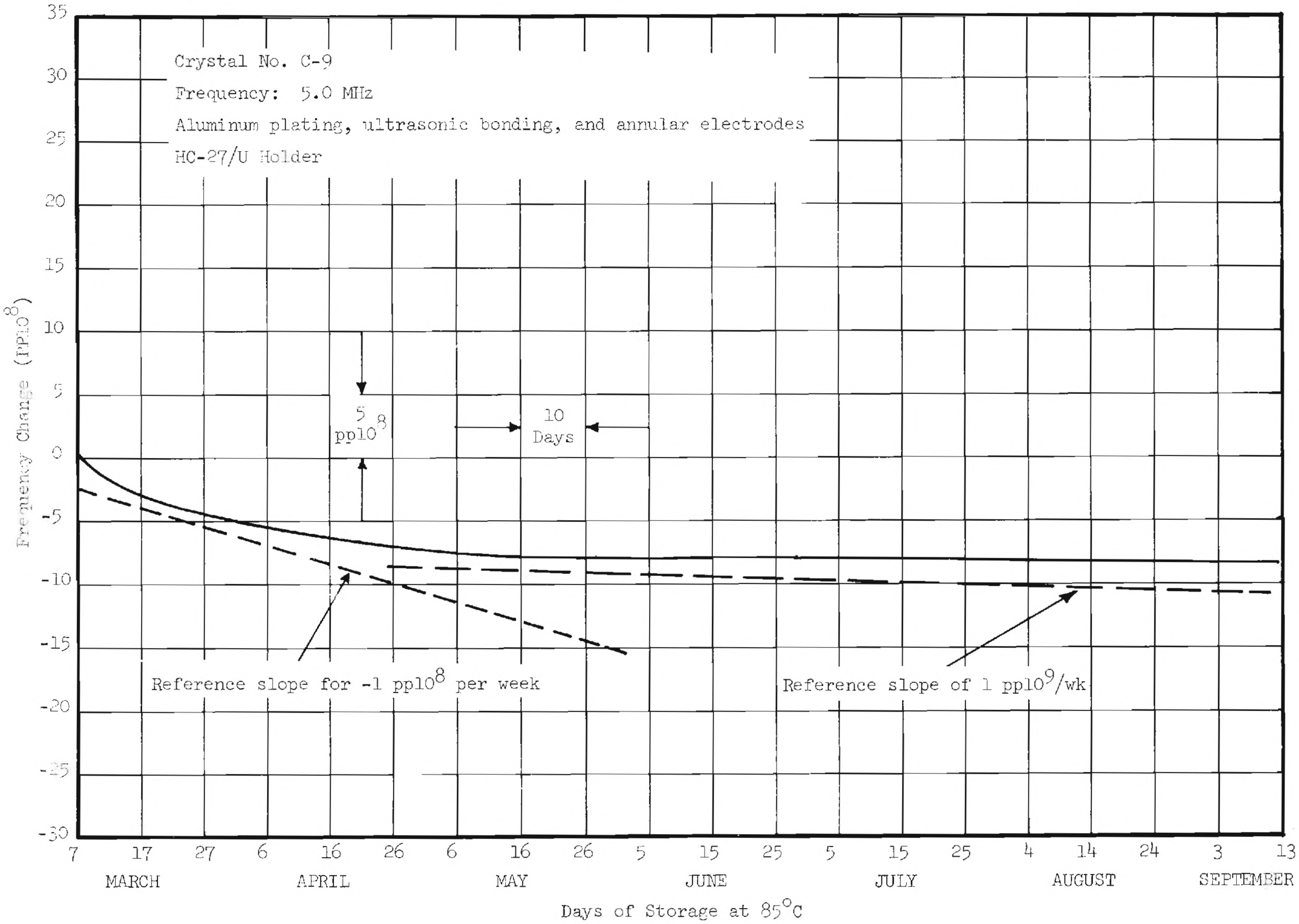

Figure 17. Aging data for 5 MHz unit No. C-9. Annular electrodes 9/32" O.D., 7/32" I.D.

TABLE 8

Average Stabilization Period of 5 MHz Units
with Respect to Excitation Method at 85°C

Excitation	Number of Units	Days	ΔF During Period ($pp10^8$)	Remarks
Perpendicular	6	66.0	83.0	Unit C-2 not included
Annular	17	12.5	13.9	Unit C-10 not included

It is quite apparent here that the resonators formed with annular electrodes display a much shorter time of stabilization by a factor of 1/5; and the total frequency change experienced by the annular plated resonators is reduced by an even greater ratio (1/6). It must be noted, however, that of the 25 resonators examined 10 (3 with conventional, 7 with annular electrodes) were plated with aluminum without preheating the quartz substrate,* a method known to be conducive to higher aging rates. The effect of the inclusion of aging data of this group of resonators is to accentuate somewhat the observed differences between resonators plated with the two different configurations. The data in the succeeding Table 9 are somewhat biased for the same reason.

A similar comparison of the post stabilization aging rates for the total period and the last 30-day period of operation is given in Table 9. Here the aging rates during the total post stabilization period are shown to be in the ratio 1/3 and during the final period to be in the ratio 1/14.

TABLE 9

Average Post-Stabilization Aging Rates of 5 MHz Units at 85°C

Excitation	Number of Units	Aging Rate Total Period ($pp10^8$/wk)	Aging Rate (last 30 days) ($pp10^8$/week)	Remarks
Perpendicular	6	0.53	0.43	Unit C-2 not included
Annular	17	0.18	0.03	Unit C-10 not included

---

*Preheating the quartz when aluminum was deposited over copper in order to form the annulus resulted in alloying of the two metals and poor resolution of the annulus by etching methods.

Another factor of interest in the comparison of the two types of resonators is the relative Q value obtained for the units of the two plating configurations.

The average Q values were 0.88×10^6 for the units having perpendicular-field excitation and 1.45×10^6 for those having annular excitation. Hence an increase in Q by a factor of about 1.6 was obtained by use of annular electrodes.

d. Aging measurements (cold-weld holders)*

Twenty-three units having annular electrodes 7/32 inch I.D. and 9/32 inch O.D. were prepared for this work. The holders used were types HC-6 and E7-1. Fifteen units were sealed for aging studies, one of which failed. The aging data for fourteen units for about 1000 hours storage are given in Table 10.

Seven of these units failed to reach an aging rate of ± 1 pp10^8/week. One unit, No. E-9, is a leaker. The others, numbers E-2, E-3, E-7, E-10, E-12, and E-16 aged highly positive. Five units achieved an aging rate of 1 pp10^8/week after an average of 17 days storage. The average ΔF during this time was +14.3 pp10^8.

Only two units, numbers E-6 and E-15 had an initial aging rate of ± 1 pp10^8/week or less.

The average aging was +2.5 pp10^8/week,** a value much higher that that obtained for similar units sealed in glass holders (HC-27/U).

Aging data for one of the better units (E-5) is shown in Figure 18. Figure 19 shows the aging for unit E-10. The latter unit has aged at an average rate of +3.2 pp10^8/week for 960 hours.

e. Comments

Although it has been conjectured by a number of investigators that a large fraction of the aging observed for relatively stable AT-cut quartz resonators in evacuated sealed containers has been due to mass transfer by an adsorption-desorption mechanism, otherwise credible evidence often has been obscured by an appreciable number of units not following the expected behavior pattern. For instance aging vectors due to strain relief, and on occasion due to defects within the quartz, have frequently counterbalanced or superimposed upon the expected vector in a manner such that the result was difficult to interpret.

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[*] Baked-out and sealing techniques were similar to those described previously for 3 MHz units.

[**] Not including unit E-9.

TABLE 10

AGING DATA FOR 5 MHz UNITS WITH
ANNULAR ELECTRODES IN COLD-WELD HOLDERS

		Vacuum Bake		Stabilization Period*		Aging After Stabilization**		
Unit	Holder Type	Time (Min.)	Temp. (°C)	Time (Days)	ΔF ($pp10^8$)	Time (Hours)	Rate ($pp10^8$/week)	Remarks
E-2	HC-6	60	250	-	-	1128	+ 1.80	Has not stabilized
E-3	E7-1	60	250	-	-	1128	+ 7.40	Has not stabilized
E-4	E7-1	60	250	25	+33.8	528	+ 0.60	
E-5	HC-6	60	300	11	+ 4.5	736	+ 0.85	
E-6	HC-6	60	300	0	0	960	+ 0.53	Initial Aging < 1 $pp10^8$/wk
E-7	E7-1	60	300	-	-	960	+ 9.17	Has not stabilized
E-8	E7-1	60	300	25	- 6.0	360	+ 0.79	
E-9	HC-6	60	300	-	-	960	- 5.90	Has not stabilized (leaker?)
E-10	E7-1	60	350	-	-	960	+ 3.20	Has not stabilized
E-11	HC-6	60	350	18	+10.0	528	+ 0.80	
E-12	E7-1	60	350	-	-	960	- 2.00	Has not stabilized
E-14	E7-1	60	400	4	-17.0	696	- 0.34	
E-15	E7-1	60	400	0	0	792	- 0.51	Initial Aging < 1 $pp10^8$/wk
E-16	E7-1	(No Bake)		-	-	792	+ 5.00	Has not stabilized

---

*Time (Days) at 85°C for unit to reach an aging rate of ± 1 $pp10^8$/week and the total ΔF during that period.

**Aging subsequent to the stabilization period except as noted in remarks column.

The data of this report have given clear-cut evidence to support the adsorption-desorption mechanism as the principle one associated with the aging of the resonators under study here. This has been accomplished in part by readucing mounting strains and by examination and elimination of atypical crystals by x-ray topography. The use of aluminum as well as gold plated electrodes and the employment of annular electrodes and cold welded containers have given new insights into aging phenomena. In aging data obtained recently it has been observed (as reported in the text and Tables 2A, 3A, 4A, and 9 and 10 of this report) that the following general types of initial aging behaviors occur:

(1) Resonators with aluminum electrodes mounted in glass envelopes age negatively.

(2) Resonators with annular electrodes mounted in glass envelopes age slightly positively.

(3) Resonators with aluminum electrodes mounted in cold-welded nickel plated containers age negatively.

(4) Resonators with annular electrodes mounted in cold-welded nickel-plated containers aged positively, the rate increasing with bake-out temperature.

(5) Resonators plated with gold and mounted in a glass container usually age positively; however, at higher temperatures (125°C), units in the T-5$\frac{1}{2}$ container aged markedly negatively.

(6) Different behaviors have been noted for the same types of units mounted in containers of small or large internal area; i.e., for the HC-27/U and T-5$\frac{1}{2}$ glass containers and the HC-6/U and E7 type cold welded containers, respectively.

(7) Resonators in leaking containers or in containers with large virtual leaks (due to an internal source) age rapidly downward.

In particular it is to be noted that the resonators with annular electrodes, exposing only a quartz surface over the active zone of the resonator, age very little or slightly upward in glass containers. The adsorption properties of the quartz surface and the interior of the glass, being very similar, lead to an early balance of mass transfer effects. For aluminum plated resonators, in glass or in nickel containers, the relatively high adsorption property of the aluminum (or its alumina coating) lead to initial loading of the aluminum and negative aging. For gold plated resonators the reverse is true; the gold is unloaded and positive aging results. However, excessive pressure within the container or outgassing due to aging at high temperatures may result in loading of the gold coated quartz and negative aging. In the cold welded containers used, either nickel or nickel plated, units with annular electrodes aged positively; and the rate and degree of aging increased as the bake-out temperature increased.

Each of these phenomena can readily be explained by the mass transport theory of aging utilizing known adsorption-desorption phenomena. Furthermore, information has been obtained which gives a clearer insight into aging behavior of quartz resonators and which provides information as to methods of reducing aging to a required or desired level.

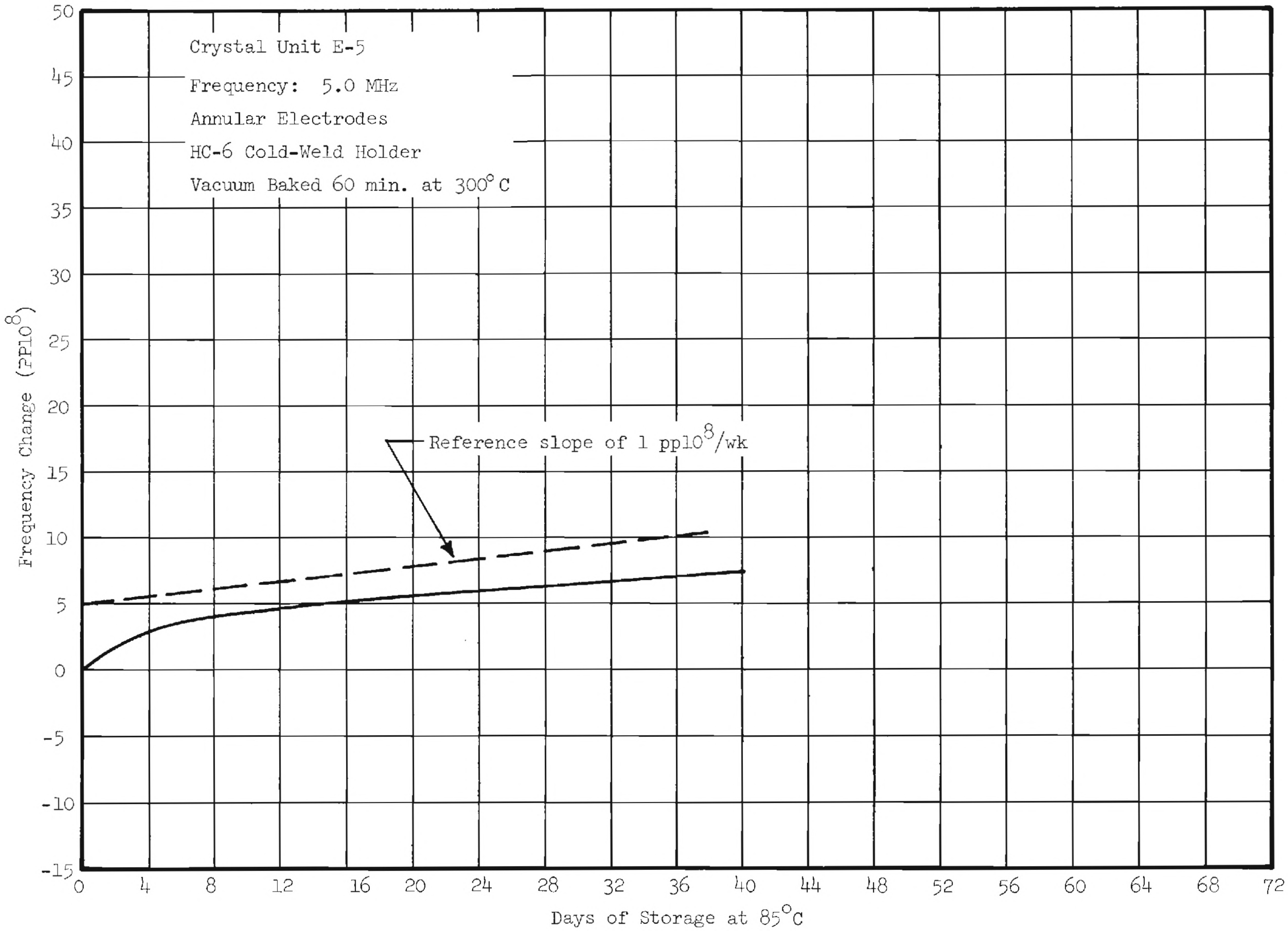

Figure 18. Aging data for 5 MHz unit No. E-5. Annular electrodes 9/32" O.D., 7/32" I.D. HC-6 type cold-weld holder.

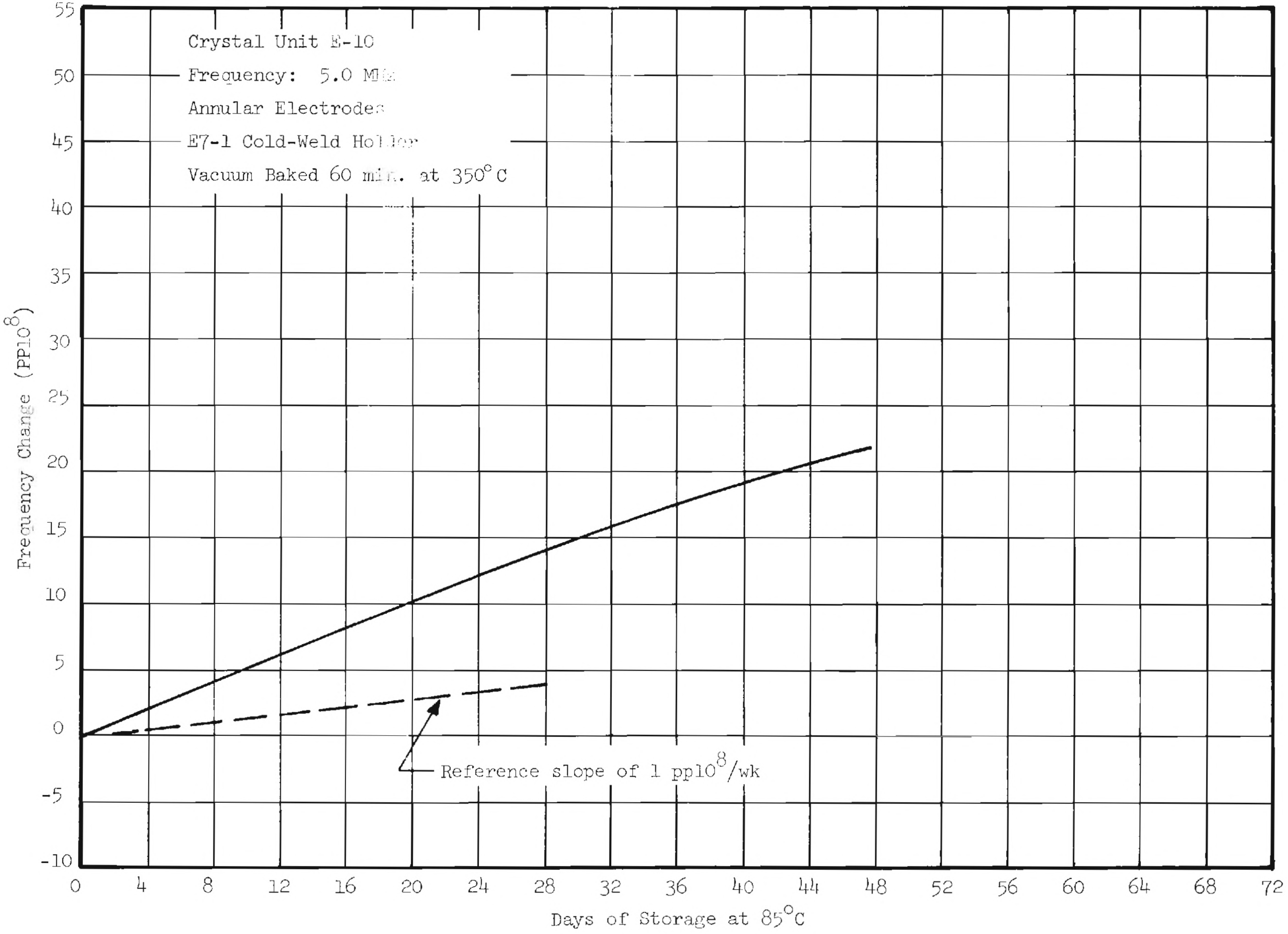

Figure 19. Aging data for 5 MHz unit No. E-10. Annular electrodes 9/32" O.D., 7/32" I.D. E7-1 type cold-weld holder.

