AGING CHARACTERISTICS OF

QUARTZ CRYSTAL RESONATORS

by

RICHARD B. BELSER

and

W. H. HICKLIN

Project No. A-552

Contract No. DA-36-039-SC-87407
DA Task No. 3A-99-15-004

Prepared for

U. S. Army

Electronics Research and Development
Laboratory, Fort Monmouth, New Jersey

Atlanta, Georgia
Engineering Experiment Station
Georgia Institute of Technology
1961 - 63

CONTENTS

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 April 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 1
Contract No. DA-36-039-SC-87407
Georgia Tech Project A-552
Period: 15 February to 31 March 1961

Dear Sir:

The purpose of this project is to delineate the factors in the fabrication and mounting of quartz crystal resonators which are related to the aging of the resonators. Of particular interest is the development of materials and techniques of fabrication which will reduce aging to a minimum. Of specific interest are units of 16.5 mc frequency operated at the fundamental and the third and fifth overtones and an evaluation of resonators sliced from Y-bar and swept quartz. Measurements are to be conducted with a maximum accuracy and a target value of a part in 10^9.

Measurement methods developed under the associated Contract DA-36-039-SC-85363 have progressed to the degree that measurement to a part in 10^9 is now feasible. This equipment will be used for this project. The Atomichron to be supplied to the Contract arrived on 10 March 1961 and is now being installed.

Procurement of quartz plates suitable for use on the project was undertaken immediately upon notification of the initiation of the project. These include blanks of synthetic Y-bar quartz and quartz swept by an electric field.

The 200 unit, 85°C crystal oven, previously used for aging studies at a frequency of 16.5 Mc, is currently being modified for use on this contract. The crystal sites are being connected to the BNC terminations outside the oven by means of short lengths of coaxial cable. The grounded terminal bridge method of frequency measurement will be used.

The vacuum equipment has been modified to produce pressures during plating in the range 10^{-7} mm to 10^{-8} mm of mercury. A combination of cold surface pumping and gettering with evaporated titanium is being used in the plating chamber. Preliminary measurements have shown that the cited pressures can readily be obtained in this manner.

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FORMAT ✓ 19 BY Flc

The need for these lower pressures is justified by an examination of the aging curves of crystal units base plated with aluminum. Whereas units base plated at monitor temperature of 450°C aged downward quite rapidly, those plated at a temperature of 250°C performed very well. This behavior was not understood originally but it was conjectured that a thicker oxide was adsorbing greater quantities of gas with time. Upon measuring pressure directly on the plating chamber it was found that the chamber pressure rose to the 10^{-4} mm Hg range when preheating the quartz to 450°C unless an extended pumping period was employed before heating. The pressure rise at 250°C was much less and recovery time was greatly reduced. As a result it is conjectured that the increased chamber pressure during plating at high temperatures has resulted in a film of smaller crystallite size and a more porous structure. This in turn resulted in higher aging rates for resonators plated with a chemically active metal such as aluminum. This explanation fits the observed behavior of resonators plated with aluminum while maintained at 450°C substrate temperatures and clarified the otherwise anomalous behavior.

An experiment to evaluate this hypothesis will be conducted in the near future.

Plans for the month of April include completion of oven, vacuum and measuring equipment modifications presently under way and of the fabrication of an initial series of resonators. These will be plated with Al + Al or Al + Au.

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Original Signed By Vernon Crawford

V. Crawford
Head, Physics Branch
Physical Sciences Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

3 May 1961

Frequency Control Division
Electronic Components Research and
Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 2
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 April to 1 May 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on the stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

Materials and Apparatus

An order has been placed for one hundred AT-cut plates of each of the three types of quartz required. In addition, one pound each of "bulk" Y-bar and swept quartz have been ordered from Sawyer Research Products, Inc.

The 200 unit oven has been modified to incorporate coaxial leads to all positions; and preliminary calibration tests are being conducted. The oven will be ready for use by the 15th of May.

The modification of the apparatus for the base plating and vacuum baking of resonators has been completed. Operating pressures are in the 10^{-7} mm of Hg range.

The design of a final plating chamber has been completed and construction started. This chamber is expected to operate at pressures in the 10^{-7} mm of Hg range and to have a rapid pump down rate.

Frequency Measurement System

In order to attain the desired level of measurement accuracy a further modification of the present frequency measurement system to insure more reliable control of bridge adjustment and to speed up the measurements has been sought. The proposed system and the progress in its development is outlined below.

The frequency measuring system currently used employs an automatic gain control circuit which maintains the crystal drive constant during adjustment of crystal bridge and oscillator frequency. This system provides the necessary accuracy in crystal frequency measurement but the procedure is somewhat tedious and lengthy where a large number of crystal units must be measured. Once the oscillator frequency is locked onto the crystal frequency several adjustment operations must be carried out on oscillator tuning, bridge balance, and detector gain to accomplish the desired bridge null condition and thus permit the frequency to be correctly recorded.

A system which will improve the resolution of the detector in indicating the null point of the bridge and also provide the possibility for automatic tracking of the oscillator frequency with the crystal frequency has been designed; and the construction of a breadboard system has been begun. A block diagram of the entire system including the proposed improved detector and frequency tracking system is shown in Figure 1 attached.

Two signal voltages are taken from the bridge and fed into a two channel superheterodyne circuit; these are the bridge input to one channel and the bridge null output to the other channel.

Mixer injection voltages are for both mixer stages derived from a common local oscillator. The output of each mixer is amplified in separate i-f amplifiers and fed to a synchronous detector. The output of the synchronous detector is a d-c voltage proportional to amplitude and phase difference between the two i-f signals derived from the bridge. Thus if the bridge is balanced the output of the detector is zero or some fixed mean value determined by the inherent constant phase value in the detector system.

When the bridge is unbalanced in one direction the detector d-c output will change and its phase relative to the balance condition will have a certain polarity. An unbalance in the opposite direction will produce a detector output of the opposite polarity. Since the output is dependent on the coherent properties of the two signals the incoherent property of noise in both channels will produce no net d-c output and therefore these high frequency noise fluctuations may be filtered out by a low pass filter having only a few cycles bandwidth. Thus the null indication is not masked by the noise voltage that is present in the envelope type of detector used in the present system; as a result, a greater resolution of null condition is obtained in the proposed system.

Since the synchronous detector output is determined by the direction of bridge unbalance, the d-c voltage derived may be used to correct the frequency of the oscillator. This action brings the bridge to balance by operating the crystal at the frequency of its true series resonance. This facility is indicated on the block diagram by the connection between the low-pass filter output and the oscillator reactance circuit input associated with the VFO.

When the oscillator frequency is tuned manually to search for the crystal resonance frequency and comes within the bandwidth of the detector system the frequency tracking circuit will automatically take over and pull the VFO frequency into the correct crystal frequency. This relieves the operator, from this point on, from having to monitor the frequency to maintain bridge balance. The only adjustment remaining for his attention is the reactance balancing adjustment to compensate for the reactive component of the crystal.

Comments

Investigations conducted at Georgia Tech during the past several years have indicated that there is no intrinsic reason why the final plating operation should degrade the frequency stability of crystal resonators provided metals chosen for the base and final plating are compatible with regard to the effects of alloying and are not highly stressed. In mass production of resonators final plating to frequency is a bottle-neck, and in effort to speed the operation plating techniques are frequently employed which are unacceptable, i.e.: high pressures, poor or no cold trapping, etc. While the chamber now under construction here may not speed the final plating operation significantly, it will improve the operation by offering quickly obtainable pressures in the 10^{-7} mm of mercury range with adequate cold trapping in the same time now required to pump to the 10^{-4} or 10^{-5} mm of Hg range. Pressure gauges have also been placed to monitor pressure in the chamber directly, since the instantaneous pressure during evaporation is the pressure of importance. In many vacuum systems the gauge position does not give a proper reading of the chamber pressure and poor exhaust methods may allow significant rises in pressure of two orders of magnitude during the plating action. Pressures of this amount may increase aging rates of the resultant resonators to an unacceptable degree. In the current study every effort will be made to delineate these factors and to point out methods of avoiding them.

Program for May 1961

Oven positions will be ready for the installation of resonators by the middle of this month. Initial resonators of 16.5 mc fundamental will be fabricated and measured. Some of the older 16.5 mc resonators will be installed as a check on the quality of the new oven and its controls. On arrival of resonator plates now on order aluminum plated resonators will be fabricated employing duPont No. 5504 A silver flake cement. Similar units will be fabricated employing aluminum and gold overcoats for frequency adjustment. Units for operation in the overtone modes will be prepared provided the quartz plates, currently on order, are received.

Respectfully submitted.

Richard B. Belser
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

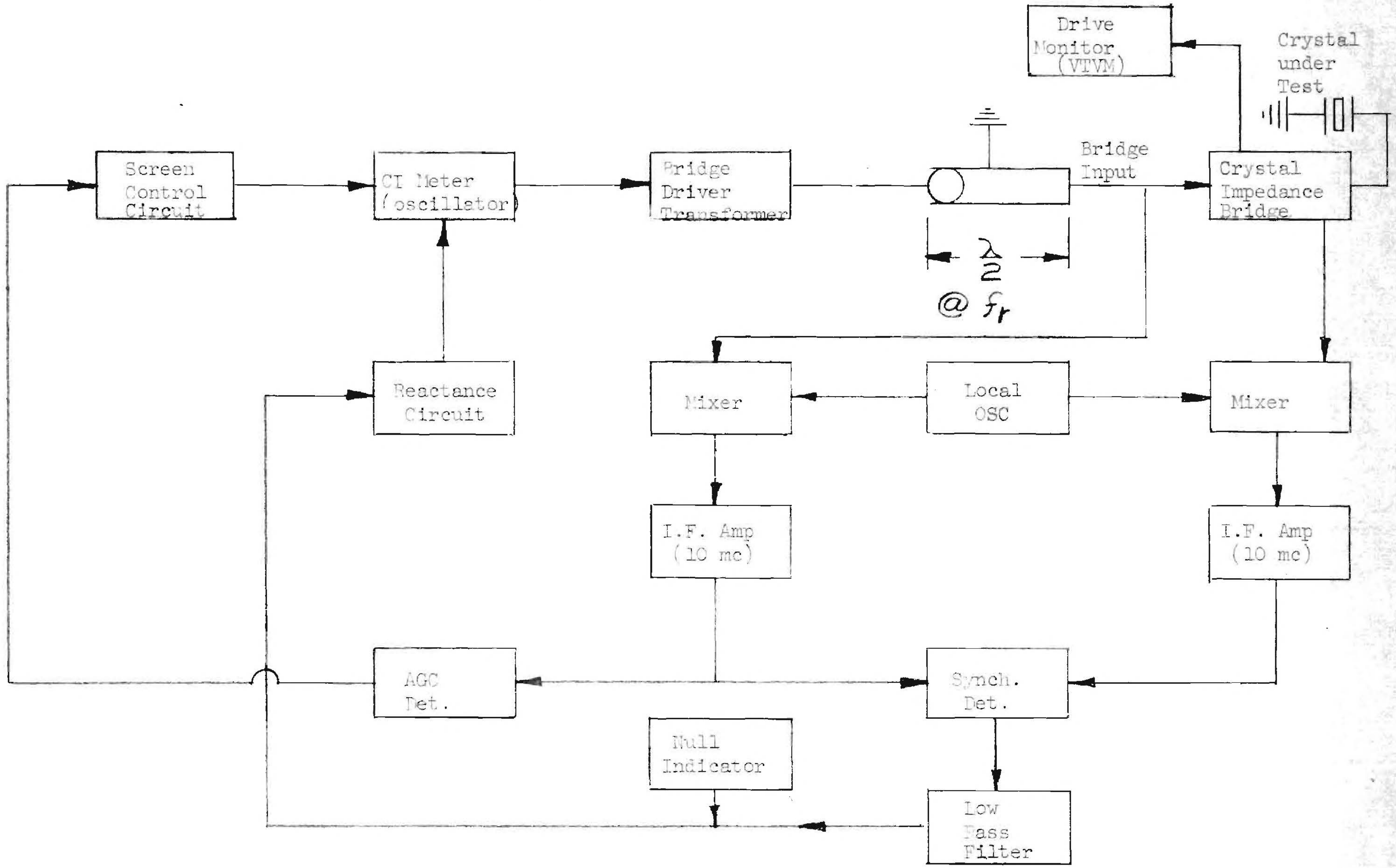

Figure 1. Crystal Frequency Measuring System Including AGC and the Proposed Improved Detector and Frequency Tracking System

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 June 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, N. J.

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 3
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 May 1961 to 1 June 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on the stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

Circuitry for the automatic nulling device to be added to the frequency measurement bridge has been completed and the apparatus is now ready for evaluation as to measurement accuracy. Repeatable measurements to a few parts in 10^9 are expected.

Modification of the 200 unit oven has been completed to incorporate a coaxial lead and BNC termination to each resonator position. This oven was placed in operation the latter part of May. Some early difficulty was encountered in temperature control but this was traced to a failure of the outer oven to cycle. By increasing the heater voltage of the outer oven the problem was remedied.

Twenty resonators were completed with parameters indicated in the attached Table. These were placed in the 85° oven for aging. Data obtained during the month was insufficient for proper interpretation of aging behavior.

Mr. R. B. Belser, W. H. Hicklin and W. Bruce Warren attended the 14th Annual Frequency Control Symposium in Atlantic City, N. J., 31 May, 1-2 June 1961.

Plans for the month of June are to complete the measurement equipment, fabricate and measure additional resonators in accordance with the scheduled program, and to complete Quarterly Report No. 1, now in preparation.

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

RBB:am

TABLE I

PARAMETERS OF RESONATORS FABRICATED DURING QUARTER

Unit No.	Type Quartz	Base Plating Metal	Base Plating Temp (°C)	Base Plating Pressure (mm Hg)*	Final Plating Metal	Final Plating Pressure	Bonding Cement	Bonding Curing Temp (°C)	Bonding Curing Time (Hours)
				Group 1 - Yield 100%					
1-1	Natural	Aluminum	300	4×10^{-6}	-	-	5504A	150	3
1-2	"	"	"	"	-	-	"	"	"
1-3	"	"	"	"	-	-	"	"	"
1-4	"	"	"	"	-	-	"	"	"
1-5	"	"	"	"	-	-	"	"	"
1-6	"	"	"	"	-	-	"	"	"
1-7	"	"	"	"	-	-	"	"	"
1-8	"	"	"	"	-	-	"	"	"
1-9	"	"	"	"	-	-	"	"	"
1-10	"	"	"	"	-	-	"	"	"
				Group 2 - Yield 90%					
2-1	Natural	Aluminum	300	2×10^{-6}	-	-	5504A	300	1
2-2	"	"	"	"	-	-	"	"	"
2-3	"	"	"	"	-	-	"	"	"
2-4	"	"	"	"	-	-	"	"	"
2-5	"	"	"	"	-	-	"	"	"
2-6	"	"	"	"	-	-	"	"	"
2-7	"	"	"	"	-	-	"	"	"
2-8	"	"	"	"	-	-	"	"	"
2-9	"	"	"	"	-	-	"	"	"
2-10	"	"	"	"	-	-	"	"	"

*This pressure is that recorded at the instant of evaporation; pressures just before and shortly after evaporation are usually an order of magnitude lower.

TABLE I (Con

	Mounting		Vacuum Baking					
Unit No.	Type	Resonator Holder	Time (Hours)	Temp (°C)	Pressure (mm Hg)	Funda		
				Group 1 - Yield 100%				
1-1	GE Glass	0.006" Springs	3	175	2×10^{-7}			
1-2	"	"	"	"	"			
1-3	"	"	"	"	"			
1-4	"	"	"	"	"			
1-5	"	"	"	"	"			
1-6	"	"	"	"	"			
1-7	"	"	"	"	"			
1-8	"	"	"	"	"			
1-9	"	"	"	"	"	-	-	22.5
1-10	"	"	"	"	"	-	-	24.5
				Group 2 - Yield 90%				
2-1	GE Glass	0.006" Springs	3	175	2×10^{-7}	4.5	-	14.0
2-2	"	"	"	"	"	4.5	-	13.0
2-3	"	"	"	"	"	6.0	-	15.0
2-4	"	"	"	"	"	5.5	-	16.5
2-5	"	"	"	"	"	6.0	-	Hi
2-6	"	"	"	"	"	6.0	-	18.0
2-7	"	"	"	"	"	6.5	-	17.5
2-8	"	"	"	"	"	7.0	-	50.0
2-9	"	"	"	"	"	7.0	-	17.5
2-10	"	"	"	"	"	6.0	-	17.5

GEORGIA INSTITUTE OF TECHNOLOGY

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ATLANTA 13, GEORGIA

5 July 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. [illegible]
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 June 1961 - 1 July 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on the stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

Thirty 80 Mc resonators were fabricated during the month of June. These consisted of 20 units fabricated of cultured quartz and 10 of natural quartz. The cultured quartz units were plated with aluminum only and half were on swept quartz and half on unswept material. The ten units on natural quartz were base plated with aluminum but plated to frequency with gold. R_s values for nearly all units were in the range 10 to 20 ohms when operated at 80 Mc (5th mode). Yield on these resonators was 100 percent.

Measurements of the fifty resonators fabricated to date have been made regularly. Some drift in parts in 10^8 was noted due to drafts about instrumentation. The CI meter, bridge and oven have been housed in insulated boxes with plastic curtains in front. These have cut down drafts and stabilized measurements.

The application of the improved measurement technique utilizing automatic nulling of the crystal bridge encountered a difficulty related to instability in the I-F amplifiers. The I-F amplifiers have been rebuilt to eliminate this problem which was primarily due to insufficient shielding.

In addition, a 10 kc amplitude modulation has been added to the error signal from the crystal bridge to facilitate drift free amplification of the synchronous detector output. The method by which this has been accomplished is indicated in the block diagram of Figure 1. The entire system diagram has been redrawn for the sake of clarity with the modifications shown inside the dotted portions of the diagram.

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The 10 kc signal from an audio oscillator is injected along with the error signal from the crystal bridge at the input mixer, with the result that the I-F signal output of the mixer is amplitude modulated at a 10 kc rate. This amplitude modulated signal is heterodyned in the synchronous detector with the unmodulated signal from the I-F reference channel to produce a 10 kc output whose phase reverses whenever the phase of the error signal from the crystal bridge reverses. The 10 kc signal is then amplified and applied to the 10 kc phase detector whose output is a D-C voltage of proper polarity to tune the CI meter oscillator to the frequency required for null in the crystal bridge.

Quarterly Progress Report No. 1 was completed and forwarded for approval.*

Plans for the month of July are to fabricate and measure resonators in accordance with the scheduled program. The measurement apparatus has now been improved to the point that good aging measurements should be obtained during the month.

Respectfully submitted,

Richard B. Belser

RBB/var

Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
Library, 2
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* The approved copy has now been received and will be reproduced and distributed shortly after the 15th of July.

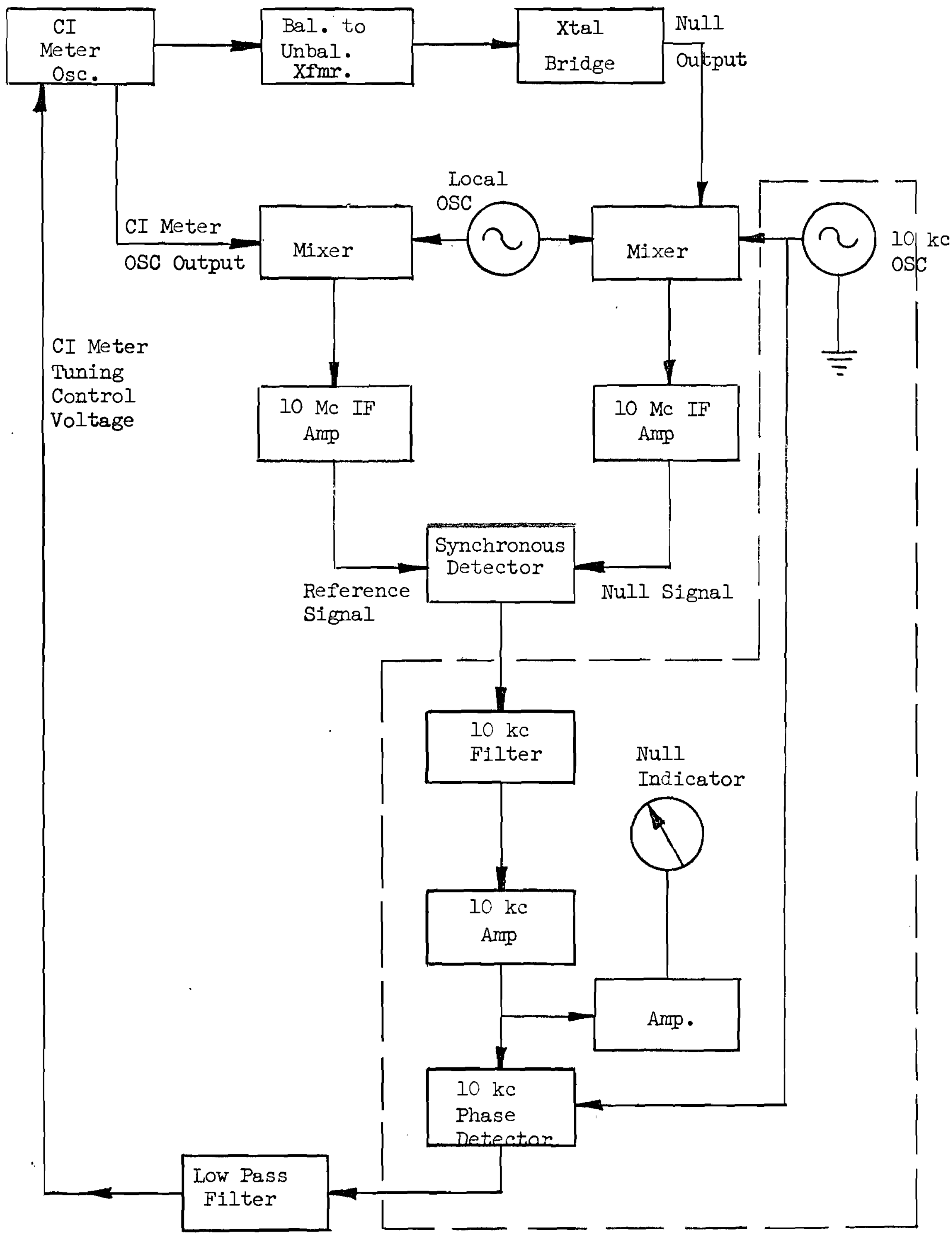

Figure 1. Modified Automatic Null Device

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

2 August 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 5
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 July to 1 August 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on the stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural synthetic and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

During the reporting period three groups of crystal units using natural quartz blanks were fabricated. The pertinent details of each group are tabulated below.

QUARTZ CRYSTALS FABRICATED DURING JULY 1961

Group	Base Plate	Final Plate	R_s*(Ω)	Yield
5	Aluminum	Gold	22.0	100%
6	Aluminum	Aluminum	15.4	50%
7	Aluminum	Gold	26.1	60%

*Average value for the operable units measured at the 5th overtone in 85°C oven.

Groups 5 and 7 differed in that group 5 units were overplated with gold without removing the blanks from the base-plating mask while those of group 7 were mounted and plated to frequency individually at the fundamental frequency (16.0 Mc). All units were mounted in glass holders, evacuated, vacuum baked and sealed in vacuum.

The modification on the 200 unit, 85°C oven to incorporate coaxial leads into the crystal positions caused a rather serious temperature control problem. This action resulted from the relatively large volume of metal in the coaxial cable outer conductor transferring heat readily between oven levels and to the outside. The measurement errors due to small oven temperature changes have been virtually eliminated by:

1. Enclosing the bottom of the oven with a styrofoam housing leaving only a plastic curtain through which the bridge enters to engage the BNC connectors.

2. Covering the sides and top of the oven with styrofoam, the top being removable to permit loading of the oven.

Frequency measurements have been made only at the fifth mode using equipment designed for use at 100 Mc on Project A-508. However, the equipment under construction for measurements at the fundamental and third overtone as well as the fifth overtone is expected to be completed shortly. The improvement in measurement obtained by correction of the oven temperature control problem is exhibited in the graph attached for unit 2-1 (aluminum plated).

The program for August is to continue fabrication and measurements of crystal units according to plan. In addition, units already on test will be removed from the aging ovens by groups and measurements will be made for calculation of the "Q" values of the resonators. The measurements will be made at the fundamental frequency only.

Respectfully submitted,

Richard B. Belser
Project Director

RBB/var

Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
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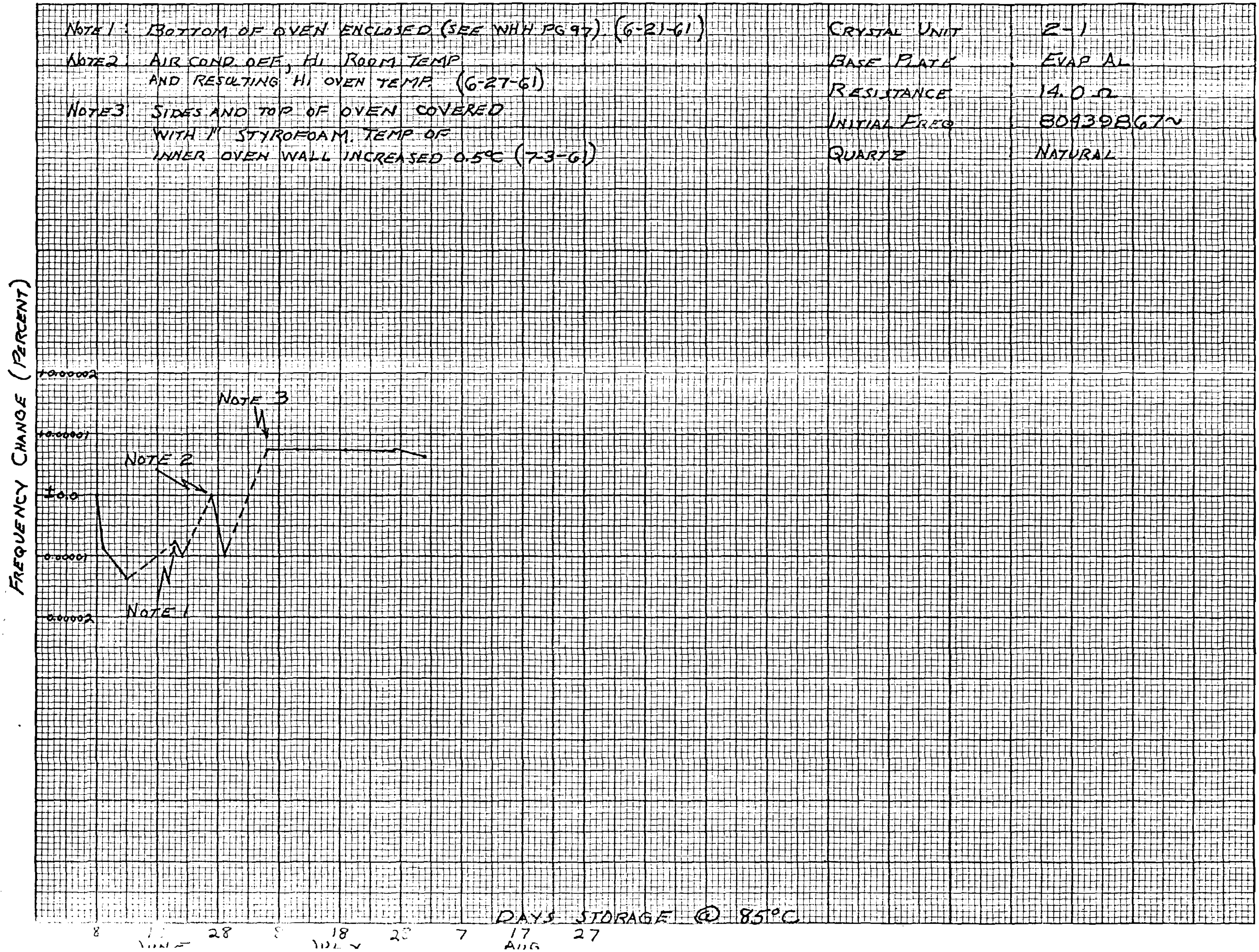
NOTE 1: BOTTOM OF OVEN ENCLOSED (SEE WHH PG 97) (6-21-61)
NOTE 2: AIR COND OFF, HI ROOM TEMP AND RESULTING HI OVEN TEMP (6-27-61)
NOTE 3: SIDES AND TOP OF OVEN COVERED WITH 1" STYROFOAM. TEMP OF INNER OVEN WALL INCREASED 0.5°C (7-3-61)
CRYSTAL UNIT 2-1
BASE PLATE EVAP AL
RESISTANCE 14.0 Ω
INITIAL FREQ 80439867~
QUARTZ NATURAL
FREQUENCY CHANGE (PERCENT)
+0.00002
+0.00001
±0.0
-0.00001
-0.00002
NOTE 3
NOTE 2
NOTE 1
DAYS STORAGE @ 85°C
8
28
18
7
17
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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 October 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 6
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 September to 1 October 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural synthetic and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

The entire effort during the month of September has been devoted to the completion of the AGC-AFC frequency measurement system. Unforeseen difficulties were encountered in the signal to interference ratio of the output of the AFC circuit. As a result inadequate resolution and sensitivity is obtained for satisfactory operation of the AFC channel. Although extensive efforts were made to overcome this difficulty no practical solution appeared to be likely within a reasonable work period. Hence, it has been decided to abandon the AFC portion of the system but to incorporate improvements in sensitivity achieved during reconstruction of the bridge assembly. The present system is expected to give measurements an order of magnitude better than that achieved previously, i.e., accurate to a few parts in 10^9.

The construction of the present system cannibalized the measuring system as it was and thus prevented frequency measurements for about thirty days. The measurement system should be operative at the higher accuracy within ten days. It also has incorporated into it a multiplier which will allow frequency measurements at both the third and fifth overtones.

It is recommended that if further improvement in measurement accuracy be necessary that sufficient equipment be provided to allow parallel development of measurement instrumentation without interruption of the operating system.

Quarterly Report No. 2 was submitted and approved except for minor corrections. It is now undergoing final reproduction in the corrected copy and will be distributed in a few days.

Notice that the balance of the financial allotment for the work for the 24-month total work period, per a telephone conversation between Dr. G. K. Guttwein and Mr. R. B. Belser, has been confirmed by the Contracting Officer and work can proceed without interference from lack of sufficient funds.

Components necessary for mounting quartz resonators in the HC-6/U glass container have been received and work is proceeding on this phase. Some experiments with a "Pyroceram" sealing and bonding are also making progress and some success along this line appears feasible.

During the month of October the frequency measurying system should be back in operation and fabrication and measurement of resonators according to schedule will be continued. Units will be mounted in the glass HC-6/U container for the first time.

Respectfully submitted,

Richard B. Belser

RBB/var

Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

November 5, 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 7
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 October to 1 November 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

The difficulties encountered with the AGC-AFC frequency measurement system have resulted in the temporary abandonment of this measurement method and a return to a system based on the original bridge measurement system. An inherent weakness of the AGC-AFC bridge system is that driving the crystal through a transformer degrades the effective Q of the crystal and gives it poor control of the CI meter. It has been found that the transformer can be eliminated by adopting a system similar to that shown in Figure 1.

This arrangement requires a stable frequency source to drive the bridge and this may be CI meter controlled by a series of crystals of closely matching frequencies to those under test or a frequency synthesizer of high short time stability such as the Rohde and Schwarz signal generator. By driving the crystal under measurement passively with the proper frequency, the resonant frequency of the crystal under examination can be determined. With refinement this technique is expected to reach the desired accuracy of measurement of a few parts in 10^9.

A large part of the time during the month of October was spent in working on the AGC-AFC measurement system. When it became apparent that this method would not become workable without extensive further development, work was immediately begun upon reestablishment of the original bridge method with some refinement. Since this held no prospect for measurement accuracies of parts in 10^9 the passive measurement outlined was adopted since it could be initiated as readily as a return to the former method. However, the Rohde and Schwarz frequency synthesizer would greatly facilitate the use of the new system.

A method for sealing the glass HC-6/U units has been perfected. After the resonator has been mounted the envelope, base and crystal are held by two jigs in a vertical evacuated Vycor tube heated externally by a gas ring-burner. The envelope, in an inverted position, is held by the lower jig. The upper jig holds the base and mounted resonator which mates with the envelope. The latter jig is spring loaded to force the two parts together as the sealing frit is melted.

The gas burner heats the parts to a temperature of about 250°C. This aids in outgassing the parts and in reducing stresses set up when the Kovar ring is heated by the induction coil. The induction coil is actuated at a current of one ampere for about 30 to 45 seconds until the Kovar ring glows at a dull red. A dial gauge monitors the relative movement between the upper and lower jigs. When this reads about 0.017" the foot switch to the induction coil is released. The dial gauge continues to move about 0.003". A motion between the jigs of 0.020" has been found to give consistently leakproof sealing as determined by the vacuum oil leak test. On completion of the seal the heat supplied by the gas burner is gradually reduced to anneal the seal. The time allowed for this is five minutes. The resultant seals have given no trouble from cracks due to residual stresses in the glass. The method also removes the necessity for careful programming of the current of the induction heater coil.

Plans for the month of November are to renew aging measurements of resonators fabricated with the new passive frequency measurement system. Resonators will be mounted in the new HC-6/U glass mounts for the first time.

Respectfully submitted,

RBB/var

Richard B. Belser
Project Director

cc: Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
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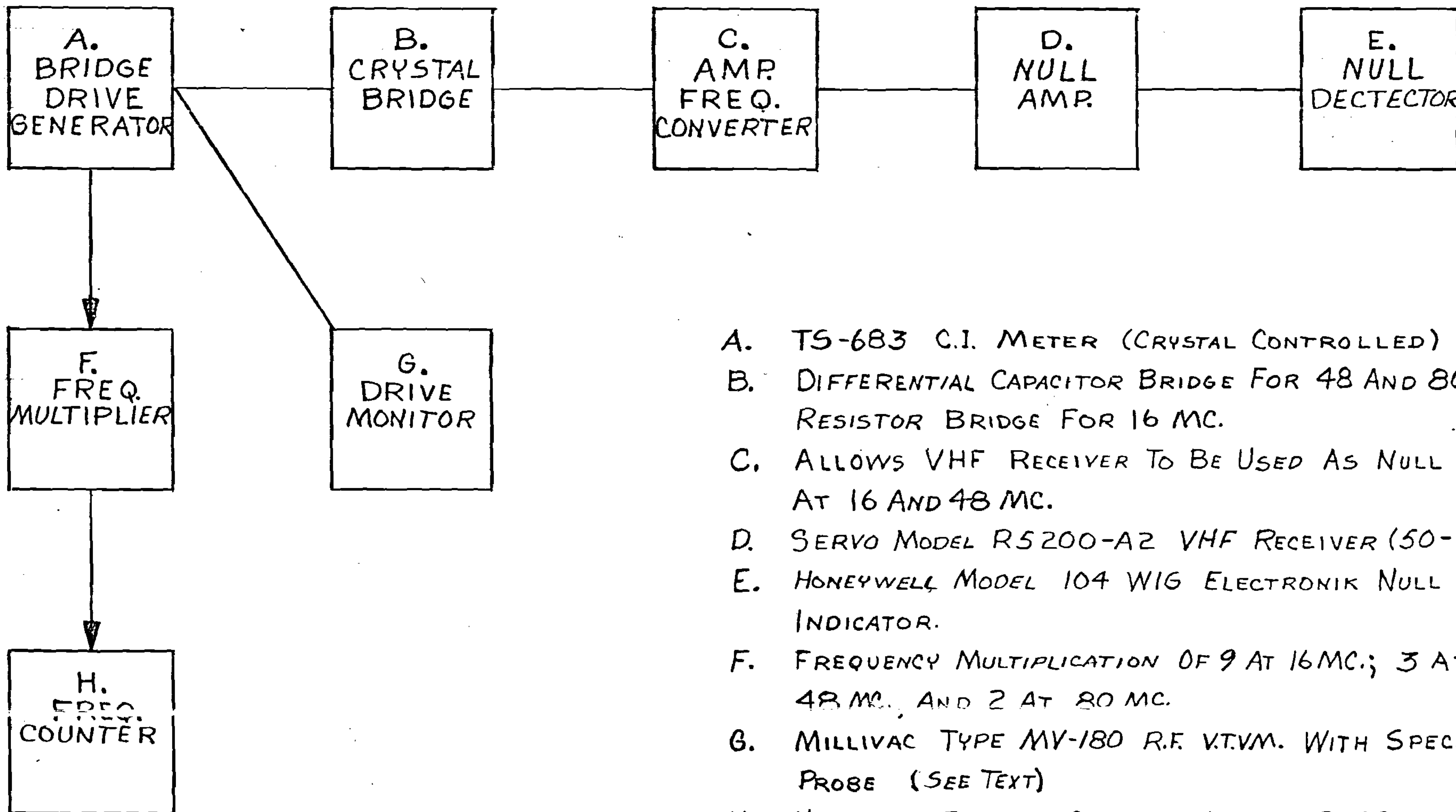
Surplus



A. TS-683 C.I. Meter (Crystal Controlled)

B. Differential Capacitor Bridge For 48 And 80 MC. Resistor Bridge For 16 MC.

C. Allows VHF Receiver To Be Used As Null Amp. At 16 And 48 MC.

D. Servo Model R5200-A2 VHF Receiver (50-200 MC.)

E. Honeywell Model 104 W1G Electronik Null Indicator.

F. Frequency Multiplication Of 9 At 16 MC.; 3 At 48 MC., And 2 At 80 MC.

G. Millivac Type MV-180 R.F. V.T.V.M. With Special Probe (See Text)

H. Hewlett-Packard Counter Model 524C

FIGURE 1. PASSIVE BRIDGE FREQUENCY MEASUREMENT SYSTEM

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 December 1961

Frequency Control Division
Electronic Components Research and Development Laboratories
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber

Subject: Progress Letter No. 8
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 November to 1 December 1961

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

The frequency measuring equipment based upon the crystal bridge method of measurement has been completed. The system was completed essentially as described in Progress Letter No. 7 and Quarterly Report No. 3. Frequency measurements of all crystals have been made at each of the operating frequencies (16, 48, and 80 Mc). Results indicate that the precision of measurements may approach a few parts in 10^9 by the use of frequency multiplications of 9 at 16 Mc, 3 at 48 Mc, and 2 at 80 Mc before counting and then counting for ten seconds.

Initial measuring of the crystal units was a laborious task because of the necessity of matching the frequencies of the crystals controlling the CI meter to the crystals stored in the oven. Twenty percent of the crystals fabricated during this project were required for use as reference frequency crystals. Resonators fabricated during previous contracts were employed to cover the lower frequency ranges at each operating frequency.

Further improvements in the 85°C oven temperature control have given a temperature stability of about ± 0.02°C maximum deviation. Additional improvements planned include full proportional control of the inner oven using a magnetic amplifier to supply the oven heater power. The D.C. control current for the amplifier will be obtained from a thermistor bridge.

Fabrication of crystal resonators was started again during November. The first group (No. 9) was base plated with evaporated aluminum without overcoating to frequency and sealed in HC-6/U glass holders. The apparatus described in Quarterly Report No. 3 was used for sealing. The units were mounted in tab-clips spot-welded to the pins and were bonded with Pyroceram-silver cement. No aging data on these units are available as yet.

Dr. G. K. Guttwein of USASRDL visited the Georgia Institute of Technology on 2 November 1961. The progress and future program of the project were discussed. Particular emphasis was placed on measurement of aging at the fundamental, 3rd, and 5th overtones for respective resonators in order to define the overtone dependence of aging.

Plans for the month of December include the fabrication of crystal units in accordance to the previous schedule with emphasis placed upon units mounted in glass HC-6/U holders. Measurements in progress will be continued and the current frequency measuring technique will be refined.

Respectfully submitted,

Richard B. Belser
Project Director

RBB/var

cc: Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
Library, 2
Surplus

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

5 January 1962

Headquarters
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber
Solid State and Frequency Control Division

Subject: Progress Letter No. 9
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 December 1961 to 1 January 1962

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

The passive bridge frequency measuring apparatus has been in use for about 45 days. The precision of measurement with few exceptions has been very good. There are, however, two major sources of measurement error:

1. The oven temperature deviates about $\pm$ 0.03°C about the mean temperature of 85°C.

2. In some cases the frequency match between the CI meter crystal and the oven crystal is poor.

This latter condition causes the frequency stability of the CI meter to be poor since the CI meter crystal must be "pulled" from its normal resonant frequency during the measurements.

Reference Item 1 above: the operation at the same temperature of each unit at the fundamental, third, and fifth modes results in a mismatch between the respective turn-over temperature of the crystal and the oven temperature except at one mode of operation. Thus the effect of the temperature changes of the crystal oven cause measurement errors to be larger for one or more of the operating modes. It is also possible, of course, that in some cases none of the operating modes will have a turn-over temperature at 85°C.

Correlation of the dependence of the frequency of the crystal units upon the oven temperature is now being determined by logging, with the resistance of a thermistor mounted in an evacuated bulb and placed in the crystal oven along with the crystal measurements.

Procurement of a magnetic amplifier which will deliver a 60-cycle AC voltage controlled by a few milliamperes of DC current has been initiated. The control current will be obtained from a thermistor bridge.

Reference item 2 above: the logical solution to this problem is the substitution of a high quality frequency synthesizer for the crystal controlled CI meter. However, some relief may be obtained as the stock of CI meter crystals increases. Frequency counting periods of ten seconds are not being used presently because of the instability of the crystal controlled CI meter.

The type of measurements being observed is illustrated in Figures 1, 2, and 3. The unit (1-2), base plated only with evaporated aluminum and sealed in an evacuated bulb, exhibits relatively large aging at the fifth mode (Figure 3) but a very small amount at the fundamental and third overtone.

Two groups of crystal units were completed during the month. Group 9 was base plated with aluminum, mounted in tab-clips, bonded with Pyroceram 95 and silver cement (five parts Pyroceram to one part silver by volume) in the manner described below and sealed in HC-6/U glass holders. The yield was 90% operable units. A second group (No. 10) was completed with plating and bonding similar to that of Group 9 for comparison with units previously prepared with other types of bonding agents. These were sealed in the glass lamp envelopes instead of the glass HC-6/U containers. The yield of the latter group was also 90%.

Considerable trouble was encountered when bonding to metal films with the Pyroceram-silver cement. Several units of Group 9 which would operate unbonded failed after the cement was cured. Several bonding and firing operations were necessary before nine operable units were obtained. During the process the following bonding method was developed and used on Group 10.

1. Dry mix 5 parts Pyroceram 95 and 1 part silver flake (by volume).
2. Add thinner until the mixture has the consistency of cream.
3. Apply a thin coat to the mounted crystals at the clip and allow to dry.
4. Apply a second thin coat and fire 5 minutes at 450°C in air.

All but one unit of Group 10 unit operated after bonding.

Part of the trouble with the Pyroceram-silver bonding appears to be the mismatch between the thermal expansion of quartz and Pyroceram. In order to investigate the bonding more thoroughly, polished plates of fused quartz were plated with evaporated aluminum and used for various bonding experiments. It was found that upon cooling the Pyroceram contracts pulling the film from the quartz at the periphery of the cement.

In several cases of extreme behavior a small chip of silica was broken from the plate. A very, slow cooling rate did not improve bond reliability.

Experiments are being extended to include bonding to films of silver and gold on fused silica substrates. Also, the silver content of the cement has been varied. Evidence recently obtained indicates that a mixture having 5 parts silver and 1 part Pyroceram by volume produces, after firing, a more ductile cement which possesses sufficient bond strength and which does not damage the film or the quartz during the cool-down cycle.

The program for the month of January includes:

Fabrication of crystal units in HC-6/U holders, continued frequency measurements, additional experiments with bonds of Pyroceram-silver cement, and completion of the oscillators required for studies of the effects on aging of continuous crystal drive.

Respectfully submitted,

Richard B. Belser
Project Director

RBB/var

Enclosures: Figures 1, 2, 3

cc: Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
Library, 2
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FIGURE 1

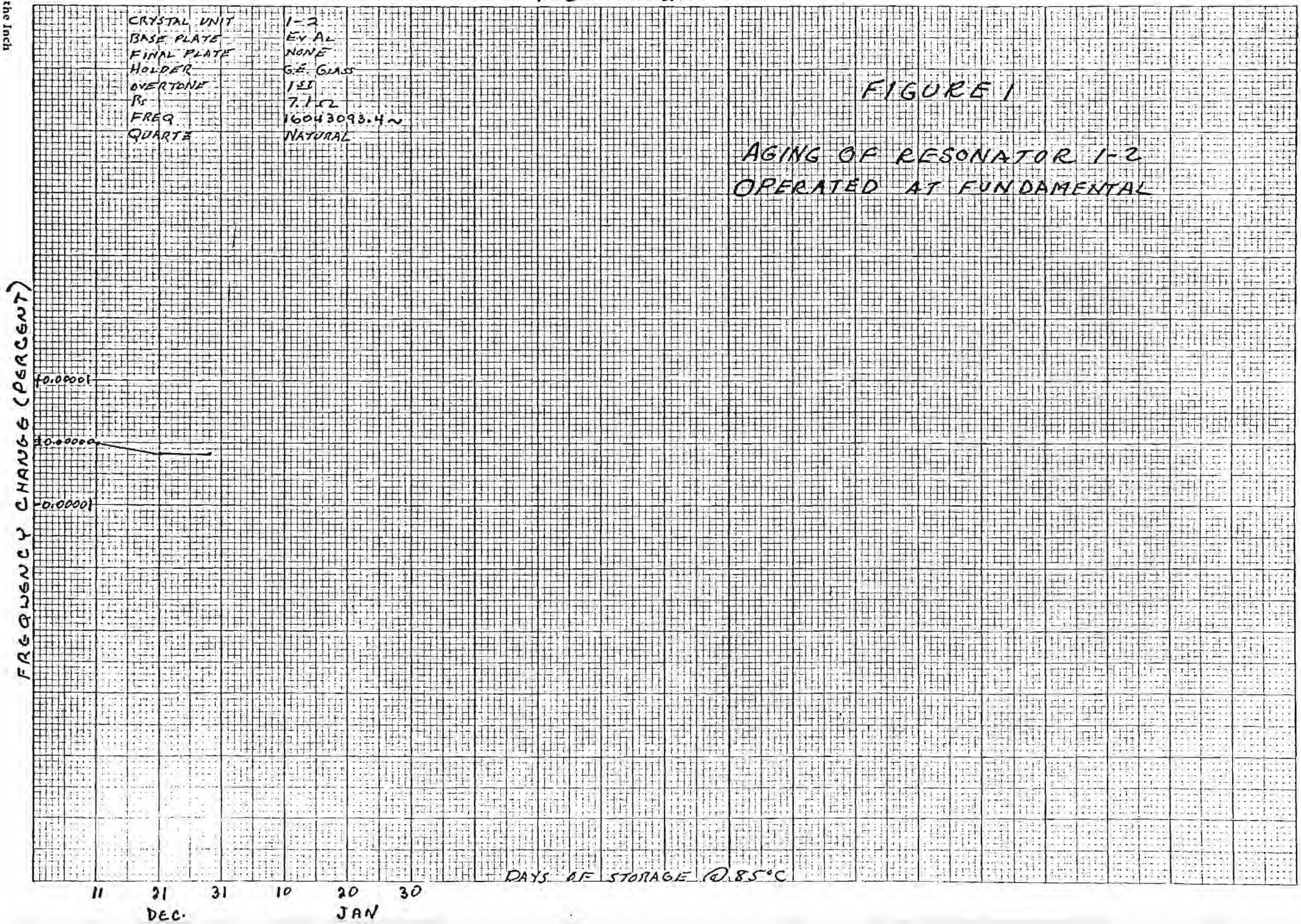
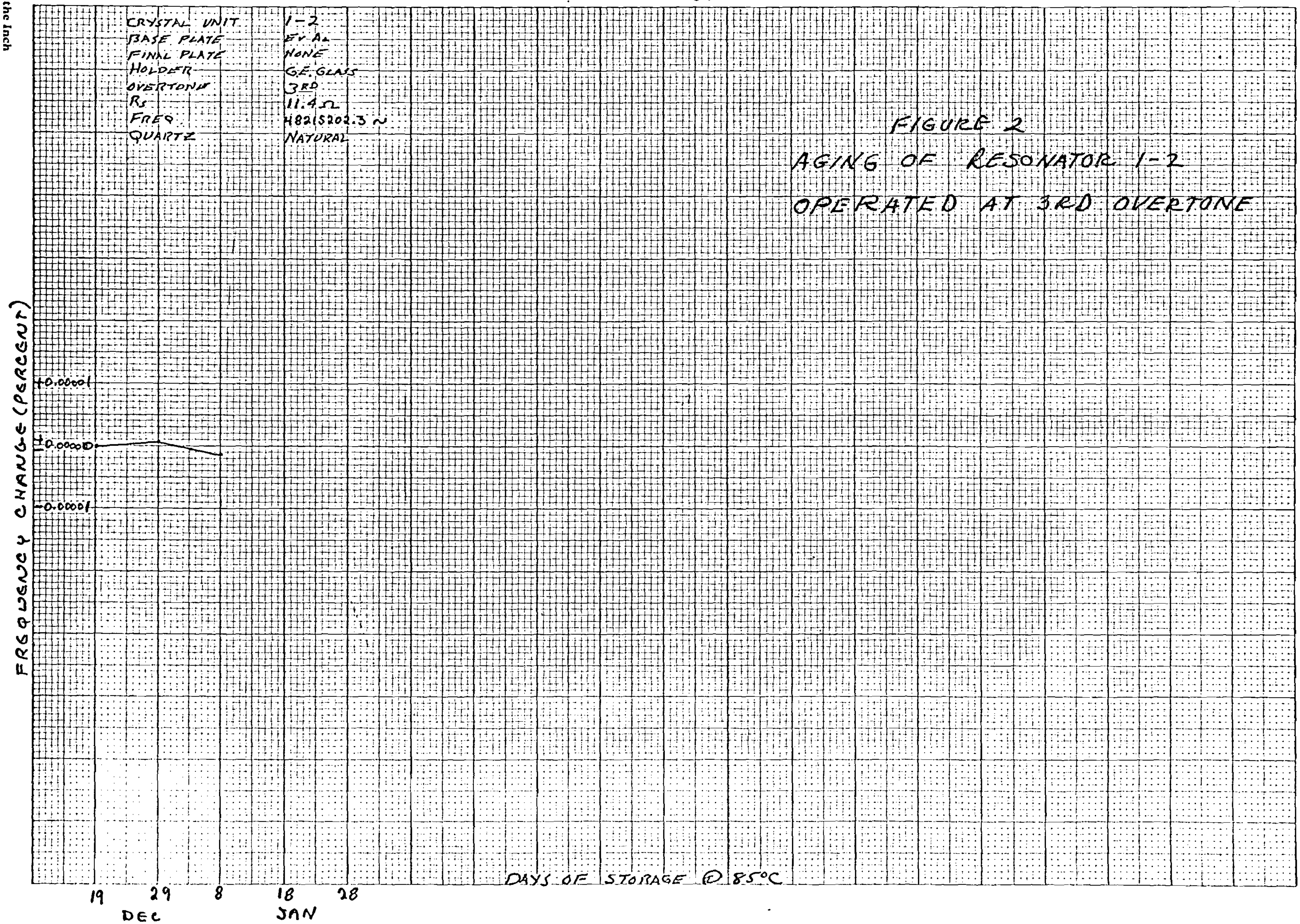
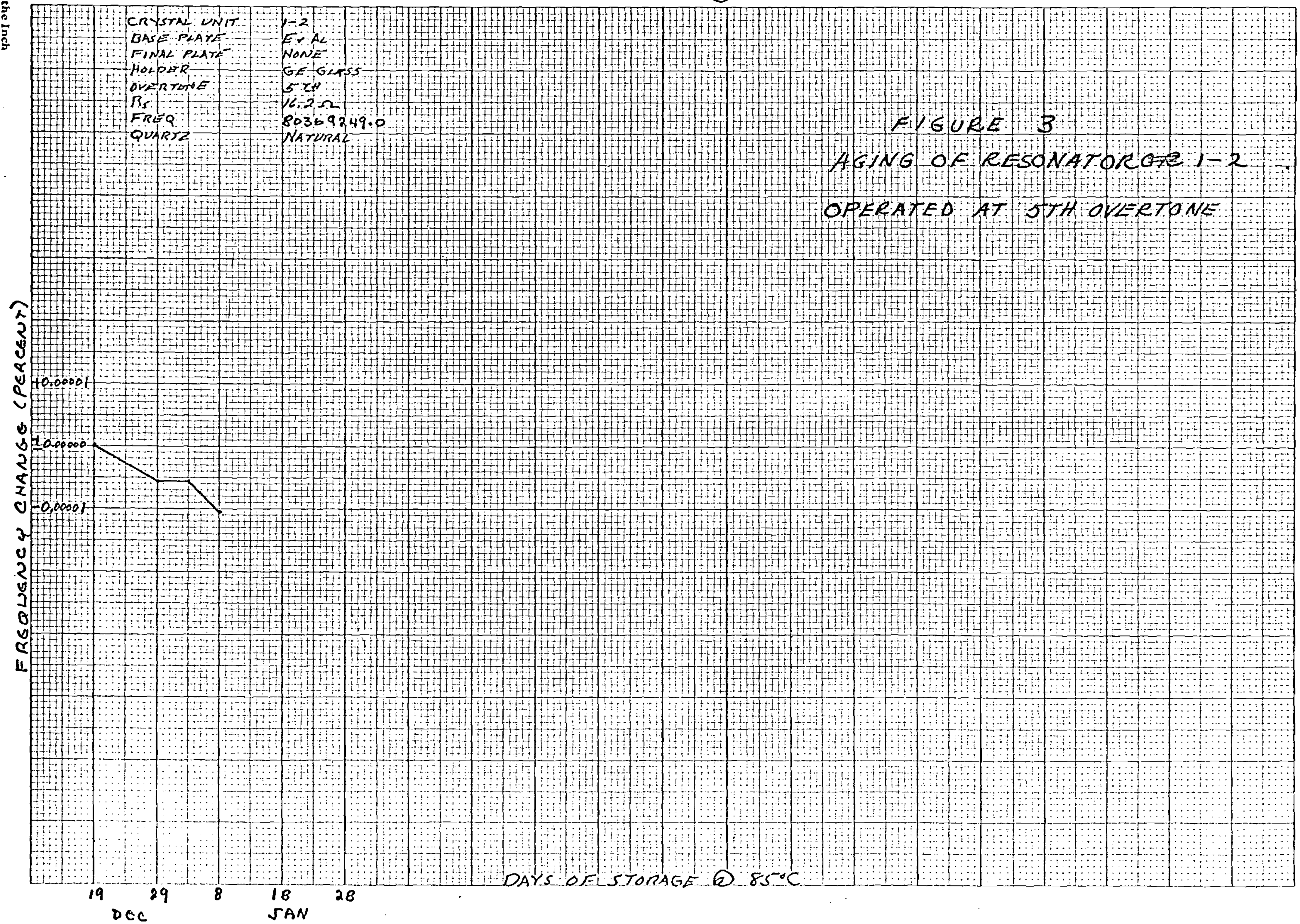

CRYSTAL UNIT 1-2
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1st
Rs 7.1 Ω
FREQ 16043093.4 ~
QUARTZ NATURAL
FIGURE 1
AGING OF RESONATOR 1-2
OPERATED AT FUNDAMENTAL
FREQUENCY CHANGE (PERCENT)
+0.00001
±0.00000
-0.00001
DAYS OF STORAGE @ 85°C
11
21
31
10
20
30
DEC.
JAN

FIGURE 2



CRYSTAL UNIT 1-2
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 3RD
Rs 11.4 Ω
FREQ 4821S202.3 ~
QUARTZ NATURAL
FIGURE 2
AGING OF RESONATOR 1-2
OPERATED AT 3RD OVERTONE
FREQUENCY CHANGE (PERCENT)
+0.00001
±0.00000
-0.00001
DAYS OF STORAGE @ 85°C
19
29
8
18
28
DEC
JAN

FIGURE 3


CRYSTAL UNIT 1-2
BASE PLATE Ev AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 5TH
Rs 16.2 Ω
FREQ 80369249.0
QUARTZ NATURAL
FIGURE 3
AGING OF RESONATOR 1-2
OPERATED AT 5TH OVERTONE
FREQUENCY CHANGE (PERCENT)
+0.00001
0.00000
-0.00001
DAYS OF STORAGE @ 85°C
19
29
8
18
28
DEC
JAN

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 February 1962

Headquarters
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber
Solid State and Frequency Control Division

Subject: Progress Letter No. 10
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 January to 1 February 1962

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

One group of crystal units was fabricated during the month. This group (No. 11) was base plated with evaporated aluminum, mounted in 0.006-inch springs, bonded with du Pont No. 5504-A cement and mounted in glass bulbs which were subsequently evacuated, baked, and sealed. The quartz used was of the swept, cultured type. The yield was 100% and all of the units were operable on the three modes of interest (1st, 3rd, and 5th).

Frequency measurements have continued using the passive bridge system. Modifications have been made subsequent to Quarterly Report No. 3 and the final design is shown in the block diagram of Figure 1. No basic change in the operation of the system resulted from the changes. However, the use of the HRO-5R receiver improved the signal-to-noise ratio by reducing the bandwidth in the null detection circuit. The frequency converter was eliminated by using the HRO-5R for a null amplifier at 16 Mc and by detuning the front end of the VHF receiver so that 48 Mc could be received directly.

Frequency measurements are considered to be accurate to a few parts in 10^9 except for a few cases in which the frequency match between the crystal controlling the CI meter and the one being measured is poor.

The primary effort during the month has been to improve the oven temperature control. Two approaches have been taken. Figure 2-A shows in block form a control system using the amplified output of a thermistor bridge to control the output voltage of a magnetic amplifier*. Power is supplied directly to the oven heater from the latter.

A second system shown in Figure 2-B consists of a fixed DC voltage across the oven heater upon which is superimposed a 10 kc AC voltage the amplifier of which is varied according to the balance condition of a thermistor bridge. Both of the temperature control systems have been constructed and are ready for final testing.

A qualitative analysis of conductive cements using a mixture of Pyroceram No. 95 and silver flake has indicated that improved results are obtained with a mixture of one part Pyroceram to 2 parts silver by volume. The dry mix is suspended in a solution of amyl acetate to which has been added a small amount (about 3% by weight) of nitrocellulose, dried at a low temperature of about 100°C for one hour and then fired for five minutes in a muffle furnace pre-set to 450°C.

An investigation by x-ray topography (as developed by A. R. Lang, University of Bristol) of the strain patterns in quartz plates caused by various cements has been initiated in conjunction with Dr. R. A. Young and Mr. N. K. Hearn, Jr., of the x-ray department. Such a study was suggested by the fracturing of silica plates by the Pyroceram-silver cements containing five parts Pyroceram to one part silver by volume. This fracture was not observed when the cement was fired onto thin quartz plates, and it was conjectured that considerable mechanical distortion of the plate would likely occur when the cement contracted upon cooling. Initial investigations of stress in quartz plates reveal considerable stress exerted on the plates by the various mounting systems being employed currently. These are being examined with the objective of devising a mounting method applying a minimum stress.

Measurements of approximately 75 resonators have been continued throughout the month. Since measuring is required at the fundamental, 3rd, and 5th modes each unit requires three measurements and a limit of about ten units per day or 50 per week may be measured. This allows daily measurement of ten units or bimonthly measurements of 100 units. A plot of a typical frequency behavior being obtained is shown in Figures 3 (1-10) and 4 (10-1). Note that positive aging was displayed in the fundamental modes in both cases but very little in the overtone modes.

- - - - -

* Freed type MAO-3

The program for the month of February includes:

1. completion of the oven temperatures control systems;

2. continued frequency measurements;

3. installation of a second storage oven operating at 85°C. This oven is to be used in conjunction with studies of the effect of continuous crystal drive and of the effects of radiation on crystal frequencies.

Respectfully submitted,

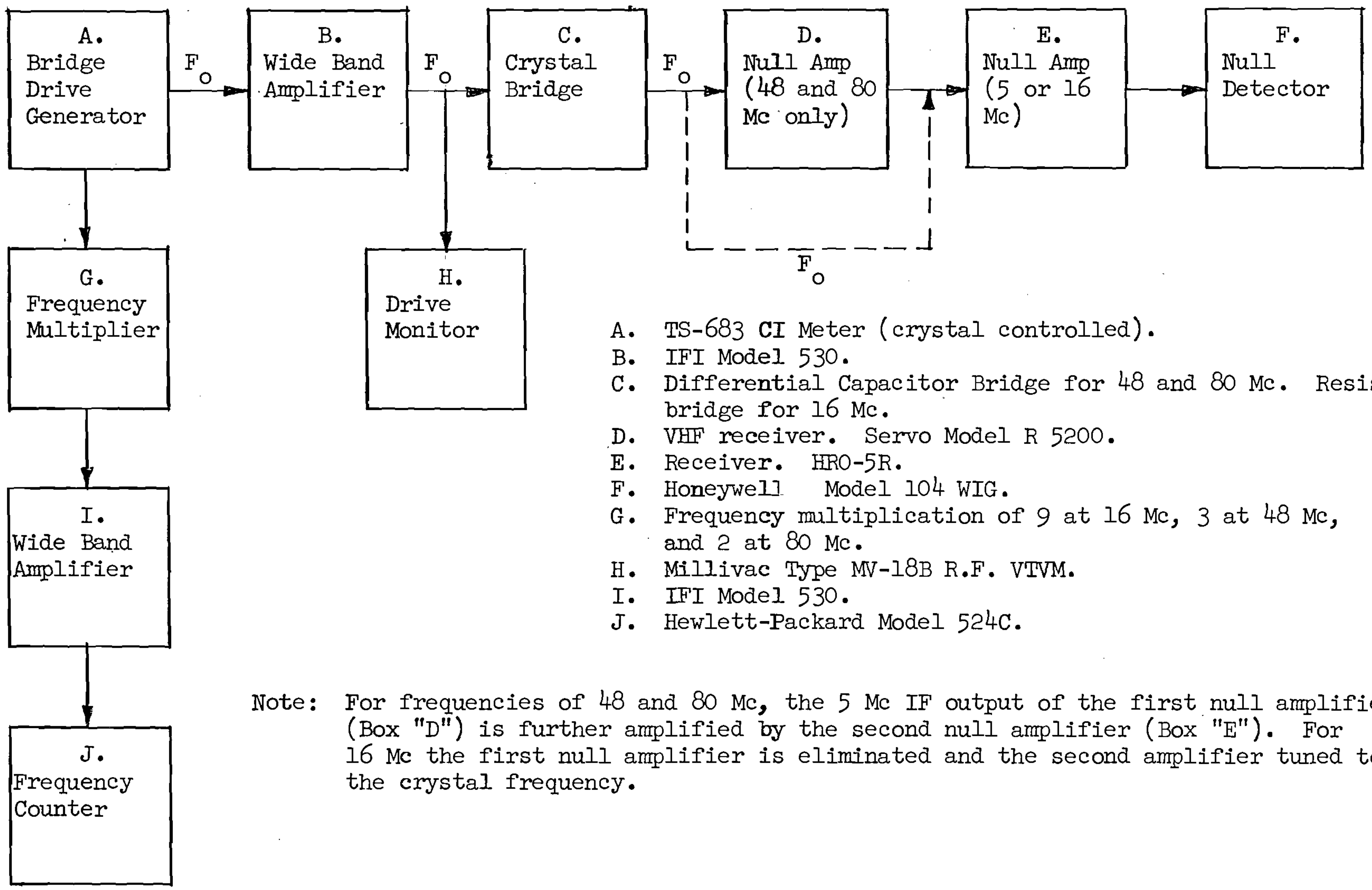
RBB/var

Richard B. Belser
Project Director

Enclosures: Figures 1; 2; 3-A, -B, -C; 4-A, -B, -C

cc: Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
Library, 2
Surplus



A. TS-683 CI Meter (crystal controlled).
B. IFI Model 530.
C. Differential Capacitor Bridge for 48 and 80 Mc. Resistor bridge for 16 Mc.
D. VHF receiver. Servo Model R 5200.
E. Receiver. HRO-5R.
F. Honeywell Model 104 WIG.
G. Frequency multiplication of 9 at 16 Mc, 3 at 48 Mc, and 2 at 80 Mc.
H. Millivac Type MV-18B R.F. VTVM.
I. IFI Model 530.
J. Hewlett-Packard Model 524C.

Note: For frequencies of 48 and 80 Mc, the 5 Mc IF output of the first null amplifier (Box "D") is further amplified by the second null amplifier (Box "E"). For 16 Mc the first null amplifier is eliminated and the second amplifier tuned to the crystal frequency.