5. Aging of 10 MHz Fundamental Resonators at 125 and 85°C

a. General

In June 1963, 42 each 10 MHz fundamental units were fabricated for aging studies at 85°C. All were base plated with about 2500 Å of evaporated gold and then overplated with 500 Å of gold. Fabrication variables were introduced as tabulated below:

Group	No. Units	Cement	Holder (evacuated)
A	10	5504	T-$5\frac{1}{2}$
B	10	5504	T-$5\frac{1}{2}$
C	11	Pyroceram + Ag	HC-27/U
D	11	5504	HC-27/U

The units were aged at 85°C for about 16 months (until September 1964). Twenty-seven of the units passed an acceptance requirement of not over ± 4 pp10^7 total aging for the first 30 days after which the aging rate was ± 1 pp10^7/week or less. The units which failed to meet the acceptance requirement were dismantled for x-ray studies. The 27 good units were stored at room temperature for 14 months, until November 1965, at which time they were placed in a 125°C oven for further aging studies.

b. Aging measurements at 125°C*

Table 11 shows the average aging rate of all units with respect to the type holder for a period of 5000 hours; and Figures 20 and 21 display aging data for typical units at both 125°C and for a subsequent period at 85°C. Data for each temperature were plotted on the same graph for comparison.

TABLE 11

Average Aging Rates of 10 MHz Units at 125°C

Holder Type	Aging Rate 1st 30 days (pp10^7/wk)	Aging Rate Last 30 days (pp10^7/wk)	Aging Rate Total Period (pp10^7/wk)	Remarks
HC-27/U	+1.01	+0.09	+0.21	
T-$5\frac{1}{2}$	-1.64	-1.85	-1.44	(not including A-4)

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[*] Measurements were also made at 30 MHz (third overtone). The data were very similar and only the fundamental frequency data were used for Tables 11 and 12 which follow.

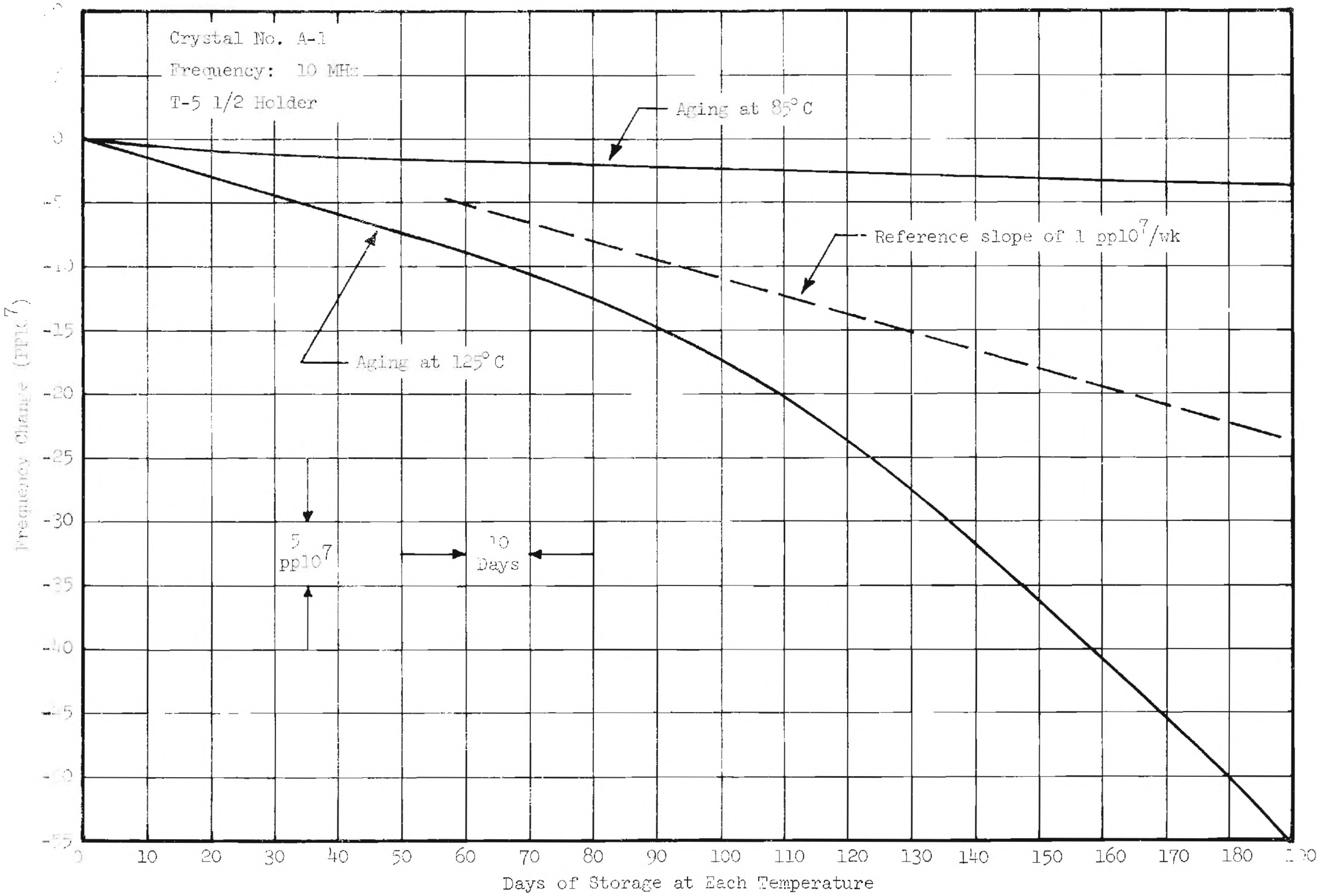

Figure 20. Aging data for gold plated 10 MHz unit No. A-1 at 85 and 125° C. Sealed in evacuated T-5 1/2 holder.

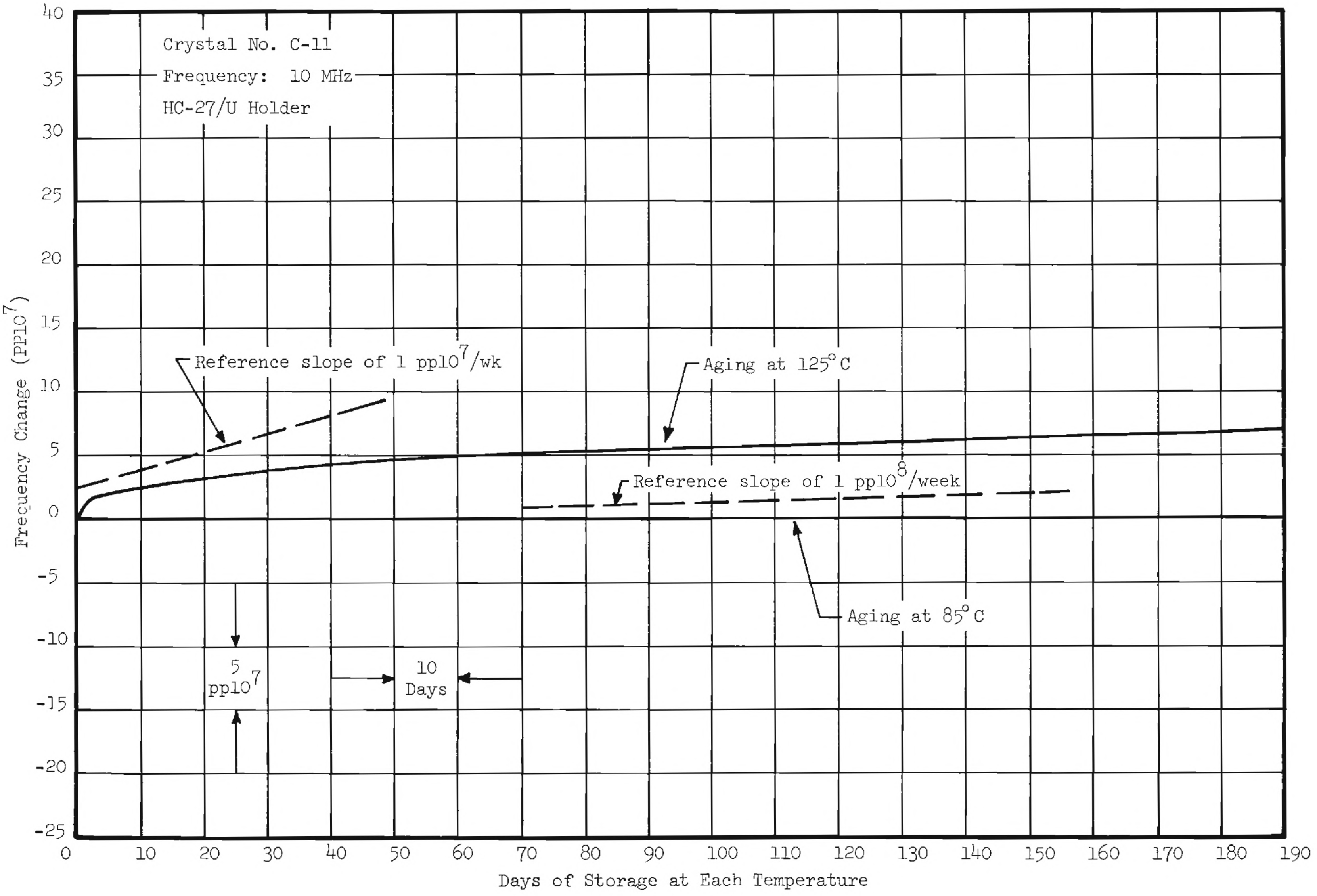

Figure 21. Aging data for gold plated 10 MHz unit No. C-11 at 85 and 125° C. Sealed in evacuated HC-27/U holder.

Examination of the data of Table 11 reveals that the aging rates of the resonators in the HC-27/U and T-5½ containers are in the respective ratio of 2/3 for the first 30 days, 1/20 for the last 30 days and 1/7 for the total period of 30 weeks. It is also noteworthy that the aging rate did not decrease for the units in the T-5½ holder but actually increased. Although the cement type is an additional variable in that pyroceram-silver was used for most of the units in the HC-27/U container, it is believed that the container is the principal variable responsible for the aging differences observed between the two types. The larger size of the T-5½ container, and thus its greater interior surface, the lower bakeout temperature (275°C compared to 450°C), and the small tubulation through which gas must be pumped result in a relatively high final pressure in the sealed unit. At any given aging temperature the available reactive gases come to some equilibrium with respect to the rate of adsorption on the enclosed resonator or its plating (including possible reaction with the plating). If the equilibrium is unbalanced by an increase in temperature, a new set of conditions exists and the equilibrium must be re-established. The larger interior size of the T-5½, the lower bakeout temperature, and the higher final pressure may be contributors to the relatively large aging rates observed in this container. It may be noted in addition that similar aging rates were observed for commercially fabricated gold plated 3 MHz resonators at 125°C indicating a behavior which appears to be characteristic of these units as now fabricated in large glass envelopes.

c. Aging measurements at 85°C

After 5000 hours of aging for the 10 MHz units at 125°C, the oven temperature was decreased to 85°C for an additional 5000 hours of measurement. The reduction of the aging rates was dramatic as shown by a comparison of the data of Tables 11 and 12 and Figures 20 and 21. All units aged at rates much less than 1 pp10^7/week during the first 30 days and reached rates well under 1 pp10^8/week during the last 30 day period of the 5000 hour period.

TABLE 12

Average Aging Rates of 10 MHz Units at 85°C

Holder Type	Last 30 days Aging Rate at 125°C* (pp10^7/wk)	Aging Rate 1st 30 days (pp10^7/wk)	Aging Rate last 30 days (pp10^7/wk)	Aging Rate Total Period (pp10^7/wk)	Remarks
HC-27/U	0.09	0.16	0.01	0.03	
T-5½	1.85	0.28	0.07	0.08	(not including A-4, B-6, and B-10)

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[*] Repeated from Table 11 for comparison.

A comparison of the aging rates for the last 30 days at 125°C and for the first 30 days at 85°C reveals that the rate of the resonator in the HC-27/U holder underwent a small increase (due probably to thermal shock) whereas the units in the T-$5\frac{1}{2}$ underwent a marked reduction in the ratio of 7/1. Nevertheless the resonators in the HC-27/U continue to show marked superiority in aging rates in the ratio 1/2, 1/7, 1/3 respectively for the first 30 days, last 30 days, and total period of 5000 hours respectively. Hence the relative advantage of the HC-27/U container for the future aging of the resonators under 85°C or 125°C temperature storage is clearly indicated.

D. SPECTRUM ANALYSIS STUDIES

1. 3 MHz Resonators with Perpendicular Excitation

The frequency spectra of a number of 3 MHz units similar to the ones aged at 85°C (discussed in Section III, C, 3) were recorded. Most of the data were obtained at 25°C. Data for a typical resonator, D-3, are shown in Figure 22. The first major response (less than 10 db down) near the fundamental response is at +170 kHz. No responses of importance below the fundamental were found for any of the units of this type examined.

One unit (No. 10-23) was very erratic at 85°C. Subsequent measurements revealed a large activity dip near 80°C. The spectrum of the main response of this unit was analyzed at several temperatures from 45 to 85°C. The data were presented in detail in Technical Report ECOM-02251-3. The spectra recorded the movement of a spurious response having a high negative temperature coefficient of frequency. At each temperature it approached more closely the main response and finally merged with it, causing an activity dip at about 77°C. As the temperature was further increased the response crossed over the main one and continued to separate from it in a negative direction. Figure 23 shows the appearance of the main response at 77°C, the approximate temperature of maximum attenuation. The erratic frequency behavior of this unit at 85°C is apparently due to the presence of some factor introducing this spurious response. The relatively large negative temperature coefficient of frequency of the response results in its interference with the fundamental response over a wide range of temperature.

2. 5 MHz Resonators with Annular Excitation

A number of frequency spectra were made for units having annular electrodes. The outside diameters of the annuli were 9/32 inch while the inside diameters were varied from 1/16 to 1/4 inches. As the I.D. of the annulus was increased the spectra revealed that the series resistance of the main thickness-shear response increased resulting in a lower amplitude of the response and the main response became sharper (i.e., higher Q).*

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*These observation were also confirmed by electrical measurements of R_s, L_1 and Q.

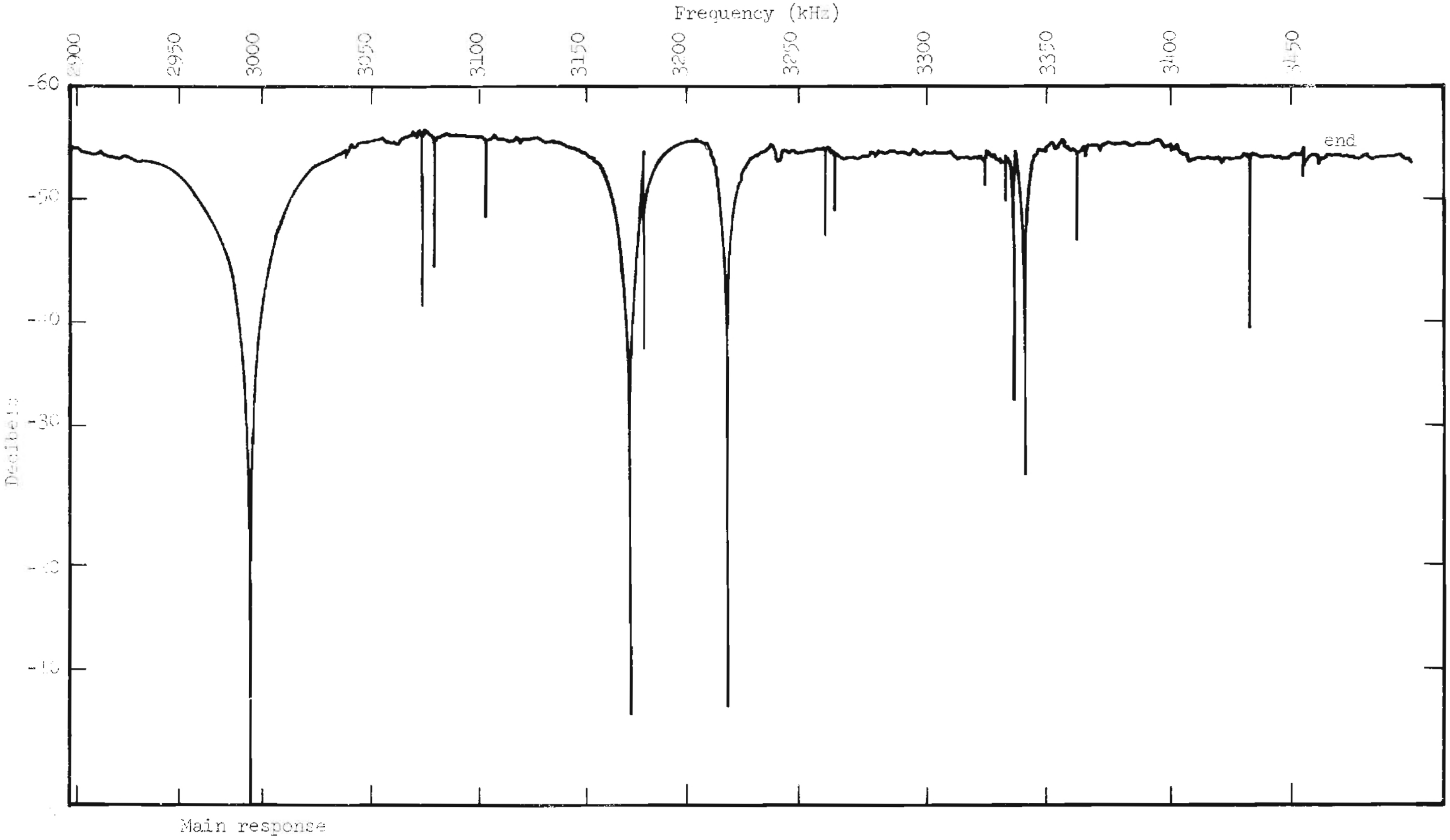

Figure 22. Spectrum of aluminum plated 3 MHz unit No. D-3. Sealed in evacuated HC-27/U holder.

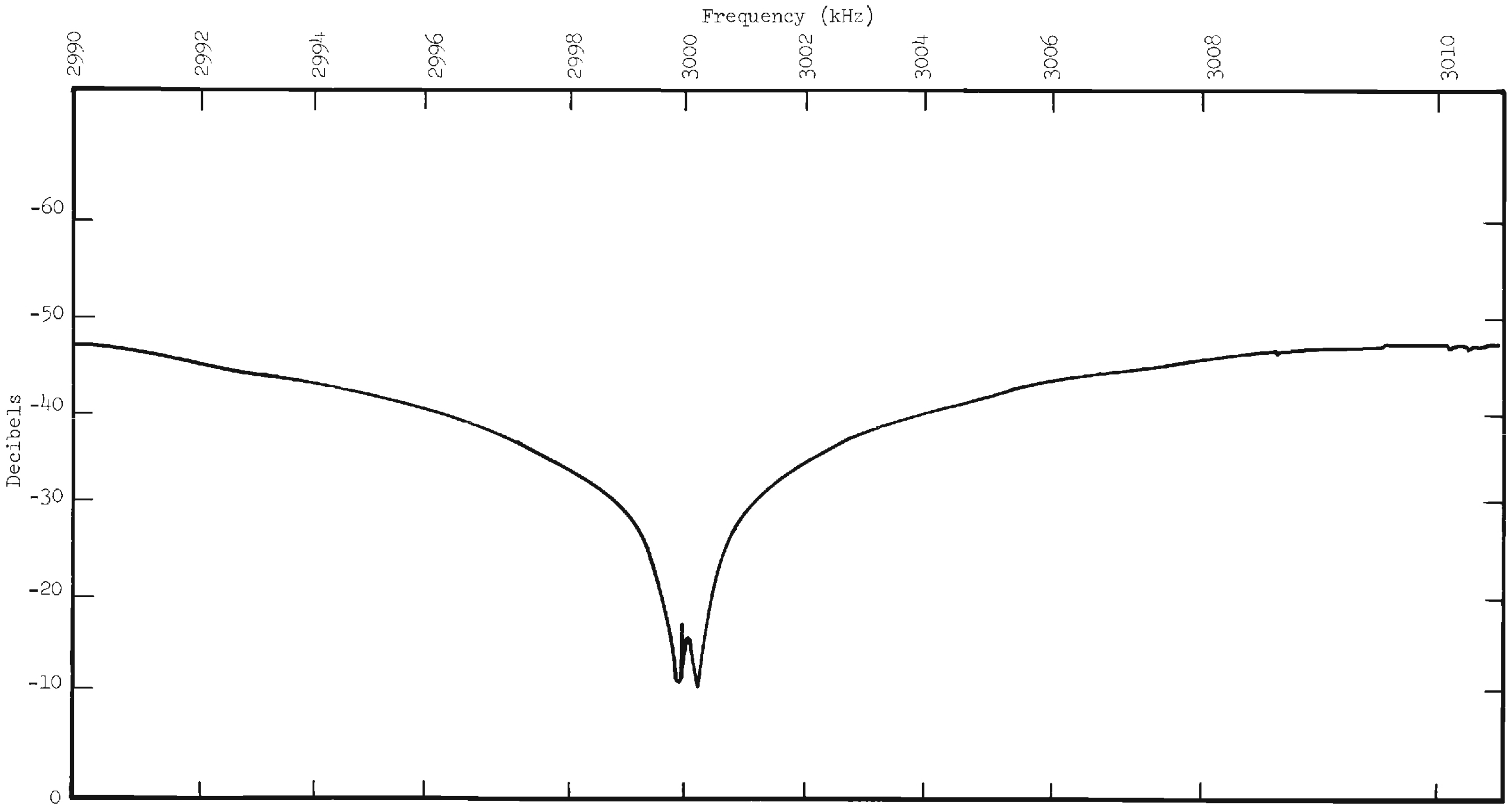

Figure 23. Spectrum of the Main response of aluminum plated 3 MHz unit No. 10-23 at 77° C.

On the basis of these and other studies, the optimum annular electrode was selected as 7/32 inch I.D. and 9/32 inch O.D. for 5 MHz units 1/2 inch in diameter and a 2.5 diopter plano-convex shape.*

A typical spectrum for a unit having the optimum annular electrode dimensions is shown in Figure 24. The main response was attenuated about 25 db after the annulus was formed and became weaker than a number of other responses, the first of which occurred at about +190 kHz. The Q, however, was increased by a factor of about two.

Annular electrodes were also applied to flat 5 MHz wafers with beveled edges and the resonators were completed as for the plano-convex units. No important attenuation of the principal response or improvement in the Q occurred for these units.

E. MISCELLANEOUS EXPERIMENTS

1. Final Frequency Adjustment of Annular-Electrode Units

a. General

In Technical Report ECOM-02251-3, November, 1966, it was demonstrated that appreciable frequency adjustment of plano-convex, annular-electrode units of the chosen annulus dimensions could not be made by plating or deplating of the electrodes.** A number of possibilities for frequency correction exists; one of these was examined during the current period.

b. Frequency adjustment by quartz etching

The annular electrodes used for the units studied for aging were of evaporated aluminum. For this experiment they were of evaporated chromium over-plated during the same evacuation with evaporated gold. This plating combination is highly resistant to an aqueous ammonium bifluoride etching solution and the quartz could be readily etched without damage to the plating or to its adherence to the quartz.

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[*] The basis for the selection was maximum Q values consistent with reasonable impedance levels. See Technical Report ECOM-02251(E)-10.

[**] The internal area of the annulus chosen was equal to or greater than the principal oscillating regions of the quartz wafer excited in first thickness shear mode.

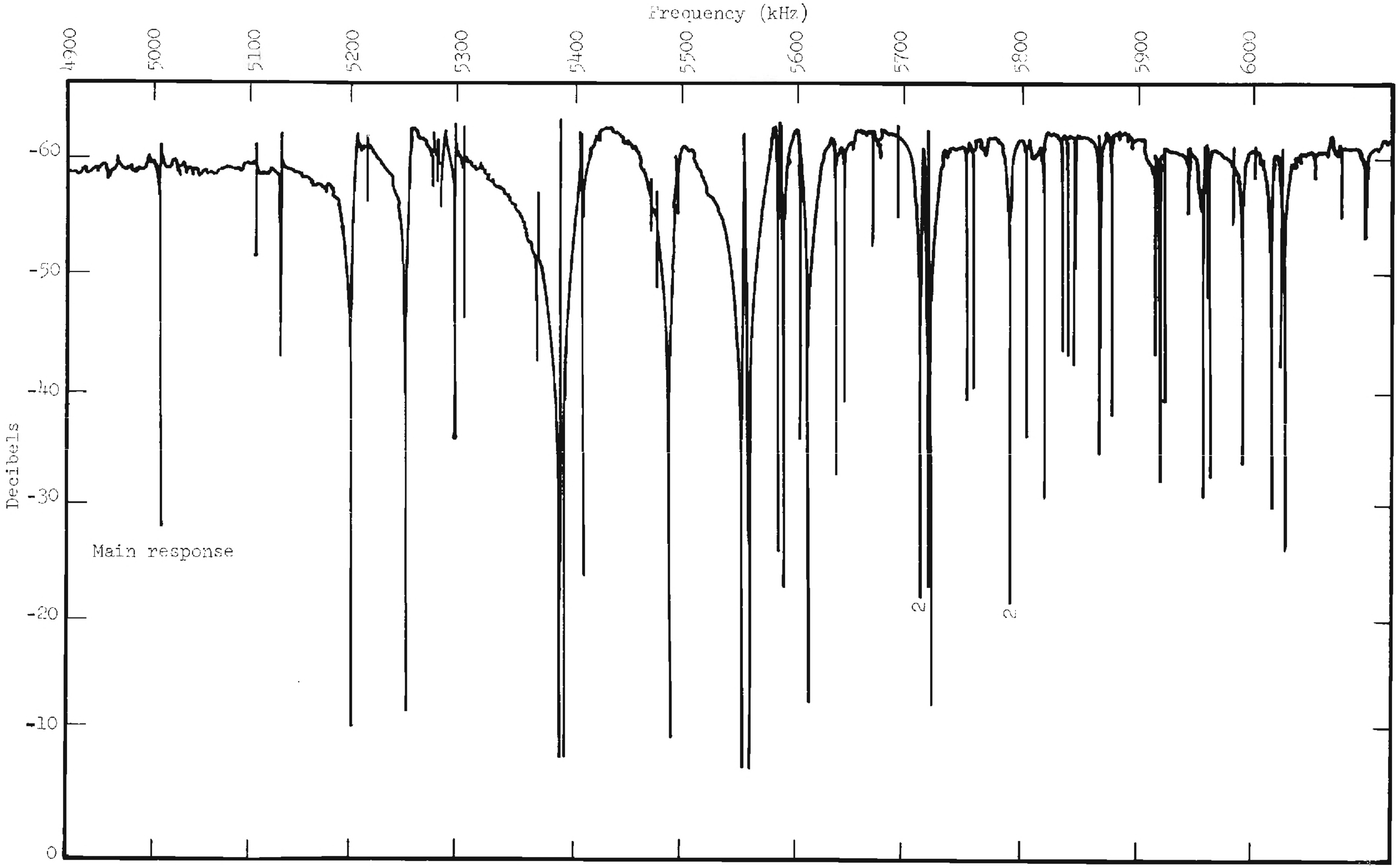

Figure 24. Spectrum of 5 MHz unit S-AR-6. Annular electrodes 9/32" O.D., 7/32" I.D.

Units plated as above were etched in ammonium bifluoride in distilled water (saturated at room temperature), and the frequency and resistance were determined at five minute intervals. The frequency change vs. etch time are plotted in Figure 25. The frequency of the unit having a 7/32 inch I.D. annulus changed at a greater rate than the one with a 1/8 inch I.D. annulus, but the rate per unit area exposed in the center was greater for the latter by about 5/3, compared to that of the 7/32 I.D. zone, indicating the greater activity of the central portion of the plate. An important observation was that the frequency of units with each configuration shifted about +2200 ppm before the series resistance increased.

The same units used for these experiments were stripped of the chrome-gold plating and replated with aluminum annuli. They were then used for frequency vs. temperature studies of units with annular electrodes reported below.

2. Frequency vs. Temperature Studies of 5 MHz Units with Annular Electrodes

a. General

At the start of this research it was assumed that the temperature coefficient of frequency (TCF) for annular excitation would be approximately the same as for perpendicular excitation. Angles were specified for the 5 MHz wafers such that the upper turning point would be 85°C for wafers excited by the perpendicular field method. Aging data at 85°C soon revealed the units with annular electrodes to be more sensitive to small oven temperature deviations than those with the normal keyhole electrode. Several units having annuli of different I.D. were fabricated and temperature cycled from 25 to 100°C. The units were not mounted in sealed containers in order to avoid temperature measurement errors which might be introduced by an evacuated container.

b. Frequency measurement vs. temperature measurements for plano-convex resonator

Figure 26 illustrates the typical frequency-temperature relations obtained for a plated unit before and after the annulus was formed. When the 1/8 inch I.D. annulus was formed the upper turning point shifted -22.5°C and the maximum frequency deviation from the 25°C value at the minimum was reduced from -46 ppm to -14 ppm.

Figure 27 shows similar data for a unit having an angle of cut of quartz giving a turn over temperature near 70° instead of 85°C. Here the upper turning point was shifted about -17.5°C; and the maximum frequency deviation for annular excitation was < ± 5 ppm from the median value over the range 25 to 90°C.

The behavior of a third unit having annular electrodes 7/32 inch I.D. is shown in Figure 28. This unit held frequency within ± 2.0 ppm from the median value between 25 and 75°C.

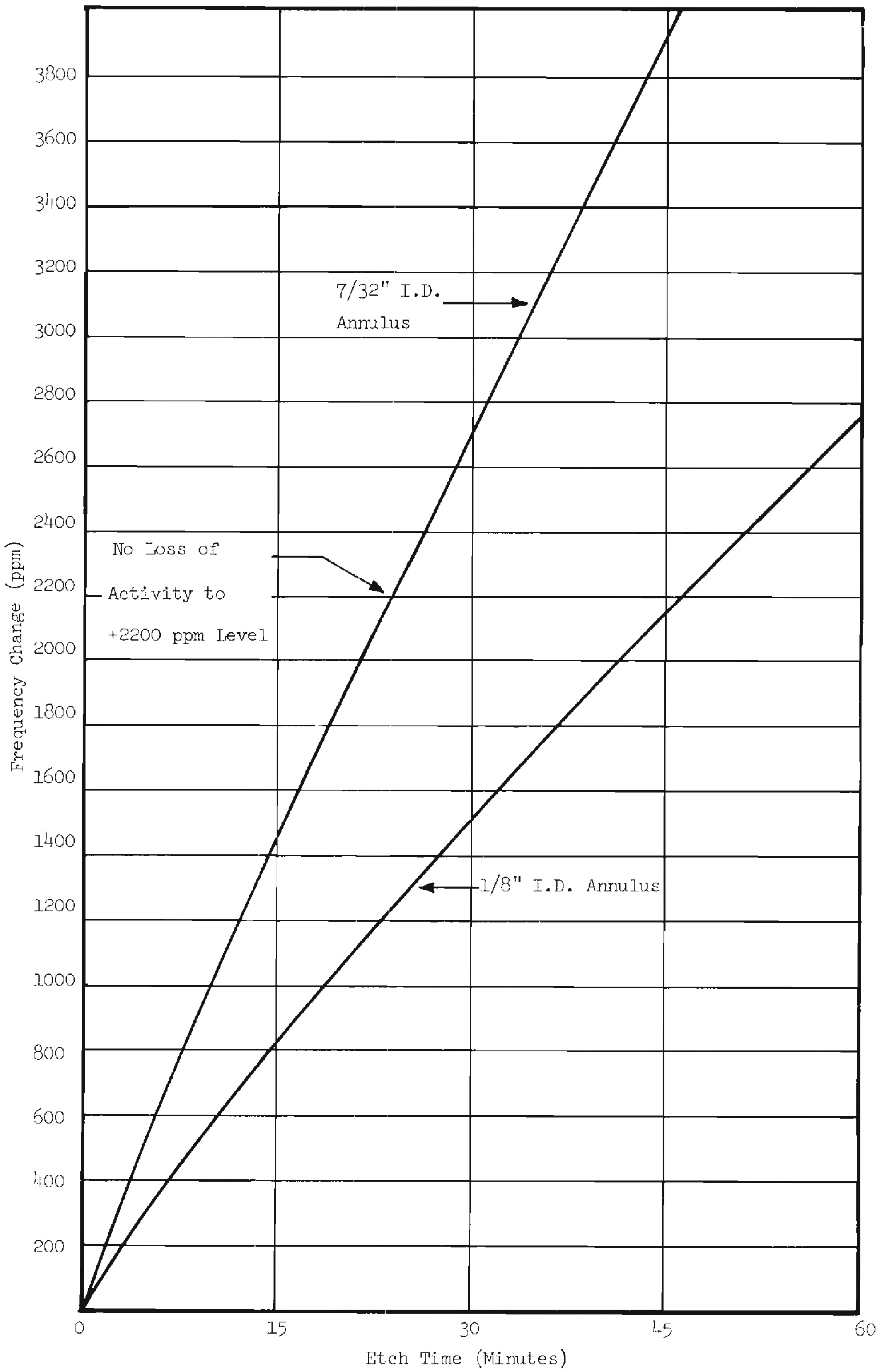

Figure 25. Frequency changes versus quartz etching time for 5 MHz units. Annular electrodes 1/8" and 7/32" I.D., 9/32" O.D.

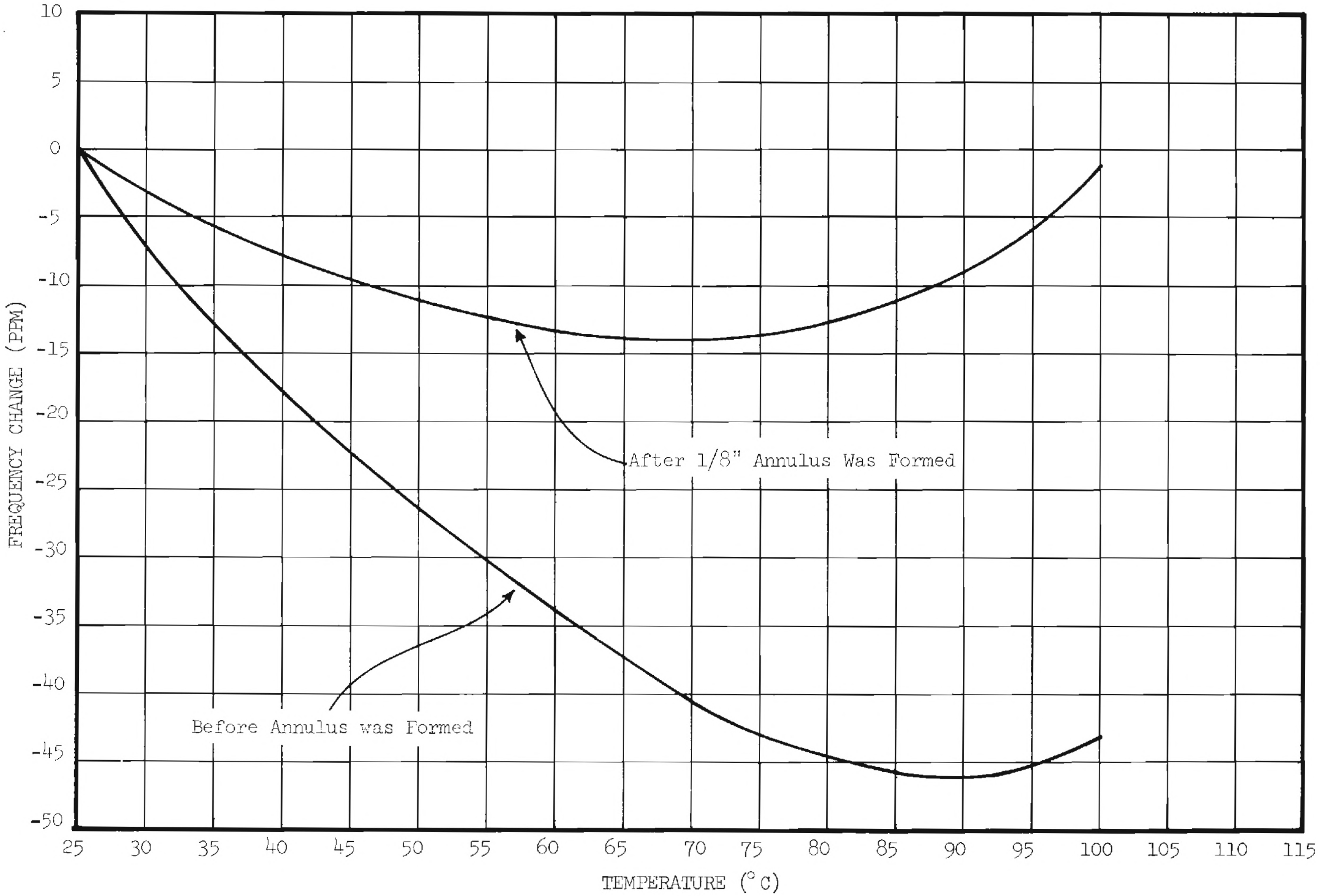

Figure 26. Frequency-temperature characteristics for a 5 MHz unit before and after the 1/8" I.D. annulus was formed.