Figure 1. Passive Bridge Frequency Measuring System

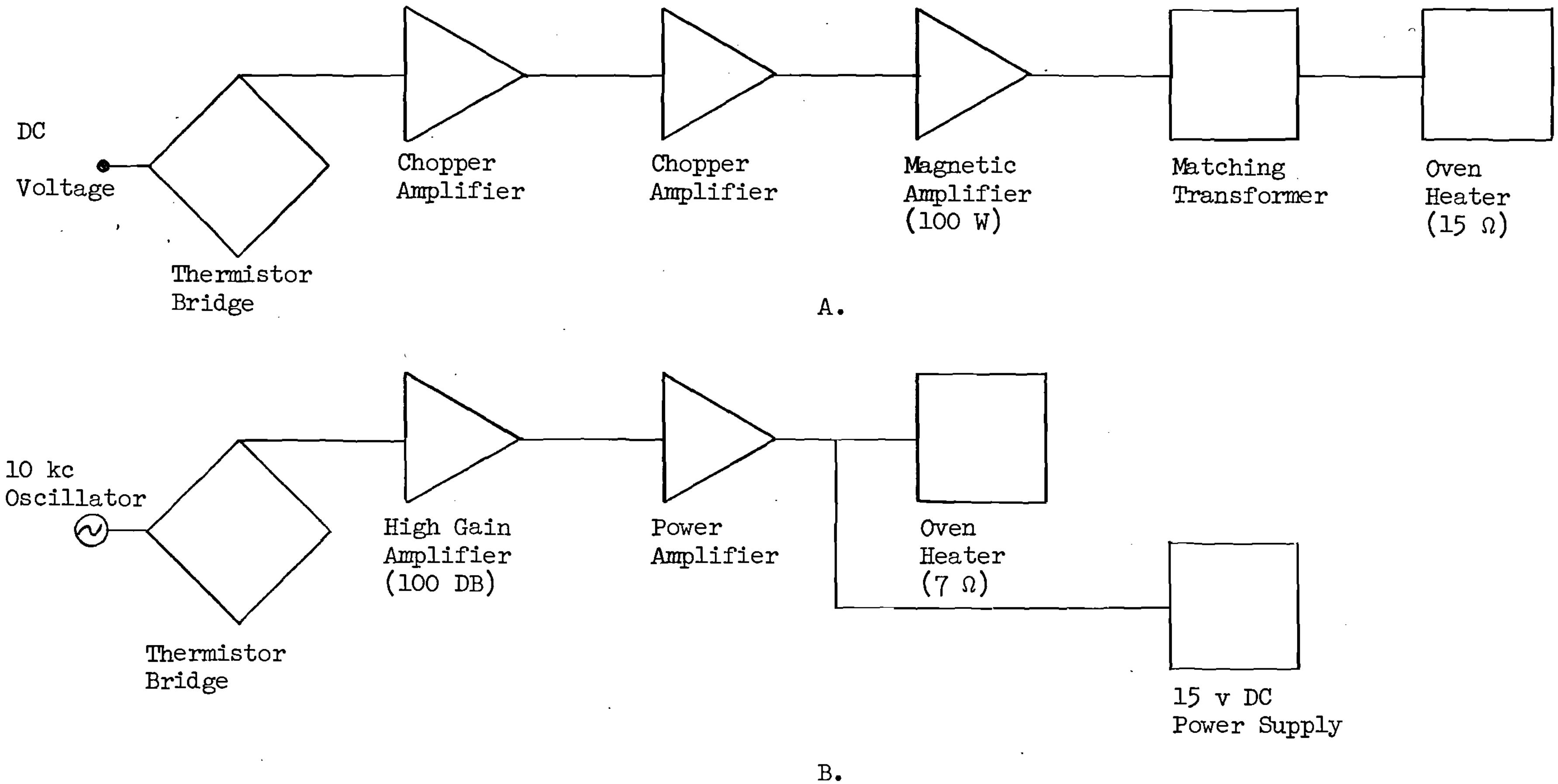


Figure 2. Proportional Oven Control Systems

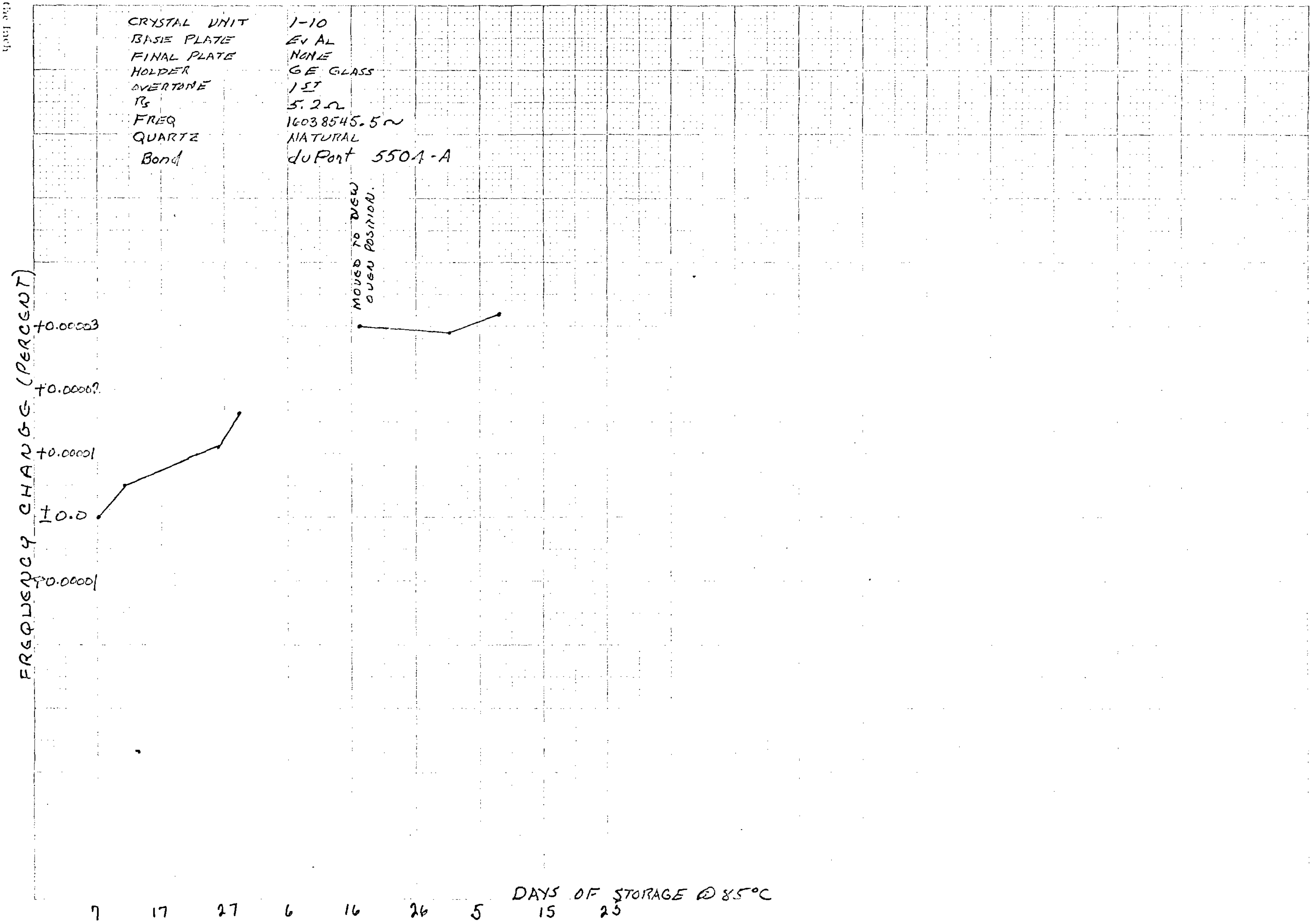

CRYSTAL UNIT 1-10
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1ST
Rs 5.2Ω
FREQ 16038545.5~
QUARTZ NATURAL
Bond duPont 5504-A
MOVED TO NEW OVEN POSITION.
FREQUENCY CHANGE (PERCENT)
+0.00003
+0.00002
+0.00001
±0.0
-0.00001
DAYS OF STORAGE @ 85°C
7
17
27
6
16
26
5
15
25
DEC
JAN
FEB

FIGURE 3A

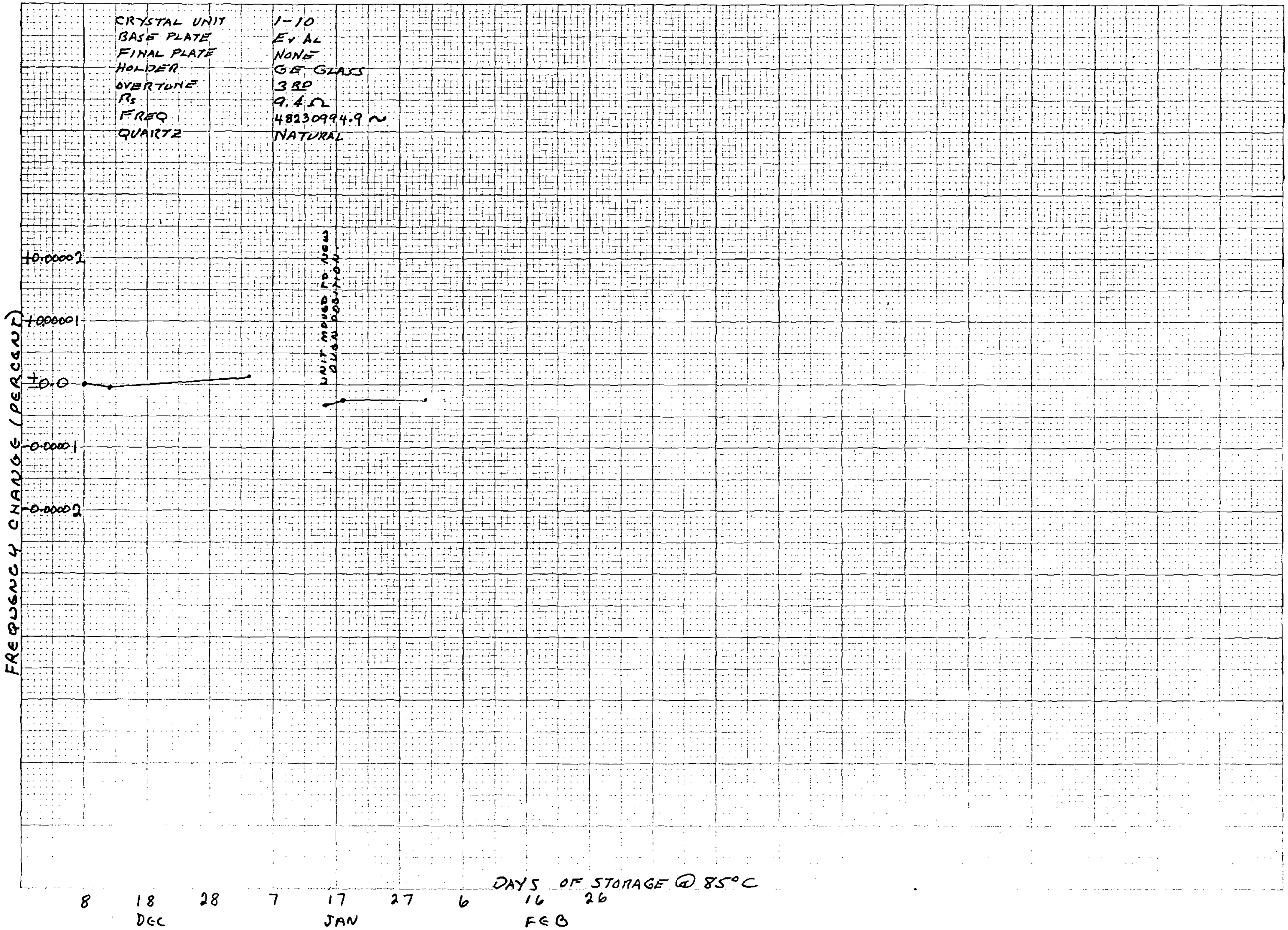

CRYSTAL UNIT 1-10
BASE PLATE Ev AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 3RD
Rs 9.4 Ω
FREQ 48230994.9 ~
QUARTZ NATURAL
UNIT MOVED TO NEW OVEN POSITION
+0.00002
+0.00001
±0.0
-0.00001
-0.00002
FREQUENCY CHANGE (PERCENT)
DAYS OF STORAGE @ 85°C
8
18
28
7
17
27
6
16
26
DEC
JAN
FEB

FIGURE 3B

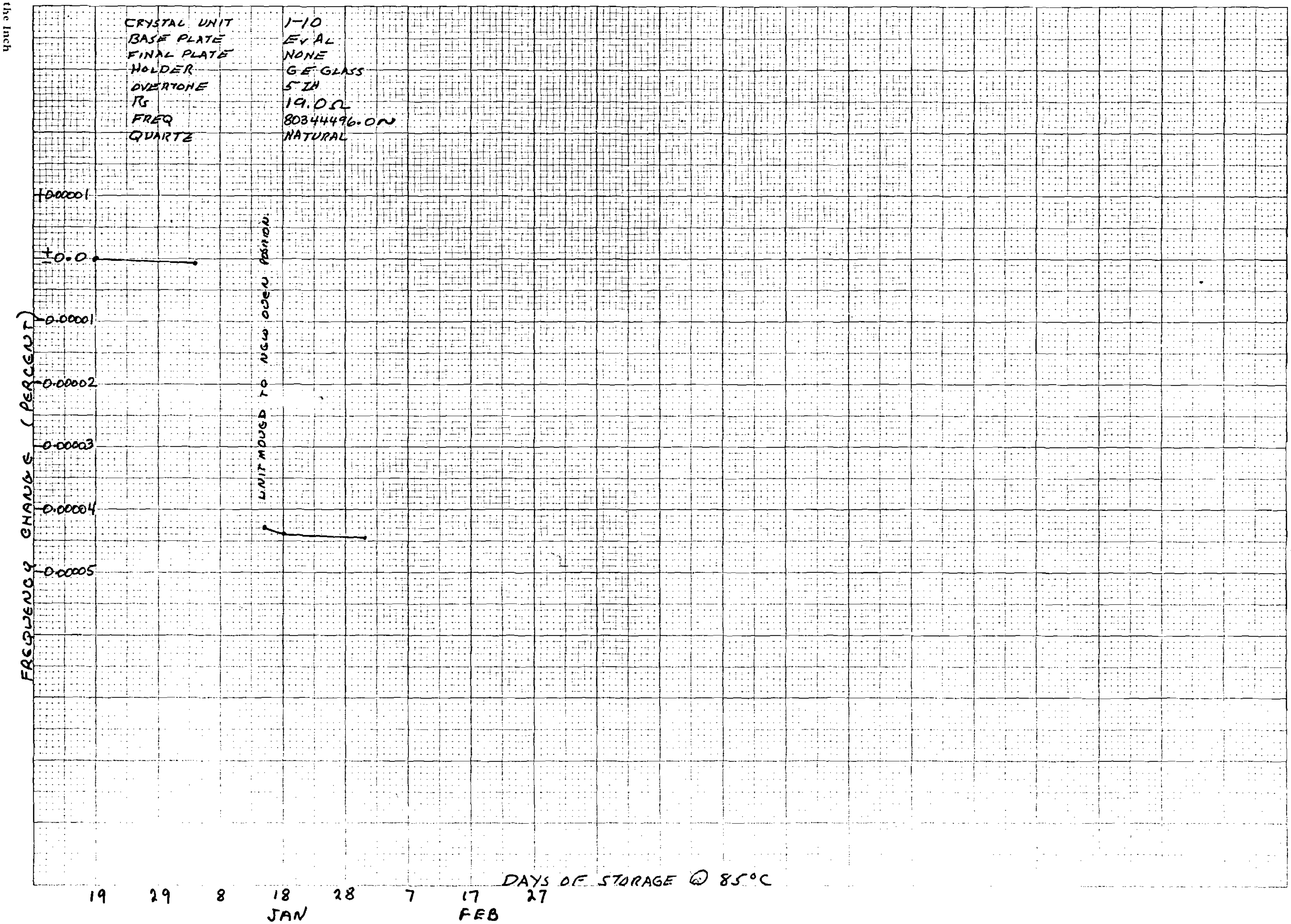

CRYSTAL UNIT 1-10
BASE PLATE Ev AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 5 TH
Rs 19.0Ω
FREQ 80344496.0N
QUARTZ NATURAL
+.000001
±0.0
-0.00001
-0.00002
-0.00003
-0.00004
-0.00005
FREQUENCY CHANGE (PERCENT)
UNIT MOVED TO NEW OVEN POSITION
DAYS OF STORAGE @ 85°C
19
29
8
18
28
7
17
27
JAN
FEB

FIGURE 3C

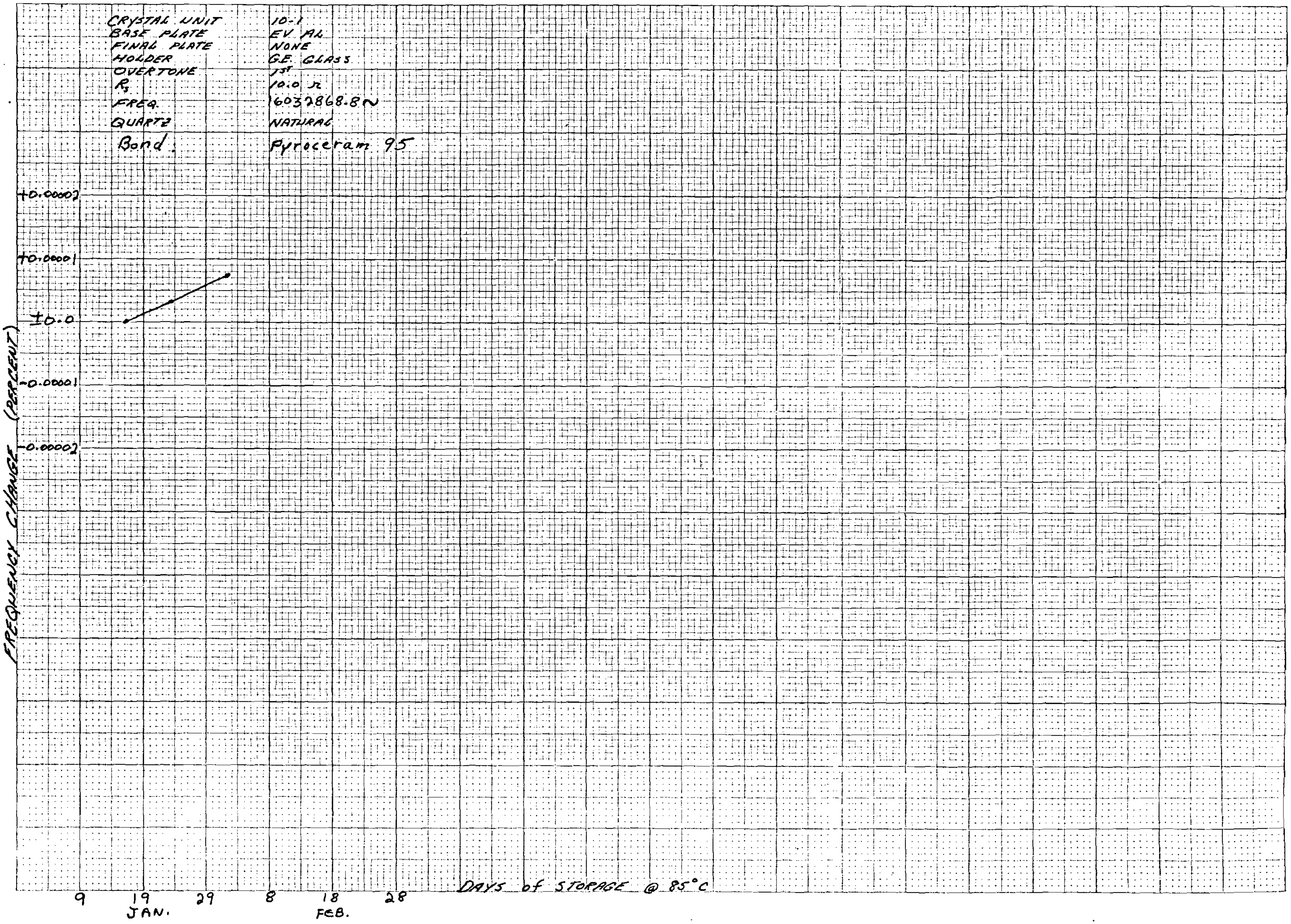
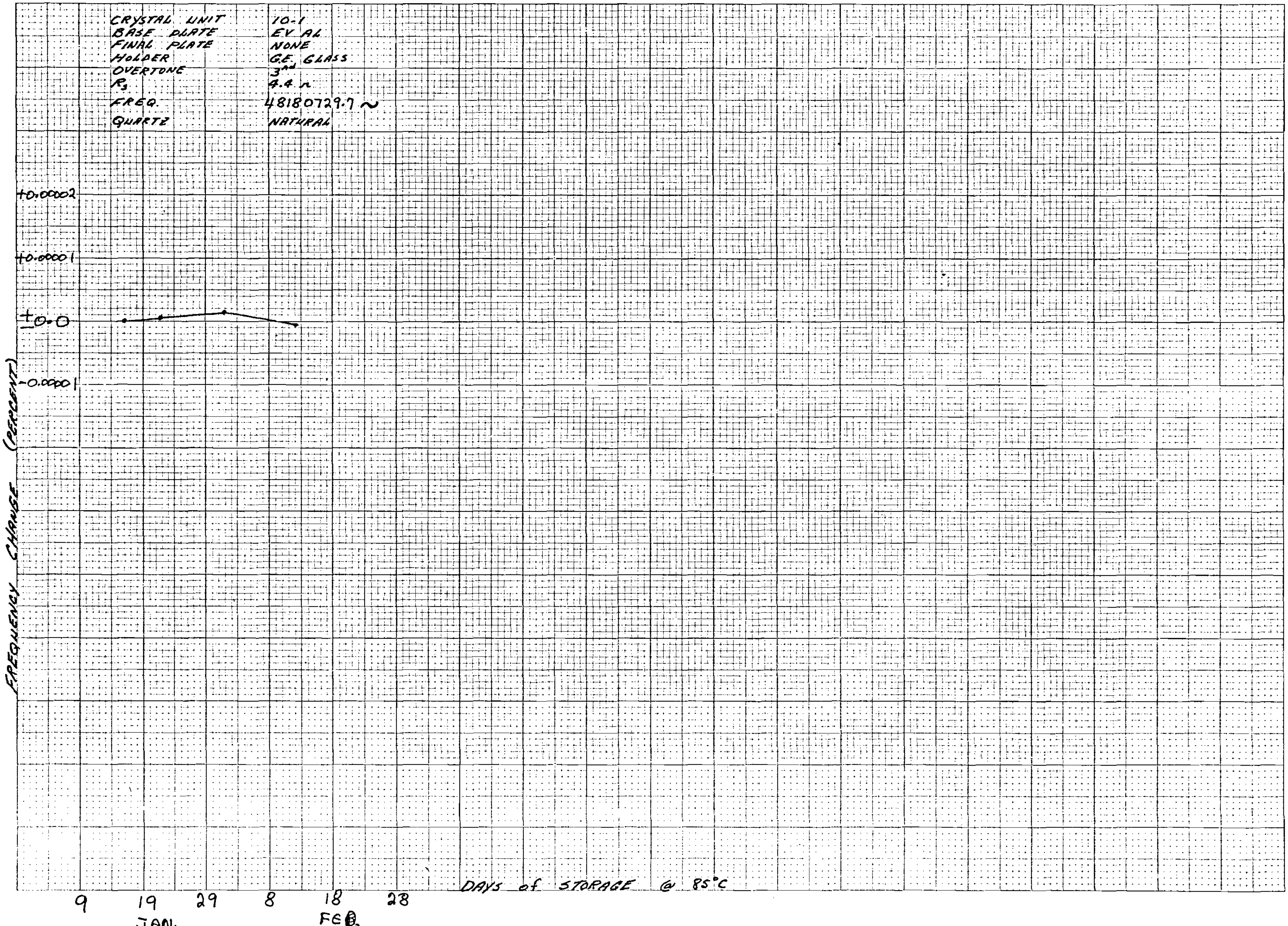

CRYSTAL UNIT 10-1
BASE PLATE EV. AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1ST
R_s 10.0 Ω
FREQ. 16037868.8 ~
QUARTZ NATURAL
Bond: Pyroceram 95
+0.00002
+0.00001
±0.0
-0.00001
-0.00002
FREQUENCY CHANGE (PERCENT)
9
19
29
8
18
28
JAN.
FEB.
DAYS of STORAGE @ 85°C

FIGURE 4-A



CRYSTAL UNIT 10-1
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 3rd
R_s 4.4 Ω
FREQ. 48180729.7 ~
QUARTZ NATURAL
+0.00002
+0.00001
±0.0
-0.00001
FREQUENCY CHANGE (PERCENT)
DAYS of STORAGE @ 85°C
9
19
29
8
18
28
JAN.
FEB.

FIGURE 4 B

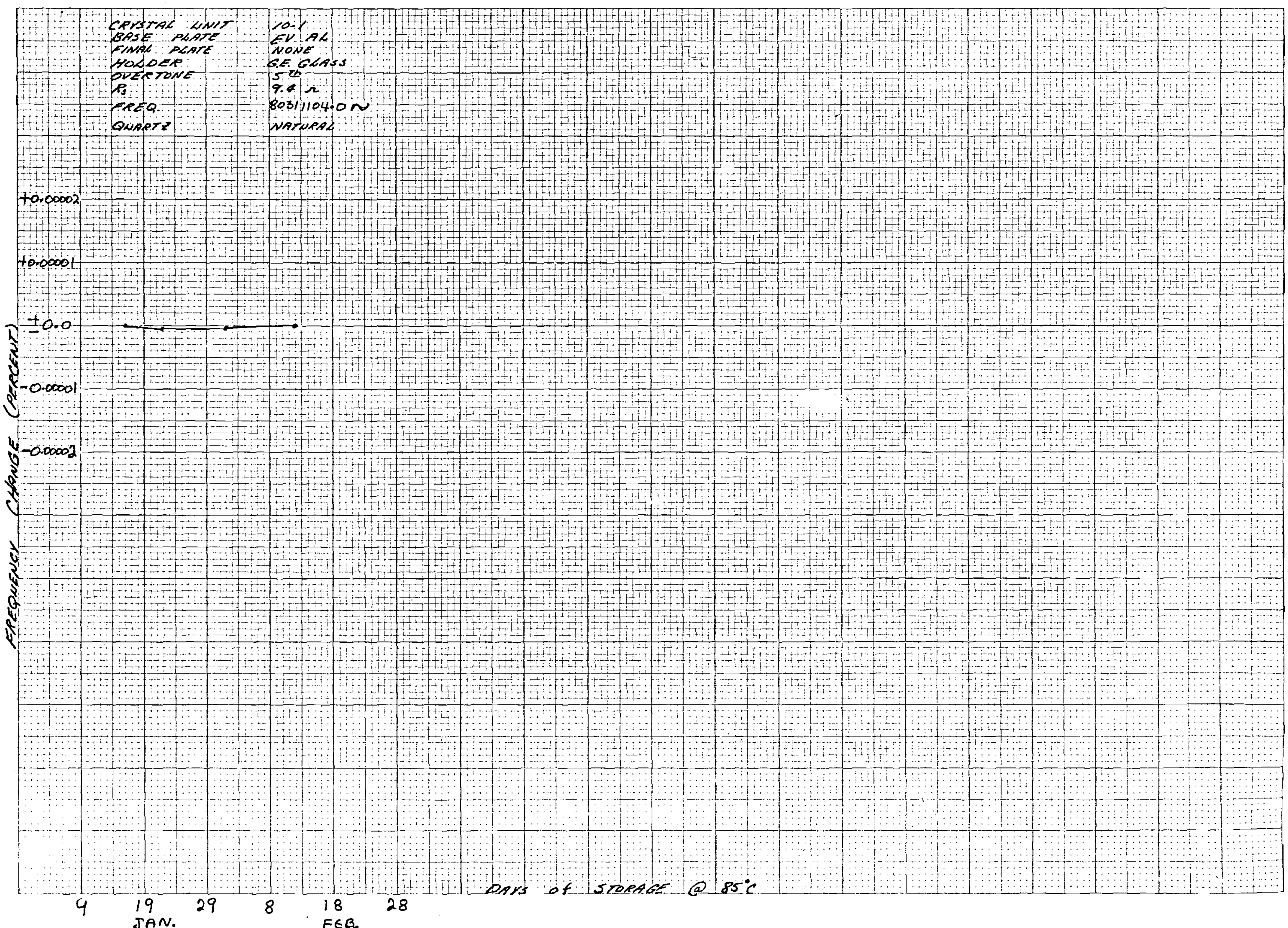

CRYSTAL UNIT 10-1
BASE PLATE EV. AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 5th
R_1 9.4 Ω
FREQ. 8031104.0 ~
QUARTZ NATURAL
+0.00002
+0.00001
±0.0
-0.00001
-0.00002
FREQUENCY CHANGE (PERCENT)
DAYS of STORAGE @ 85°C
9
19
29
8
18
28
JAN.
FEB.

Figure 4.C

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

8 March 1962

Headquarters
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber
Solid State and Frequency Control Division

Subject: Progress Letter No. 11
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 February to 1 March 1962

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

Two groups of crystal units were fabricated during the month. The pertinent details of each group are given in Table I. All of the units of group 12 were operable at the 1st, 3rd, and 5th modes. Unfortunately there were reference crystals for but two of the units at the 5th mode. Measurements were made on all of the units at the 1st and 3rd modes.

The passive bridge frequency measuring equipment has operated during the month without modification or major repair. The principal disadvantages (as stated before) are the necessity of maintaining a large file of reference crystals for controlling the CI meter and the loss of precision when the reference crystal must be "pulled" well out of the maximum effective Q range.

Standard frequency signals required for the frequency counter are obtained from an O-76/U 100-kc oscillator. The beat of the local oscillator with the 20-kc transmission from WWVL is monitored continuously. The oscillator is maintained at a frequency of 14 ± 2 pp 10^9 above the frequency of WWVL.

The proportional oven control system shown in Figure 2-A of Progress Letter No. 10 has been placed in service. Operation has been limited to periods when frequency measurements are being made since an unreliable chopper amplifier can not be operated unattended. This unit will be replaced or repaired. Experiments indicate that the control system will hold the oven to a maximum temperature deviation of $\pm$ 0.01°C and possibly better. When the high-sensitive thermistors now available are installed in the control system some further improvement is anticipated.

An oven providing 36 additional positions for aging studies at 85°C has been placed in operation. The temperature stability of this latter oven is very good. When control voltage refinements are completed the stability without proportional control should be as good or better than the 200-position oven with proportional control. A second 36-unit oven is now being modified for use on this project.

Three units of Group 1 (natural, unswept quartz with aluminum base plate) were exposed to gamma radiation for 24 hours at an intensity of 1.6×10^6 rad/hour. This irradiation level is the maximum obtainable with a readily available source. The frequency changes produced are given in Table II.

TABLE II

Frequency change (ppm)*

Unit	Fund.	3rd Mode	5th Mode
1 - 2	+ 3.8	+ 0.33	+ 0.35
1 - 5	+ 10.1	+ 6.8	+ 7.15
1 - 6	- 0.81	- 1.5	- 1.64

*The changes shown were measured at 85°C before and after irradiation.

These results confirm previous experiments indicating that crystal resonators exposed to gamma radiation at an intensity of 1.6×10^6 rad/hour for several hours usually exhibit positive frequency shifts. The shifts were not predictable but generally fell in the range of 2 to 15 ppm. The subsequent aging trends of these crystals are being measured. Initial measurements indicate small positive aging with a tendency to reach stability in a few days.

Measurements of approximately 80 units have been continued throughout the month. Typical data are shown in Figures 1, 2, and 3. The aging illustrated by units of Group 11 as depicted in Figure 3 is especially interesting. These units were inadvertently vacuum baked at 225°C rather than the normal temperature of 175°C. The cement (duPont #5504A) had turned brown and probably started to decompose. The generally poor initial aging of this group is considered due to contamination of the holder and quartz plate by some component of the epoxy cement.

The program for the month of March includes:

1. complete installation of the third 85°C oven making 172 positions available for aging studies;

2. continue frequency measurements;

3. make initial studies of the effect of continuous drive on crystal aging;

4. complete one crystal group. A maximum of two groups a month can be completed without overloading the measurement laboratory;

5. time permitting, the radiation studies will be expanded to include resonators of other types of quartz.

Respectfully submitted,

for Richard B. Belser
Project Director

RBB/var

Enclosures: Table I
Figures 1A, B,
2A, B, C
3A, B, C

cc: Addressee, 5

TABLE I

Group	Quartz	Base Plate*	Mounting	Bonding	Sealing	Average R_s (ohms) 1st	3rd	5th
12(A)	swept natural	Evap. Al.	0.006" springs	5504-A	3 hour vacuum bake	5.6	9.3	15.2
12(B)	swept cultured	Evap. Al.	0.006" springs	5504-A	3 hour vacuum bake	6.7	10.1	15.0
13(A)	natural	Evap. Al.	0.006" springs	5504-A	3 hour vacuum bake	processing incomplete		
13(B)	cultured	Evap. Al.	0.006" springs	5504-A	3 hour vacuum bake	processing incomplete		

*No final plating.