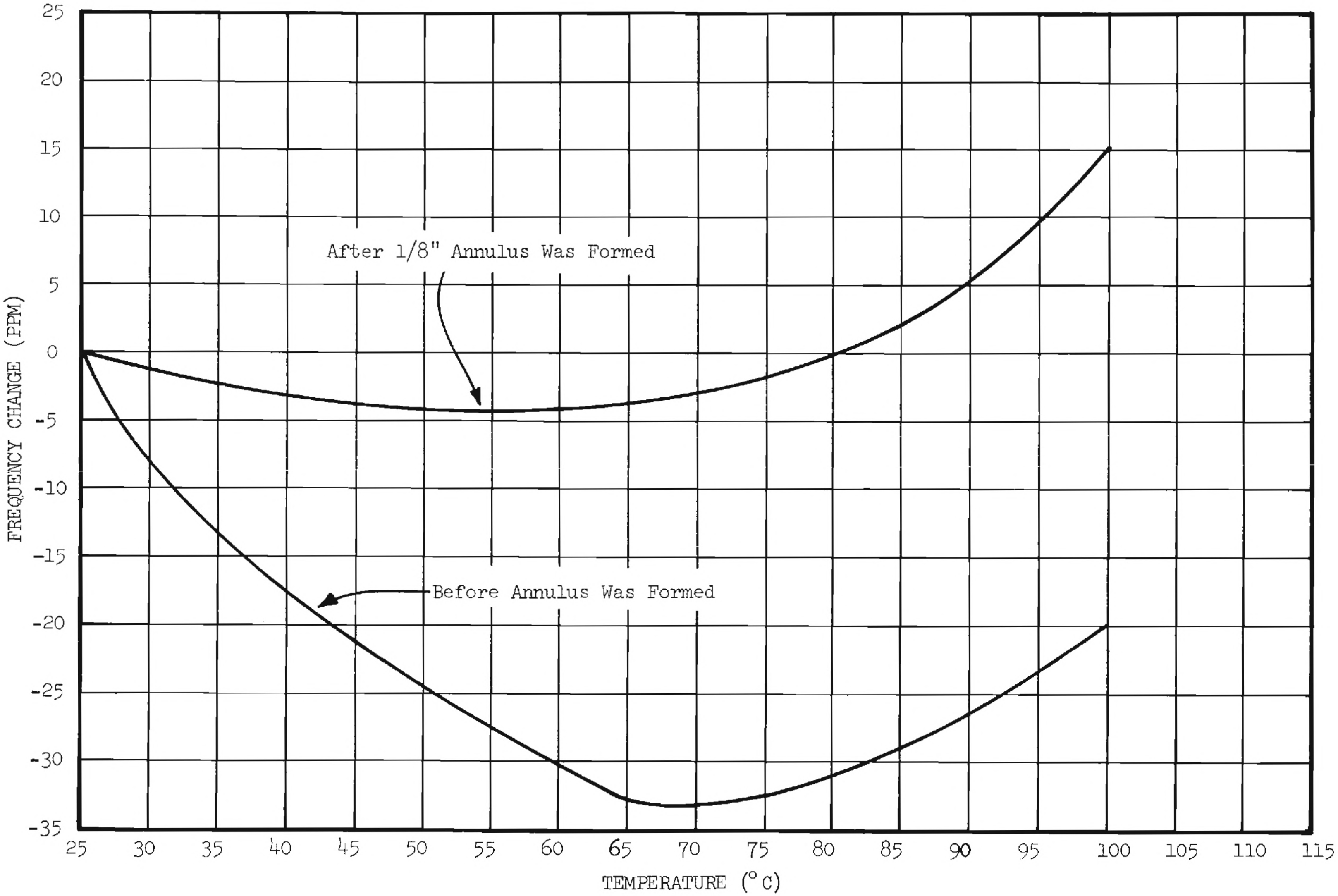

Figure 27. Frequency-temperature characteristics for a 5 MHz unit before and after the 1/8" I.D. annulus was formed.

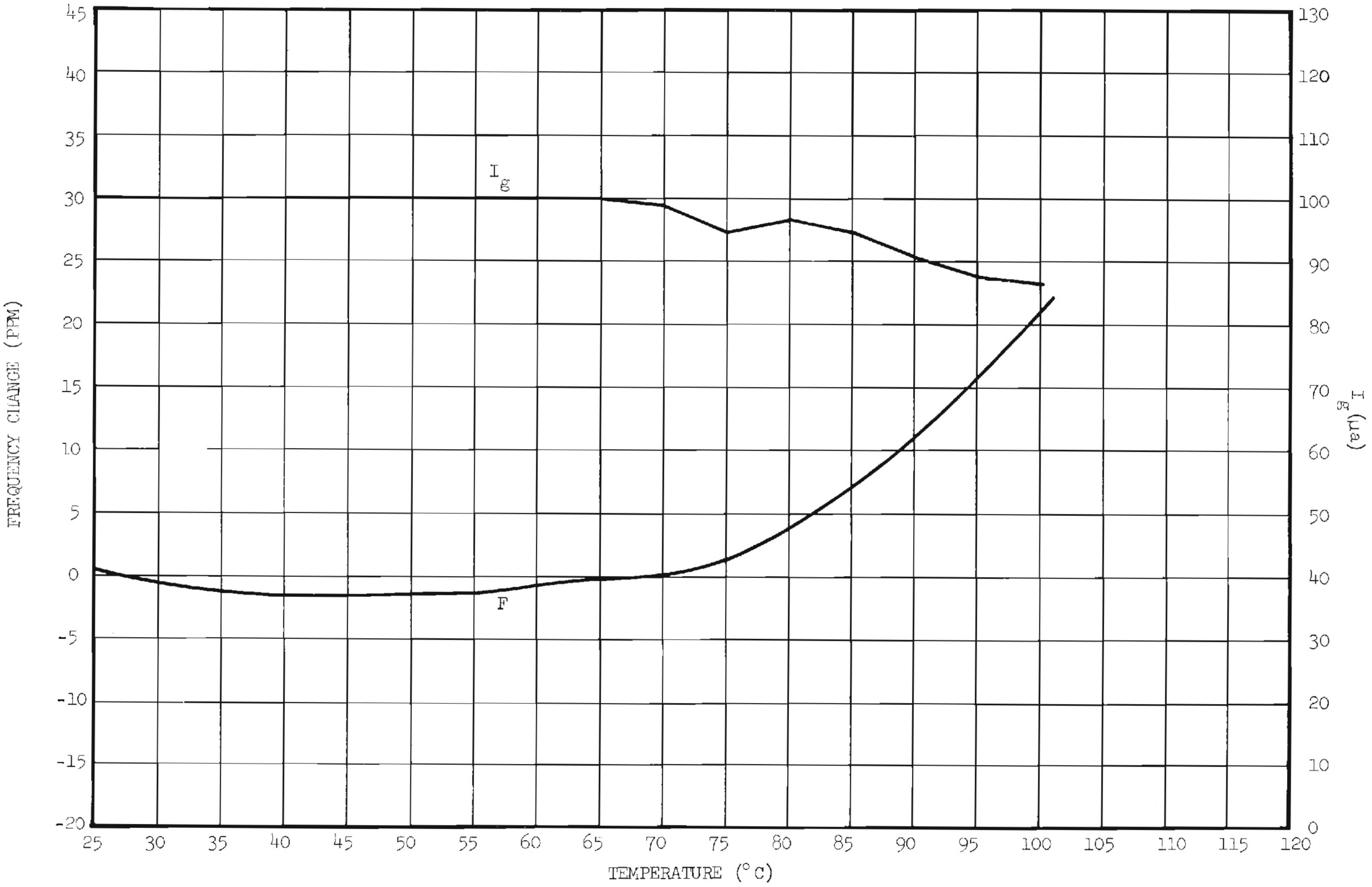

Figure 28. Frequency-temperature characteristics of a 5 MHz unit having annular electrodes 9/32" O.D., 7/32" I.D.

When the I.D. of the annulus was reduced to 1/16 inch the frequency-temperature curve was similar to that obtained for units of conventional electrode configuration.

c. 5 MHz resonators fabricated from flat wafers with beveled edges

Several 5 MHz units fabricated of flat wafers with beveled edges were investigated. The results were obscured by numerous activity dips. However, enough data were obtained to indicate that the TCF of the beveled-edge wafers is not improved by the use of annular electrodes.

d. Comments

During the frequency vs. temperature measurements it was observed that the annular electrode units subjected to etching for frequency adjustment experiments, described in Section III, E, 1, b, preceding, were remarkably free of activity dips occurring during temperature cycling of the units. This observation indicates a need for a study of the effect of etching on the spurious responses of resonators of plano-convex configuration. Preliminary data give evidence that etching may be an important method of reducing the number of units with undesired temperature sensitive responses leading to activity dips similar to the one, depicted in Figure 23.

3. Aging Studies of 3 MHz Unit NS-1* Comparing the Effect of Intermittent and Continuous Oscillation

The temperature stabilities of the 85°C ovens in use are determined by using commercial 3 MHz units operated at 3.22 MHz, the third inharmonic response in Z'. Figure 8 of Interim Report No. 8 of this contract** shows the frequency vs. temperature relation of this response. Similar units having an 85°C upper turning point and operated on the main response (111 mode) were intended to be used for thermometer crystals at 125°C. However, the high negative aging rate at 125°C precluded their use as will be noted in Figure 29; the aging of unit NS-1 was -8.2 ppm in 160 days at 125°C even though the unit had previously been aged about one year at 85°C. This rapid rate confirms the unsuitability of the T-5½ type container for the enclosure of resonators to be exposed to high temperatures as discussed previously in Section III, C, 5, b. The measurements were made with a crystal impedance bridge and the unit was oscillated only during measurements.

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*Commercially fabricated of swept natural quartz mounted in T-5½ holder.

**Contract DA-36-039-AMC-02251(E), February 15, 1965.

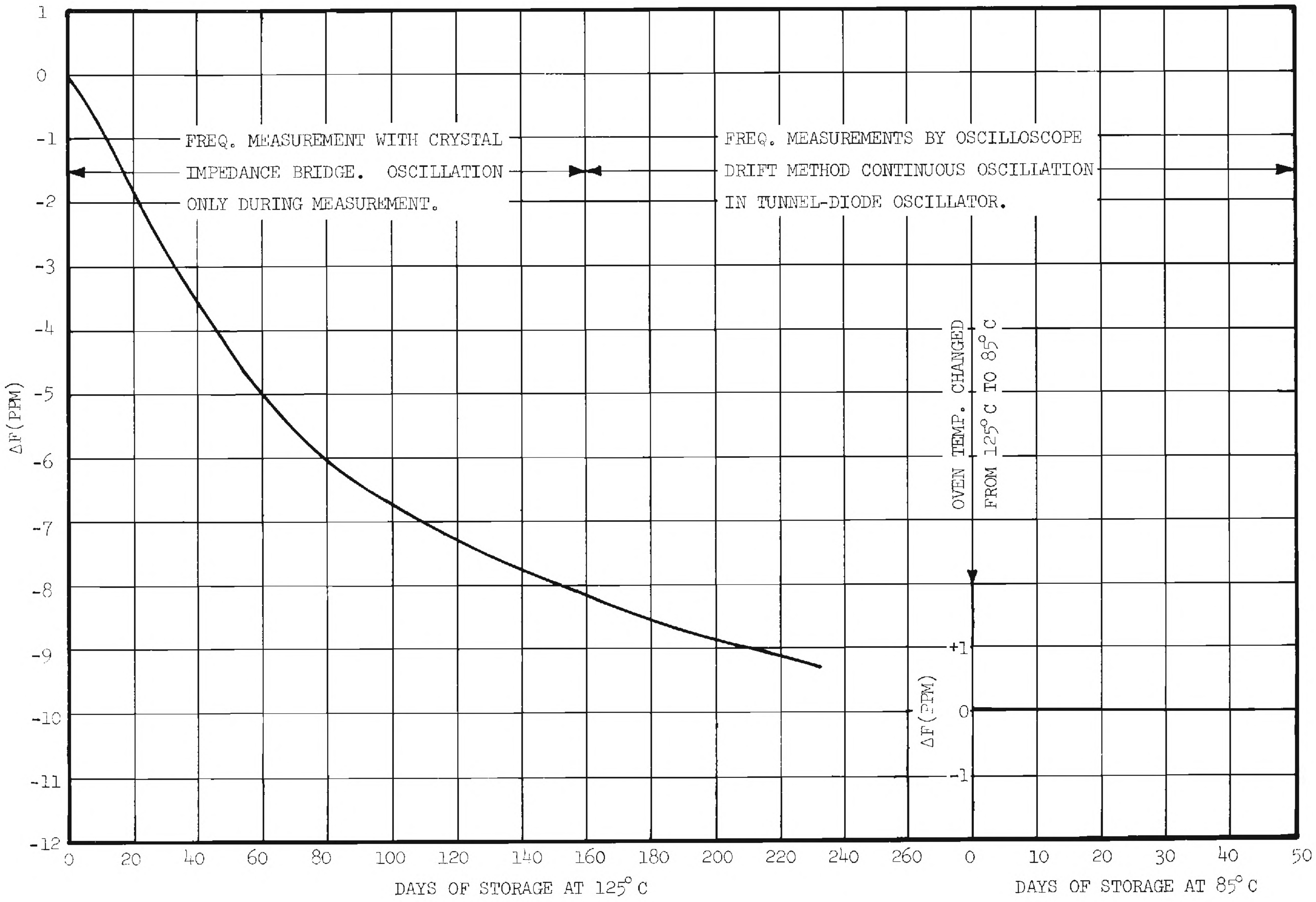

Figure 29. Aging data for gold plated 3 MHz unit No. NS-1 showing the effect of continuous and intermittent operation.

A tunnel-diode oscillator was designed and built for continuous oscillation of resonators concurrently with this program. One of these was used to provide continuous oscillation of unit NS-1. The oscillator was installed on the 160th day at 125°C and the oscillation of NS-1 was continued until the 232nd day at which time the oven temperature was reduced to 85°C. An inspection of the aging data obtained during the period of continuous oscillation at 125°C shows excellent agreement in the aging rate while oscillating continuously with that obtained previously for the unit by the crystal impedance bridge method. The tunnel-diode oscillator was maintained at ambient room temperature since previous experiments had indicated that temperature control was probably unnecessary except for very critical applications. Figure 29, in addition, presents the aging data for the crystal unit operated with the tunnel-diode oscillator after reducing the oven temperature to 85°C. The aging at 85°C has been essentially zero and frequency measurements using the oscilloscope-drift technique have been stable within ± a few pp10^9. The coarse frequency scale on which these latter data are plotted was selected to dramatize the remarkable reduction in aging rate when the oven temperature was reduced and in order to display the data on a single page.

The design of the tunnel-diode oscillator used to operate unit NS-1 at 85 and 125°C is shown in Technical Report ECOM-02251-3, November, 1966, Appendix A.

F. X-RAY DIFFRACTION STUDIES OF VARIOUS RESONATORS*

1. Aging Analysis by X-ray Topography

a. Low frequency resonators

As reported in Technical Report ECOM-02251-3, the low frequency resonators removed from the ovens due to their poor aging characteristics were examined by x-ray methods. In order to detect as many defects as possible, two SID patterns were made of each unit utilizing Bragg planes whose normals were as nearly mutually perpendicular and parallel to the crystal face as possible. The two 100 kHz units, which exhibited a very high initial positive aging, have strained regions over about 25 per cent of their surface area. These imperfect regions were produced by the plating separation process, the lead attachment process, and the edge finishing process. In contrast to 100 kHz units previously investigated, these two units showed no twist due to the mounting wires, and the imperfection produced at the points of attachment was less than that usually observed.

The three square CT-cut and two rectangular SL-cut 455 and 500 kHz units were examined. Two of the three square units had a chip on one edge, but

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* This section contributed by C.E. Wagner and R.A. Young of the Diffraction Laboratories, Georgia Institute of Technology.

otherwise the edges of all these units were relatively perfect. There were wide, straight bands of defects characterized by a single fault vector in four of the units, and the fifth showed long defects that are probably surface scratches. There are also other defects present, most of which are probably scratches.

b. 10 MHz reliability units

The results of x-ray studies of the 10 MHz reliability units passing the aging requirements were reported in Technical Report ECOM-02251(E)-9. As a whole these units were relatively free from areas of high defect concentrations and, in all cases but one, the SID patterns showed no scratches. However, the defect types and concentrations (excluding scratches) present in some of the units passing the aging requirements were similar to those of the reliability units failing the requirements.

Two SID patterns were made of each of the twenty-seven 10 MHz reliability units passing the aging requirements and the data obtained are summarized in Table II Technical Report ECOM-02251(E)-9. The patterns were made with the $2\bar{1}0$ and $0\bar{1}2$ reflections while the units were still encapsulated. (The exposure times were 30 to 90 minutes depending on the reflection and type container used, compared with 6 to 8 minutes for units not encapsulated.) The observed defects were divided into four types: spot or clump defects, line defects, planar defects, and plating outline.

The planar defects are thought to be sheets of impurities or defects of a similar nature lying on a plane. For the reliability units examined here all the lines of intersection of the planar defects with the crystal surface made an angle of about 65° with the x axis. It is quite possible that these defects are similar to the "phantom defects" of G. W. Willard.*

The line defects observed in these units were generally too straight to be scratches produced in polishing, and in some cases may have been narrow planar defects. It was noted that although scratches were observed visually on almost all of the units, most were not observed in the SID patterns. The spot or clump defects are perhaps small regions of clustered impurities or small inclusions of foreign matter. Some of the shorter line defects may also be of this nature.

The intensity enchancement at the edge of the plating represents a strain gradient at the surface of the quartz. It was found that the strain is anisotropic with a maximum strain gradient in the $0\bar{1}2$ direction and a minimum in the $2\bar{1}0$ direction. There is enough difference in these two directions that the plating outline seen in a $0\bar{1}2$ pattern is often not visible in a $2\bar{1}0$ pattern.

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*Willard, G. W., "Quartz Crystals for Electric Circuits," by R. A. Heising, D. Van Nostrand (New York: 1952), 140.

The SID patterns of the units and their aging characteristics were reviewed to determine if any correlation could be found between the defects and aging characteristics (initial and final slope and sign of frequency changes vs. time). Previous investigation by etching, remounting, and reaging some 10 Mc units with poor aging histories suggested a correlation between poor aging and surface defects. The existence of the plating outline on twelve of the twenty-seven reliability units passing the aging requirements shows that surface defects of the plating outline type are not always associated with poor aging in the pp10^7 range for these AT-cut crystals. It should be noted, however, that the plating outline was observed in both the $0\bar{1}2$ and $2\bar{1}0$ reflections in only one instance, and in all cases the outline was not prominent. In addition, there were only two crystals with defects which could have been scratches, and only one or two scratches would have been in the oscillating region. Therefore, surface defects were not prominent in the group.

c. Activity dip

X-ray diffraction patterns were made of an oscillating 3.00 MHz crystal exhibiting an activity dip. The patterns were made over a range of temperatures at and near the temperature of the activity dip in an effort to determine if any change occurred in the mode of oscillation. This work is reported in Technical Report ECOM-02251-3. Although no concrete evidence was found showing a difference in the modes below and above the dip, neither could any definite difference be seen between the mode patterns of the two responses present at the temperature of the dip. Since some difference would be expected between these modes, further investigations (made under better experimental conditions) might show a difference in the modes. It is obvious, however, that there are an unusually large number of defects in the crystal.

d. Annular electrode

Both plano-convex and plane-parallel, beveled-edge 5 MHz crystals with and without annular ring electrodes were examined to determine if the plating configuration had any effect on the size or placement of the oscillating region. The study in Technical Report ECOM-02251-3 showed that the plating configuration had no observable effect, but rather, for these 5 MHz crystals, the thickness of the wafer was the controlling factor.

e. Topographs of damage produced by ultrasonic bonding

A preliminary investigation of the damage produced by ultrasonically bonding a metal strip to a quartz oscillator was made by making topographs of two units with several bonds on each. It was found that intensity enhancement (a result of lattice distortions) occurred at each bond site, and that the area of the damaged region was approximately the same size as the bond area. Figure 30, a $2\bar{1}0$ topograph of a unit with ten bond areas, is an example. No attempt has yet been made to determine the depth of the damage.

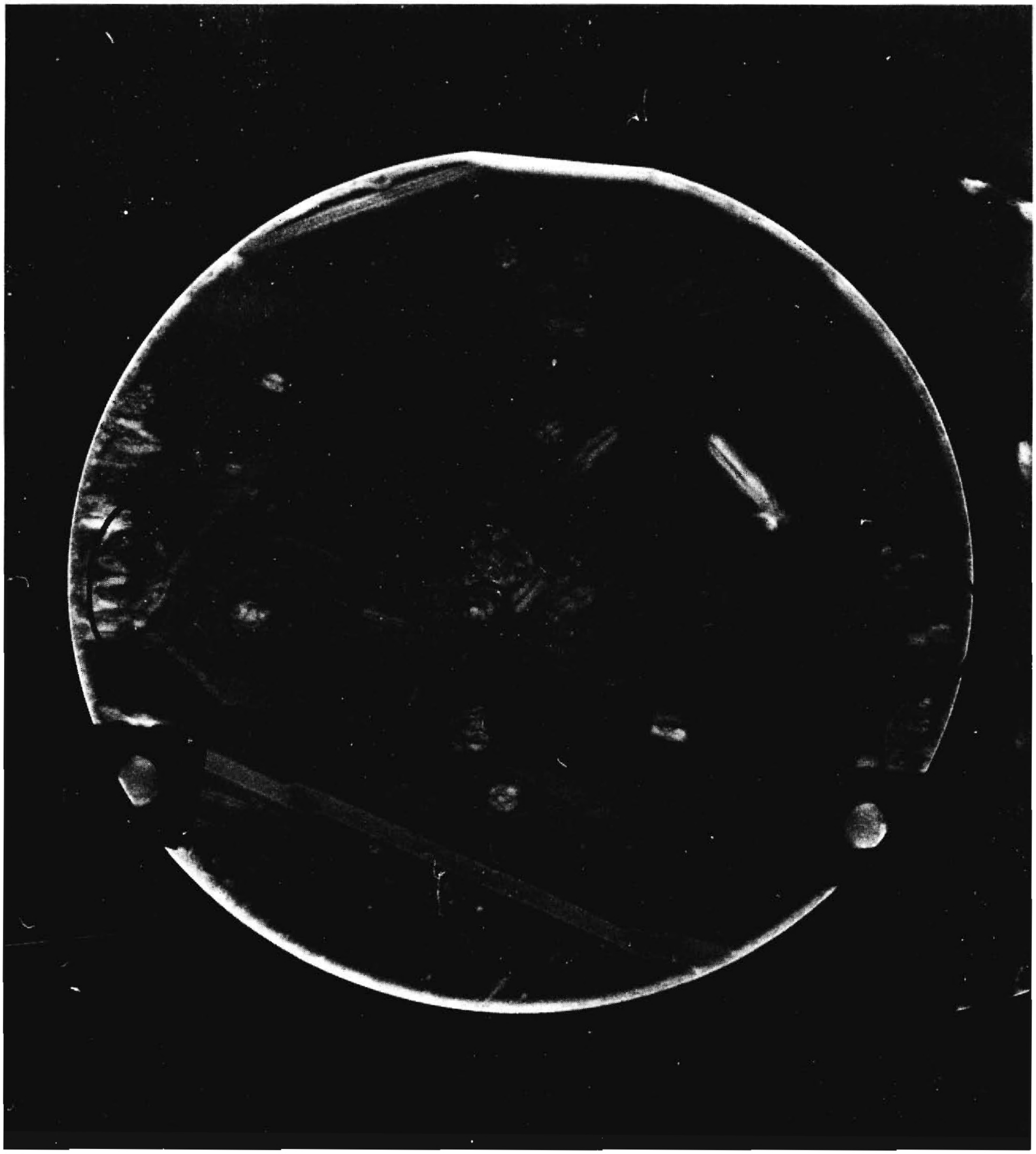

Figure 30. Topograph of quartz unit with ten bond regions (located in circles).

2. Measurement of Amplitude by an X-Ray Diffraction Technique

a. Amplitude distribution

The amplitude distribution for an AT-cut quartz resonator was determined by the x-ray Source-Image Distortion technique. The general technique is described in Report No. 7, USAECOM Contract No. DA-36-039-AMC-02251 (E), 15 November 1964, and in our paper "X-Ray Source-Image Distortion Technique for the Study of Crystal Distortion and Vibration," R. A. Young and C. E. Wagner, J. Appl. Phys. 37, 4070-4076 (1966), reprints of which were bound in USAECOM 02251(E)-3, November, 1966.

The experimental configuration used for the present work is shown in Figure 31. The crystal is aligned to diffract the characteristic $K\alpha_1$ radiation from a micro-focus spot source. For most Bragg reflections and x-ray wavelengths used, the $K\alpha_2$ component also diffracts when the crystal is set to diffract the $K\alpha_1$ component, as depicted in Figure 31. There is no collimation of the beam. Slits are used only to keep the incident beam from striking the film, and for safety reasons. Thus, any portion of the crystal in which the Bragg planes make the Bragg angle with the source will diffract. Recording the diffracted image on film, one determines the locations of the portions of the crystal that make the Bragg angle with a ray from the source. These images of the diffracting regions are called SID lines. For undistorted Bragg planes the loci of the diffracting regions are bounded by essentially straight lines. Knowing the displacement of the diffracting region from its undistorted (straight line) position, one can determine the difference in angle between the ray that would have been diffracted were the crystal undistorted, and the ray that is actually diffracted, and hence the angular distortion of the lattice. Figure 32 is a sketch of the diffracting regions for a crystal which is distorted only in the center area. The dashed lines are the edges of the diffracting regions for the undistorted crystal. The distance D is directly proportional to the distortion at point (x,z') on the crystal.

A lattice distortion can be a simple tilting of the Bragg planes, a strain $\Delta d/d$, or a combination of both. However, the relative contributions of the two can be separated because a strain produces a displacement of the image proportional to $\Delta d/d \tan \theta$, where θ is the Bragg angle, while there is no dependence on θ for a displacement produced by tilt. For the first order thickness-shear mode, if the displacement is assumed to be a sinusoidal function of the thickness, the maximum tilt will occur midway between the crystal faces and the maximum displacement at the surface. Thus if the displacement is given by $A_o \sin y' (2\pi/\lambda)$ (origin at the center of the wafer, y' measured normal to the surface), the tilt, which in this case is the first derivative of the displacement with respect to y', will have a maximum of magnitude $2\pi/\lambda\ A_o$ midway between the crystal surfaces. If λ, the wavelength, is equal to twice the crystal thickness, t, then A_o will be the maximum amplitude of oscillation at the surface. However, for example, if $\lambda/2 > t$, then the maximum amplitude of oscillation at the surface will not be A_o but will be some smaller value A, where $A = A_o \sin \pi/\lambda\ t$. Thus the actual amplitude would be less than the amplitude calculated from the tilt by an amount depending on the difference between the actual half-wavelength and the crystal thickness. Any unknown deviation from the assumption of sinusoidal waves would also cause the amplitude measurements to be in error.

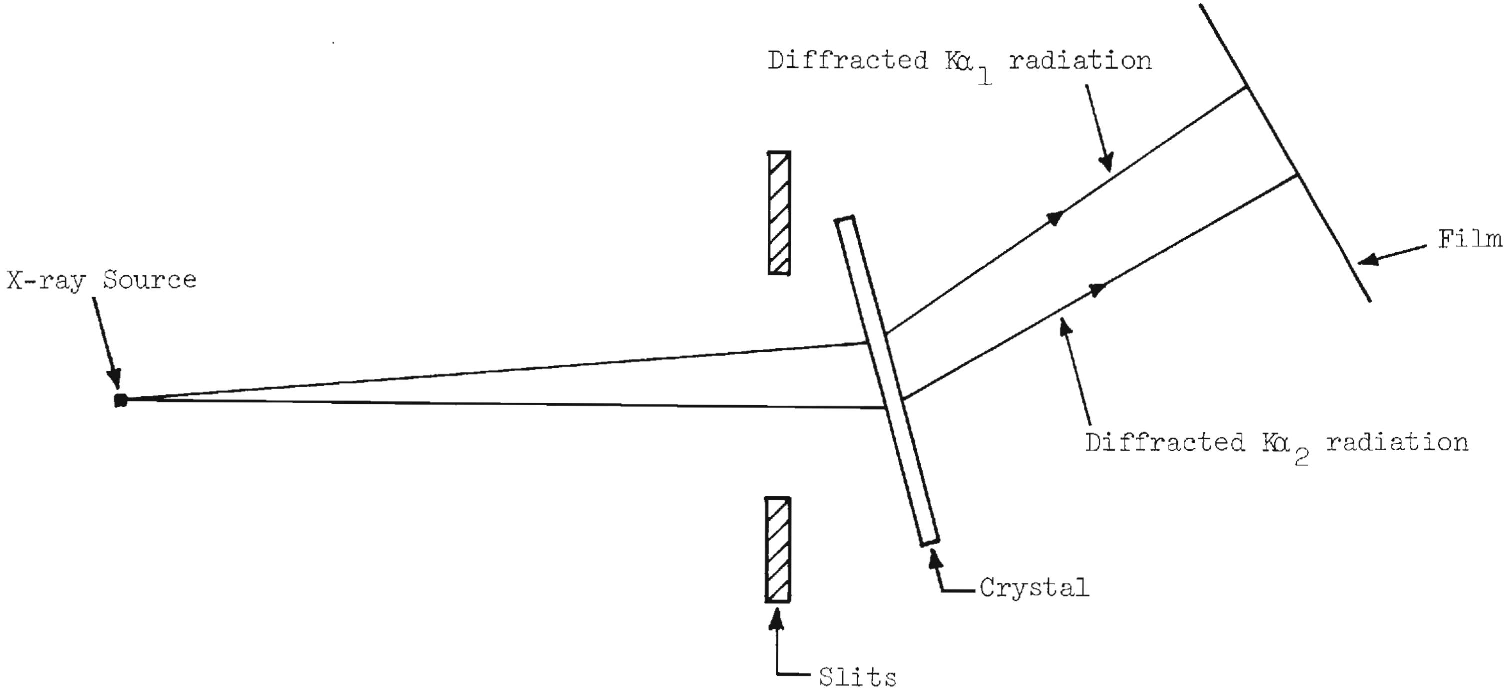

Figure 31. Sketch of source-image distortion layout showing different ray paths of diffracted Kα$_1$ and Kα$_2$ radiations.

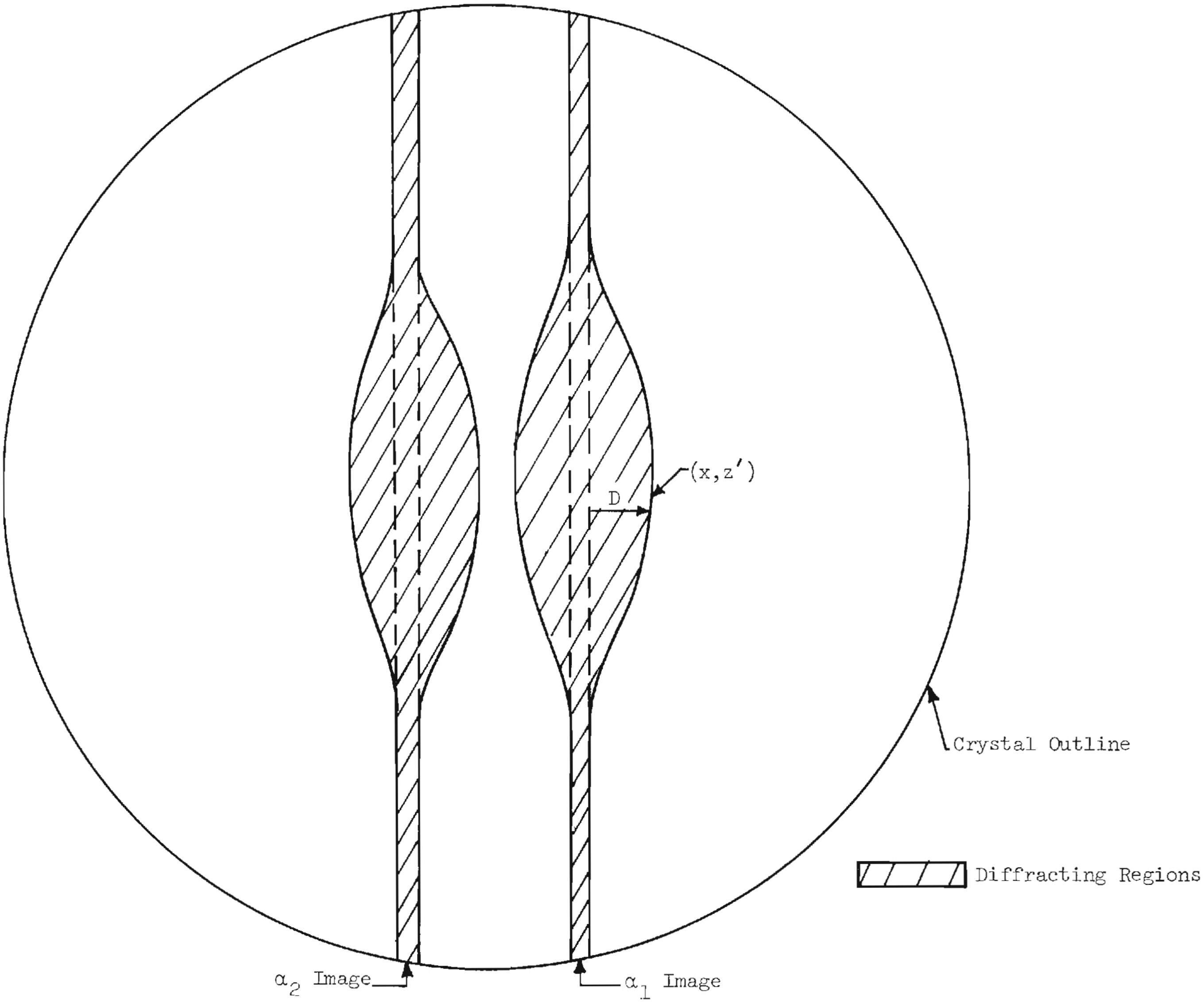

Figure 32. Sketch of diffracting regions for an oscillating crystal whose amplitude is appreciable only in the middle area.

When the distortion in a crystal is not constant throughout its thickness, a correction must be applied to the SID data. This correction represents a minimum detectable distortion of which the magnitude depends, among other things, on the depth of the distortion within the crystal and the side of the SID lines on which the measurements are made.

The minimum distortion detectable is determined as follows. When the crystal is not distorted (such as during the phase of the oscillation when the displacements are zero) and for sufficiently small μt, where μ is the x-ray absorption coefficient and t the crystal thickness, the diffracting portion of the crystal in the plane of incidence will be a triangular shaped region with apex angle 2θ as shown in Figure 33 for the transmission case with the active Bragg planes perpendicular to the crystal surface. When the crystal is deformed the location of the diffracting region will be moved to that part of the crystal that does make the Bragg angle with a ray from the source. To find the minimum detectable distortion then, one must determine what point in the crystal will diffract such that its image will lie at the edge of the image formed when the crystal is undistorted. One can then calculate the distortion necessary to produce diffraction at such a point, and the distortion found will be the minimum detectable distortion for that depth in the crystal. We will consider now tilts occurring midway between the crystal faces, where the maximum deformation is produced in a first order thickness-shear mode.

If the Bragg planes are tilted at an angle $\Delta\beta$ with respect to their undistorted positions, then one edge of the perfect crystal image and distorted crystal image will coincide when $S \cdot \Delta\beta \approx \ell$, where S is the crystal to film distance and ℓ and m are defined in Figure 33.