FIGURE 1A

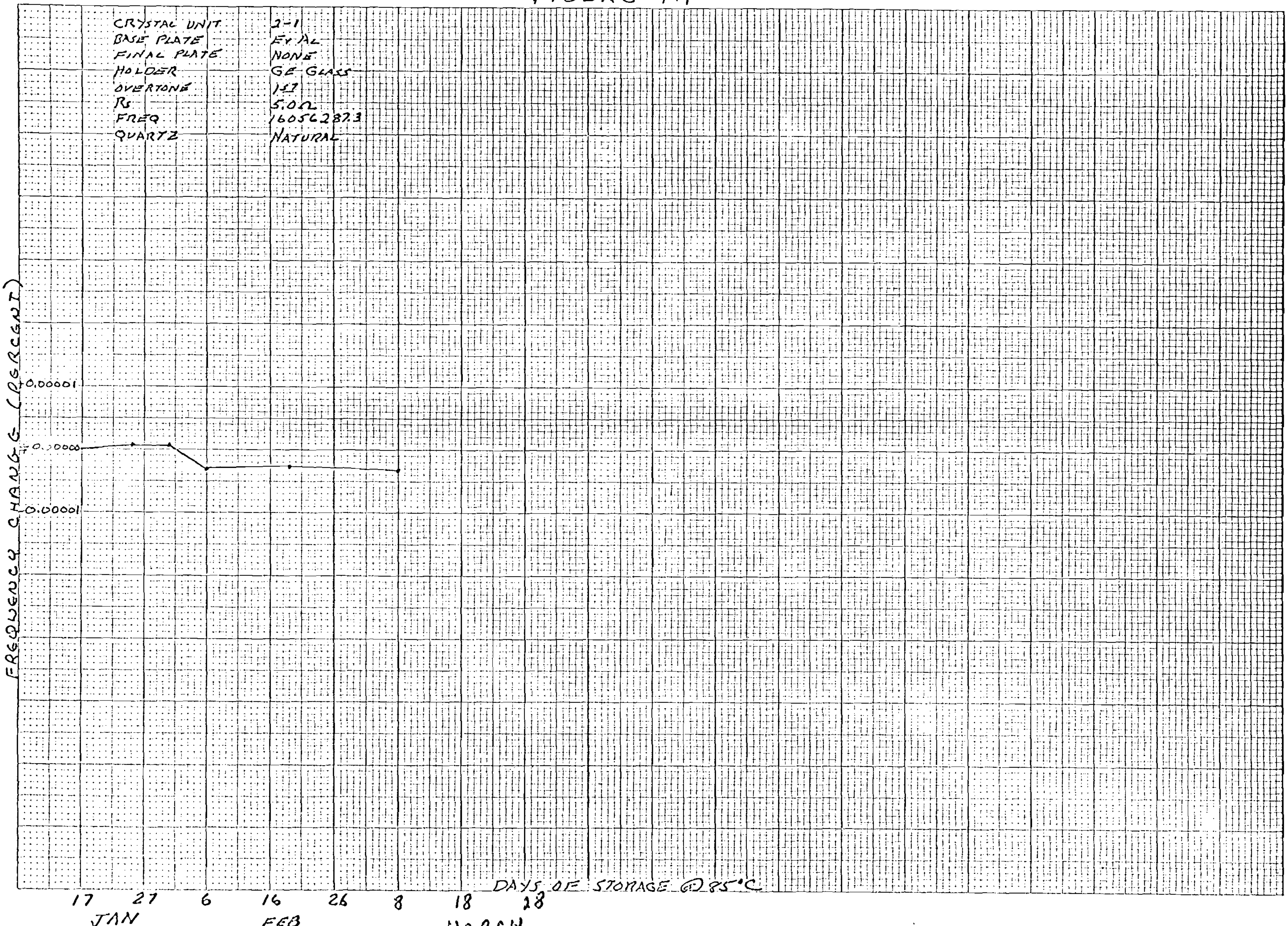


FIGURE 1A

FIGURE 1B

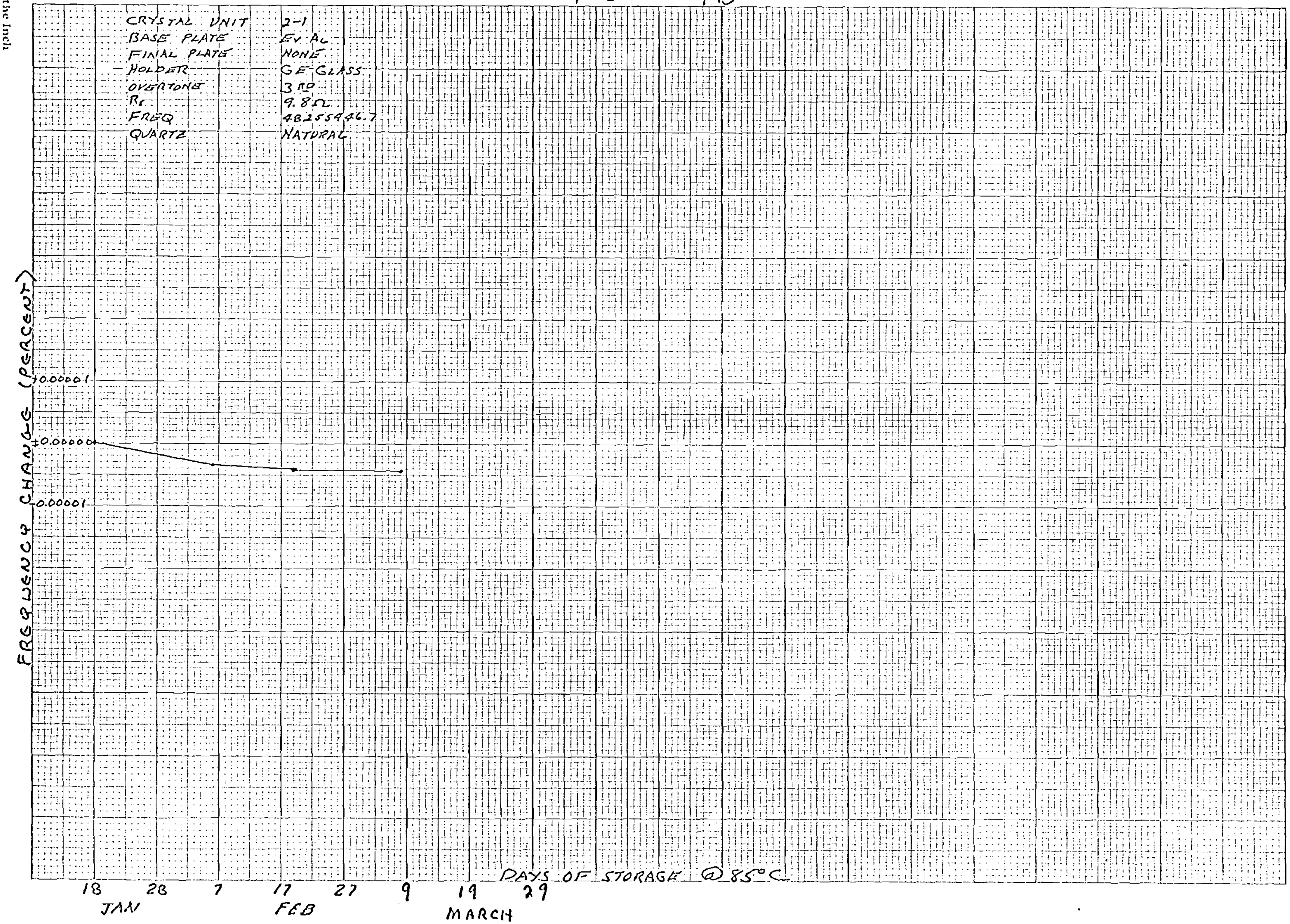


FIGURE 1B

FIGURE 2A

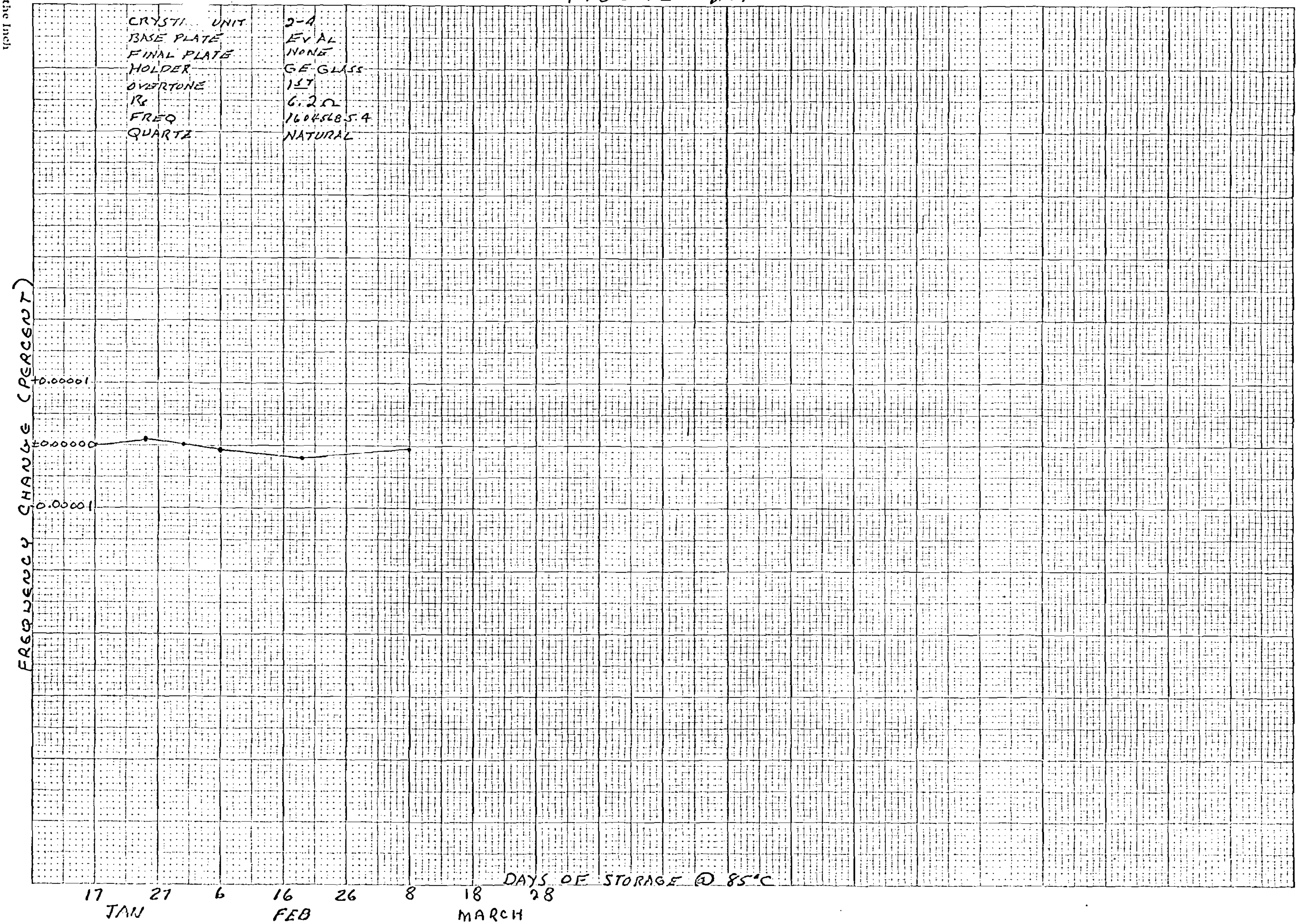

CRYSTAL UNIT 2-4
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1ST
Re 6.2Ω
FREQ 1604568.5.4
QUARTZ NATURAL
FREQUENCY CHANGE (PERCENT)
+0.00001
±0.00000
-0.00001
DAYS OF STORAGE @ 85°C
17
21
6
16
26
8
18
28
JAN
FEB
MARCH

FIGURE 2B

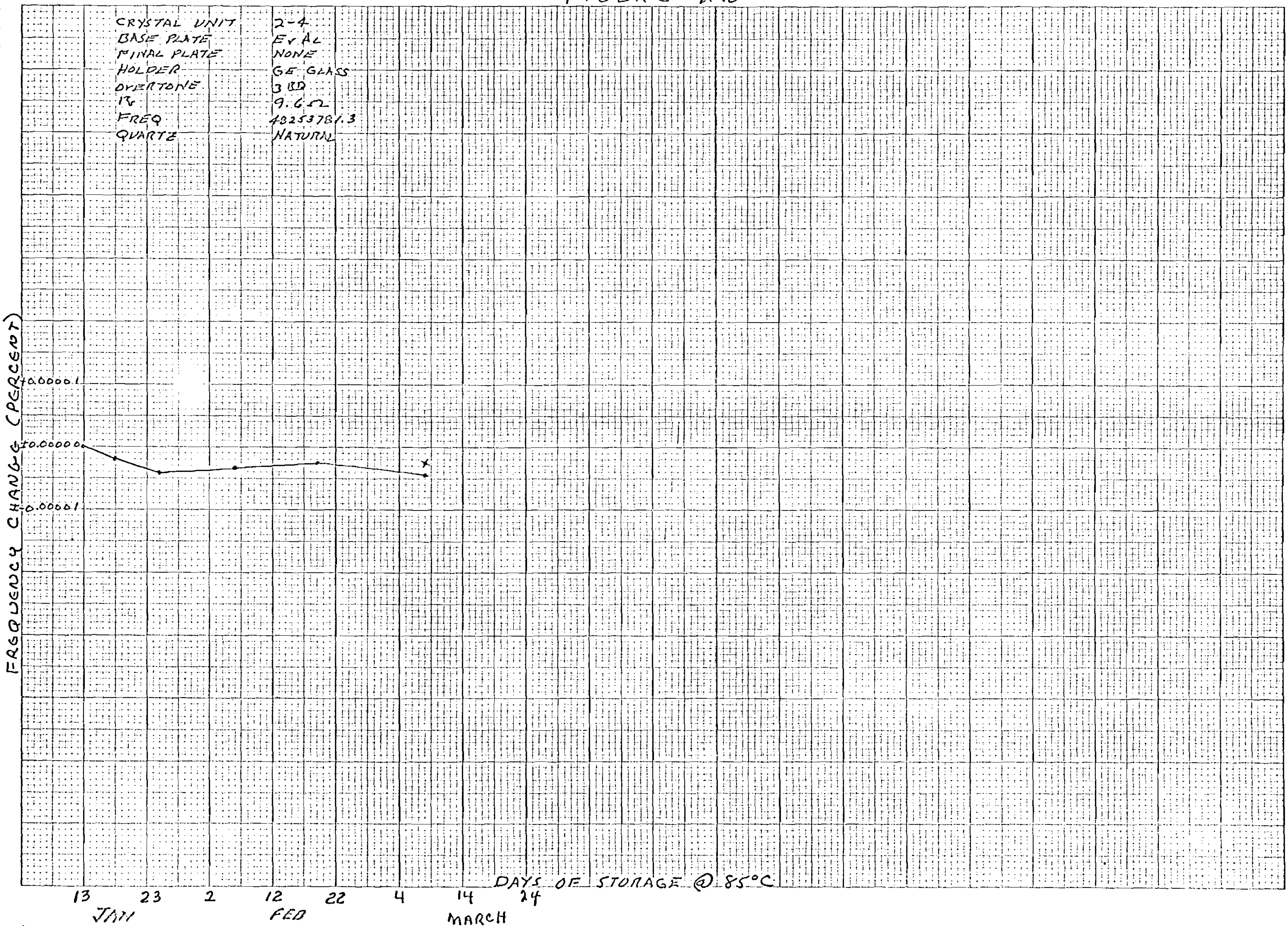

CRYSTAL UNIT 2-4
BASE PLATE Ev AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 3RD
R 9.6 Ω
FREQ 48253781.3
QUARTZ NATURAL
FREQUENCY CHANGE (PERCENT)
+0.00001
+0.00000
-0.00001
DAYS OF STORAGE @ 85°C
13
23
2
12
22
4
14
24
JAN
FEB
MARCH

FIGURE 2C

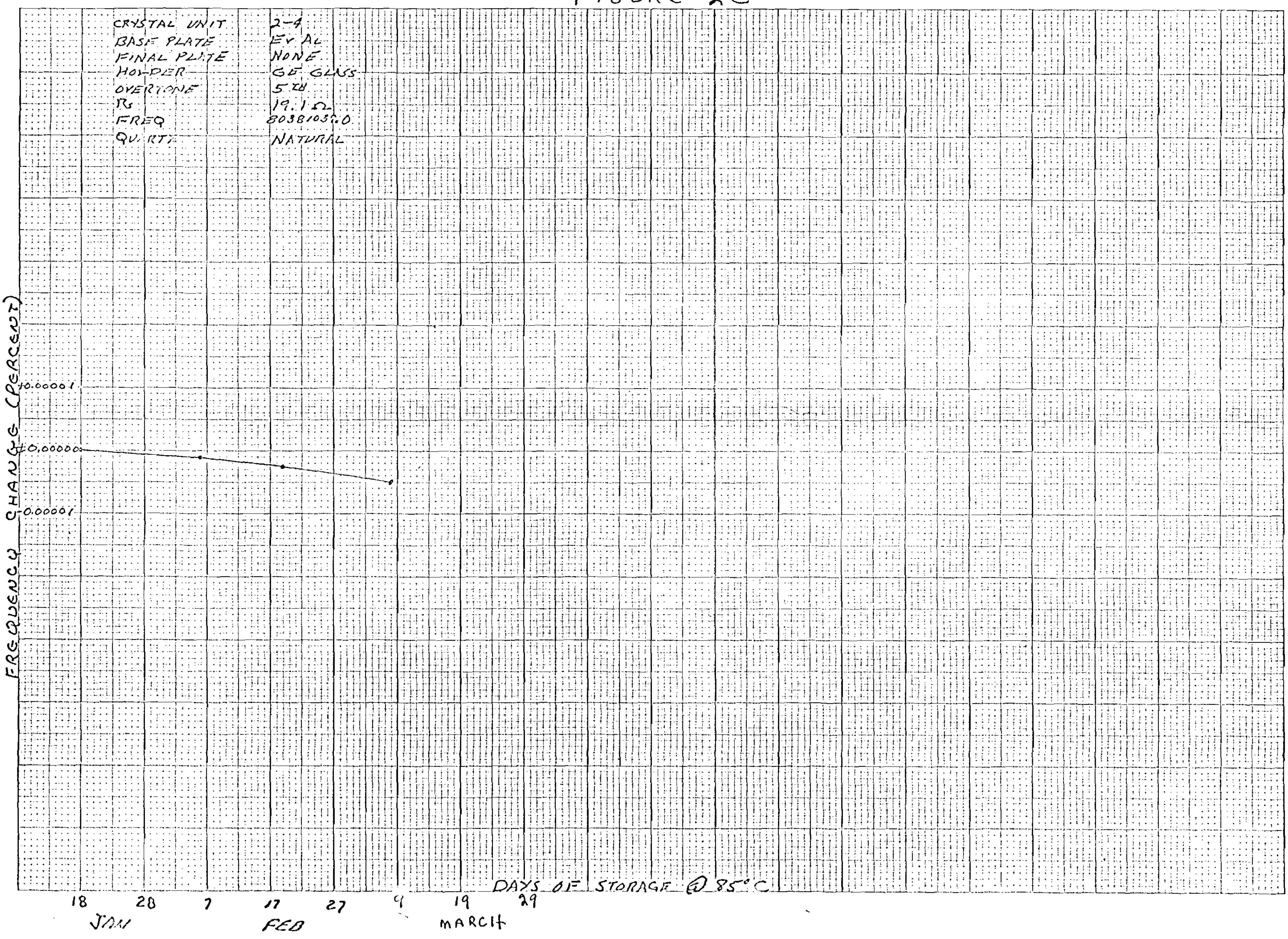

CRYSTAL UNIT 2-4
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 5th
Rs 19.1 Ω
FREQ 80381035.0
QUARTZ NATURAL
FREQUENCY CHANGE (PERCENT)
+0.00001
±0.00000
-0.00001
DAYS OF STORAGE @ 85°C
18
28
7
17
27
9
19
29
JAN
FEB
MARCH

FIGURE 3A

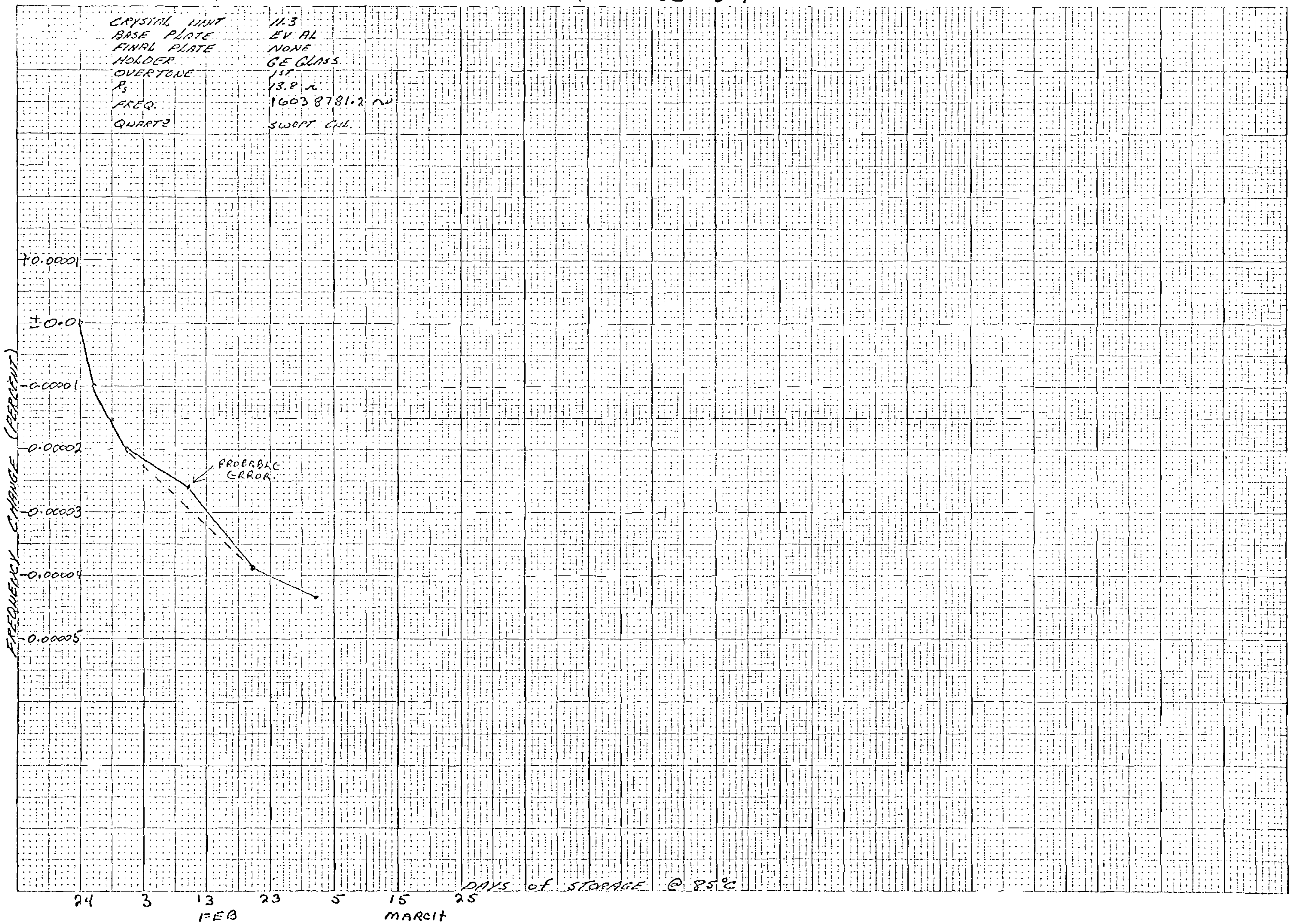


FIGURE 3A.

FIGURE 3B

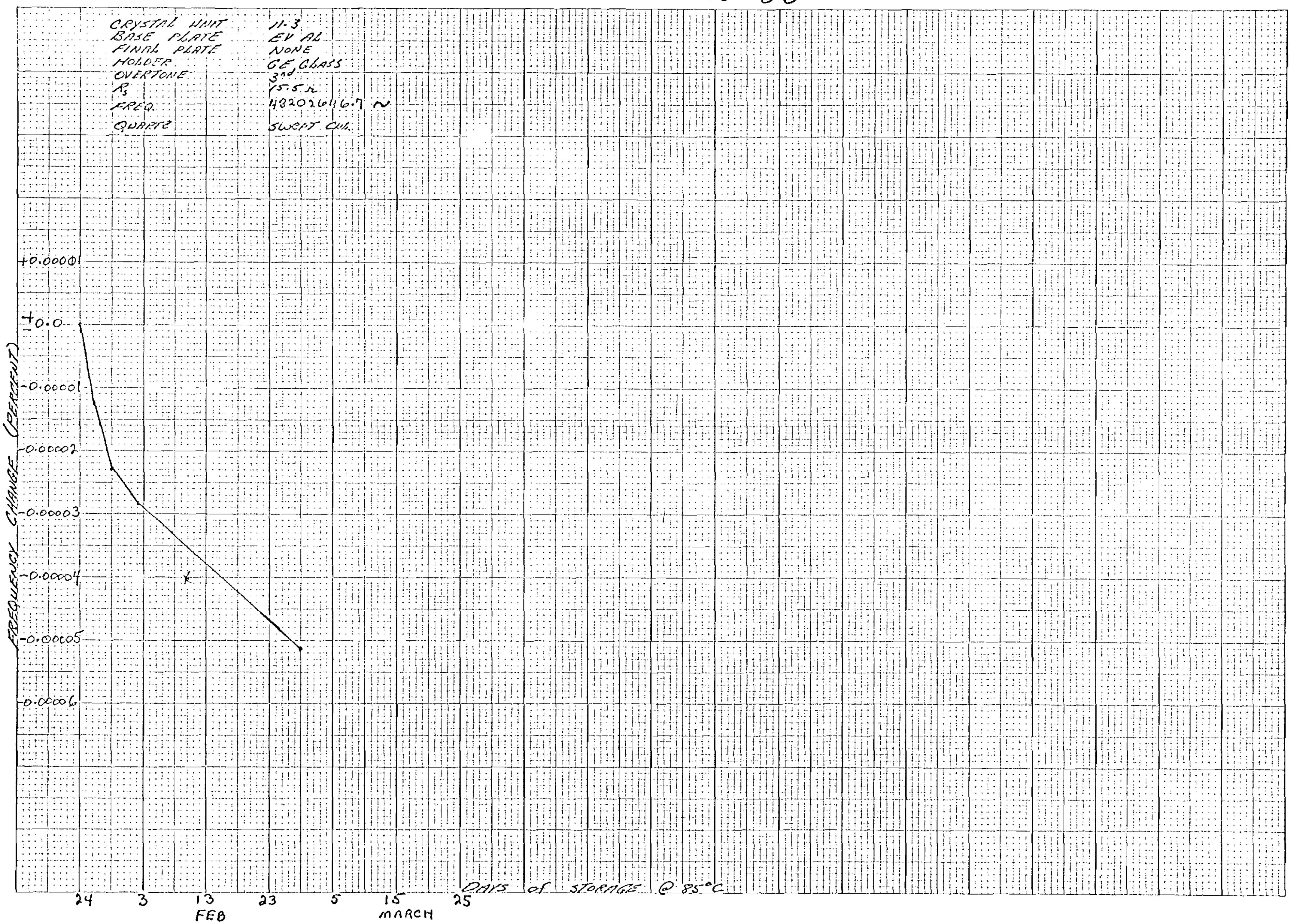


FIGURE 3B

FIGURE 3C

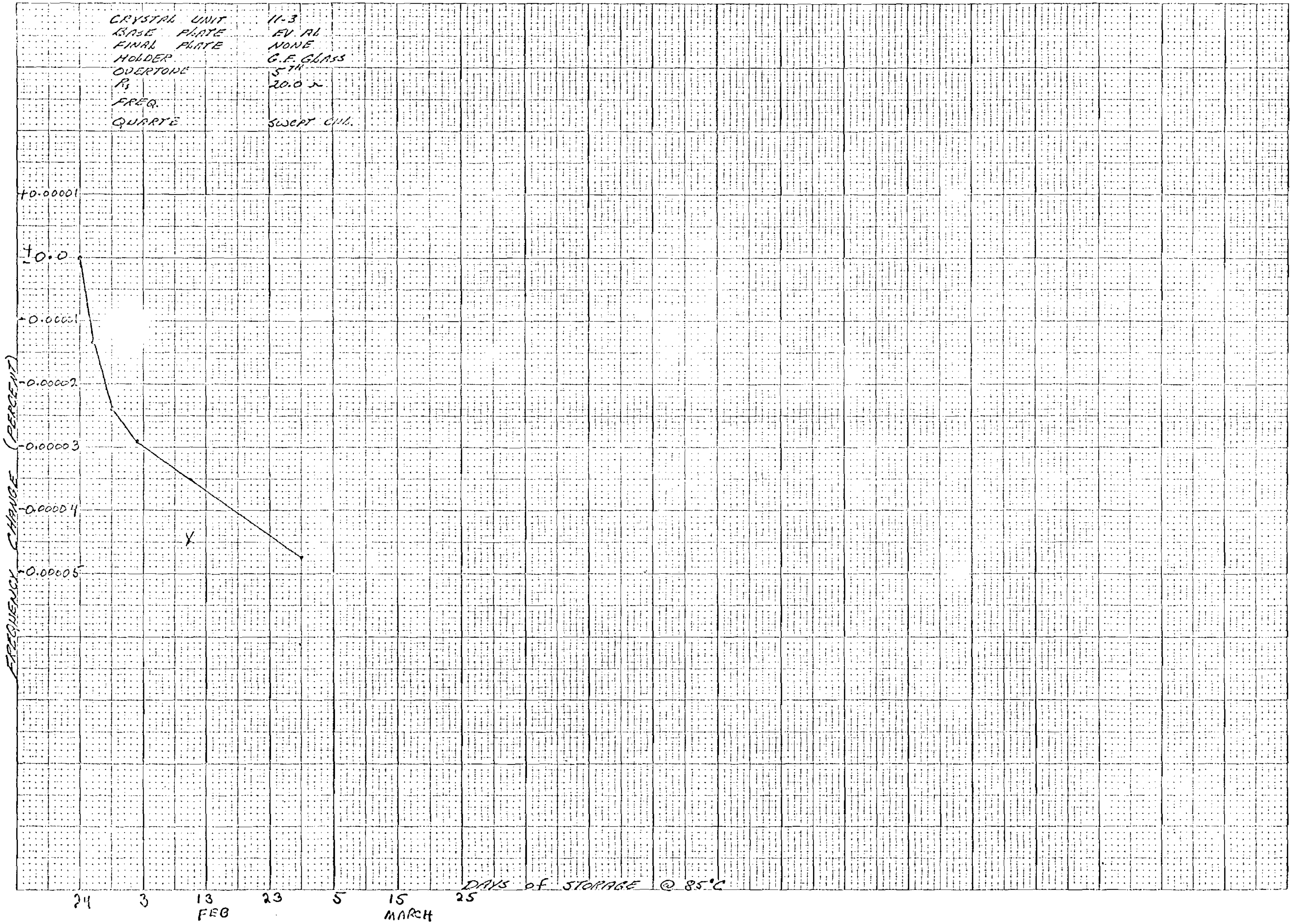


FIGURE 3C.

12-282

FIGURE 1A

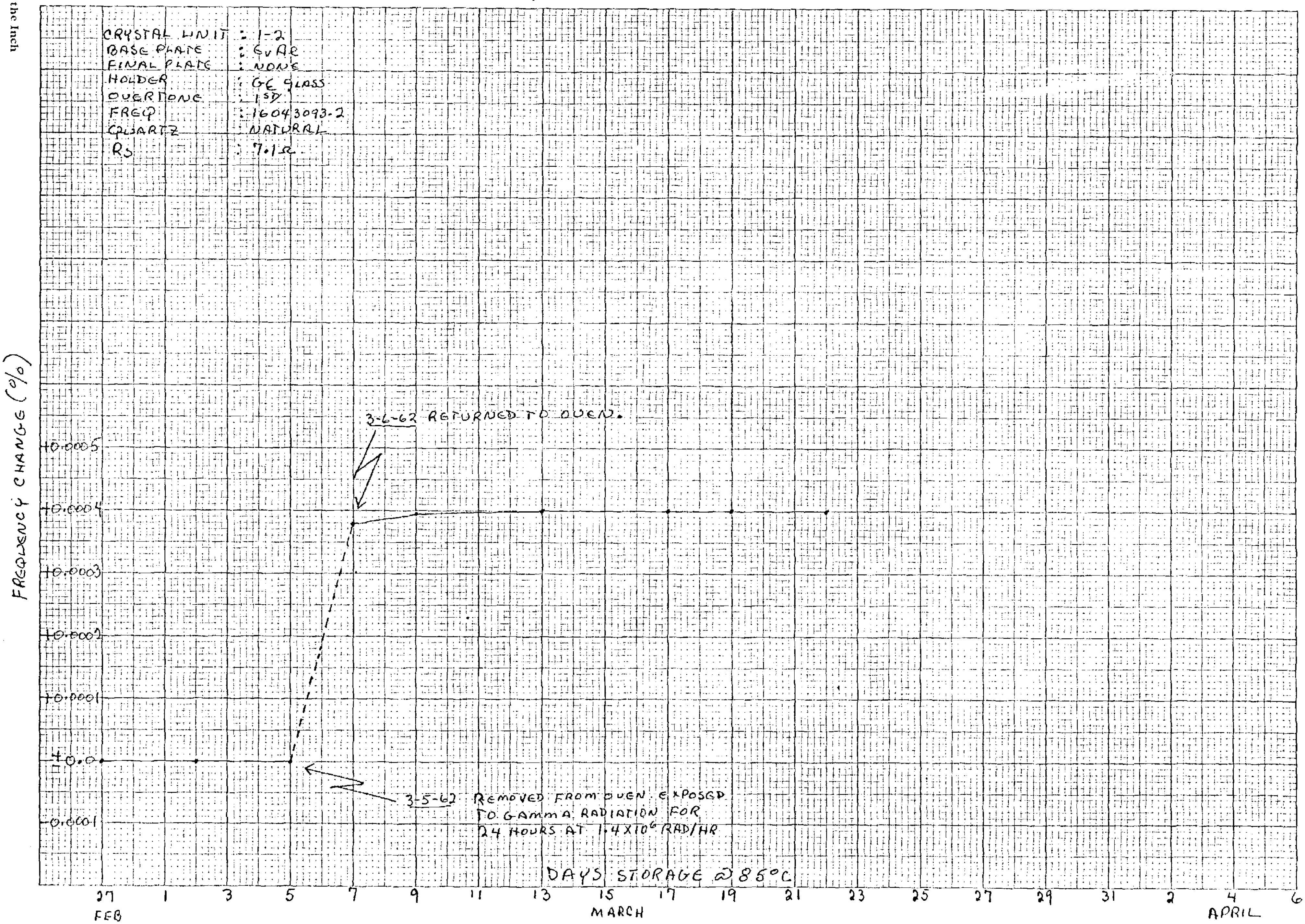


FIGURE 1 B

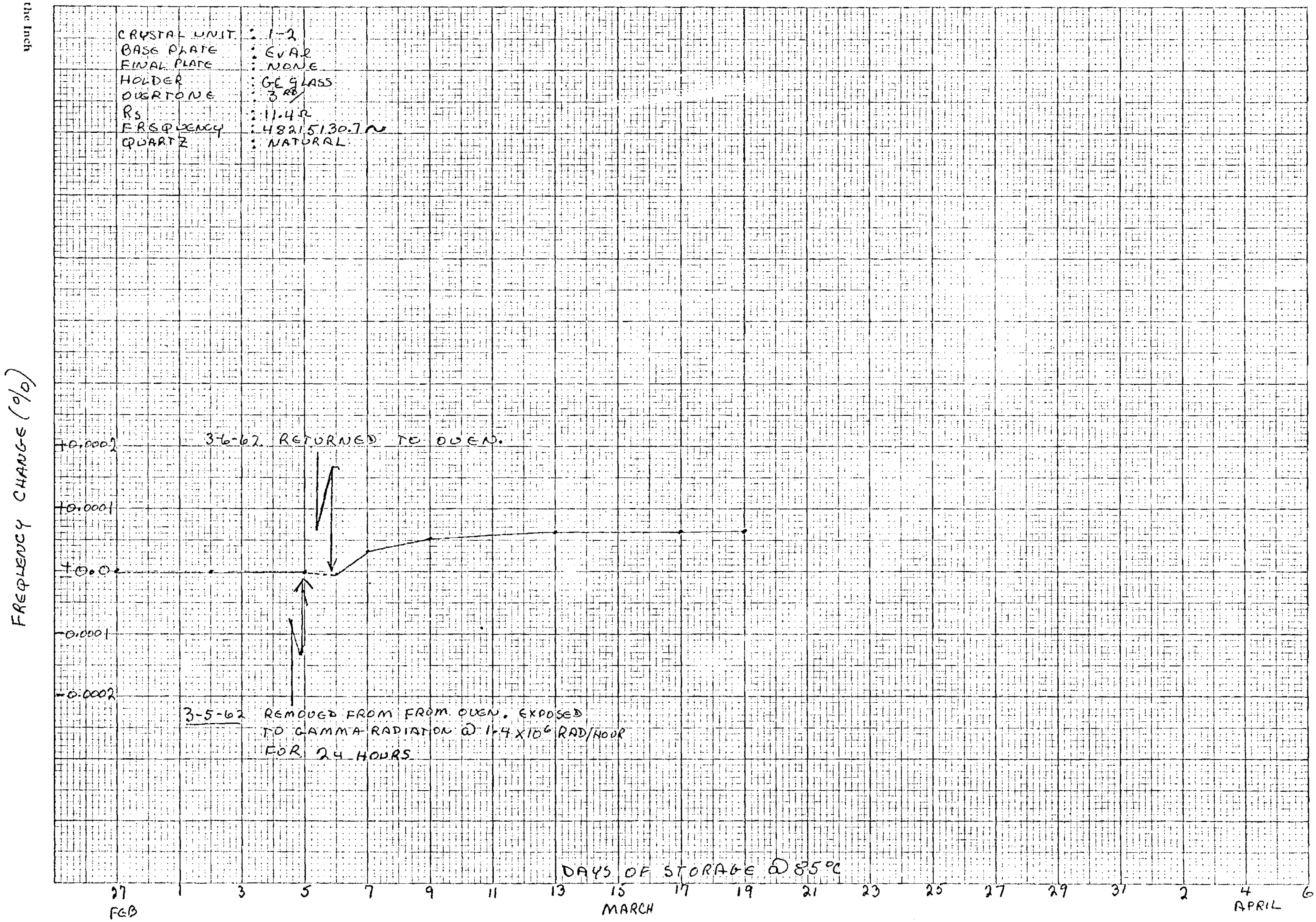

CRYSTAL UNIT : 1-2
BASE PLATE : EVAR
FINAL PLATE : NONE
HOLDER : GE GLASS
OVERTONE : 3 RD
Rs : 11.4Ω
FREQUENCY : 48215130.7 ~
QUARTZ : NATURAL
3-6-62 RETURNED TO OVEN.
3-5-62 REMOVED FROM FROM OVEN. EXPOSED TO GAMMA RADIATION @ 1.4 x 10^6 RAD/HOUR FOR 24 HOURS
FREQUENCY CHANGE (%)
+0.0002
+0.0001
±0.0
-0.0001
-0.0002
DAYS OF STORAGE @ 85°C
27 FEB
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
2
4
6
MARCH
APRIL