Now

$$L \cdot \Delta\beta \approx m,$$

and

$$\frac{\ell}{\cos\theta} + \frac{m}{\cos\theta} = t \cdot \tan\theta,$$

so

$$\ell + m = t \cdot \sin\theta$$

Thus the minimum angular deviation detectable on the right side of the SID line image is found from

$$\ell + m = t \cdot \sin\theta = \Delta\beta_{min} \cdot (S + L),$$

so that

$$\Delta\beta_{min} = \frac{t \cdot \sin\theta}{L + S}$$

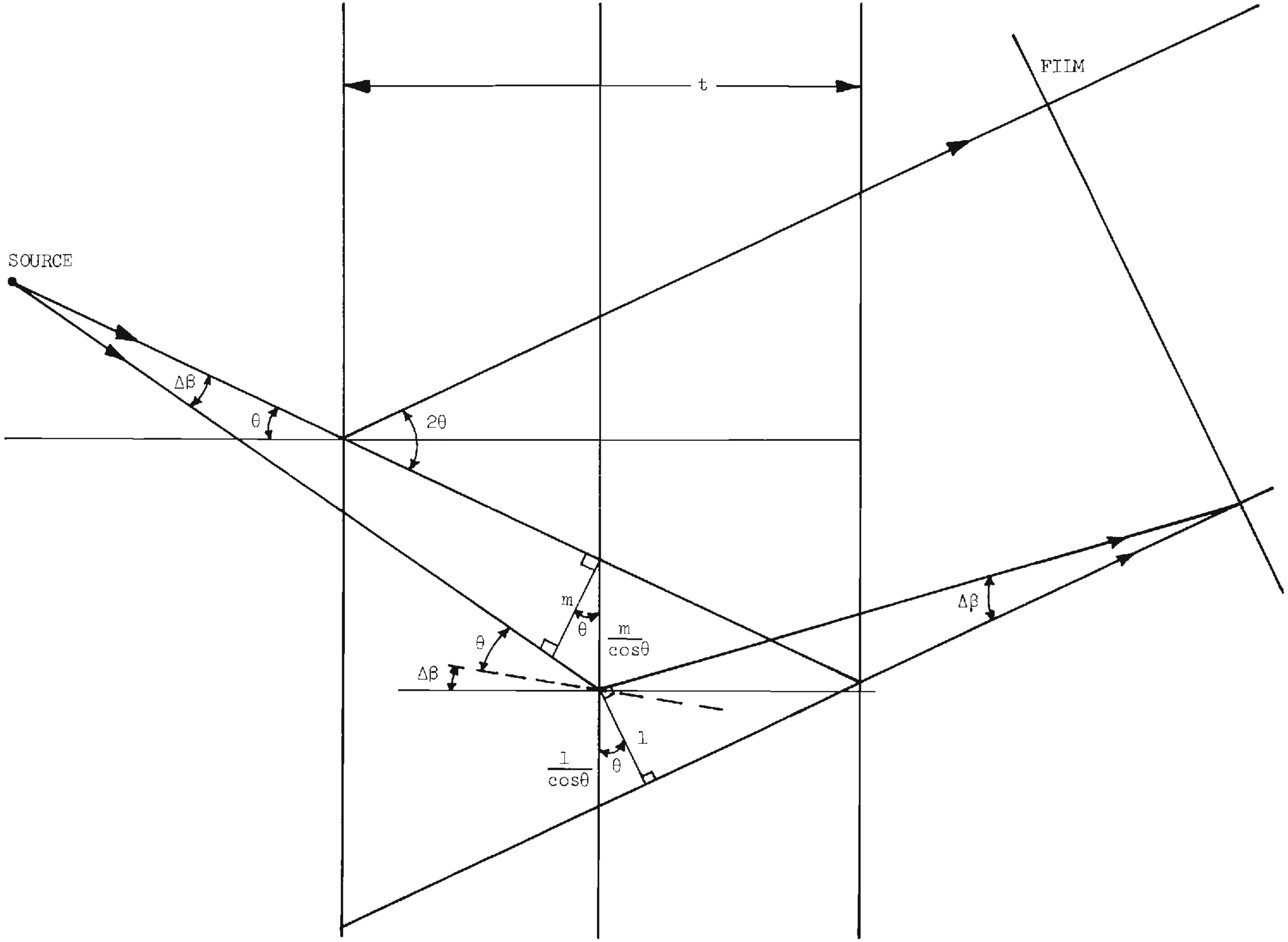

Figure 33. Diagram of diffraction geometry in the plane of incidence. Solid line is for the undistorted crystal case, dashed line is for distorted crystal case.

This amount of tilt must be added to each measurement made on the right hand side of the SID line. When the left side of the SID line is considered, the same equations result, so that to correct the measurements one needs to increase the measurements on each side of the SID line by the amount $\Delta\beta_{min}$.

If the maximum tilt were not in the center of the crystal, the correction on each side would be different. If the maximum tilt were not localized, but, rather, were constant throughout the entire crystal thickness, then there would be no minimum detectable distortion and no correction to make to either side. Thus, the fact that in the following section a crystal-thickness-correction is necessary (to make the tilt versus voltage curve go through the origin) shows that the displacement is not a linear function of thickness. If the position of maximum tilt were to lie on a plane parallel to the crystal surface at some arbitrary depth, this depth could be determined from the difference in the correction for each side that was necessary to make the plots of the data for each side pass through the origin. The fact that in the following section the correction is the same for data from both sides of the SID lines shows that the maximum tilt is midway between the crystal surfaces.

The preceding discussion was couched in terms of tilts of the Bragg planes; however, there was nothing essential to the derivation of the minimum detectable deformations that necessitates that tilt the origin of the change, $\Delta\beta$, in the apparent Bragg angle. In fact, the derivation of the minimum detectable distortion for changes, $\Delta\beta$, due to changes in d-spacing, can be obtained from the argument above by substituting "$\Delta\beta/d \tan\theta$" for "tilt" throughout.

To obtain data over an entire crystal, one translates the crystal a known amount between exposures. Ten to fifteen exposures are usually made for a crystal 1 cm in diameter. The usual exposure time is about 8 minutes, so the total exposure time is less than two hours.

The diffracted images were recorded on a fine-grained emulsion and were measured on their projected images formed on a screen by a lantern slide projector. This method was used because it was found that prints made directly from the negatives did not produce sufficient magnification or contrast for the analysis. The errors present in the measurements from the screen are, however, larger than desired, and some improvement can be made by measuring the images on the emulsion with a traveling microscope. The precision could also be improved by making some changes in the experimental configuration.

The amplitude distribution was determined for a plano-convex 5 MHz unit with annular electrodes. The outer plating diameter was 9/32 in. and the inside diameter was 7/32 in. The resistance of the unit was 490Ω and it was operated at a drive level of 0.60 milliwatts.

On the assumptions that the maximum crystal thickness is a half wavelength, that all of the crystal vibrates at the same frequency, that the wavelength does not change (even though the crystal thickness changes), and that the displacement is a sinusoidal function of y', a tilt of 10^{-2} radians corresponds to a displacement of 2,800 Å at the surface of the crystal. The results are shown in Figure 34 by contour of equal amplitude. The numbers on the countour lines are radians x 10^3 since the quantity actually measured is tilt. The geometrical center of the crystal face is indicated with a "+". It is seen that the center of the oscillation is off the face center by about 0.6 mm. (A much greater displacement and distortion of the amplitude distribution has been noted in another crystal in Semiannual Report No. 3 USAECOM Contract No. DA-36-039-AMC-02251(E), August,1966.)

The error in each measurement was about $\pm 1 \times 10^{-3}$ radians, due primarily to the difficulty of determining precisely the edge of the diffracted image projected on the screen.

b. Maximum amplitude as a function of voltage

The maximum amplitude of oscillation as determined from the maximum tilt observed in a SID pattern was determined as a function of voltage drop across the crystal in the range 0.03 to 0.14 volts (0.06 to 1.3 milliwatts, respectively). The sample was a 5 MHz AT-cut flat quartz crystal with beveled edges and conventional (perpendicular field) electrodes. The results are shown in Figure 35. The functional form of the voltage-amplitude relationship is seen to be linear over the range investigated. The three sets of data points represent data from three points on the crystal less than 0.2 mm apart. These points are from three of the four edges of the diffracted images depicted in Figure 32.

There are no data points for a tilt $< 0.83 \times 10^{-4}$ radians because this is the minimum detectable tilt for this reflection, x-ray wavelength, and crystal thickness, as explained in the previous section.

G. DISCUSSION

1. Relative Merits of Aluminum Plating for Semiprecision Resonators

As communication systems become more sophisticated (i.e., SSB), the aging requirements of crystal resonators become more stringent. Many of the present requirements for general use are equivalent to those of the frequency standards of the past.

Electrodes of evaporated gold are still considered by many as the only choice when a low value of long term aging is required. However, gold has certain disadvantages; the intrinsic adherence to quartz is poor, and the subsequent processing temperatures are limited by the agglomeration temperature of the gold. The latter temperature is well under 450°C for a gold film less than 1500 angstroms thick.

The principal advantages of gold are that relatively pure films having near bulk density may be obtained even when evaporated in poor vacuum conditions and corrosion of the film does not occur in any reasonably expected container atmosphere.

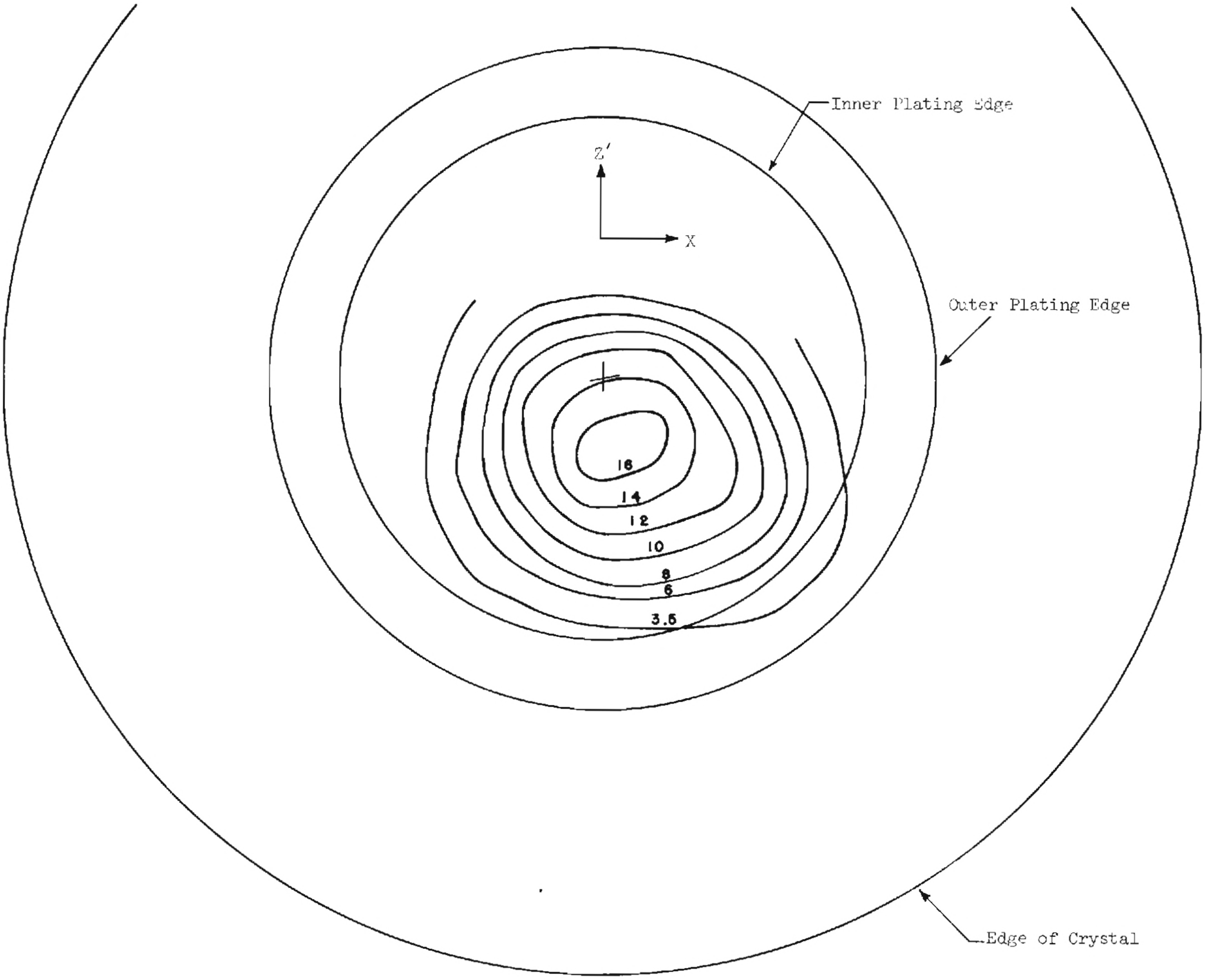

Figure 34. Lines of equal amplitude for a flat 5 MHz crystal with beveled edges. Numbers are tilts x 10^3 (radians). (10 x 10^{-3} radians here correspond to a displacement at the surface of 2,800 A). The center of the crystal face is indicated by the "+".

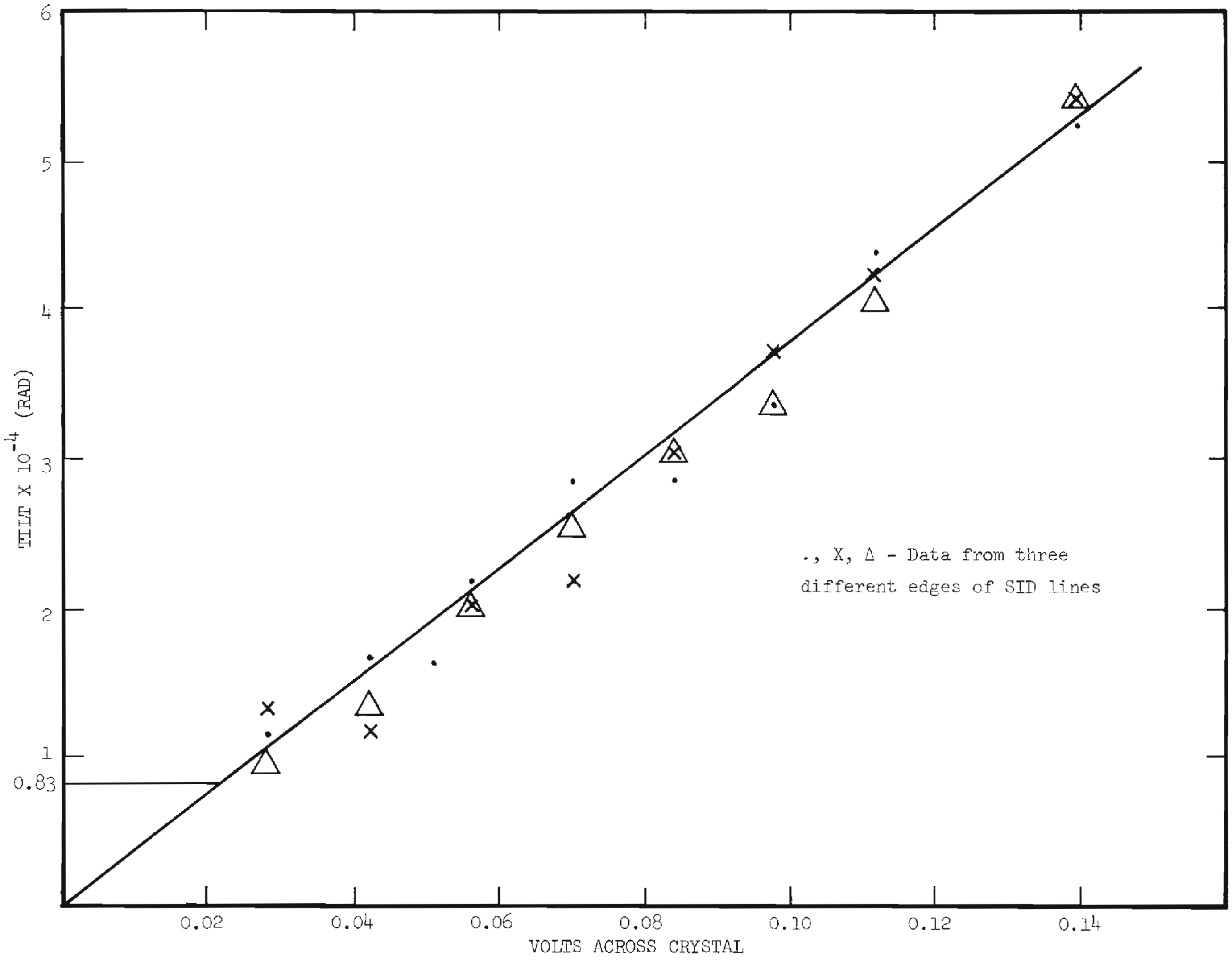

Figure 35. Plot of tilt produced by oscillation (which is proportional to amplitude of oscillation) versus voltage drop across the crystal.

Aluminum, on the other hand, has none of the disadvantages of gold but has some intrinsic to itself, particularly with respect to the chemically active nature of the metal. As a result, certain precautions must be taken in the plating process. However, when these conditions have been met, aluminum plated resonators have consistently performed better than gold plated ones as noted in Section III, C, 3, c.

For best results pressure in the plating chamber must be lower for evaporating aluminum than for evaporating gold. This requirement is necessary because of the chemical activity of aluminum previously noted. The aging rates of aluminum plated resonators are related to the oxide (Al_2O_3) content of the electrodes and the resultant porosity of the films as well as to the surface oxidation effects.

The surfaces of the quartz to be plated must be degassed in vacuum by heating for best results. The adsorbed gas, unless removed, will react with the aluminum and may produce aging similar to that obtained due to high chamber pressure.

A film stabilization step* was added to the fabrication process here and consisted of heating the plated wafers overnight (~16 hours) in air at 200°C. This action increased the adherence of the aluminum plating to a very high value as required for the subsequent ultrasonic bonding and stabilized the oxide surface to diminish further growth.

The aluminum films on polished quartz when processed as described are bright, remarkably adherent, and may be cleaned in hot chromic acid. They may be easily bonded by ultrasonic methods, and processing temperatures of over 450°C may be used if desired. The frequency changes during the evacuation, baking (up to 450°C), and sealing of the HC-27/U holders was held to a consistent, average value of -5 ppm.

2. Relative Merits of the HC-27/U Glass Holder Compared to the T-5½ Holder

The aging of the gold-plated 10 MHz units at 125°C showed a consistent holder-dependent behavior. The units in the T-5½ holder, which were evacuated by means of a small-bore tube, aged at much higher rates than those in HC-27/U holders. These observations were again apparent during aging studies of one group of 3 MHz units (group 14) sealed in the HC-27/U holders, the caps of which were fitted with evacuation tubes through which the units were subsequently evacuated.

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*This step should not be used if the wafers were not degassed in the vacuum chamber before plating.

The fact that the baking temperature before sealing is usually higher for the HC-27/U units is probably one beneficial factor. However, the major difference seems to be the low pumping rate attainable for the small-bore tubes commonly used to evacuate the T-5$\frac{1}{2}$ holder.

Experiments made here indicated that the T-5$\frac{1}{2}$ holder could not be evacuated even to a pressure of one micron after several hours of pumping and baking although a five order pressure differential existed across the evacuation path through the tube. The larger internal surface area of the T-5$\frac{1}{2}$ envelope is also a highly undesirable feature since increase in temperature may result in high desorption from the envelope.

For the reasons cited and because of its convenient size and shape the HC-27/U holder is superior to the T-5$\frac{1}{2}$ holder as a container for quartz resonators of suitable size.

IV. CONCLUSIONS AND RECOMMENDATIONS

It would be premature to state that the edge finish of low-frequency, center-mount crystal units has no effect on the aging rate. However, there are obviously more important aging factors; two of these are the methods of mounting and of bonding the resonator. The newer bonding techniques, such as the ultrasonic and, possibly, the thermo-compression methods should give resonators with improved aging characteristics. Development studies of the latter bonding methods for low frequency units should be made.

Excellent performance has been obtained for aluminum-plated 3 MHz resonators. Two major problems remaining are the following: final frequency correction methods which will not degrade the aging, and mounting and ultrasonic bonding techniques which will allow the units to meet military shock and vibration requirements.

The fabrication techniques for all units should be upgraded. In particular, the new oil-free pumping methods should be evaluated with respect to contribution to improvements in resonator aging and Q.

The relatively new annular-excitation technique shows promise of making the following important improvements in resonator performance: (1) lower long-term aging, (2) higher Q, and (3) improved frequency-temperature behavior.

Much additional work needs to be done before annular excitation can be accepted for general use by the defense forces. Three areas for future work are the determination of the optimum shape of the wafer (i.e., plano-convex or biconvex and the proper contour), the optimum angle or cut*, and final frequency adjustment methods.

The aging data measured here at 85 and 125°C for similarly fabricated units mounted in HC-27/U and T-$5\frac{1}{2}$ holders prove that the T-$5\frac{1}{2}$ holder (or any holder evacuated through small-bore tubes) is inferior to the HC-27/U container with respect to the long-term aging of resonators mounted therein.[**] It is recommended that the T-$5\frac{1}{2}$ holders not be used for semiprecision units unless the sealed holder is gettered.

The aging data available at this time for units sealed in evacuated and baked cold-welded holders is insufficient for a direct comparison with similar units in HC-27/U holders. However, the mounting of units in cold-weld holders has proven useful where the high sealing temperature of the glass holders has presented problems. A further study of units in cold-welded holders is needed in order to establish the procedures necessary to achieve the desired aging rates. When these procedures are established aging rates for units mounted in the cold-weld holder comparable to those for units mounted in the HC-27/U glass container are expected.

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[*] Published data for perpendicular excitation do not apply.

[**] This statement may not apply to resonators in containers which have been internally gettered after sealing.

APPENDIX

TABLE 1-A

AGING DATA FOR RESONATORS OF 81.9 TO 500 kHz FREQUENCY AND OF DIFFERENT EDGE FINISH

		Aging Rates					
Unit No.	Edge Finish	1st 30 days (ppm/week)	Last 6 mo. (ppm/week)	Total Period (ppm/week)	Total Period (Hours)	R_s at Room Temp (kΩ)	Comments
			81.9 kHz Units, NT Cut, Conventional Bonding				
1	OP	+11	0.300	+0.57	10,128	14	OP (Optically polished edge)
2	OP	+11	0.185	+0.38	"	11.5	
3	OP	+6	0.165	+0.24	"	12	
4	SP	+7	0.496	+0.77	"	17	SP (Semi polished edges)
5	SP	+7.5	0.192	+0.28	"	15.5	
6	SP	+7	0.127	+0.25	"	15	
43	OP+E	+6.5	0.154	+0.31	9,120	10.4	OP+E (Optically polished and etched edges)
44	OP+E	+4	0.005	+0.06	"	7.25	
45	OP+E	+7	0.058	+0.19	"	11.3	
46	SA	+7.5	0.112	+0.30	"	10.8	SA (State-of-art edge)
47	SA	+9	0.192	+0.50	"	10.5	
48	SA	+8.5	0.316	+0.56	"	9.2	
Averages		7.7	0.19	0.36			
			100 kHz, NT Cut, Conventional Bonding				
7	OP	+10.5	0.723	+0.77	9,120	24	
8	OP	+10.6	--	--	--	28	Removed from oven 10-22-65
9	OP	+12	0.366	+0.60	10,128	19.5	
10	SP	+7.5	0.170	+0.25	"	23.5	
11	SP	+14.5	0.142	+0.42	"	20	

(Continued)

TABLE 1-A (Continued)

Unit No.	Edge Finish	Aging Rates			Total Period (Hours)	R_s at Room Temp (kΩ)	Comments
		1st 30 days (ppm/week)	Last 6 mo. (ppm/week)	Total Period (ppm/week)			
12	SP	+1.5	0.135	+0.12	10,128	19.5	
49	OP+E	+24	0.408	+0.95	9,120	23.2	
50	OP+E	+9	0.208	+0.39	"	25.6	
51	OP+E	+7.5	0.216	+0.33	"	23.7	
52	SA	+5.5	0.069	+0.25	"	17.8	
53	SA	+63	--	--	--	28.1	Removed from oven 10-22-65
54	SA	-5.5	0.270	+0.50	9,120	140	
Averages		9.7	0.27	0.46			(Not including Units 8 and 53)
		250 kHz, DT Cut, Conventional Bonding					
13	OP	+12	0.192	+0.46	10,128	1.08	
14	OP	+22	0.112	+0.60	"	1.08	
15	OP	+7.5	0.062	+0.03	"	1.57	
16	SP	+17.5	0.254	+0.73	"	1.29	
17	SP	+12.5	0.127	+0.46	"	1.41	
18	SP	+11.5	0.169	+0.41	"	1.40	
55	OP+E	+14.5	0.231	+0.60	9,120	1.37	
56	OP+E	+8.5	0.216	+0.44	"	1.08	
57	OP+E	+8.5	0.223	+0.46	"	1.00	
58	SA	+17.5	0.019	+0.41	"	1.78	
59	SA	+18	0.181	+0.61	"	1.17	
60	SA	+22.5	0.296	+0.91	"	1.27	
Averages		14.4	0.17	0.51			

(Continued)

TABLE 1-A (Continued)

Unit No.	Edge Finish	Aging Rates 1st 30 days (ppm/week)	Last 6 mo. (ppm/week)	Total Period (ppm/week)	Total Period (Hours)	R_s at Room Temp (kΩ)	Comments
		455 kHz, SL or CT Cut, Conventional Bonding					
19	SP	+9.0	0.008	+0.29	10,128	0.75	SL-cut
20	SP	+9.0	0.127	+0.29	"	0.90	SL-cut
21	SP	--	--	--	--	0.92	SL-cut; Erractic unit
22	OP	-28.0	--	--	--	2.1	CT-cut; Bad unit
23	OP	+10.5	--	--	--	0.96	CT-cut; Removed from oven
24	OP	+8.0	0.058	+0.11	10,128	1.05	CT-cut 10-22-65
25	SP	+9.0	0.154	+0.39	"	1.0	CT-cut
26	SP	--	--	--	--	1.05	CT-cut; Bad unit
27	SP	+20.0	0.189	+0.64	10,128	0.94	CT-cut
28	OP	--	--	--	--	1.98	SL-cut; Removed from oven
29	OP	-3.0	0.142	-0.17	10,128	1.3	SL-cut 9-13-65
30	OP	-2.5	0.595	-0.52	"	1.4	SL-cut
61	OP+E	+7.0	0.119	+0.29	9,120	0.85	CT-cut
62	OP+E	+6.5	0.088	+0.31	"	0.94	CT-cut
63	OP+E	+2.5	0.111	+0.19	"	0.90	CT-cut
64	OP+E	+29.0	0.230	+1.03	"	1.20	SL-cut
65	OP+E	-34.0	--	--	--	1.10	SL-cut; Removed from oven
66	OP+E	-5.5	0.111	-0.27	9,120	1.25	SL-cut 10-22-65
67	SA	+8.0	0.092	+0.28	"	0.86	SL-cut
68	SA	+9.5	0.154	+0.43	"	1.00	SL-cut
69	SA	-1.0	0.046	+0.04	"	0.94	SL-cut
70	SA	+6.0	0.054	+0.16	"	1.20	CT-cut
71	SA	+12.0	0.085	+0.31	"	0.95	CT-cut
72	SA	+16.5	0.22	+0.63	"	0.90	CT-cut
Averages		9.[illegible]	0.14	0.35			(Not including Units 21, 22, 23, 26, 28, 65)

(Continued)

TABLE 1-A (Continued)

Unit No.	Edge Finish	Aging Rates 1st 30 days (ppm/week)	Last 6 mo. (ppm/week)	Total Period (ppm/week)	Total Period (Hours)	R_s at Room Temp (kΩ)	Comments
			500 kHz Conventional Bonding				
31	SP	+7.3	0.085	+0.31	10,128	1.15	SL-cut
32	SP	+32	--	--	--	0.95	SL-cut; Removed from oven 10-22-65
33	SP	+9.5	0.004	+0.19	10,128	1.32	SL-cut
34	OP	+15.5	0.308	+0.68	"	1.10	CT-cut
35	OP	+11.0	0.228	+0.26	"	1.55	CT-cut
36	OP	+13.0	0.220	-0.33	"	1.10	CT-cut
37	SP	-17.5	0.058	-0.25	"	1.12	CT-cut; Slightly erratic unit
38	SP	+33.5	--	--	--	1.30	CT-cut; Removed from oven 10-22-65
39	SP	+22.5	--	+0.30	10,128	1.27	CT-cut; Erratic unit
40	OP	+7.5	0.066	+0.22	"	0.97	SL-cut
41	OP	+17.0	0.595	+0.92	"	2.30	SL-cut
42	OP	+4.0	0.270	-0.30	"	1.72	SL-cut
73	OP+E	+8.5	0.177	+0.42	9,120	1.04	CT-cut
74	OP+E	+6.5	0.127	+0.26	"	1.12	CT-cut
75	OP+E	+32.5	--	--	--	1.20	CT-cut; Removed from oven 10-22-65
76	OP+E	-19.0	0.027	-0.24	9,120	1.27	SL-cut
77	OP+E	+2.5	0.002	+0.09	"	1.08	SL-cut
78	OP+E	+4.8	0.021	+0.14	"	1.08	SL-cut
79	SA	+1.3	0.061	-0.06	"	1.26	CT-cut
80	SA	+16.0	0.346	+0.62	"	1.06	CT-cut
81	SA	+3.0	0.108	+0.20	"	0.94	CT-cut

(Continued)

TABLE 1-A (Continued)

		Aging Rates					
Unit No.	Edge Finish	1st 30 days (ppm/week)	Last 6 mo. (ppm/week)	Total Period (ppm/week)	Total Period (Hours)	R_s at Room Temp (kΩ)	Comments
82	SA	+3.5	0.012	+0.15	9,120	1.10	SL-cut
83	SA	+7.5	0.135	+0.35	"	1.13	SL-cut
84	SA	+3.8	0.039	+0.16	"	1.13	SL-cut
Averages		9.6	0.14	0.29			(Not including Units 32, 38, and 75)

TABLE 2-A

AGING DATA FOR ULTRASONICALLY BONDED AT-CUT 3MHz UNITS

	Stabilization Period (1)		Subsequent Aging (2)				
Unit	Days	ΔF ($pp10^8$)	Period (Hours)	Rate Total Period ($pp10^8$/week)	Rate Last 6 mo.(3) ($pp10^8$/week)	Q ($X10^{-6}$)	Comments
Group 1 (Al plating, HC-27/U holder)							
1-1	0	-	12524	0.033	0.015	1.49	
1-6	3	-1.5	12452	0.067	0.019	1.50	
1-8	1	-1.0	12500	0.220*	0.190*	0.38	Erratic, temp. sensitive
1-10	3	-3.0	12452	0.053	0.015	0.74	
1-11	6	-6.0	12380	0.080	0.054	1.55	Temp. sensitive
Ave.	2.6	-2.3	-	0.058	0.026	1.13	
Group 2 (Evap. Au Plating, HC-27/U Holder)							
2-2	4	+1.0	12456	0.120	0.054	1.13	
2-3	22	+7.0	11952	0.230	0.110	0.57	
2-4	45	+18.0	11400	0.190	-	0.66	Erratic
2-5	22	+7.0	11952	0.200	0.120	0.90	
2-6	43	+15.5	11348	0.290	0.150	0.90	
2-8	4	+1.0	12384	0.090	0.042	0.45	
Ave.	23.3	+5.7	-	0.190	0.095	0.76	
Group 3 (Al Plating, HC-27/U Holder)							
3-5	7	-3.5	12144	0.050	0.013	0.75	
3-6	21	-12.0	11808	0.140	0.046	1.48	
3-8	3	-3.0	11240	0.180	0.110	0.57	
3-10	21	-11.0	11808	0.130	0.058	1.48	
Ave.	13.0	-7.4	-	0.130	0.057	1.07	

(Continued)

TABLE 2-A (Continued)

Unit	Stabilization Period (1) Days	ΔF (pp10^8)	Period (Hours)	Subsequent Aging (2) Rate Total Period (pp10^8/week)	Rate Last 6 mo. (3) (pp10^8/week)	Q (X10^{-6})	Comments
				Group 4 (Al Plating, HC-27/U Holder)			
4-1	7	-14.5	12144	0.170	Total ΔF <0.003Hz	0.90	Very low aging last 6 mo.
4-2	10	-17.0	12072	0.042	"	1.10	Very low aging last 6 mo.
4-3	14	-16.5	12976	0.028	"	1.50	Very low aging last 6 mo.
4-4	4	- 2.5	12218	0.140	0.042	0.56	
4-5	7	- 2.0	12144	0.090	0.026	0.37	
4-6	8	-11.5	11952	0.010	Total ΔF <0.003Hz	0.37	Very low aging last 6 mo.
4-7	10	-18.0	11904	0.001	"	0.91	Very low aging last 6 mo.
4-8	4	- 4.5	12048	0.042	0.008	1.50	
4-10	8	-12.0	11952	0.070	0.008	1.12	Sensitive to thermal shock
Ave.	8.0	-10.9	-	0.066	0.010	0.93	
				Group 5 (4) (Al plating, HC-27/U holder)			
5-2	28	-16.0	11404	0.149	0.077	1.13	
5-4	10	-10.0	11736	0.043	0.031	1.12	
Ave.	19.0	-13.0	-	0.096	0.054	1.125	
				Group 7 (Sputtered Au Plating, HC-27/U Holder)			
7-1	28	+ 9.5	9968	0.169	0.100	0.56	
7-2	35	+10.5	9800	0.200	0.140	0.50	
7-3	2	+ 1.0	10592	0.195	0.120	0.20	
7-7	35	+10.0	9800	0.230	0.027	0.56	
7-8	21	+ 5.0	10136	0.200	0.110	0.56	
Ave.	24.2	+ 7.2	-	0.200	0.099	0.48	

(Continued)

TABLE 2-A (Continued)

	Stabilization Period (1)		Subsequent Aging (2)				
		ΔF		Rate Total Period	Rate Last 6 mo. (3)	Q	
Unit	Days	($pp10^8$)	Period (Hours)	($pp10^8$/week)	($pp10^8$/week)	($X10^{-6}$)	Comments
Group 8 (Sputtered Au Plating, HC-27/U Holder)							
8-2	36	+11.0	10464	0.530	0.280	1.14	
8-3	36	+10.0	10464	0.210	0.084	1.14	
8-8	36	+13.5	10464	0.320	0.170	1.14	
8-10	15	+ 5.0	10968	0.230	0.120	1.14	
8-11	-	-	-	-	-	0.39	Erratic, temp. sensitive
8-13	29	+11.5	10632	0.330	0.096	0.76	
Ave.	30.4	+10.2	-	0.320	0.150	0.92	
Group 9 (Al plating, HC-27/U Holder)							
9-1	21	-14.5	10632	0.079	0.023	0.75	
9-2	14	-14.5	10800	0.100	0.038	0.42	
9-4	7	- 5.0	10968	0.038	0.019	0.59	
9-6	7	-11.0	10968	0.110	0.065	1.11	
9-10	14	- 8.0	10800	0.070	0.077	1.11	
9-12	7	- 6.0	10968	0.170	0.077	0.63	Temp. sensitive
9-13	0	-	11136	0.068	0.035	0.64	
9-14	0	-	11136	0.180	0.019	0.64	
9-16	29	-16.0	10440	0.230	0.200*	0.75	Erratic
Ave.	11.0	- 8.3	-	0.120	0.044	0.74	
Group 10 (Al Plating, HC-27/U Holder)							
10-1	8	- 2.0	10536	0.260	0.096	1.13	
10-4	15	- 5.0	10368	0.110	0.031	1.12	
10-6	2	+ 1.0	10704	0.120	0.010	0.39	
10-7	4	- 1.0	10632	0.110	0.026	1.13	

(Continued)

TABLE 2-A (Continued)

	Stabilization Period (1)		Subsequent Aging (2)				
		ΔF		Rate Total Period	Rate Last 6 mo. (3)	Q	
Unit	Days	(pp10^8)	Period (Hours)	(pp10^8/week)	(pp10^8/week)	($X10^{-6}$)	Comments
			Group 10 (Al Plating, HC-27/U Holder)				
10-8	0	-	10728	0.130	Total ΔF <0.003Hz	1.50	Very low aging last 6 mo.
10-10	8	- 2.0	10536	0.140	0.077	0.64	
10-18	7	- 2.0	10560	0.120	0.058	1.10	
10-19	-	-	-	-	-	0.30	Very temp. sensitive
10-22	7	- 5.0	10560	0.032	Total ΔF <0.003Hz	0.20	Very low aging last 6 mo.
Ave.	6.0	- 2.5	-	0.130	0.037	0.83	
			Group 11 (Al Plated, HC-27/U Holders)				
11-1	0	-	10560	0.270	0.089	1.14	Preaged 16 hrs @ 170°C
11-7	21	- 9.5	10056	0.100	Total ΔF <0.003Hz	0.90	Preaged 16 hrs @ 170°C
11-8	14	- 4.0	10224	0.200	0.023	0.90	Preaged 16 hrs @ 170°C
11-9	20	- 7.5	10080	0.360	0.115	1.10	Preaged 16 hrs @ 170°C
11-11	42	-13.0	9552	0.210	0.046	0.90	Preaged 16 hrs @ 170°C
11-12	21	- 5.0	10056	0.200	0.019	0.56	Preaged 16 hrs @ 170°C
11-13	4	- 1.0	10464	0.320	0.210*	1.10	Preaged 16 hrs @ 170°C
11-14	4	- 2.0	10464	0.056	0.012	0.60	Temp. sensitive
11-15	28	-17.5	9888	0.110	0.031	0.50	
11-17	0	-	10560	0.370	0.096	1.10	
11-19	4	- 1.5	10464	0.220	0.096	-	
11-20	0	-	10560	0.040	0.031	-	
Ave.	13.2	- 5.1	-	0.200	0.051	0.88	