FIGURE 1C

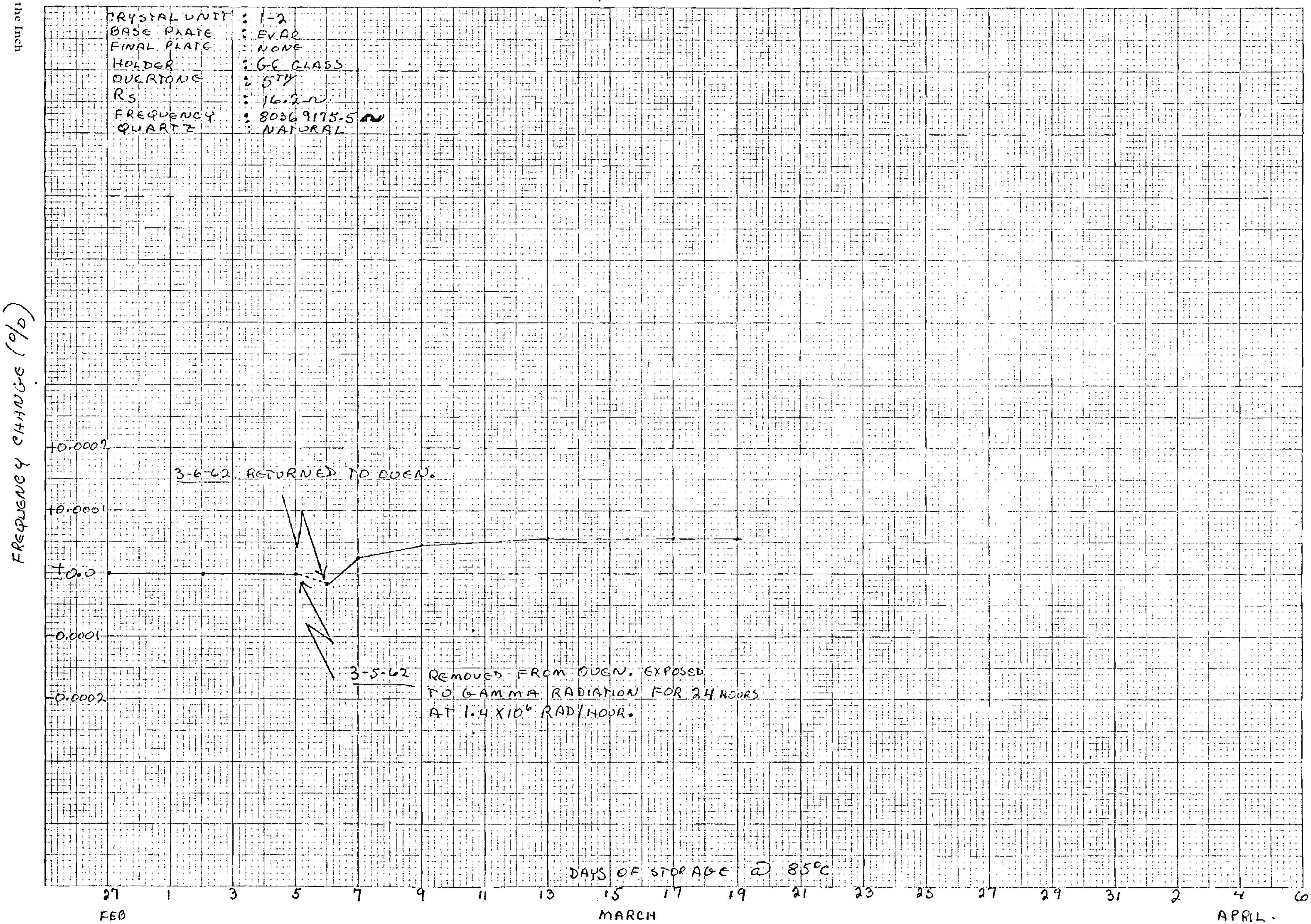
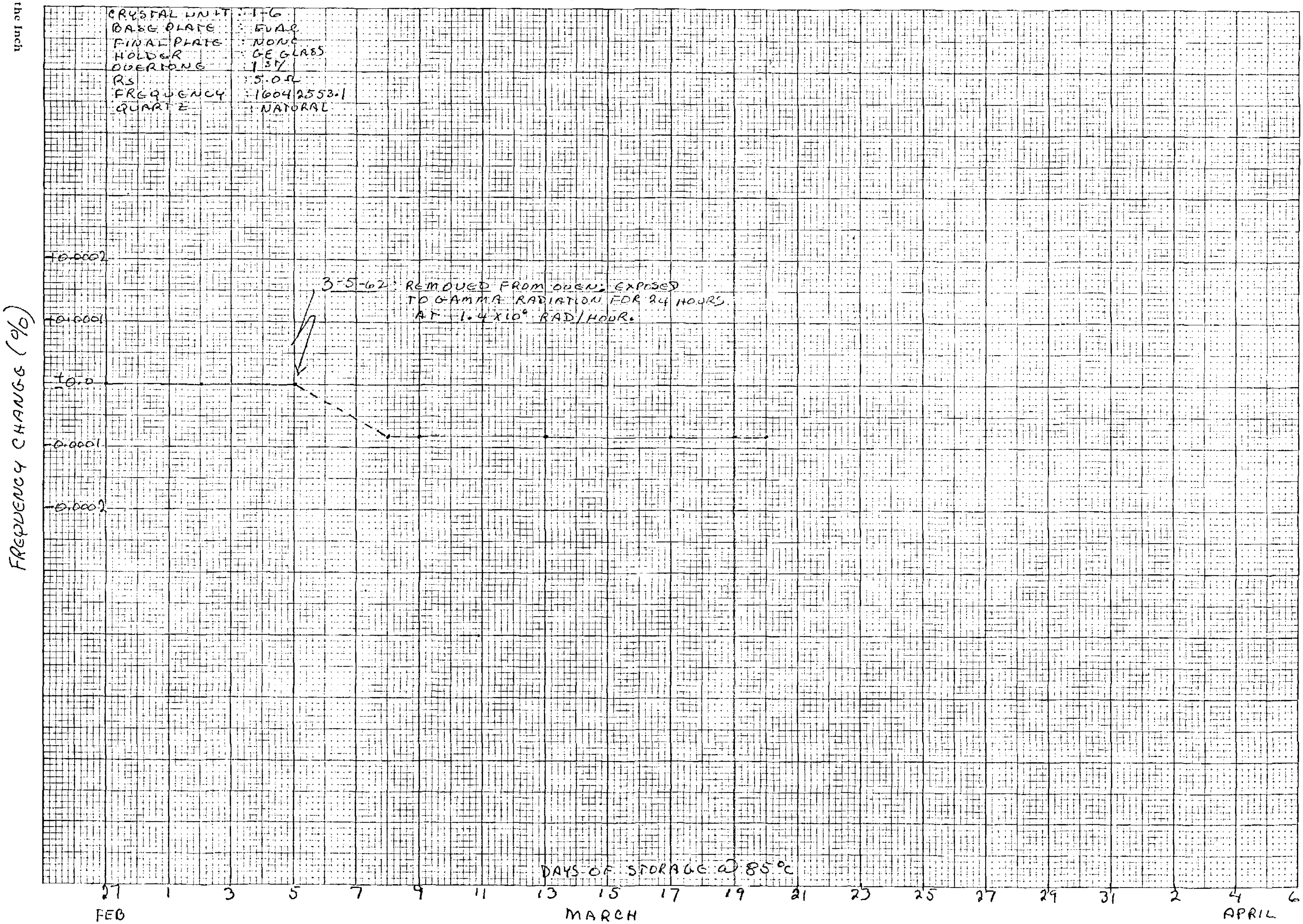
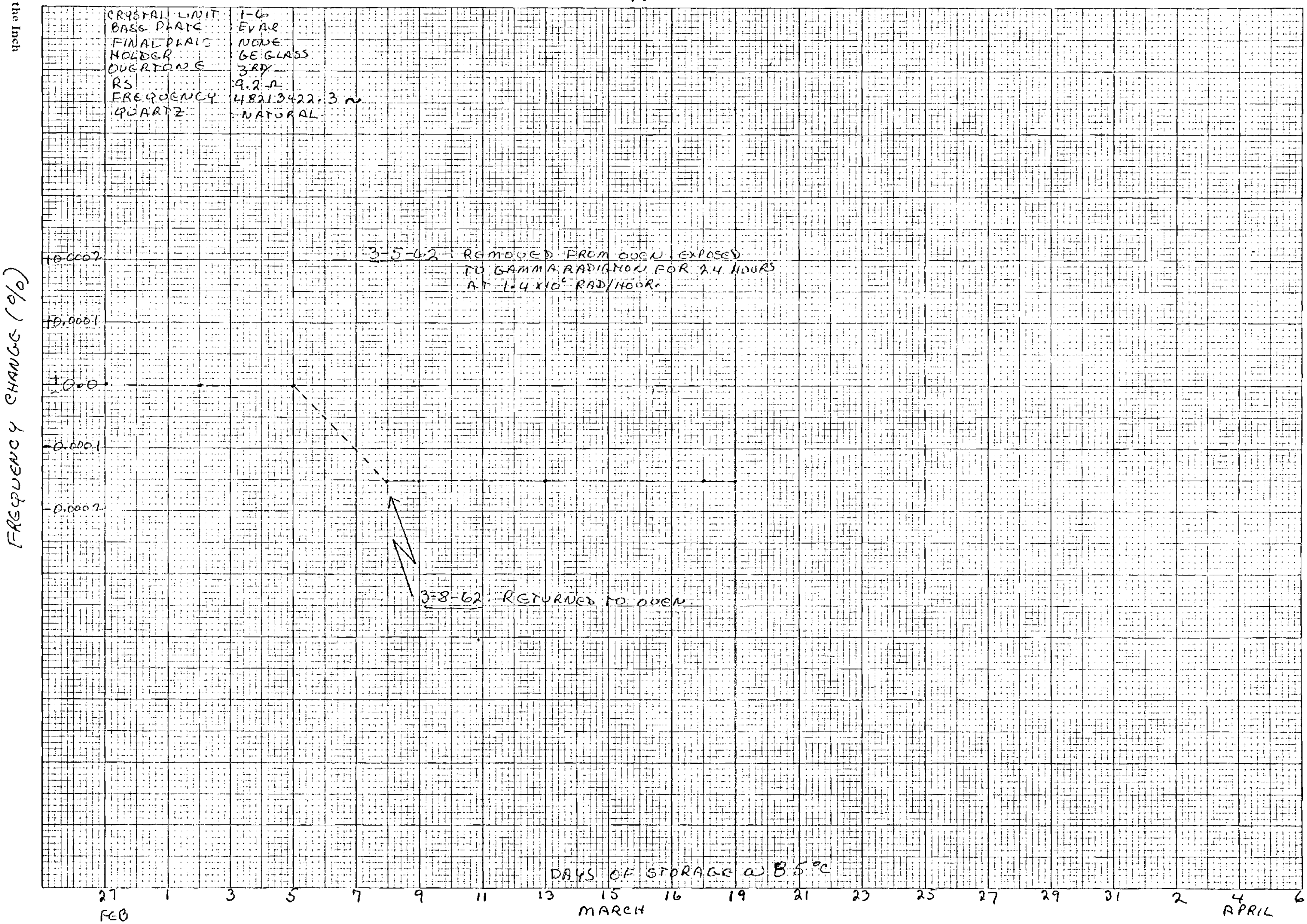

CRYSTAL UNIT : 1-2
BASE PLATE : EVAR
FINAL PLATE : NONE
HOLDER : GE GLASS
OVERTONE : 5TH
Rs : 16.2 Ω
FREQUENCY : 80369175.5 ~
QUARTZ : NATURAL
FREQUENCY CHANGE (%)
+0.0002
+0.0001
±0.0
-0.0001
-0.0002
3-6-62 RETURNED TO OVEN.
3-5-62 REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION FOR 24 HOURS AT 1.4 X 10^6 RAD/HOUR.
DAYS OF STORAGE @ 85°C
27
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
2
4
6
FEB
MARCH
APRIL

FIGURE 2A



Squares to the Inch

FIGURE 2B



CRYSTAL UNIT 1-6
BASE PLATE EVAR
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 3RD
RS 9.2 Ω
FREQUENCY 4821 3422.3 ~
QUARTZ NATURAL
3-5-62 REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION FOR 24 HOURS AT 1.4 x10^6 RAD/HOUR.
3-8-62 RETURNED TO OVEN.
FREQUENCY CHANGE (%)
+0.0002
+0.0001
±0.0
-0.0001
-0.0002
DAYS OF STORAGE @ 85°C
27 FEB
1 3 5 7 9 11 13 15 16 19 21 23 25 27 29 31 MARCH
2 4 6 APRIL

FIGURE 2C

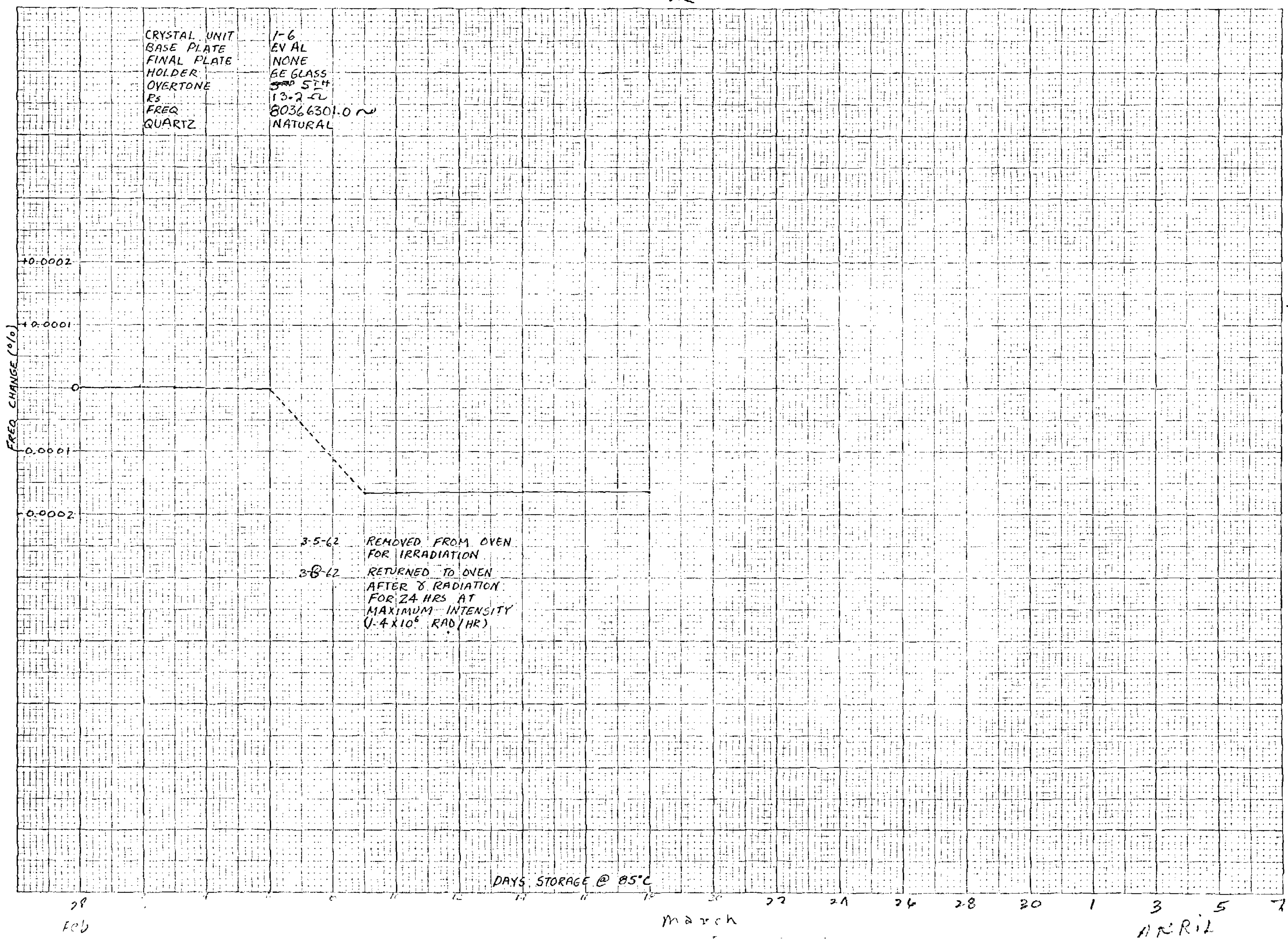

CRYSTAL UNIT 1-6
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 5TH
Rs 13.2 Ω
FREQ 80366301.0 ~
QUARTZ NATURAL
+0.0002
+0.0001
0
-0.0001
-0.0002
FREQ CHANGE (%)
3-5-62 REMOVED FROM OVEN FOR IRRADIATION
3-8-62 RETURNED TO OVEN AFTER γ RADIATION FOR 24 HRS AT MAXIMUM INTENSITY (1.4 X 10^6 RAD/HR)
DAYS STORAGE @ 85°C
28
Feb
March
22
24
26
28
30
1
3
5
7
APRIL

FIGURE 3A

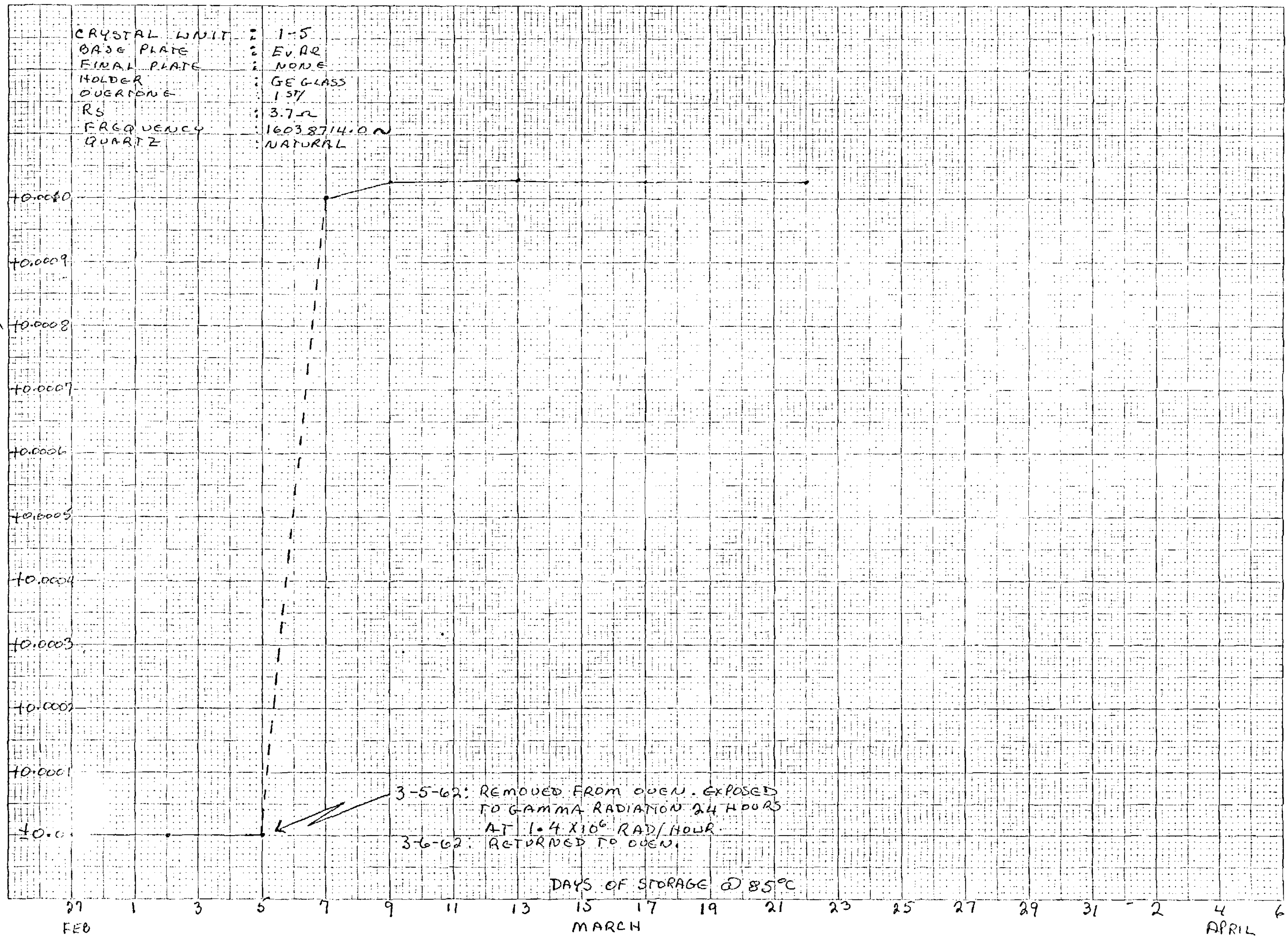

CRYSTAL UNIT : 1-5
BASE PLATE : EV AG
FINAL PLATE : NONE
HOLDER : GE GLASS
OVERTONE : 1ST
RS : 3.7 Ω
FREQUENCY : 16038714.0 ~
QUARTZ : NATURAL
FREQUENCY CHANGE (%)
+0.0010
+0.0009
+0.0008
+0.0007
+0.0006
+0.0005
+0.0004
+0.0003
+0.0002
+0.0001
±0.0
3-5-62: REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION 24 HOURS AT 1.4 X10⁶ RAD/HOUR.
3-6-62: RETURNED TO OVEN.
DAYS OF STORAGE @ 85°C
27 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 2 4 6
FEB
MARCH
APRIL

FIGURE 3B

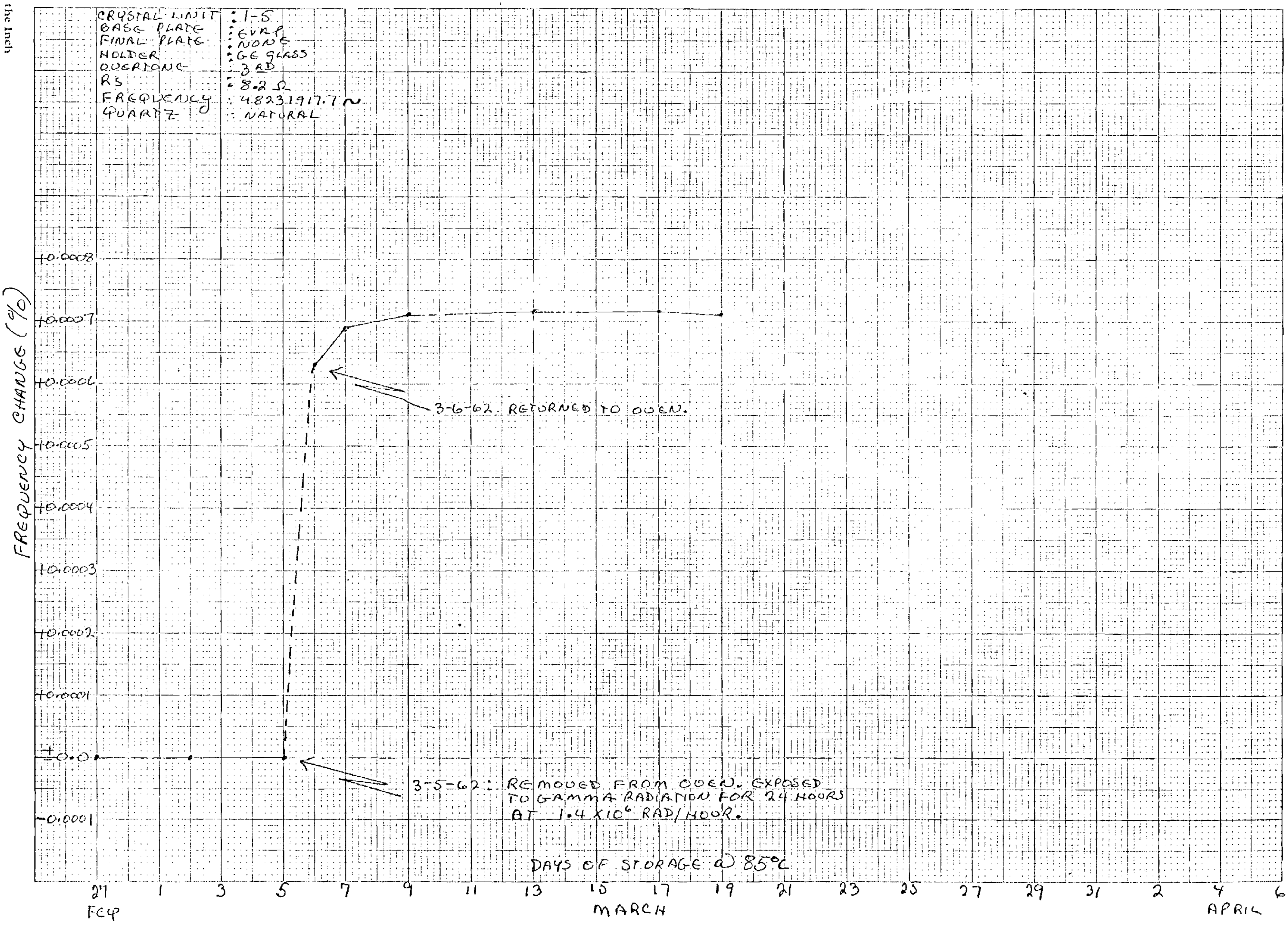
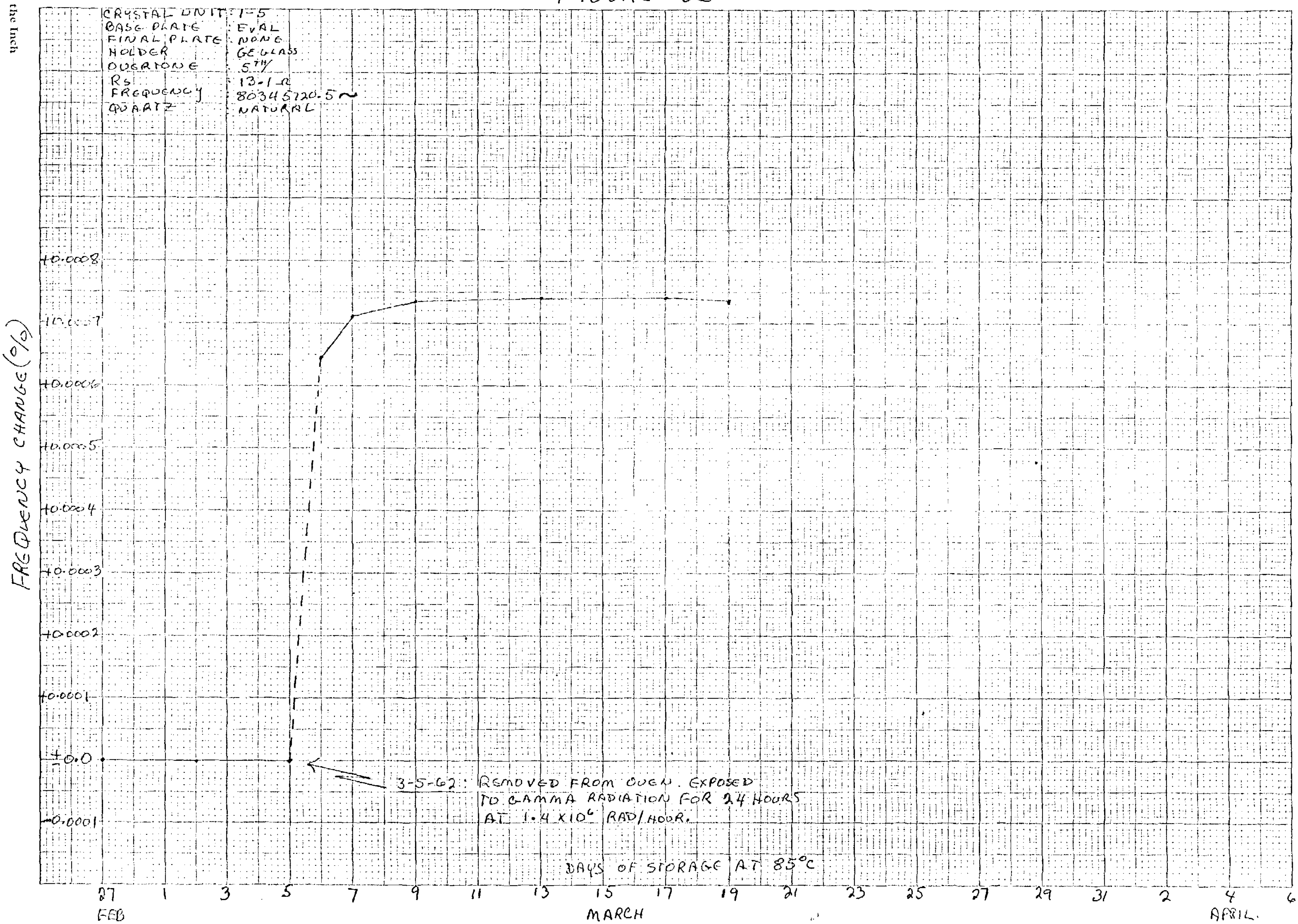

CRYSTAL UNIT : 1-5
BASE PLATE : EVRP
FINAL PLATE : NONE
HOLDER : GE GLASS
OVERTONE : 3RD
RS : 8.2 Ω
FREQUENCY : 48231917.7 ~
QUARTZ : NATURAL
FREQUENCY CHANGE (%)
+0.0008
+0.0007
+0.0006
+0.0005
+0.0004
+0.0003
+0.0002
+0.0001
±0.0
-0.0001
3-6-62. RETURNED TO OVEN.
3-5-62: REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION FOR 24 HOURS AT 1.4 X 10^6 RAD/HOUR.
DAYS OF STORAGE @ 85°C
27
FEB
1
3
5
7
9
11
13
15
17
19
21
23
25
27
29
31
MARCH
2
4
6
APRIL

FIGURE 3C


CRYSTAL UNIT : 1-5
BASE PLATE : EVAL
FINAL PLATE : NONE
HOLDER : GE GLASS
OVERTONE : 5TH
Rs : 13.1 Ω
FREQUENCY : 80345720.5 ~
QUARTZ : NATURAL
FREQUENCY CHANGE (%)
+0.0008
+0.0007
+0.0006
+0.0005
+0.0004
+0.0003
+0.0002
+0.0001
±0.0
-0.0001
3-5-62: REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION FOR 24 HOURS AT 1.4 X10^6 RAD/HOUR.
DAYS OF STORAGE AT 85°C
27 1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 2 4 6
FEB
MARCH
APRIL

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

4 [illegible]

Headquarters
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber
Solid State and Frequency [illegible]

Subject: Progress Letter No. [illegible]
Contract No. DA-[illegible]
Georgia Tech Pro[illegible]
Period: 1 March [illegible]

Dear Sir:

The purpose of [illegible] t [illegible] materials and fabrication tech[illegible] [illegible] nators. Of particular inter[illegible] [illegible] modes and a comparison between [illegible] fabricated [illegible] natural, synthetic, and swept [illegible] requency measurement accuracy of a few parts in [illegible]

During the month [illegible] the paper for the 16th Frequency [illegible] Quarterly Report No. 4 was received [illegible] [illegible] department.

On April 2[illegible] [illegible] from Georgia Tech attended the 16th [illegible] Sy[illegible]

Dr. [illegible] Ph[illegible]
Mr. W. H. Hi[illegible]
Mr. C. M. Smi[illegible]

A paper on the current [illegible] [illegible] by W. H. Hicklin. Dr. [illegible] as ch[illegible] of d[illegible]ions.

During the Sym[illegible] conference [illegible] with [illegible] M. Gutt-wein of US[illegible] included: (1 [illegible] of the conducting cement [illegible] and silver flake [illegible] crystal units, and (2) [illegible] of the HC-27/U holder for high-precision crystal reson[illegible]

During [illegible] period all of the crystal units stored in the 100-unit oven were [illegible] and placed in the two small (36-unit) ovens. The large oven was then modified to improve the temperature stability by removal of one-half of the coaxial lines into the crystal positions. The heat loss path represented by these lines was thus reduced. Studies have indicated the temperature variation after modification is about one-half the previous value.

Crystal fabrication has been concentrated upon the units required for the pulsed nuclear radiation study. Twenty [illegible] silver plated units mounted in T-5½ bulbs and 22 gold plated units mounted in HC-6/U holders were completed. Several gold plated units were lost due to agglomeration of the gold during the Pyroceram cement curing at [illegible]°C for [illegible]. These were units coated with the thinner films, <1500 Å. Silver plated units will not withstand the curing temperature of Pyroceram without aggregation. Permission was obtained from Dr. Guttwein to bond the silver plated units with duPont No. 5504A cement and to seal them in the T-5½ bulbs.

Some trouble was encountered with the high frequency bridge during the month which made necessary the replacement of two of the BNC connectors on the bridge; frequency changes due to the above changes average - 3 pp 10^7 at 48 Mc and - 6 pp 10^7 [illegible].

The following table [illegible] frequency changes for three aluminum plated units which resulted from continuous drive at 2 mw on the 5th mode for one week.

TABLE I

Frequency Changes (pp 10^7)

Unit	Mode 1st	3rd	5th
1-7	+ 1.25	+ 2.[illegible]	+ 1.7[illegible]
1-9	--	+ 1.78	--
1-10	- 0.44	- 1.12	- 1.06

Subsequent measurements of frequency have shown an initial positive aging trend for all units on all modes of operation. The results of these studies are inconclusive, and the information has been obscured somewhat by the necessary repairs to the H.F. bridge.

The Rhode and Schwarz Model XUA Frequency Synthesizer was received during the month. It was quickly determined that the instrument would not be suitable for use without repair because the signal from it contained AM and probably FM modulation. Repairs could not be undertaken until the arrival of the instruction manual for the synthesizer (received 3 May 1962).

The program for the month of April will include:

1. Continuation of frequency measurements;

2. Completion of all units for the pulsed radiation study;

3. Expansion of continuous wave studies and

4. Studies of the effects of gamma radiation on the cultured and swept quartz.

A high priority will be given to the repair of the frequency synthesizer because it is urgently needed.

Respectfully submitted,

RBB/var

Richard B. Belser
Project Director

cc: Addressee, 5

bcc: A. L. Bennett
R. B. Belser
W. H. Hicklin
Library, 2

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

5 July 1962

Headquarters
U.S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. E. A. Gerber
Solid State and Frequency Control Division

Subject: Progress Letter No. 14
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 June to 1 July 1962

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

During the month of June Quarterly Report No. 5 was completed and copies were sent to USASRADL for approval.

On 22 May 1962 a group of twelve crystal units was removed from the aging ovens and sent to Mr. Stanley of USASRADL for exposure to a high intensity neutron radiation pulse. The group was comprised of four units fabricated of natural quartz, four of cultured quartz, and four of swept, cultured quartz. All of the units were base plated with evaporated aluminum and mounted in evacuated glass bulbs.

Two groups of crystal units were fabricated during the quarter for inclusion in the study of the effect of pulsed radiation on resonator performance. Group Al-3 (10 units) was fabricated of cultured quartz and mounted in HC-27/U holders after base plating with evaporated aluminum and bonding with Pyroceram 95 plus silver cement*. Group Al-4 (8 units) was fabricated in a similar manner using swept, cultured quartz. These units are now in an 85°C oven for aging measurements on the third mode.

The frequency measurements of the crystals for the pulsed radiation study are being made at the third overtone using the Rohde and Schwarz Frequency Synthesizer as the R.F. generator. The synthesizer delivers

- - - - -

* 2 parts silver plus 1 part Pyroceram by volume.

about 24 Mc to a frequency doubler which develops 48 Mc for driving the crystal impedance bridge. The spurious signals out of the synthesizer have been reduced and the precision of measurement is about 6 parts in 10^8. A complete set of replacement tubes for the device was ordered. The types ECH-81 and EF-800 have been received and installed. Some improvement in the performance was obtained.

Frequency measurements at the fundamental mode and on the third and fifth overtones have been continued during the quarter. Evidence has been accumulated to indicate that crystal units will have the maximum stability with time when continuously stored at a constant temperature. If the storage oven is opened and the units subjected to a thermal shock, a restabilization period of at least several days is required before the frequency stability is reestablished. The frequency of the unit may then be different from the original by a small amount. Such action may be associated with changes in the mechanical stress exerted by the mounting support on the thin quartz plates when the temperature is varied. An interesting experiment, although beyond the scope of the present project, would be to (1) establish a frequency vs. time trend at a constant temperature such as 85°C and then (2) change the temperature a few degrees (plus or minus) and observe the resulting effect on the resonator frequency. The temperature change should be made without a thermal shock such as would be obtained if ovens of the present design were opened to change the mercury thermostats.

A frequency measuring system capability study was made during the quarter using the crystal controlled CI meter as the R.F. generator. The results of these studies are shown in Figures 1, 2, and 3. The excellent measurements indicate that the system will measure the resonator frequencies with a precision of a few parts in 10^9. More studies of this type are planned but will be limited by the fact that the measuring system is in almost continuous use due to the number of units being studied.

Another experiment completed during the month was the following:

1. A 16 Mc unit was uncanned and mounted in a vacuum system near the intake of a hot filament ionization gauge*.

2. The system was pumped to 5×10^{-7} Torr and the unit oscillated over a range of drive levels on the fundamental mode.

3. Observations of the system pressure were made at each drive level.

There was no apparent change in the system pressure at any drive level up to the maximum obtainable with a TS-683 CI meter. Calculations show that one layer of adsorbed gas on the surface of the crystal would be of the order of 10^{14} molecules which is approximately the number in the system at 10^{-6} Torr.

- - - - -

* Veeco type RG-75P.

Hence, the evidence appears to indicate that positive changes in the frequency of a crystal resonator at the higher drive levels is not due to the removal of adsorbed gas by the vibration of the quartz.

The program for the month of July includes:

1. Continued frequency measurements of crystal units.

2. The design and construction of a crystal oven and holder so that quartz plates may be temperature cycled up to 100°C on the fundamental and overtone modes without plating and mounting. Such a device could be used to advantage in production as well as in the laboratory for the reduction of rejects due to poor angle control.

3. The design and construction of a pilot model aging oven which will allow precise temperatures to be maintained. Full proportional control will be used. The oven will house a maximum of ten units. The temperature control circuit will permit small temperature changes if desired without loss of precise control.

Respectfully submitted,

RBB/var

Richard B. Belser
Project Director

Enclosures: Figures 1, 2, 3

cc: Addressee, 5

bcc: E. J. Scheibner
R. B. Belser
W. H. Hicklin
Library, 2

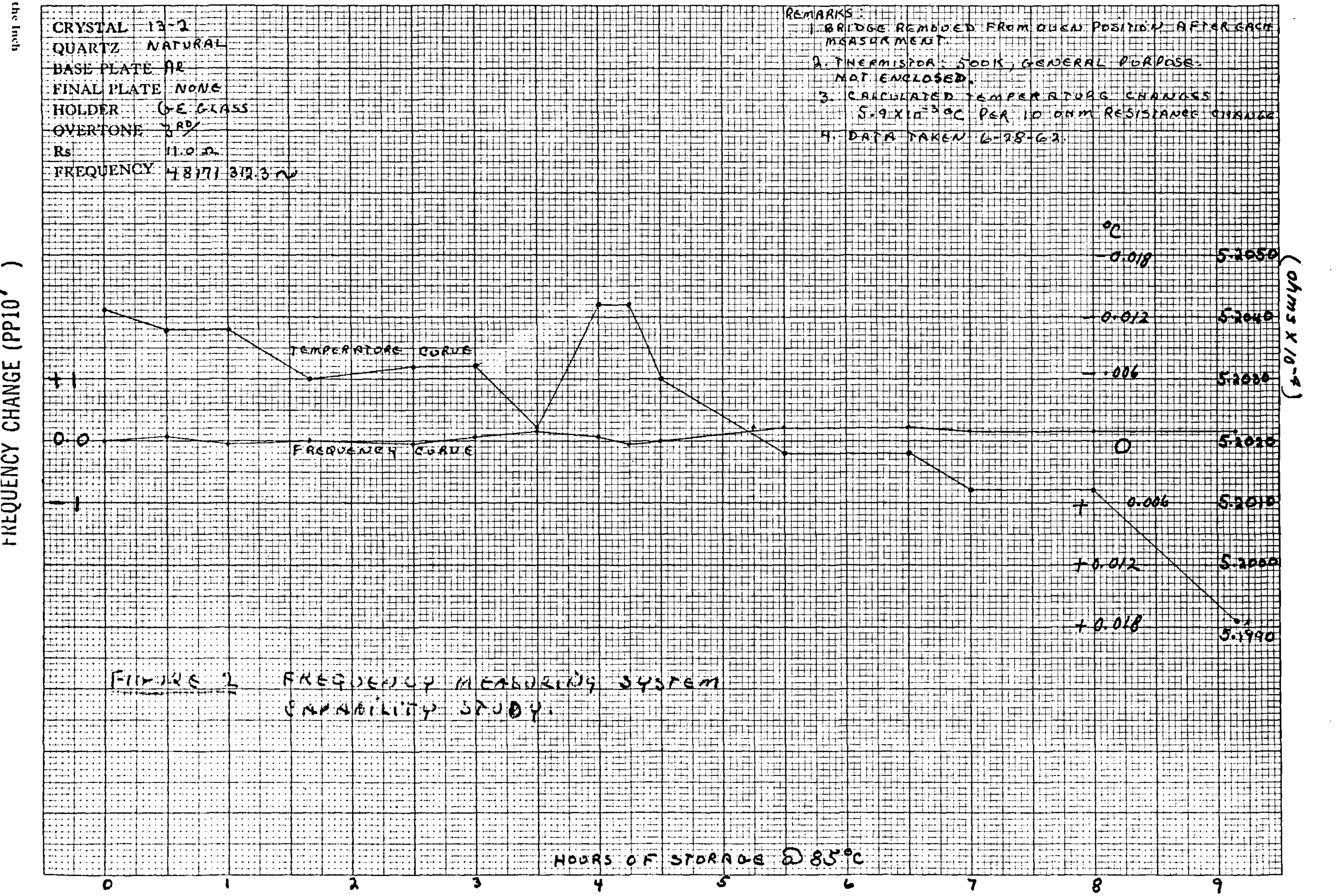


FIGURE 2 FREQUENCY MEASURING SYSTEM CAPABILITY STUDY.

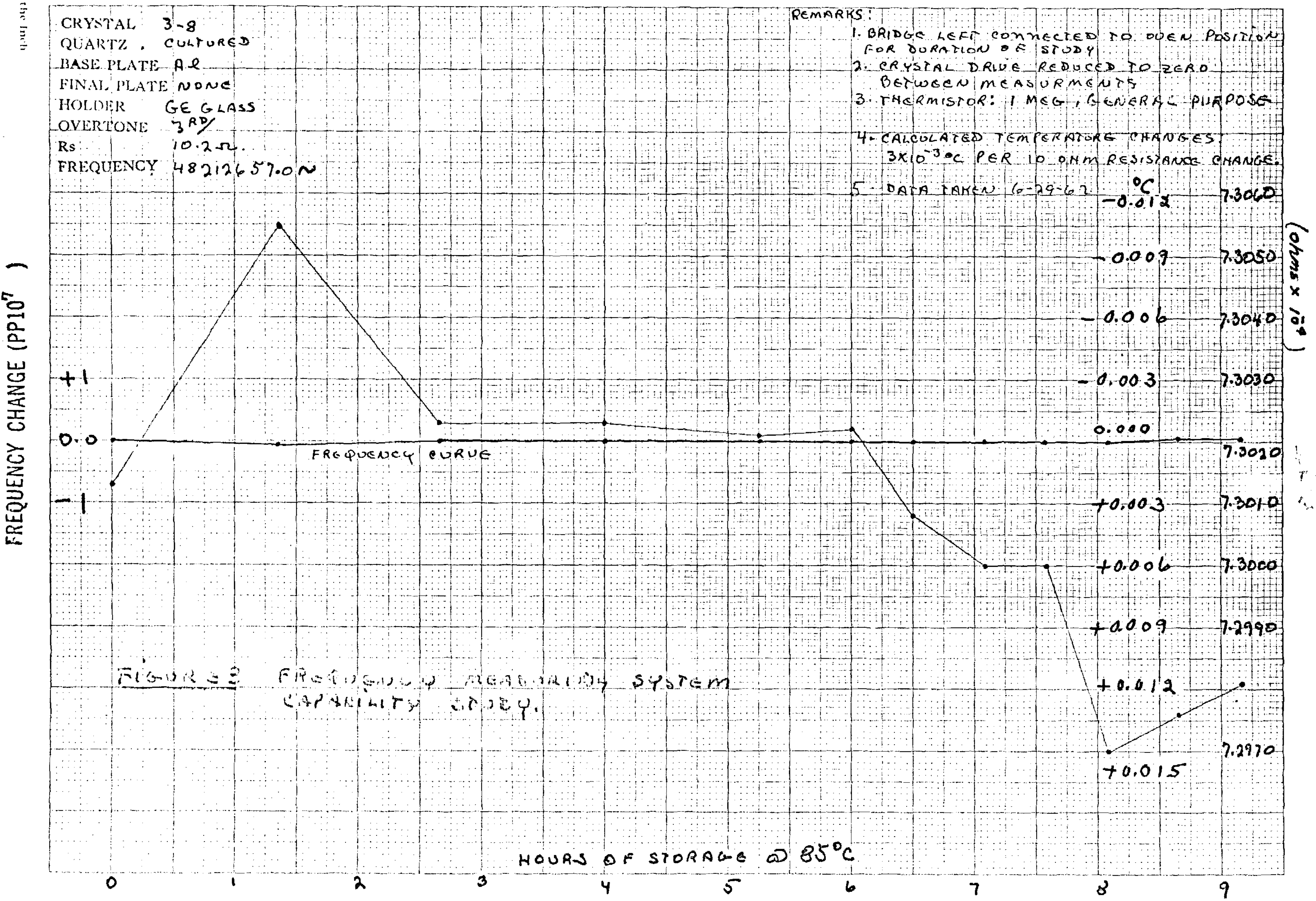


FIGURE 32 FREQUENCY MEASURING SYSTEM CAPABILITY STUDY.

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

3 August 1962

U. S. Army Signal Research and Development Laboratory
Solid State and Frequency Control Division
Piezoelectric Crystal and Circuitry Branch
Fort Monmouth, New Jersey

Attention: Dr. G. K. Guttwein

Subject: Progress Letter No. 15
Contract No. DA-36-039-sc-87407
Georgia Tech Project No. A-552
Period: 1 July to 1 August 1962

Dear Sir;

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

During the month of July principle effort has been directed to keeping up measurements of approximately 150 crystal units already fabricated and on storage. About ninety of these are for the pulsed radiation studies and have been measured principally at the third mode. The remaining 60 are the units devoted to the study of long term aging effects and have been measured at two or three modes, dependent on availability of units of matching frequencies. More recently the Rohde and Schwarz Frequency Synthesizer has been improved to the point that reasonably accurate measurements can be obtained at all modes.

No additional units were fabricated during the month because of the measuring load and the fact that annual summer vacations resulted in reduced manpower available to the project for this particular effort.

A considerable amount of recent data has implied that crystal resonators on storage are suffering some thermal shock whenever the oven is opened to insert or remove specimens. Secondly, it has appeared that stabilities of many of the resonators on storage are varying more from temperature variation within the storage ovens than from other causes. Thirdly, it is apparent that a specific cut for zero temperature coefficient at one mode of operation may not be satisfactory for the respective unit at another mode of operation. Data which exhibit some facets of these behaviors are discussed below.

Two series of successive frequency measurements over a period of 34 hours were made on crystal unit 3-8. The results of these measurements for the first and fifth modes are shown in Figures 1 and 2. Similar measurements for the same unit (3-8) operated at the third mode were illustrated in Figure 3 of Progress Letter No. 14.

These measurements indicate the accuracy capability of the frequency measurements and temperature control. They also indicate slight differences in behavior at the various modes of operation. A large part of the frequency shifts (of one or two parts in 10^8) are ascribable to temperature shifts within the oven. In general these temperature changes are not greater than ±0.015 °C in the total range of thermistor readings exhibited in 34 hours.

The frequency aging data for crystal unit 7-9 in its various modes of operation are shown in Figures 3, 4, and 5, for the first, third and fifth modes respectively. Attention is directed to the frequency changes which occurred due to opening of the oven, power failure, etc. The frequency shifts due to these temperature changes are larger at the first mode than at the other modes of operation. A similar behavior has been generally noted for other similar crystal units exposed to such inadvertent temperature changes. It is conjectured that the behavior noticed is due to changes in the strains in the quartz applied by the support system (0.006" steel springs). Temperature variations of the environment would cause dimensional changes in the support members and thus effect strain variation.

Frequency data for approximately 60 days operation have been obtained for crystal units fabricated for the pulsed radiation damage study. Typical aging curves for units plated with silver, gold and aluminium are shown in Figures 6, 7, and 8 respectively.

Arrangements are currently being made for transporting these units to the Sandia Pulsed Reactor Facility for exposure to a single radiation burst of high intensity (10^{13} nvt.). This experiment is expected to be performed in about 60 days.

A Marconi oven Type No. F 3006-01 provided through Georgia Tech funds has been recieved for use on this project. The oven after installation will be used for checking the measuring equipment and for short term studies of crystal stability.

In addition, a Manson oscillator, model RD 180A, was purchased and installed during July. The frequency stability, after less than one month of operation, is a few parts in 10^9 per day. The ultimate stability should be about two parts in 10^{10} per day.

The approval copy of Quarterly Report No. 5 was returned from USASRDL. The required corrections were made and the report was sent to the reproduction department. It is expected to be completed and distributed about 10 August 1962.

The program for the month of August includes:

1. Continued routine frequency measurement of units on long term agings,
2. installation of the Marconi oven; and
3. a continuation of the short term frequency stability studies.

In view of the recent directive of Dr. Guttwein with regard to the proposed work on temperature cycling some of the work proposed in Progress Letter No. 13 will be delayed. However, it is believed that additional frequency versus temperature information may be required for thorough interpretation of current measurements. This need suggested the proposed work rather than the technical detail as to whether or not it was specifically within the areas authorized within the terms of the contract.

Respectfully submitted,

Richard B. Belser
Project Director

Enclosures: Figures 1 through 8

cc: Addressee, 5

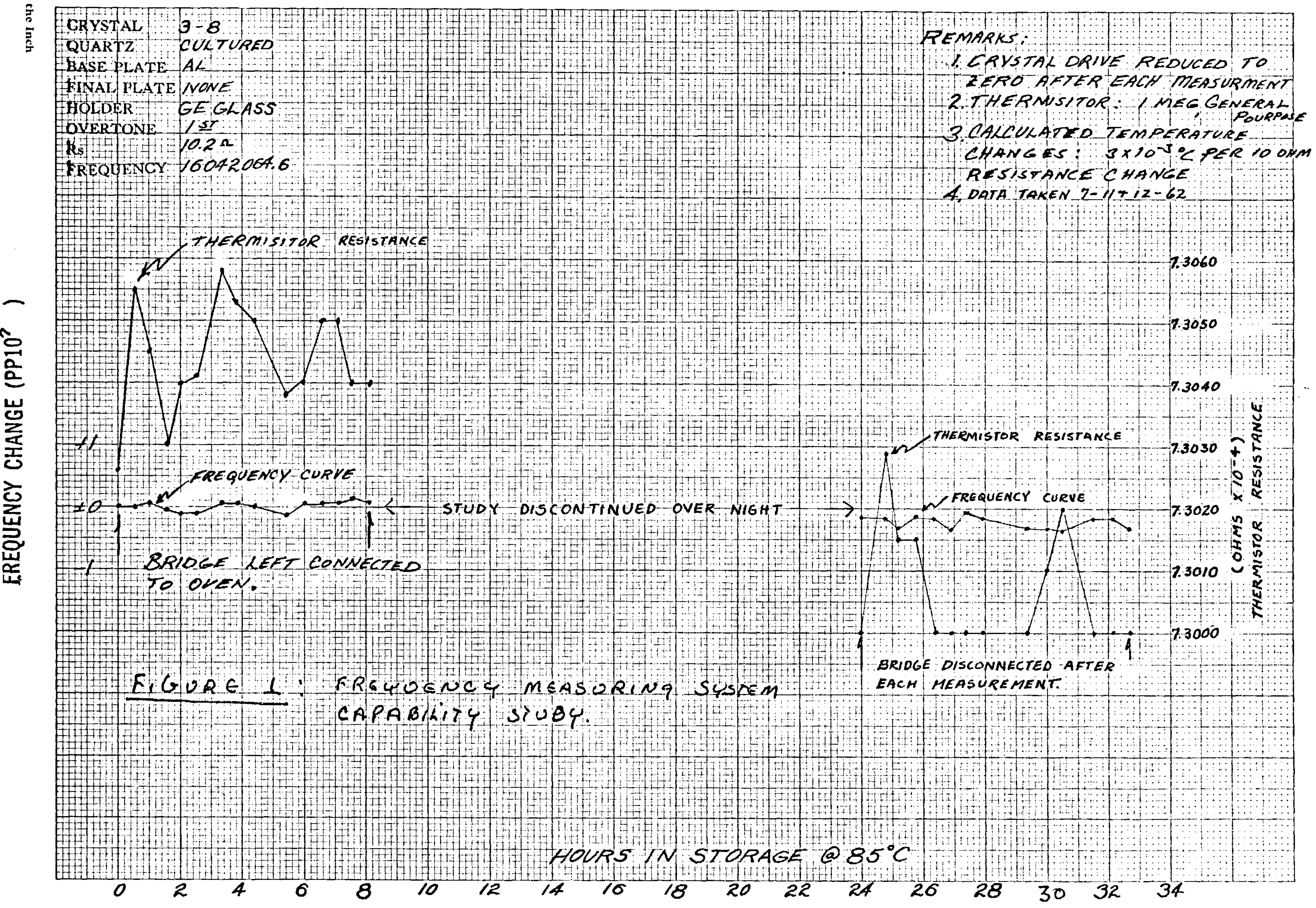


FIGURE 1: FREQUENCY MEASURING SYSTEM CAPABILITY STUDY.

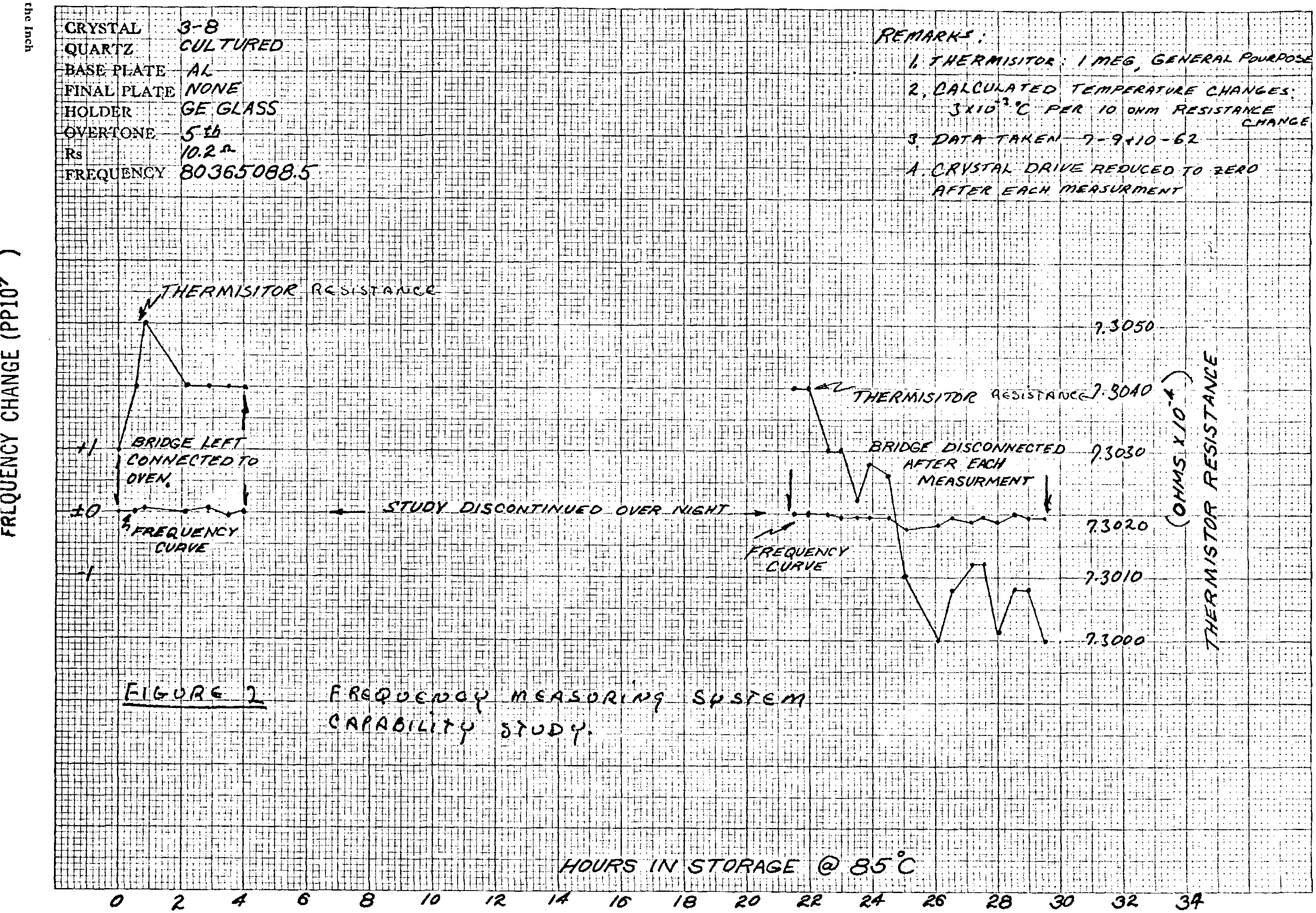


FIGURE 2 FREQUENCY MEASURING SYSTEM CAPABILITY STUDY.

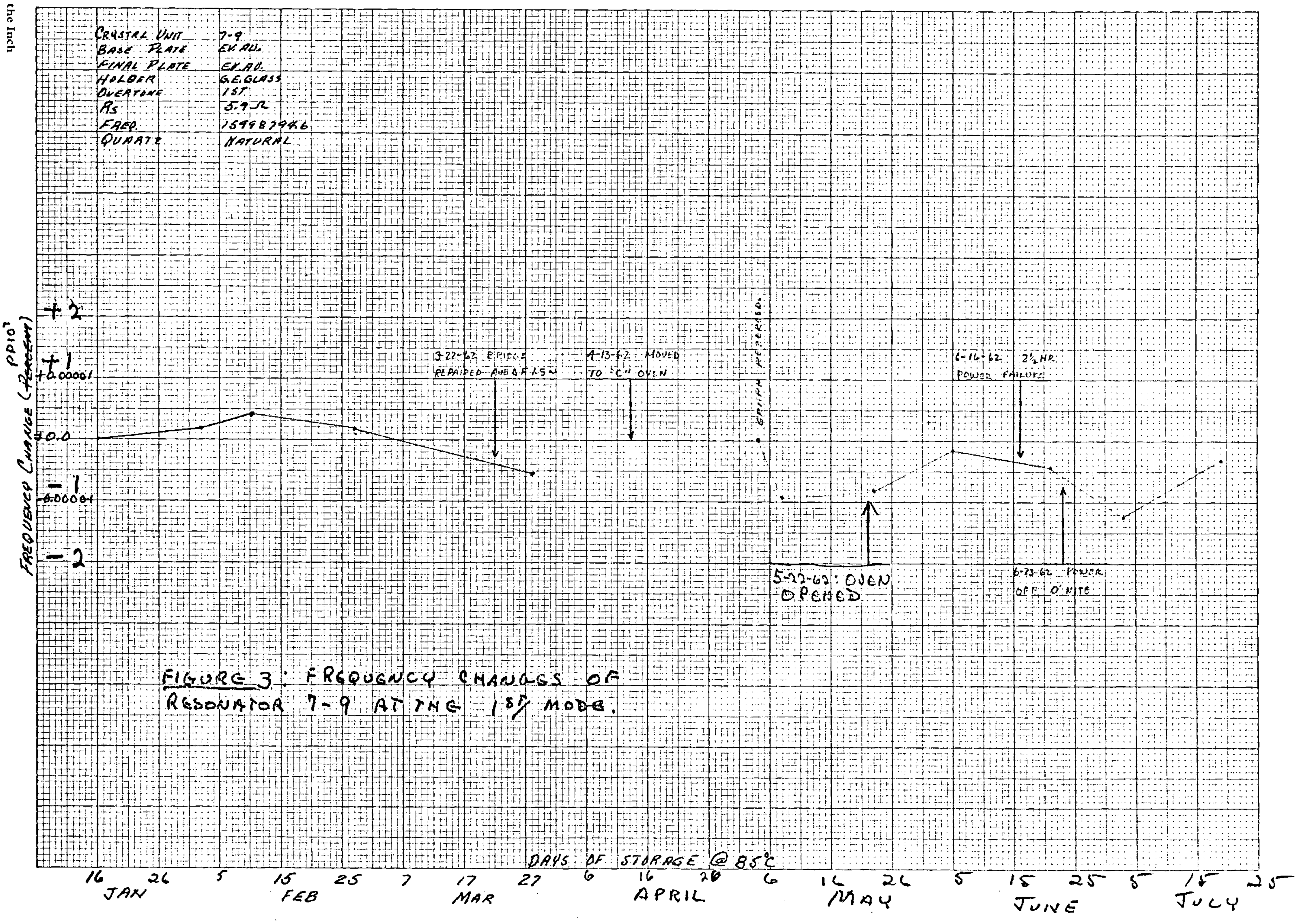


FIGURE 3: FREQUENCY CHANGES OF RESONATOR 7-9 AT THE 1ST MODE.