(Continued)

TABLE 2-A (Continued)

	Stabilization Period (1)		Subsequent Aging (2)				
Unit	Days	ΔF ($pp10^8$)	Period (Hours)	Rate Total Period ($pp10^8$/week)	Rate Last 6 mo.(3) ($pp10^8$/week)	Q ($X10^{-6}$)	Comments
			Group 12 (Al Plated, HC-27/U Holders)				
12-1	0	-	10296	0.390*	0.290*	0.78	Preaged 72 hrs @ 100°C
12-3	-	-	-	-	-	0.50	Preaged 72 hrs @ 100°C (Temp. Sens.)
12-4	4	- 2.0	10200	0.058	0.019	0.58	Preaged 72 hrs @ 100°C
12-5	4	- 2.0	10200	0.033	Total ΔF <0.003Hz	0.90	Preaged 72 hrs @ 100°C
12-6	0	-	10296	0.110	0.008	0.30	Preaged 72 hrs @ 100°C
12-7	0	-	10296	0.110	0.019	1.10	Preaged 72 hrs @ 100°C
12-9	0	-	10296	0.100	0.026	0.90	Preaged 72 hrs @ 100°C (See Fig)
12-10	56*	+13.0	9000	0.320*	0.180*	1.17	Preaged 72 hrs @ 100°C (+ aging)
12-11	7	- 4.0	10128	0.100	0.027	1.10	
12-12	7	+ 3.0	10128	0.250	0.077	0.26	+ aging
12-13	14	- 7.5	9960	0.025	Total ΔF <0.003Hz	1.48	
12-14	14	- 7.5	9960	0.025	0.011	1.50	
12-15	-	-	-	-	0.077	0.90	+ aging, temp. sensitive
12-16	14	- 5.0	9960	0.120	0.031	1.50	
12-17	7	- 4.5	10128	0.150	0.012	1.50	
12-18	14	-12.0	9960	0.051	0.019	1.50	
12-20	35	-11.0	9456	0.280	0.058	1.48	
Ave.	9.2	- 4.8	-	0.110	0.027	1.03	

(Continued)

TABLE 2-A (Continued)

	Stabilization Period (1)		Subsequent Aging (2)				
				Rate	Rate		
Unit	Days	ΔF (pp10^8)	Period (Hours)	Total Perod (pp10^8/week)	Last 6 mo. (3) (pp10^8/week)	Q (X10^{-6})	Comments
			Group 13 (Al Plated, HC-27/U Holders)				
13-1	7	- 4.5	10128	0.084	0.019	0.90	
13-2	14	- 9.5	9960	0.140	0.096	1.49	
13-4	4	+ 2.0	10200	0.084	0.038	0.42	
13-5	0	-	10296	0.082	0.077	1.49	
13-9	0	-	10128	0.190	0.096	0.90	Preaged 115 hours @ 100°C
13-10	-	-	-	-	-	0.90	Preaged 115 hours @ 100°C (Erratic)
13-11	0	-	10128	very low	Total ΔF <0.003 Hz	1.50	Preaged 115 hours @ 100°C
13-12	0	-	10128	0.058	0.031	1.12	Preaged 115 hours @ 100°C
13-13	0	-	10128	0.033	0.008	1.50	Preaged 115 hours @ 100°C
Ave.	3.1	- 2.0	-	0.084	0.046	1.14	
			Group 14 (Al Plated, HC-27/U Holder(5))				
14-1	14	-13.0	9456	0.027	0.038	1.50	
14-2	49	-24.5	8716	0.150	0.023	1.50	
14-3	35	-12.5	8952	0.057	0.034	1.50	
14-4	56	-20.5	8448	0.330	0.092	2.20	
14-5	70	-28.0	8112	0.580	0.346	2.20	
14-6	56	-28.0	8448	0.360	0.150	1.50	
14-7	49	-22.0	8716	0.200	0.058	2.20	
14-8	84	-37.5	7776	0.370	0.130	2.20	
14-9	42	-37.0	8784	0.077	0.019	2.20	
14-10	0	-	9792	0.340	0.078	1.50	
Ave.	46.0	-23.3	-	0.250	0.098	1.90	

(Continued)

TABLE 2-A (Continued)

	Stabilization Period (1)		Subsequent Aging (2)				
				Rate	Rate		
Unit	Days	ΔF (pp10^8)	Period (Hours)	Total Period (pp10^8/week)	Last 6 mo. (3) (pp10^8/week)	Q (X10^{-6})	Comments
			Group 15 (Al Plated, HC-27/U Holder)				
15-3	4	- 2.5	9432	0.080	0.058	1.12	
15-4	29	-18.5	8832	0.140	0.034	1.13	Slightly erratic
15-6	12	- 5.0	9240	0.240	0.110	2.20	
15-7	29	- 9.0	8832	0.430	0.250	2.20	
15-8	0	-	9360	0.360	0.210	1.49	Preaged 72 hours @ 100°C
15-9	-	-	-	-	-	2.20	Preaged 72 hours @ 100°C (erratic)
15-10	0	-	9360	0.072	Total ΔF <0.003Hz	1.10	Preaged 72 hours @ 100°C
15-11	28	- 6.5	8688	0.390	0.190	2.20	Preaged 72 hours @ 100°C
15-12	7	- 1.5	9192	0.180	0.050	1.50	Preaged 72 hours @ 100°C
15-13	0	-	9360	0.098	0.058	2.20	Preaged 72 hours @ 100°C
15-14	35	- 9.5	8520	0.260	0.250	0.91	Preaged 120 hours @ 100°C
15-16	0	-	9360	0.190	0.084	1.50	Preaged 120 hours @ 100°C
15-17	7	- 2.0	9252	0.220	0.120	2.20	Preaged 120 hours @ 100°C
15-18	0	-	9360	0.110	0.130	2.20	Preaged 120 hours @ 100°C
15-19	0	-	9360	0.130	0.077	1.50	Preaged 168 hours @ 100°C
15-20	14	+ 7.5	9030	0.093	0.077	0.26	Preaged 168 hours @ 100°C
15-21	0	-	9360	0.072	0.115	1.50	Preaged 168 hours @ 100°C
15-22	0	-	9360	0.470	0.370	1.50	Preaged 168 hours @ 100°C
15-23	0	-	9360	0.027	0.058	1.50	Preaged 168 hours @ 100°C
Ave.	9.2	- 3.4	-	0.200	0.120	1.60	

(1) The stabilization period is the number of days at 85°C required to reach an aging rate of 1 pp10^8/week. A value of zero hours indicates the initial aging rate to be 1 pp10^8/week or less.

(2) The subsequent aging rate is the total average aging rate following the stabilization period.

(Continued)

TABLE 2-A (Concluded)

(3) The date in this column is the average aging rate for the period 15 Aug. 1966 to 15 Feb 1967.

(4) Activated alumina pellets sealed in holder.

(5) Tubulation attached to HC-27/U cover. Evacuation and baking then done as for T-5½ holders.

* Value not included in group average

TABLE 5-A

AGING DATA FOR ULTRASONICALLY BONDED 5 MHz UNITS

	Stabilization Period (1)		Subsequent Aging (2)				
				Rate	Rate		
Unit	Days	ΔF ($pp10^8$)	Period (Hours)	Total Period ($pp10^8$/week)	Last 4 weeks ($pp10^8$/week)	Q ($X10^{-6}$)	Comments
			Group A (Al plating, HC-27/U Holder)				
A-2	27	-8.0	4272	-0.32	-0.10	0.82	Conventional electrodes
A-6	0	-	4920	+0.31	+0.30	0.87	Annular-Ring electrodes
			Group B (Al plating, HC-27/U Holder)				
B-1	0	-	4920	-0.45	-0.23	0.80	Conventional electrodes
B-2	0	-	4920	-0.45	-0.20	0.80	Conventional electrodes
B-4	16	+4.6	4536	+0.59	+0.45	0.68	Annular-Ring electrodes
B-5	37	-40.6	4032	-0.10	Total ΔF <0.005 Hz	1.33	Annular-Ring electrodes
B-6	0	-	4920	+0.17	Total ΔF <0.005 Hz	0.59	Annular-Ring electrodes
B-7	0	-	4920	+0.29	-0.10	1.49	Annular-Ring electrodes
B-8	2	4.8	4872	+0.01	Total ΔF <0.005 Hz	1.18	Annular-Ring electrodes Erratic Behavior
B-9	4	2.6	4824	+0.19	Total ΔF <0.005 Hz	2.28	Annular-Ring electrodes
B-10	4	1.6	4824	+0.11	Total ΔF <0.005 Hz	1.85	Annular-Ring electrodes
B-12	0	-	4920	+0.09	Total ΔF <0.005 Hz	1.52	Annular-Ring electrodes
B-13	16	6.8	4536	+0.01	Total ΔF <0.005 Hz	2.00	Annular-Ring electrodes

(Continued)

TABLE 3-A (Continued)

AGING DATA FOR ULTRASONICALLY BONDED 5 MHz UNITS

	Stabilization Period (1)		Subsequent Aging (2)				
Unit	Days	ΔF (pp10^8)	Period (Hours)	Rate Total Period (pp10^8/week)	Rate Last 4 weeks (pp10^8/week)	Q (X10^{-6})	Comments
			Group C (Al plating, HC-27/U Holder)				
C-1	135	-111.0	2512	-0.45	-0.65	0.82	Conventional electrodes
C-2	Never reached aging rate of ≤ 1 pp10^8/week		4752	-7.06	-1.40	0.82	Conventional electrodes
C-3	170	-171	96	-0.98	-0.98	1.22	Conventional electrodes
C-4	51	- 22.0	3528	-0.19	Total ΔF <0.005Hz	1.65	Annular-Ring electrodes
C-5	51	- 14.8	3528	-0.29	-0.10	1.62	Annular-Ring electrodes
C-6	0	-	4752	-0.35	Total ΔF <0.005Hz	1.38	Annular-Ring electrodes
C-7	16	- 3.8	4368	-0.05	Total ΔF <0.005Hz	1.35	Annular-Ring electrodes
C-8	0	-	4752	-0.03	+0.20	0.53	Annular-Ring electrodes
C-9	4	- 2.2	4656	-0.17	+0.10	1.90	Annular-Ring electrodes
C-10	79	- 48.8	2856	-0.38	Total ΔF <0.005Hz	2.38	Annular-Ring electrodes

(1) The stabilization period is the number of days at 85°C required to obtain an aging rate of 1 pp10^8/week or less. A value of zero indicates the initial aging rate to be 1 pp10^8/week or less.

(2) The subsequent aging rate is the aging following the stabilization period.

TABLE 4-A

AGING OF 10 MHz (FUND.) UNITS AT 125°C, Au + Au RELIABILITY SERIES (1)

Unit No.	Holder Type	Bond Cement	Aging Rates (2)			Total Period (Hours)	Comments
			1st 30 days (pp10^7/week)	Last 30 days (pp10^7/week)	Total Period (pp10^7/week)		
C-1	HC-27/U	Pyroceram	+0.93	-0.04	+0.29	5328	
C-2	"	"	+0.65	-0.02	+0.18	"	
C-3	"	"	-0.23	+0.19	+0.04	"	
C-6	"	"	+0.84	+0.04	+0.24	"	
C-9	"	"	+0.77	+0.14	+0.18	"	
C-10	"	"	-0.07	0	+0.01	"	
C-11	"	"	+0.93	+0.14	+0.25	"	
C-12	"	"	+0.72	+0.02	+0.20	"	
Ave.			0.64	0.07	0.17		
D-7	HC-27/U	5504	+2.88	+0.23	+0.40	5328	
D-12	"	"	+2.11	+0.09	+0.30	"	
Ave.			2.50	0.16	0.35		
A-1	T-5$\frac{1}{2}$	5504	-0.93	-4.40	-2.36	5328	
A-3	"	"	-1.47	-5.86	-4.04	"	
A-4	"	"	-1.80	-	-	-	Unit failed due to external solder joint
A-6	"	"	-1.17	-0.21	-0.37	5000	
A-7	"	"	-0.81	-0.89	-0.66	"	
A-9	"	"	-2.33	-0.89	-1.20	"	
A-10	"	"	-1.51	-0.84	-0.81	"	
B-1	"	"	-0.77	-8.26	-3.86	"	
B-2	"	"	-1.63	-0.91	-0.92	"	
B-3	"	"	+0.58	-1.61	-1.17	"	

(Continued)

TABLE 4-A (Continued)

AGING OF 10 MHz (FUND.) UNITS AT 125°C,
Au + Au RELIABILITY SERIES (1)

Unit No.	Holder Type	Bond Cement	Aging Rates (2) 1st 30 days ($pp10^7$/week)	Aging Rates (2) Last 30 days ($pp10^7$/week)	Aging Rates (2) Total Period ($pp10^7$/week)	Total Period (Hours)	Comments
B-4	T-5½	5504	-0.70	-0.82	-0.61	5000	
B-5	"	"	-0.23	-1.35	-0.76	"	
B-6	"	"	-2.22	-0.23	-0.69	"	
B-7	"	"	-1.87	-0.33	-0.77	"	
B-8	"	"	-7.47	-1.42	-3.23	"	
B-9	"	"	-0.23	-1.31	-0.65	"	
B-10	"	"	-2.22	-0.30	-0.91	"	
Ave.			1.63	1.85	1.44		

(1) All listed measurements for fundamental frequency; overtone data very similar.

(2) Zero indicates an aging rate which is too low to accurately determine.

TABLE 5-A

AGING OF 10 MHz (FUND.) UNITS AT 85°C,
Au + Au RELIABILITY SERIES (1)

			Aging Rates (2)				
Unit No.	Holder Type	Bond Cement	1st 30 days ($pp10^7$/week)	Last 30 days ($pp10^7$/week)	Total Period ($pp10^7$/week)	Total Aging Time (Hours)	Comments
C-1	HC-27/U	Pyroceram	+0.09	+0.02	+0.02	4920	
C-2	"	"	+0.09	0	+0.01	"	
C-3	"	"	+0.07	0	0	"	
C-6	"	"	-0.19	0	+0.03	"	
C-9	"	"	-0.04	0	0	"	
C-10	"	"	+0.02	0	0	"	
C-11	"	"	+0.02	0	+0.01	"	
C-12	"	"	-0.77	-0.02	-0.13	"	
Ave.			0.16	0	0.02		
D-7	HC-27/U	5504	+0.07	-0.02	0	4920	
D-12	"	"	-0.21	-0.02	-0.06	"	
Ave.			0.14	0.02	0.03		
A-1	T-5$\frac{1}{2}$	5504	-0.26	-0.05	-0.12	4920	
A-3	"	"	+0.07	-0.07	-0.05	"	
A-4	"	"	-	-	-	"	Unit failed at 125°C
A-6	"	"	-0.35	-0.13	-0.11	"	
A-7	"	"	-0.44	-0.10	-0.14	"	
A-9	"	"	+0.07	-0.02	-0.01	"	
A-10	"	"	-0.12	-0.06	-0.07	"	
B-1	"	"	-0.42	-0.16	-0.22	"	
B-2	"	"	+0.26	-0.09	0	"	

(Continued)

TABLE 5-A (Continued)

AGING OF 10 MHz (FUND.) UNITS AT 85°C, Au + Au RELIABILITY SERIES (1)

			Aging Rates (2)				
Unit No.	Holder Type	Bond Cement	1st 30 days ($pp10^7$/week)	Last 30 days ($pp10^7$/week)	Total Period ($pp10^7$/week)	Total Aging Time (Hours)	Comments
B-3	T-5½	5504	+0.54	-0.07	+0.06	4920	
B-4	"	"	-0.04	0	-0.03	"	
B-5	"	"	-0.44	-0.09	-0.15	"	
B-6	"	"	+0.19	-	-	"	Erratic
B-7	"	"	+0.09	-0.05	-0.01	"	
B-8	"	"	-0.26	-0.07	-0.08	"	
B-9	"	"	-0.49	0	-0.14	"	
B-10	"	"	0	-	-	"	Erratic
Ave.			0.28 (3)	0.07 (3)	0.09 (3)		

(1) All listed measurements for fundamental frequency; overtone data were very similar.

(2) Zero indicates an aging rate which is too low to accurately determine.

(3) Not including Units A-4, B-6, and B-10.

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13. ABSTRACT

The purpose of this research is to reduce the aging and increase the reliability of quartz resonators. Average aging rates of 81.9 to 500 kHz units at 85°C ranged from 0.35 to 0.51 ppm/wk for a period of 9000 hours subsequent to an initial aging phase of $\sim$ 60 days. Units having polished edges performed less well than others having a "state-of-the-art" edge finish. The average aging of 123 3MHz resonators at 85°C was 2.0 pp10^9/wk during 10,000 hours. Aluminum plated units mounted in evacuated HC-27/U holders averaged 1.2 pp10^9/wk versus 2.3 pp10^9/wk for gold plated ones. The average Q values were 1.2 and 0.75 x 10^6 respectively. Annular-field excitation of plano-convex 5 MHz units reduced aging rates to 1/10 that of conventionally-plated control units, and the Q was doubled. X-ray topography indicated oscillation was confined to the central 3/16" diameter zone for plano-convex units but extended over the entire plane-parallel zone (0.340" diameter) of units with beveled edges. The annulus was external to the active zone in the case of the plano-convex units and their Q values were four times greater. Aging of 10 MHz resonators at 125°C indicated container dependency; rates for units in T-5$\frac{1}{2}$ holder were greater than for those in HC-27/U. Serious outgassing or higher initial pressures in the T-5$\frac{1}{2}$ holder are indicated. Initial aging studies of 5 MHz resonators in cold welded containers (in vacuo) indicated degradation of aging by sealing at high temperatures (400°C) instead of improvement. Outgassing and adsorption imbalances appear to occur in containers heated to high temperature.

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3

15

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