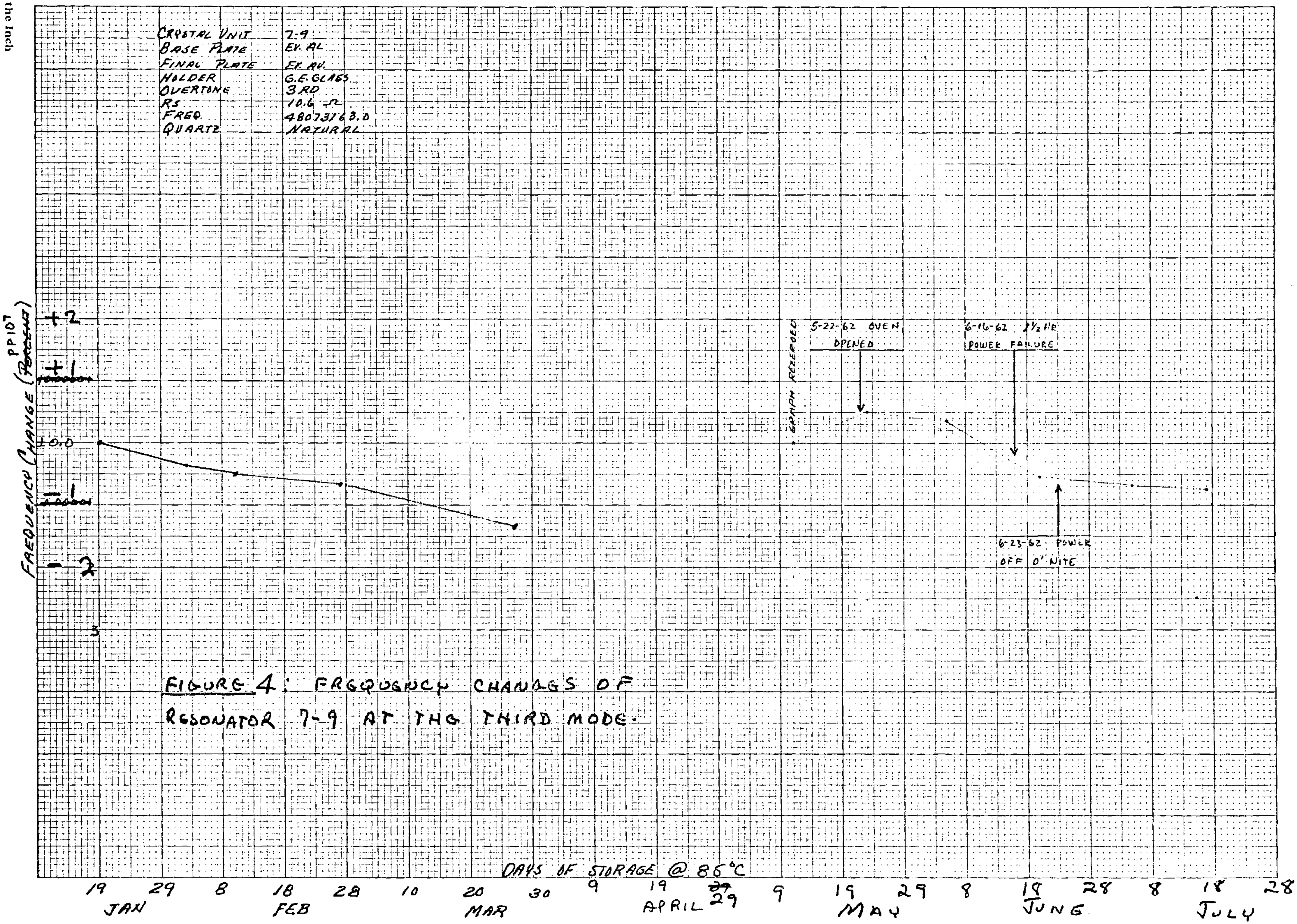


FIGURE 4: FREQUENCY CHANGES OF RESONATOR 7-9 AT THE THIRD MODE.

squares to the inch

12-282

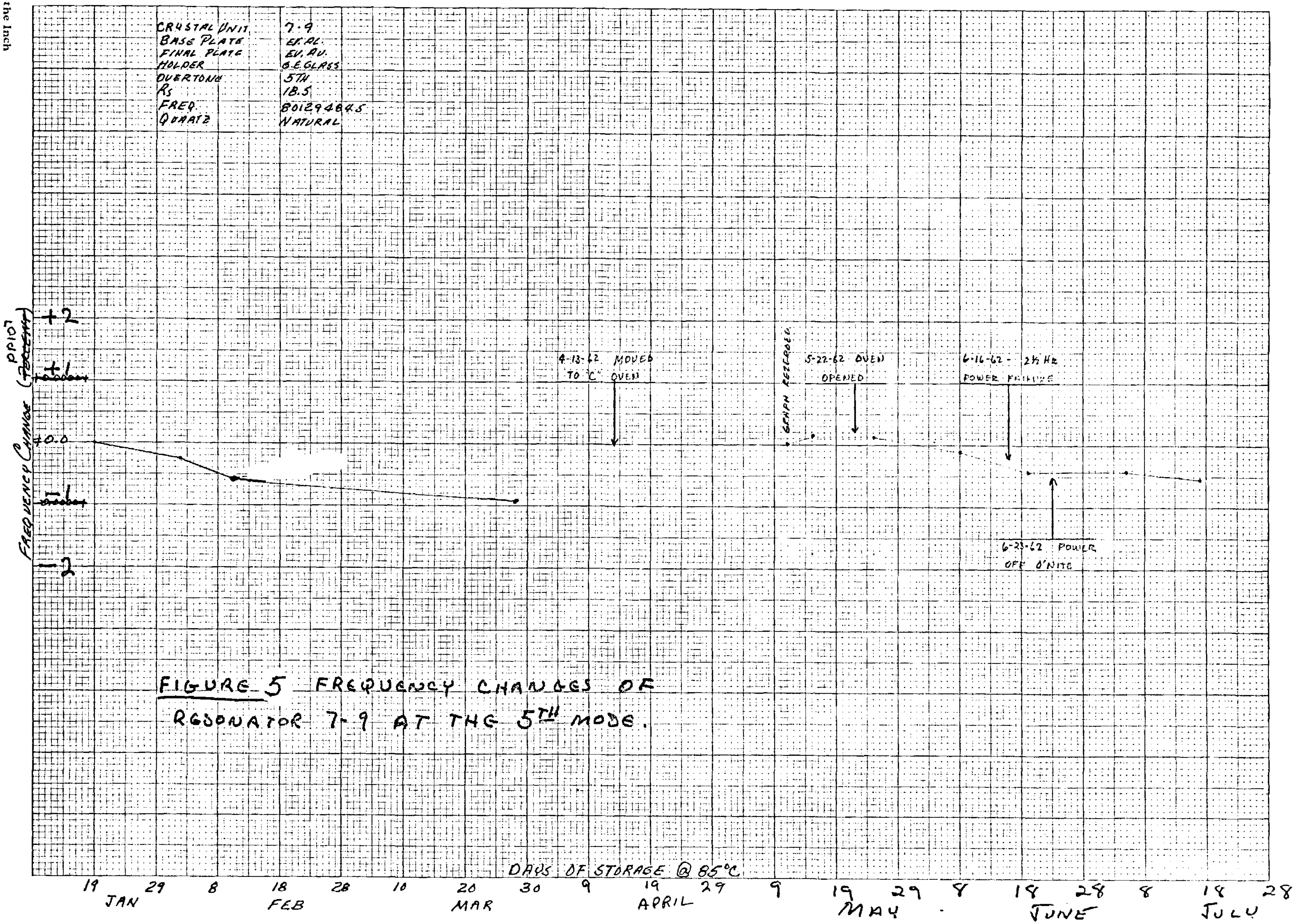


FIGURE 5 FREQUENCY CHANGES OF RESONATOR 7-9 AT THE 5TH MODE.

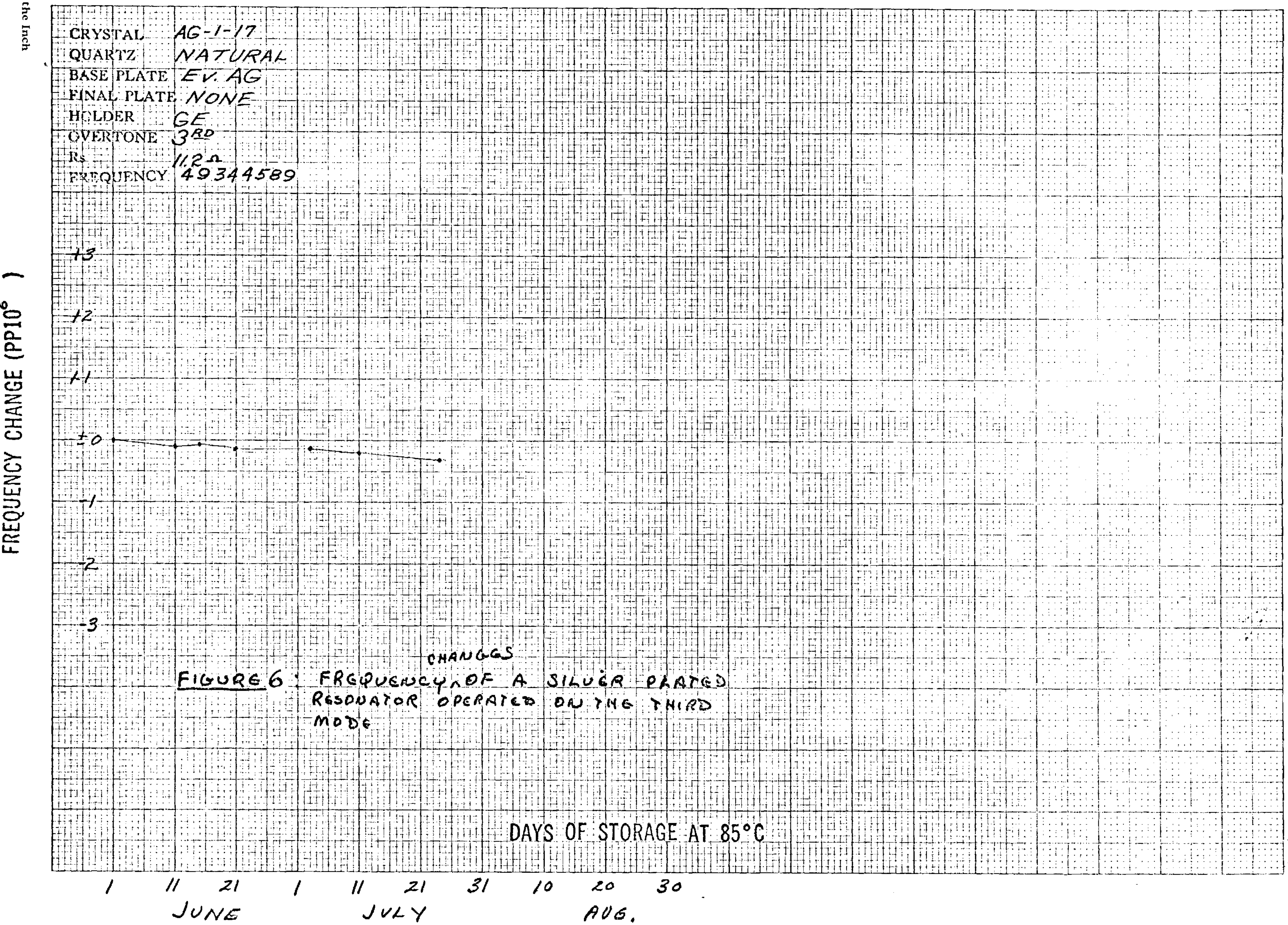


FIGURE 6: FREQUENCY CHANGES OF A SILVER PLATED RESONATOR OPERATED ON THE THIRD MODE

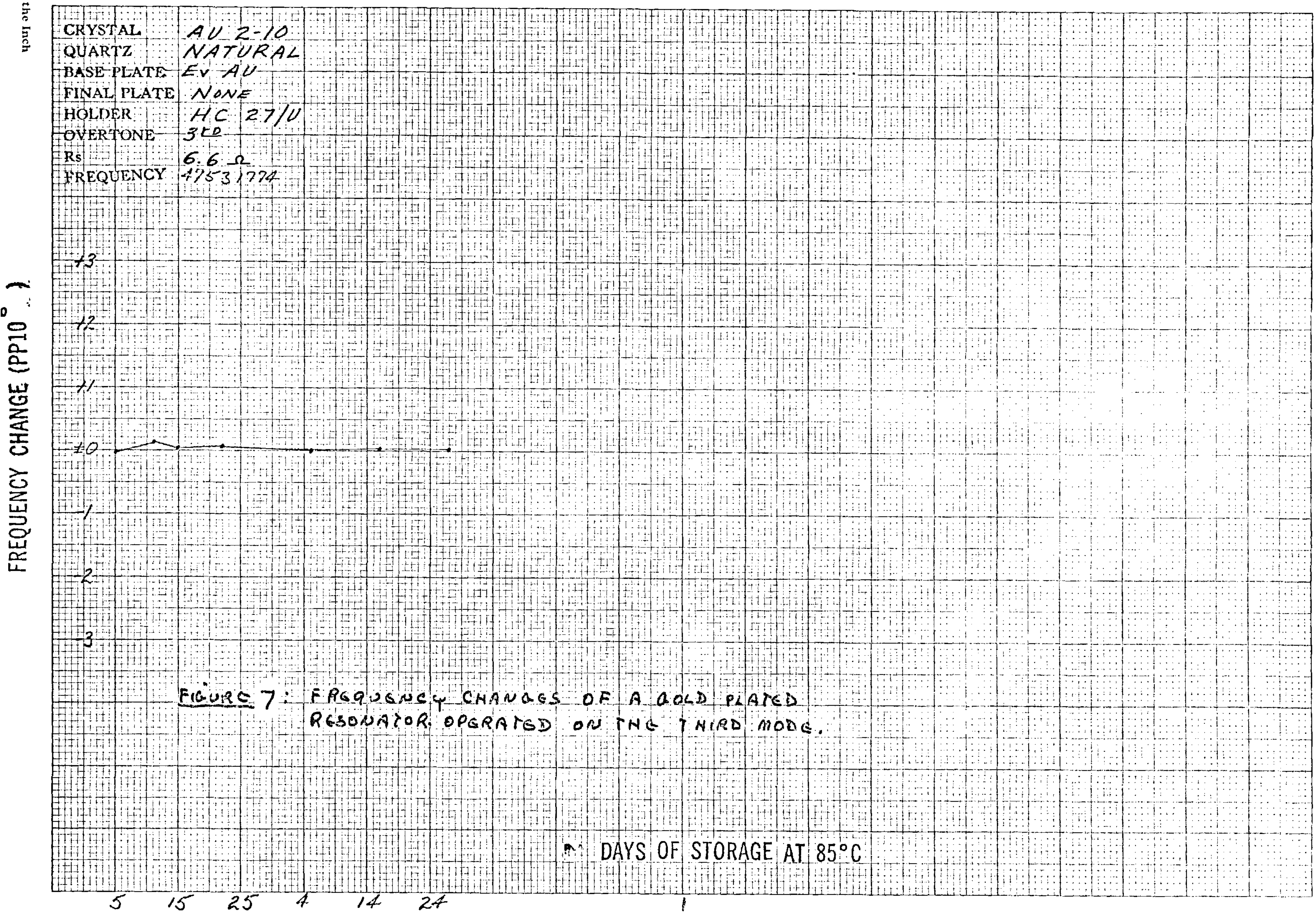


FIGURE 7: FREQUENCY CHANGES OF A GOLD PLATED RESONATOR OPERATED ON THE THIRD MODE.

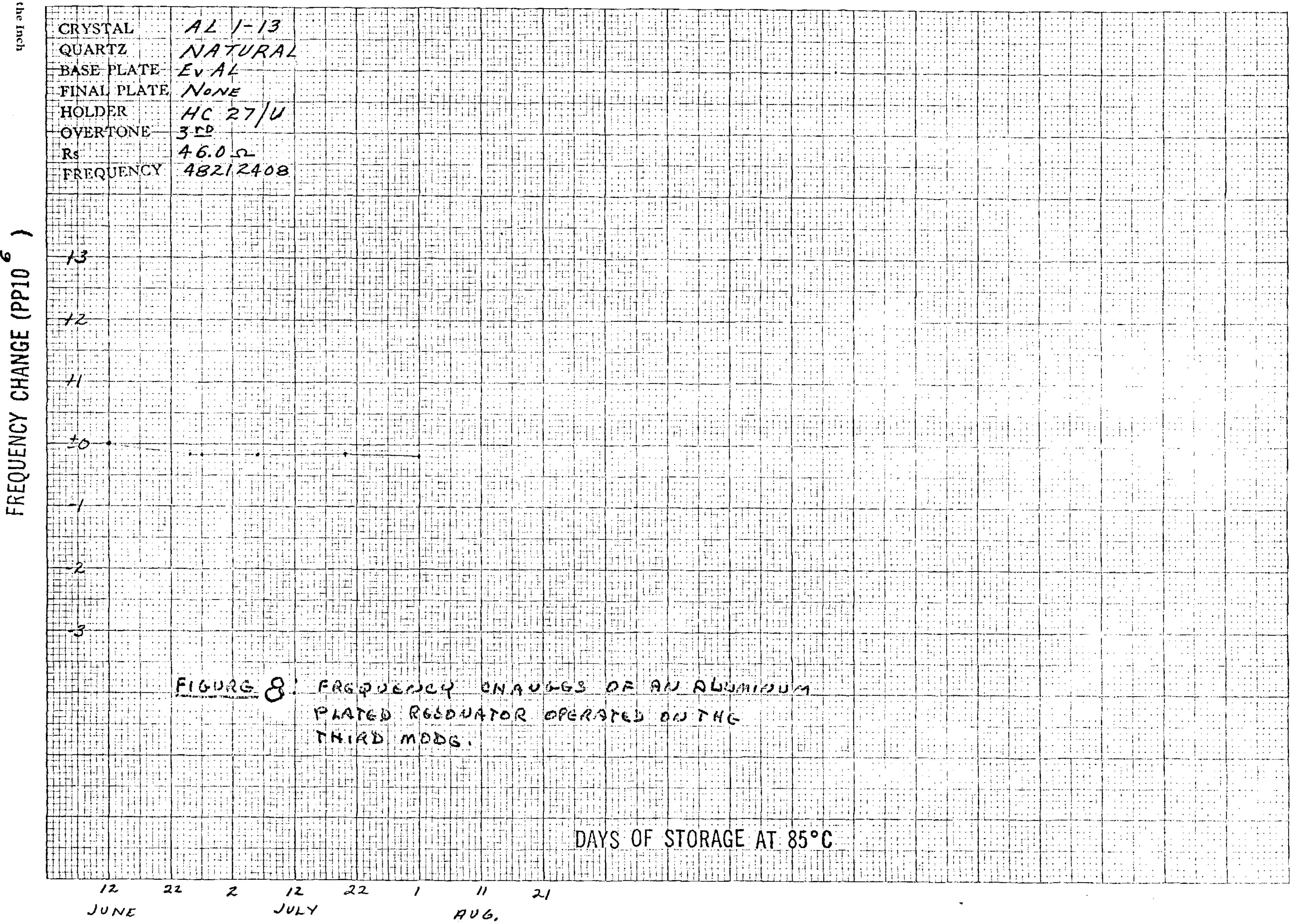


FIGURE 8: FREQUENCY CHANGES OF AN ALUMINUM PLATED RESONATOR OPERATED ON THE THIRD MODE.

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

October 5, 1962

Headquarters
U.S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. G. K. Guttwein
Solid State and Frequency Control Division
Piezoelectric Crystal and Circuitry Branch

Subject: Progress Letter No. 16
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 September to 1 October

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

On 26 September 1962 Dr. R. A. Young, Mr. R. B. Belser and Mr. W. H. Hicklin of Georgia Tech met with Dr. E. A. Gerber, Dr. G. K. Guttwein, Dr. E. Hafner, Mr. J. M. Stanley and Mr. P. E. Mulvihill of the U. S. Army Signal Research and Development Laboratories at Fort Monmouth, New Jersey. Plans for the proposed continuation of the research program on aging studies of quartz resonators were established and the scope of the technical requirements was decided. A discussion of a technique of examining stresses, electrical twinning, and other faults in quartz resonators by X-ray diffraction topography was presented by Dr. R. A. Young.

In September, Quarterly Report No. 6 was completed and copies were forwarded to USASRDL for approval before publication.

No new units were fabricated during the month, principally because the controlled temperature ovens had no positions open for additional resonators.

During the month one of the principal efforts has been directed toward completing measurements of about 150 resonator units stored at 85°C. About ninety-five of these units were fabricated for the pulsed neutron radiation study and were measured on the third overtone only. The remaining fifty-five units were fabricated for the study of long term aging effects and were measured at the first, third and fifth modes.

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Measurements of long term aging effects have continued for sufficient time to allow definite patterns of behavior to appear. These may be summarized as follows:

1. The aging rates of the third and fifth overtone modes usually agree very closely;

2. the frequency behavior at the fundamental mode is often more erratic than at the overtone modes and appears to be the result of sensitivity of this mode to thermal shock; and.

3. overplating the base plate with a second metal film, as commonly done on a cold substrate, increases the aging rate of the respective unit.

Typical data which illustrate the behavior patterns obtained for various resonators are shown in Figures 1 through 8.

Continuous drive studies for a series of resonators were conducted during the month. The general procedures followed are outlined below.

1. The values of the bridge parameters were determined for the series resistance of the particular units;

2. the input voltage to the bridge to produce the desired drive level was then calculated;

3. using the Rohde and Schwarz synthesizer as the R. F. generator, the required voltage at the proper frequency was applied to the bridge. The latter was determined by location of the null in the usual manner;

4. the units were driven for the desired period (about 3 days) at a temperature of 85°C.

Since changing the drive level from the normal micro-watt range to 2 MW caused no change in series resistances, no final adjustments on drive level were necessary.

Two units were driven as described with the results illustrated in Figures 9 and 10. Unit 3-6 was driven 88.3 hours at the fundamental and unit 10-1 was driven 64 hours at the third mode. The unit driven at the fundamental changed more than the unit driven at the third mode. Since the former was driven for 24 hours longer than the latter, no determination of whether the magnitude of the changes are due to the time difference or the apparent intrinsic sensitivity of the units at the fundamental mode can be made at this time. More experiments of this type are planned during which the units will be driven for equal periods of time at each mode.

On 10 September 1962 selected units were removed from oven A for exposure to pulsed irradiation; about 30 specimens were reserved as control specimens and kept in the laboratory at room temperature. The units to be irradiated were taken to the Sandia Pulsed Reactor Facility on 11 September and irradiated on 12 September. The irradiated units were returned to the laboratory on 14 September 1962, and nine of the irradiated units were immediately replaced in the oven. On 17 September the parameters of the nine units were measured; immediately afterwards the oven was opened again to return the balance of the units to their original test positions. The measurements of frequency changes experienced by the various resonators are summarized in Table I. In general, frequency changes noted were only a few parts in 10^7 and of the same order of magnitude as that of the control units kept at room temperature in the laboratory. There appeared to be a slight negative change indicated for the aluminum plated resonators. The significance of this at this time has not been ascertained.

During the conference on 26 September, Mr. J. M. Stanley displayed an interest in some of the gamma irradiation experiments made here earlier; a discussion of these is given below.

On 5 March 1962 three natural quartz units were exposed to gamma radiation from a Cesium 137 source for 24 hours at a dose rate of 1.4×10^6 rad/hour. A typical example of frequency changes observed are shown in Figure 11. The frequency versus time data obtained subsequent to exposure are illustrated in Figures 12, 13 and 14. Figures 12 and 13 indicate that the initial frequency change is greater on the fundamental than in the overtone modes and that the third and fifth overtones agree in behavior very closely with each other. Figure 14 illustrates the behavior of a unit which has been irradiated into the "cross-over" region - that portion of the frequency - time curve for gamma irradiation where the frequency after having been below the initial frequency has returned approximately to the original frequency as shown in Figure 11.

The program for October includes:

1. Fabrication of one group of crystals mounted in gettered T 5-1/2 bulbs,

2. a continuation of the drive level studies and,

3. continued frequency measurements of both regular and irradiated resonators.

Respectfully submitted,

Richard B. Belser
Project Director

Addressee: 5
Enclosures - Figures 1-14, Table I

Squares to the Inch

12-282

FIG. 1

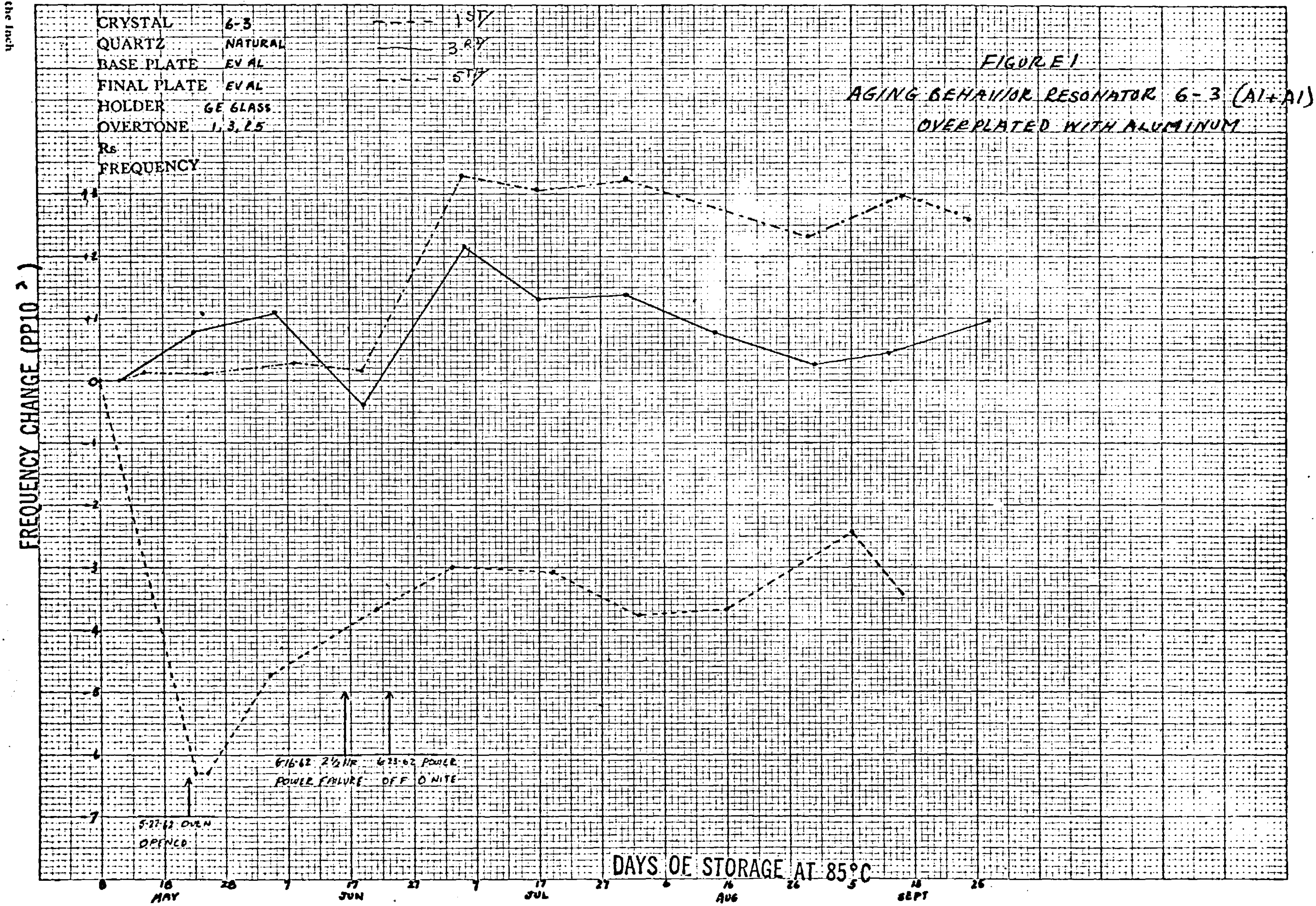
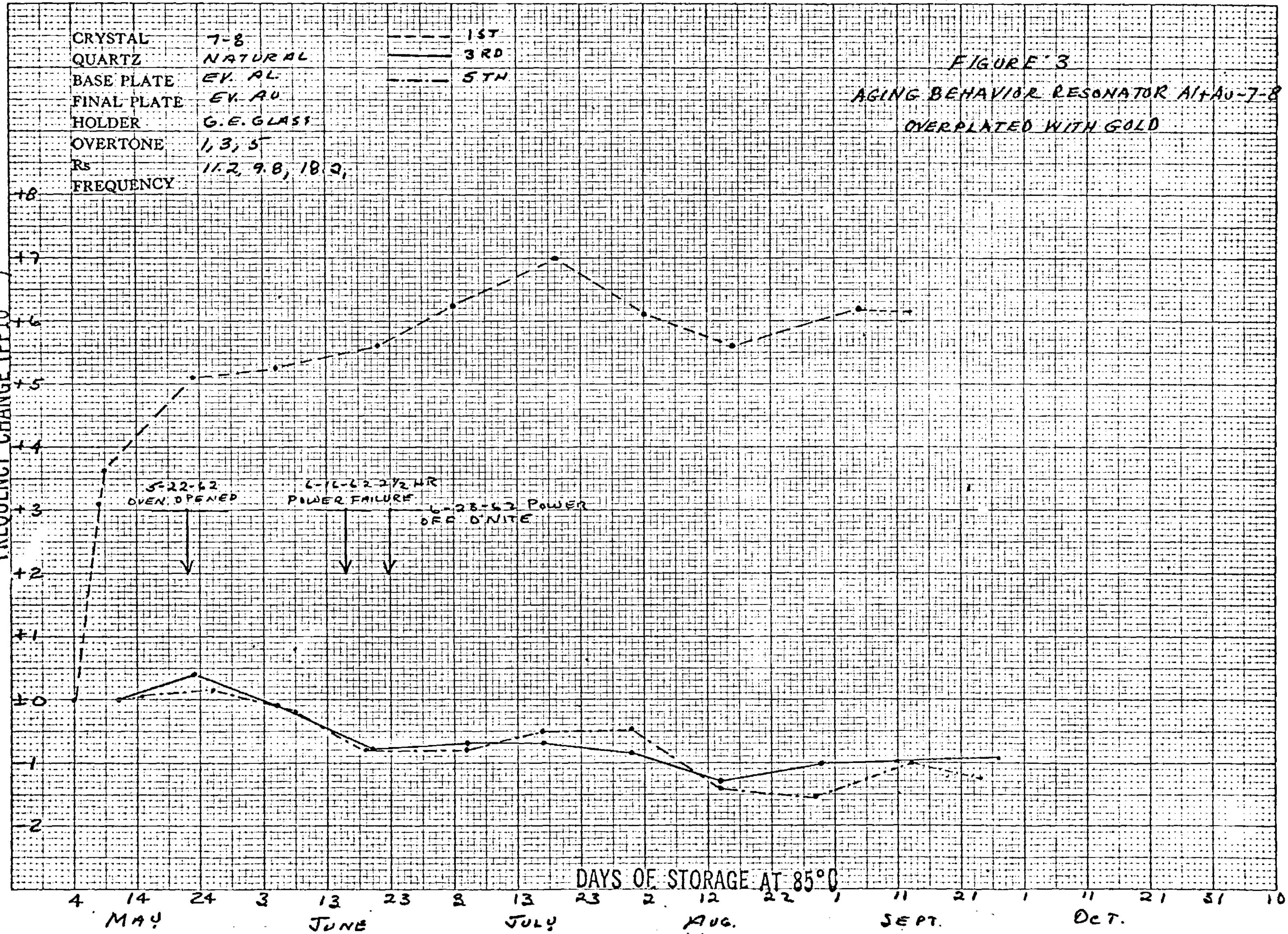
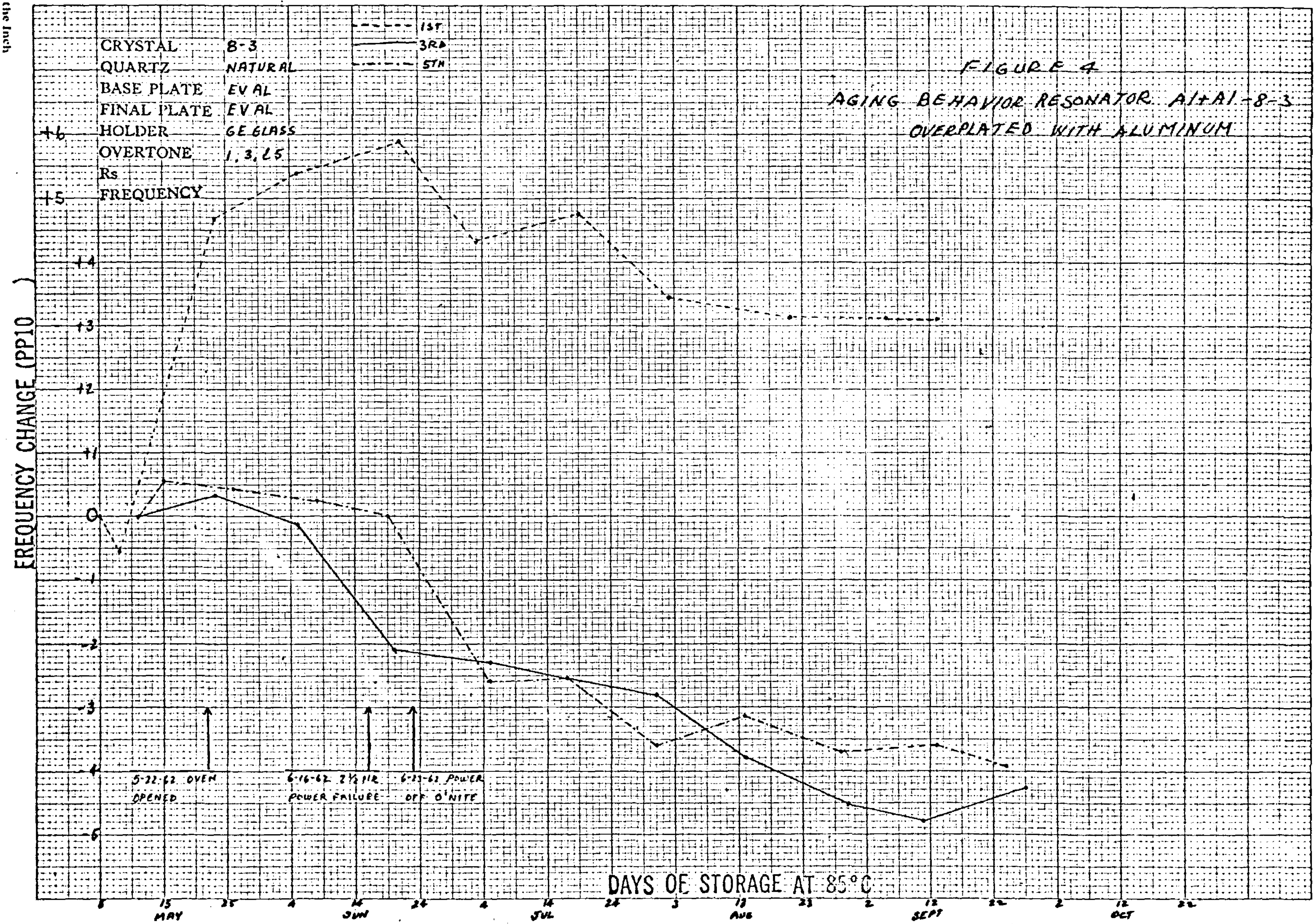


Fig 3



CRYSTAL 7-8
QUARTZ NATURAL
BASE PLATE EV. AL
FINAL PLATE EV. AU
HOLDER G.E. GLASS
OVERTONE 1, 3, 5
Rs 11.2, 9.8, 18 Ω
FREQUENCY
1ST
3RD
5TH
FIGURE 3
AGING BEHAVIOR RESONATOR Al+Au-7-8
OVERPLATED WITH GOLD
5-22-62
OVEN OPENED
6-16-62 2½ HR
POWER FAILURE
6-23-62 POWER
OFF O'NITE
FREQUENCY CHANGE (PP10
+8
+7
+6
+5
+4
+3
+2
+1
±0
-1
-2
DAYS OF STORAGE AT 85°C
4
14
24
3
13
23
2
13
23
2
12
22
1
11
21
1
11
21
31
10
MAY
JUNE
JULY
AUG.
SEPT.
OCT.

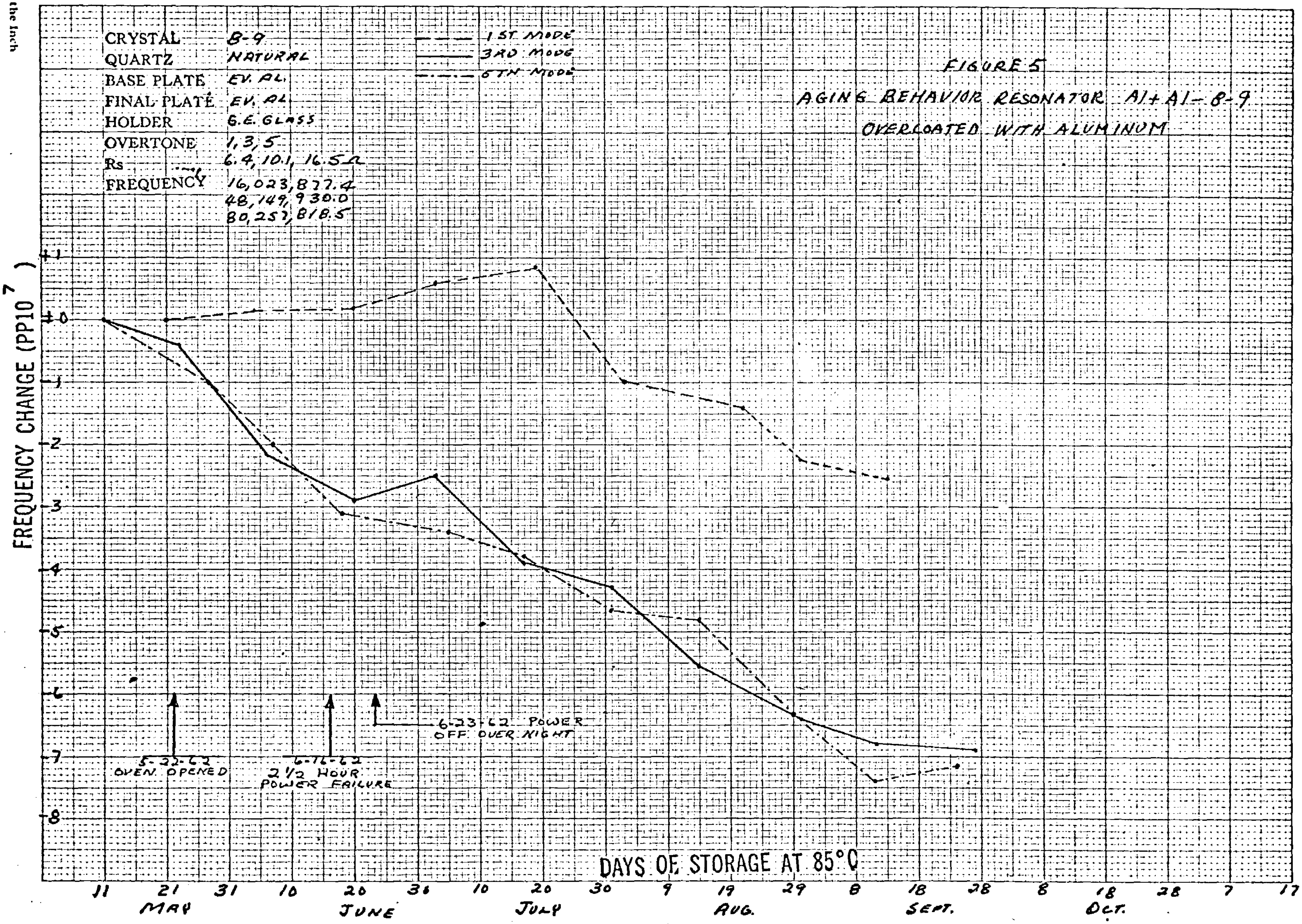
FIG 4



CRYSTAL 8-3
QUARTZ NATURAL
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER GE GLASS
OVERTONE 1, 3, & 5
Rs
FREQUENCY
1ST
3RD
5TH
FIGURE 4
AGING BEHAVIOR RESONATOR Al+Al-8-3
OVERPLATED WITH ALUMINUM
FREQUENCY CHANGE (PP10
5-22-62 OVEN OPENED
6-16-62 2½ HR POWER FAILURE
6-23-62 POWER OFF O'NITE
DAYS OF STORAGE AT 85°C
MAY
JUN
JUL
AUG
SEPT
OCT

FIG 6

FIG 5



Square to the Inch

12-282

FIG 6

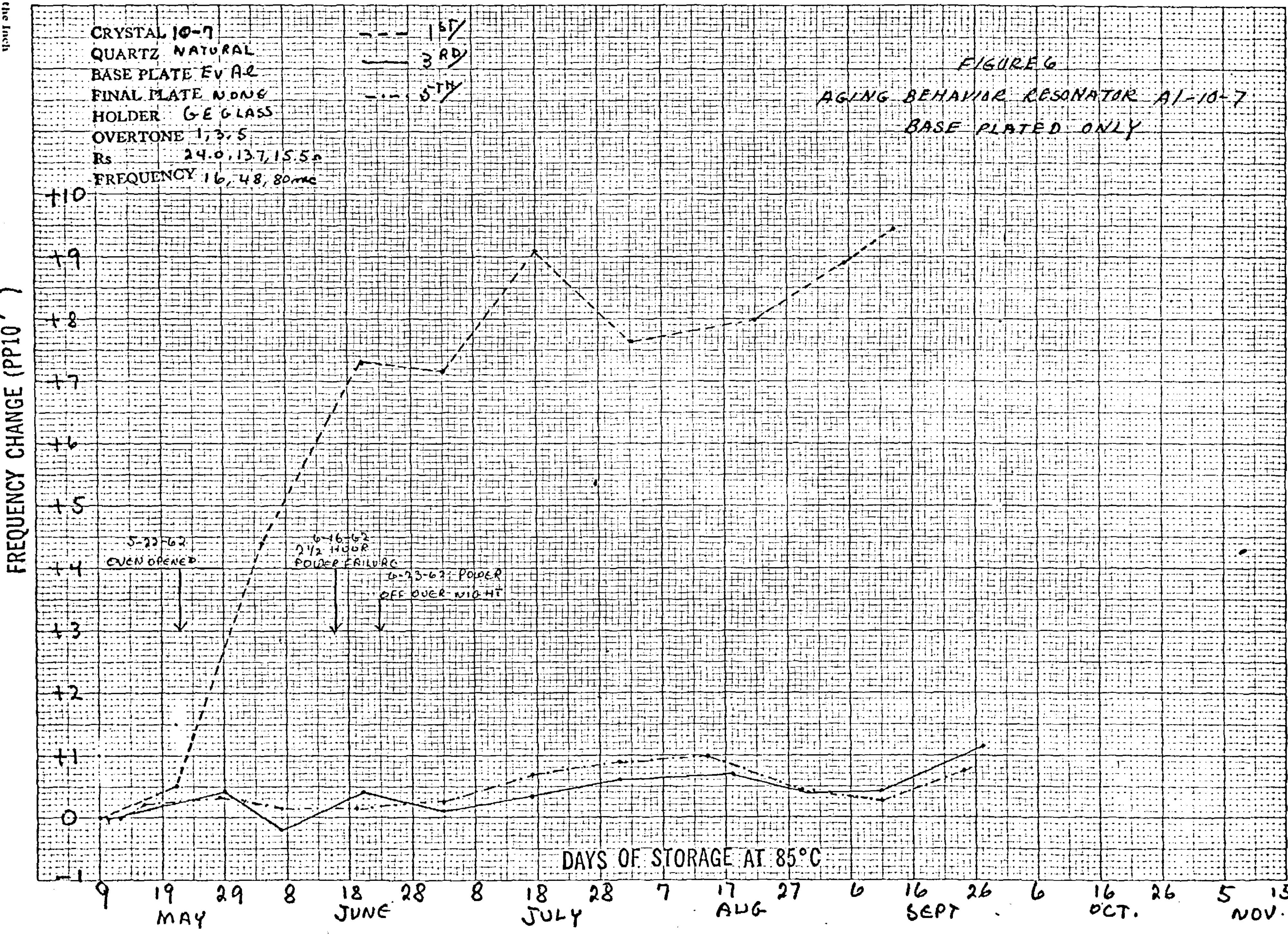

CRYSTAL 10-7
QUARTZ NATURAL
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1, 3, 5
Rs 24.0, 137, 15.5Ω
FREQUENCY 16, 48, 80mc
1ST
3RD
5TH
FIGURE 6
AGING BEHAVIOR RESONATOR A1-10-7
BASE PLATED ONLY
FREQUENCY CHANGE (PP10^7)
+10
+9
+8
+7
+6
+5
+4
+3
+2
+1
0
-1
5-23-62
OVEN OPENED
6-16-62
2½ HOUR
POWER FAILURE
6-23-62 POWER
OFF OVER NIGHT
DAYS OF STORAGE AT 85°C
9
19
29
8
18
28
8
18
28
7
17
27
6
16
26
6
16
26
5
15
MAY
JUNE
JULY
AUG
SEPT
OCT.
NOV.

FIG 7

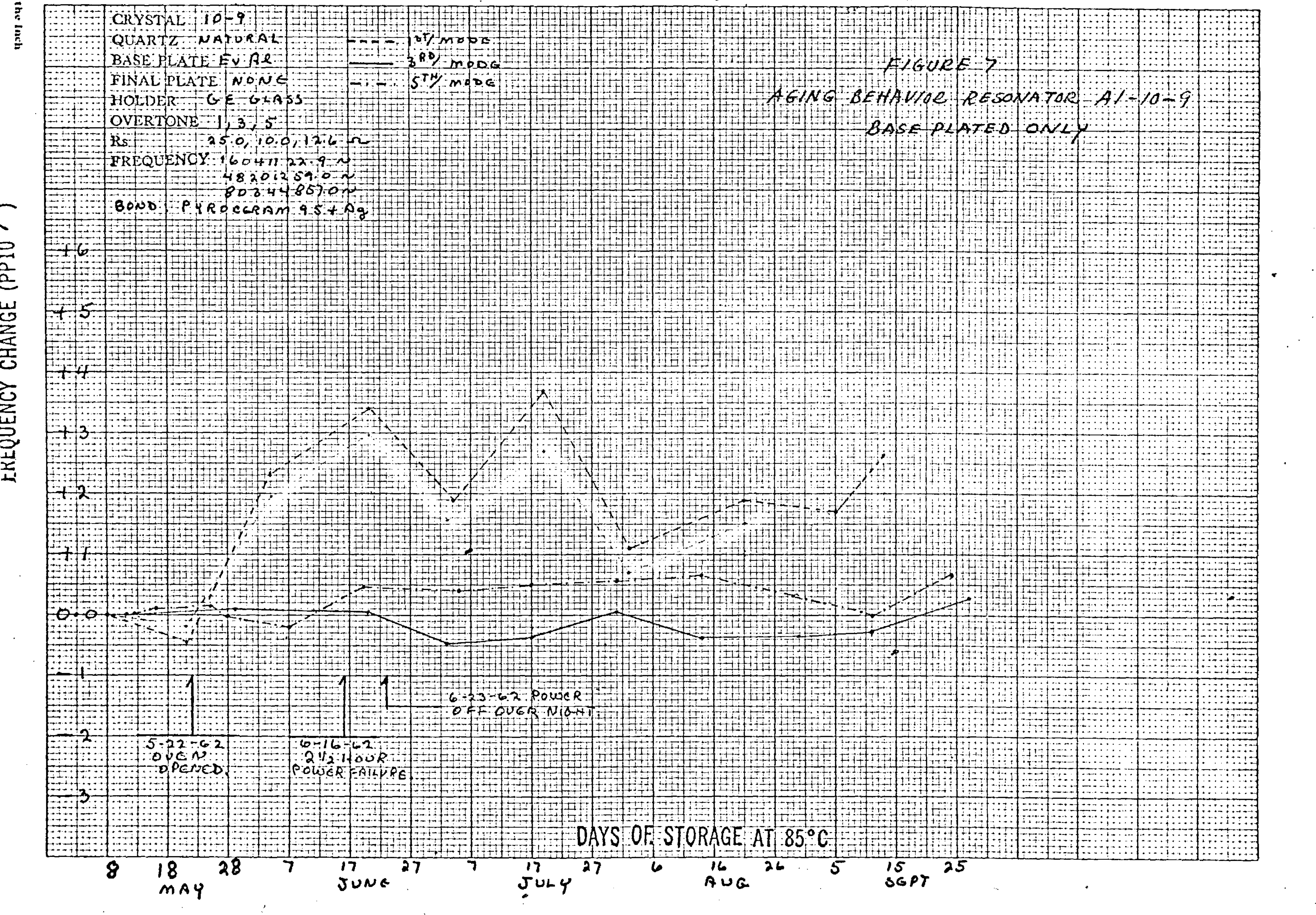

CRYSTAL 10-9
QUARTZ NATURAL
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1, 3, 5
Rs 25.0, 10.0, 12.6 Ω
FREQUENCY 16041122.9 ~
48201259.0 ~
80344857.0 ~
BOND: PYROCERAM 95 + Ag
1ST MODE
3RD MODE
5TH MODE
FIGURE 7
AGING BEHAVIOR RESONATOR A1-10-9
BASE PLATED ONLY
FREQUENCY CHANGE (PP10⁷)
+6
+5
+4
+3
+2
+1
0.0
-1
-2
-3
5-22-62
OVEN
OPENED
6-16-62
2 1/2 HOUR
POWER FAILURE
6-23-62 POWER
OFF OVER NIGHT
DAYS OF STORAGE AT 85°C
8
18
MAY
28
7
17
JUNE
27
7
17
JULY
27
6
16
AUG
26
5
15
SEPT
25

FIG 8

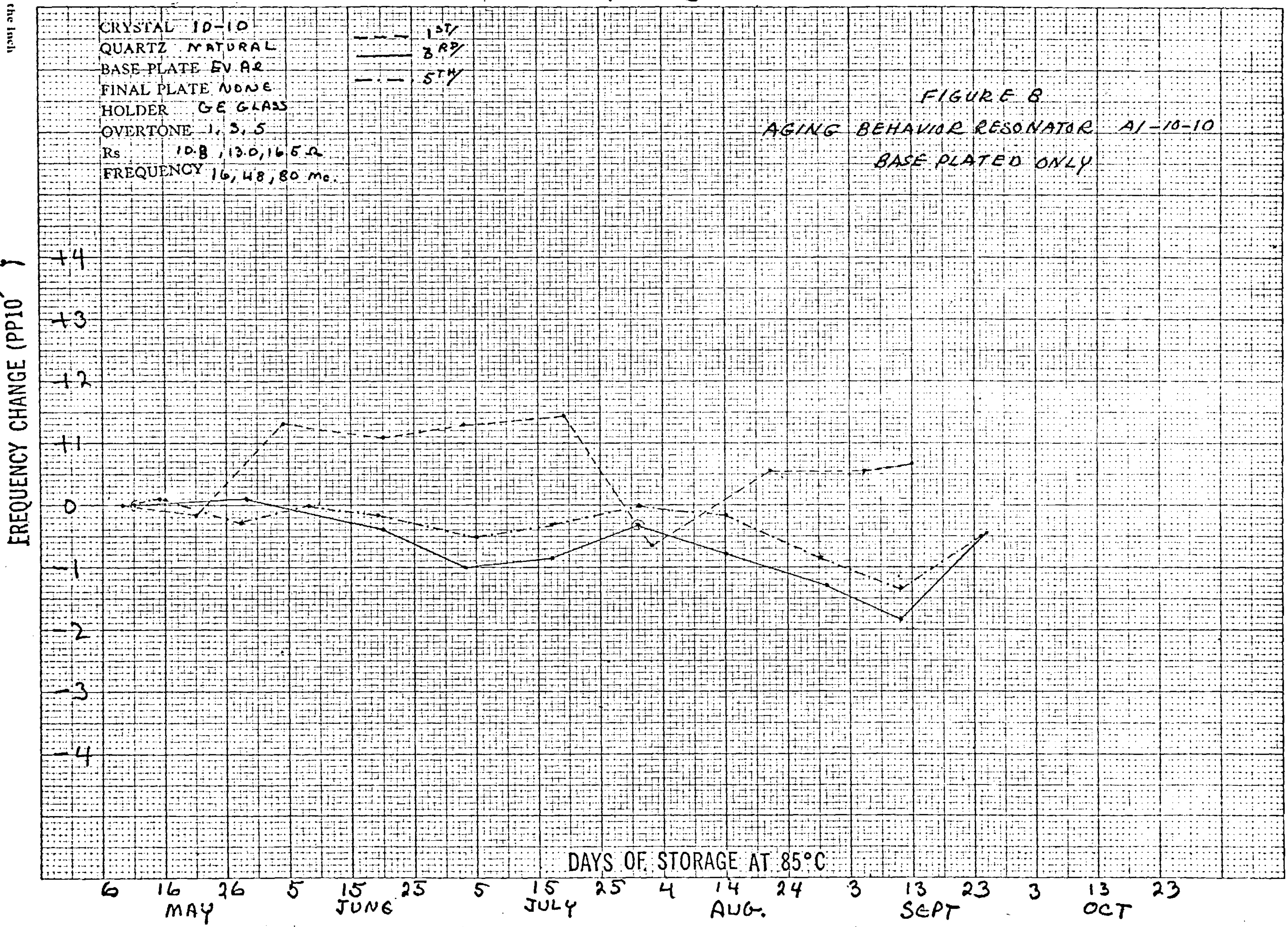
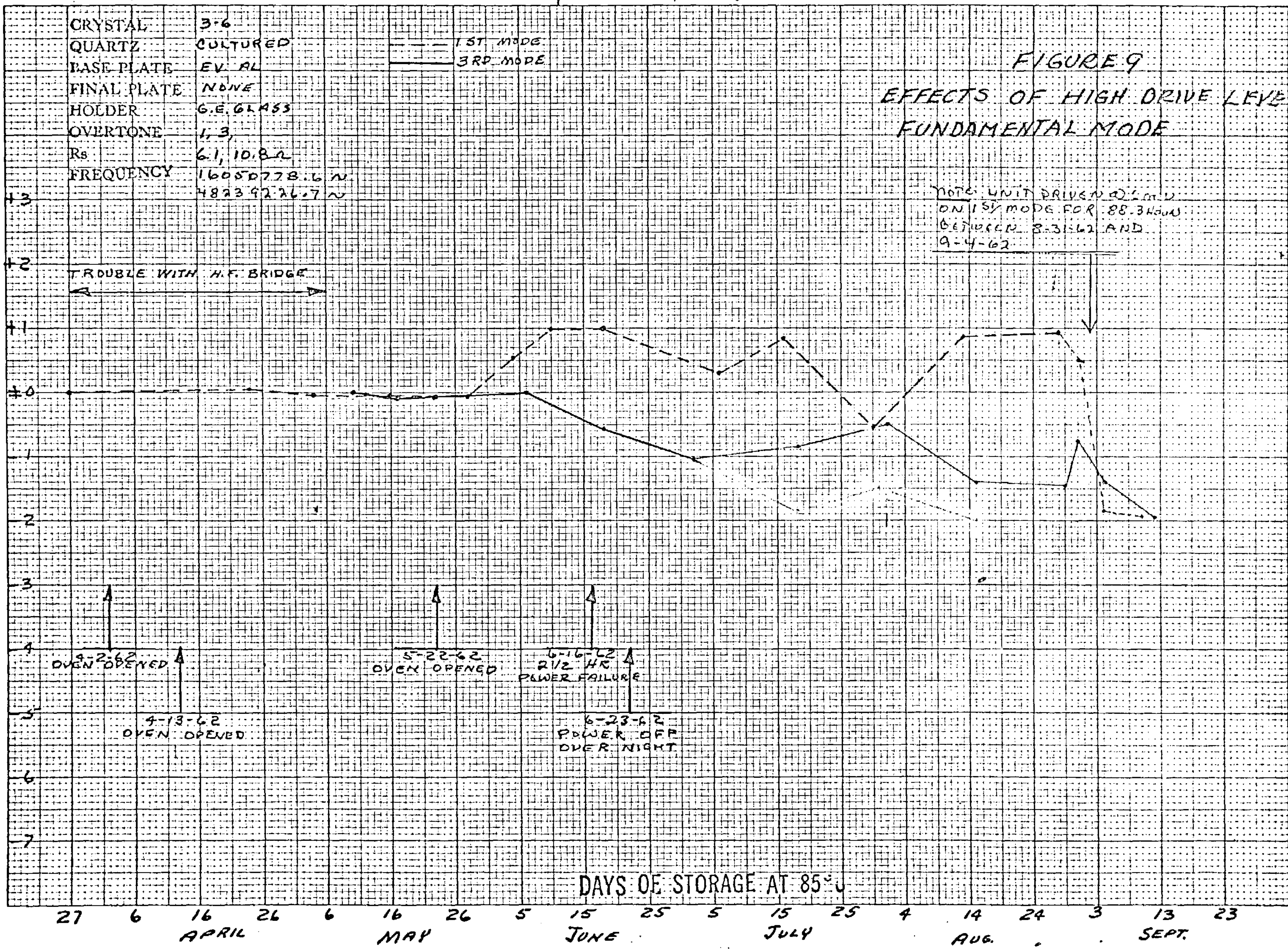
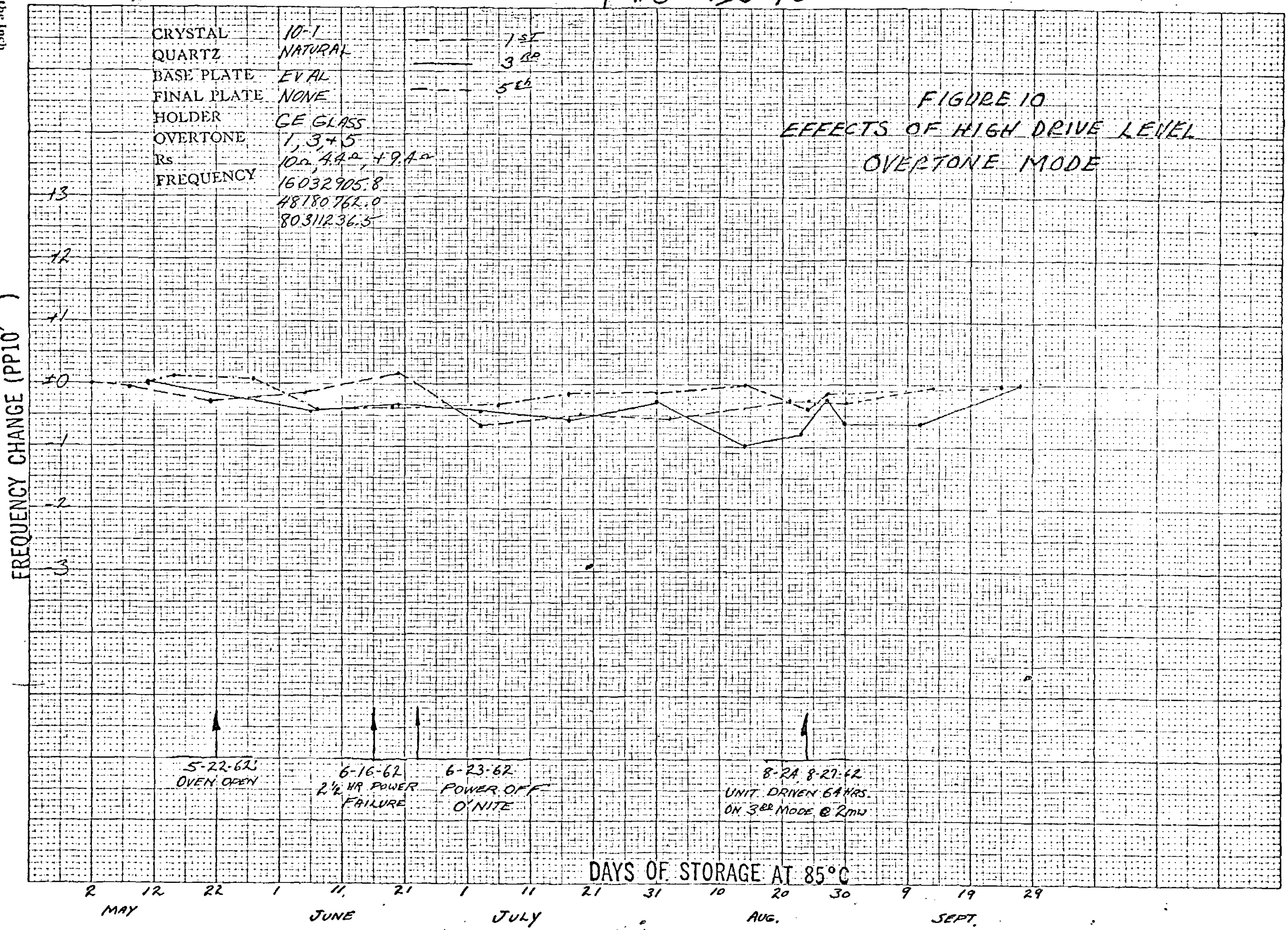

CRYSTAL 10-10
QUARTZ NATURAL
BASE PLATE EV AR
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1, 3, 5
Rs 10.8, 13.0, 16.5 Ω
FREQUENCY 16, 48, 80 Mc.
1ST
3RD
5TH
FIGURE 8
AGING BEHAVIOR RESONATOR A1-10-10
BASE PLATED ONLY
FREQUENCY CHANGE (PP10⁷)
+4
+3
+2
+1
0
-1
-2
-3
-4
DAYS OF STORAGE AT 85°C
6 16 26 5 15 25 5 15 25 4 14 24 3 13 23 3 13 23
MAY JUNE JULY AUG. SEPT OCT

FIG ~~12~~ 9



CRYSTAL 3-6
QUARTZ CULTURED
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1, 3,
Rs 6.1, 10.8Ω
FREQUENCY 16050778.6 ~
48239226.7 ~
1ST MODE
3RD MODE
FIGURE 9
EFFECTS OF HIGH DRIVE LEVEL
FUNDAMENTAL MODE
NOTE UNIT DRIVEN
ON 1ST MODE FOR 88.3 HOUR
BETWEEN 8-31-62 AND
9-4-62
TROUBLE WITH H.F. BRIDGE
FREQUENCY CHANGE (PP10 7)
4-2-62 OVEN OPENED
4-13-62 OVEN OPENED
5-22-62 OVEN OPENED
6-16-62 2 1/2 HR. POWER FAILURE
6-23-62 POWER OFF OVER NIGHT
DAYS OF STORAGE AT 85°C
27 6 16 26 6 16 26 5 15 25 5 15 25 4 14 24 3 13 23
APRIL MAY JUNE JULY AUG. SEPT.

FIG - ~~13~~ 10



CRYSTAL 10-1
QUARTZ NATURAL
BASE PLATE EV AL
FINAL PLATE NONE
HOLDER GE GLASS
OVERTONE 1, 3 + 5
Rs 10Ω, 44Ω, +9.4Ω
FREQUENCY 16032905.8
48180762.0
80311236.5
1ST
3RD
5th
FIGURE 10
EFFECTS OF HIGH DRIVE LEVEL
OVERTONE MODE
FREQUENCY CHANGE (PP10^7)
+3
+2
+1
±0
-1
-2
-3
5-22-62
OVEN OPEN
6-16-62
2½ HR POWER
FAILURE
6-23-62
POWER OFF
O'NITE
8-24 8-27-62
UNIT DRIVEN 64 HRS.
ON 3RD MODE @ 2mw
DAYS OF STORAGE AT 85°C
2 12 22 1 11 21 1 11 21 31 10 20 30 9 19 29
MAY
JUNE
JULY
AUG.
SEPT.

FIG. 11

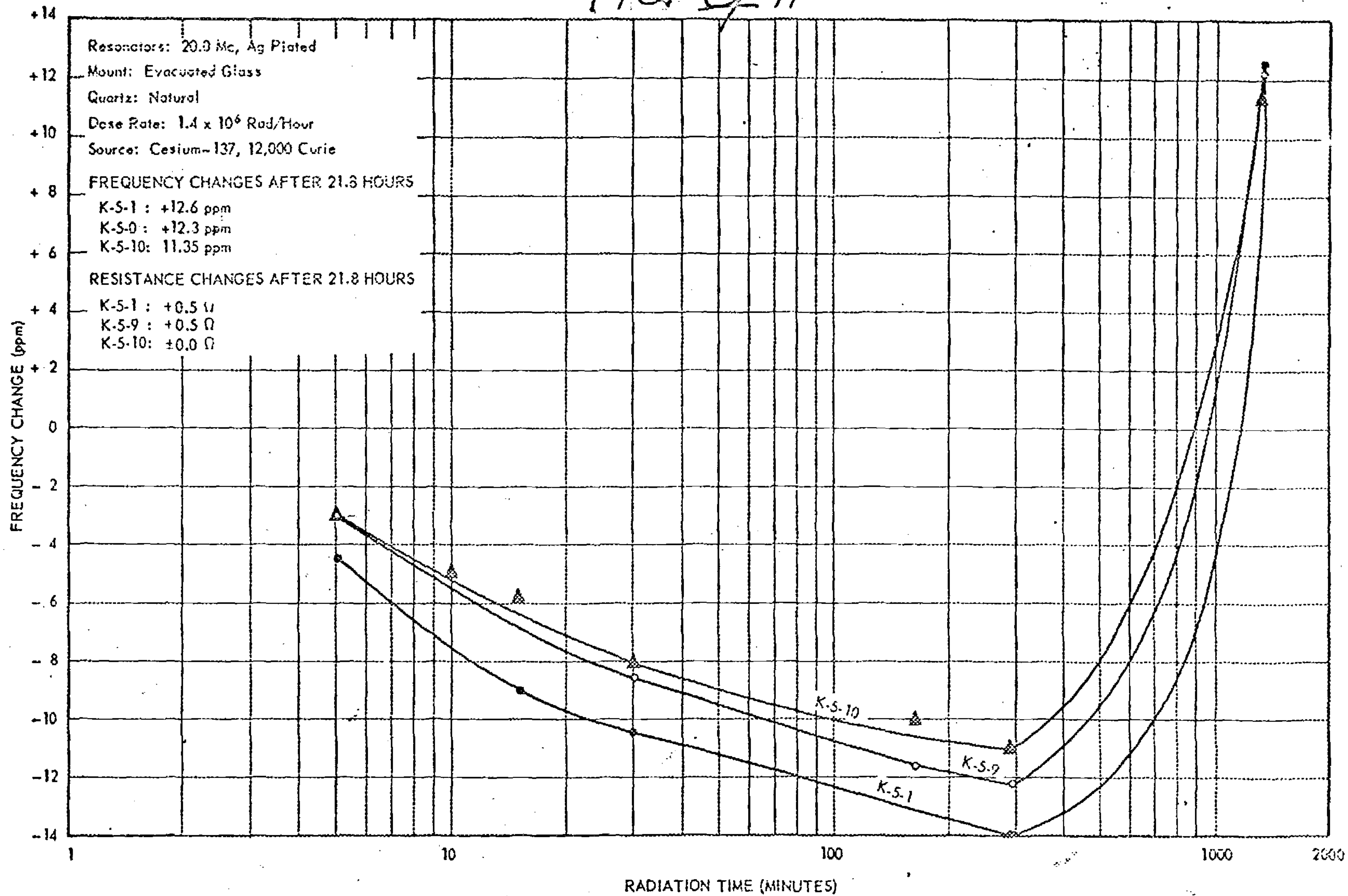
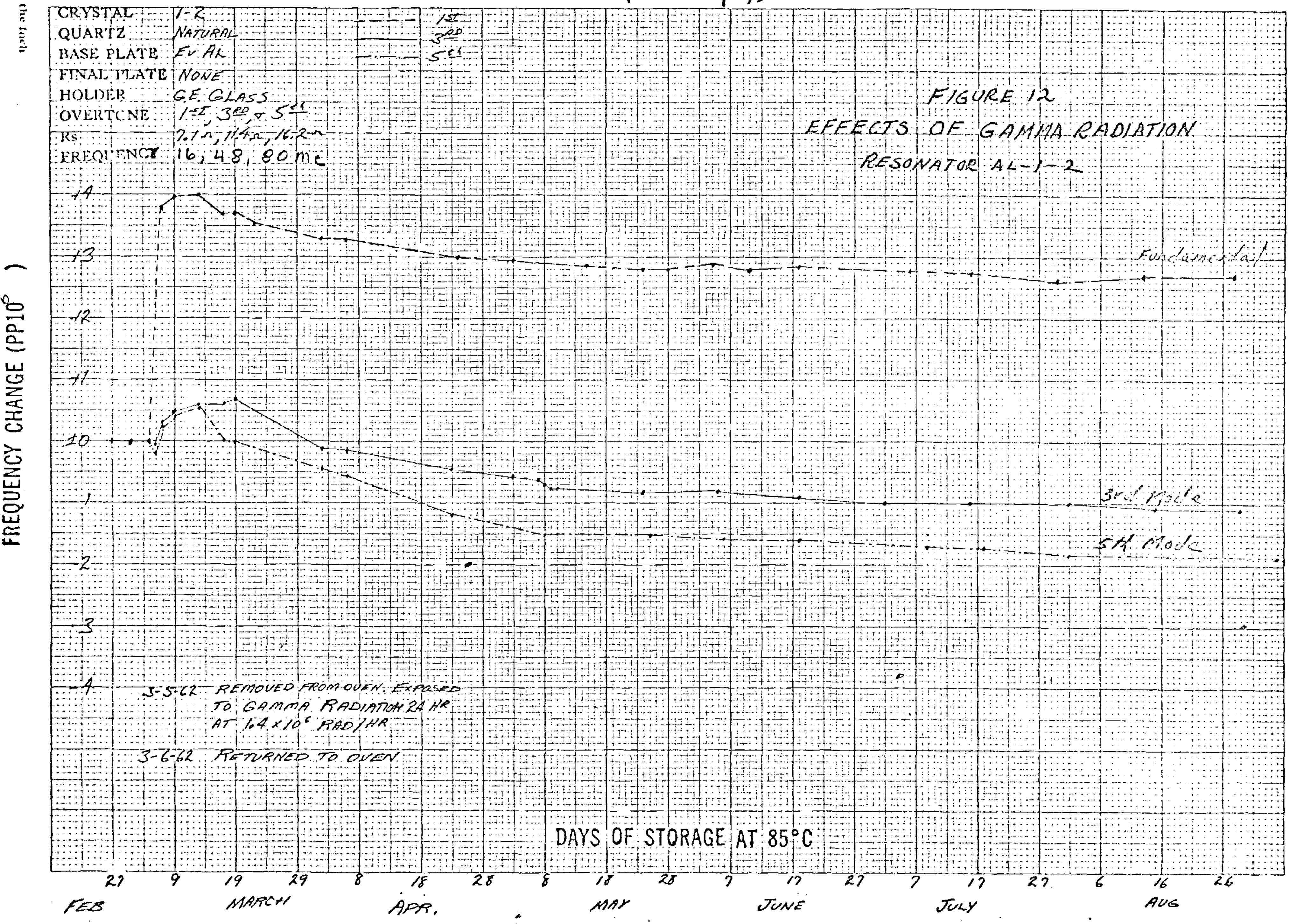


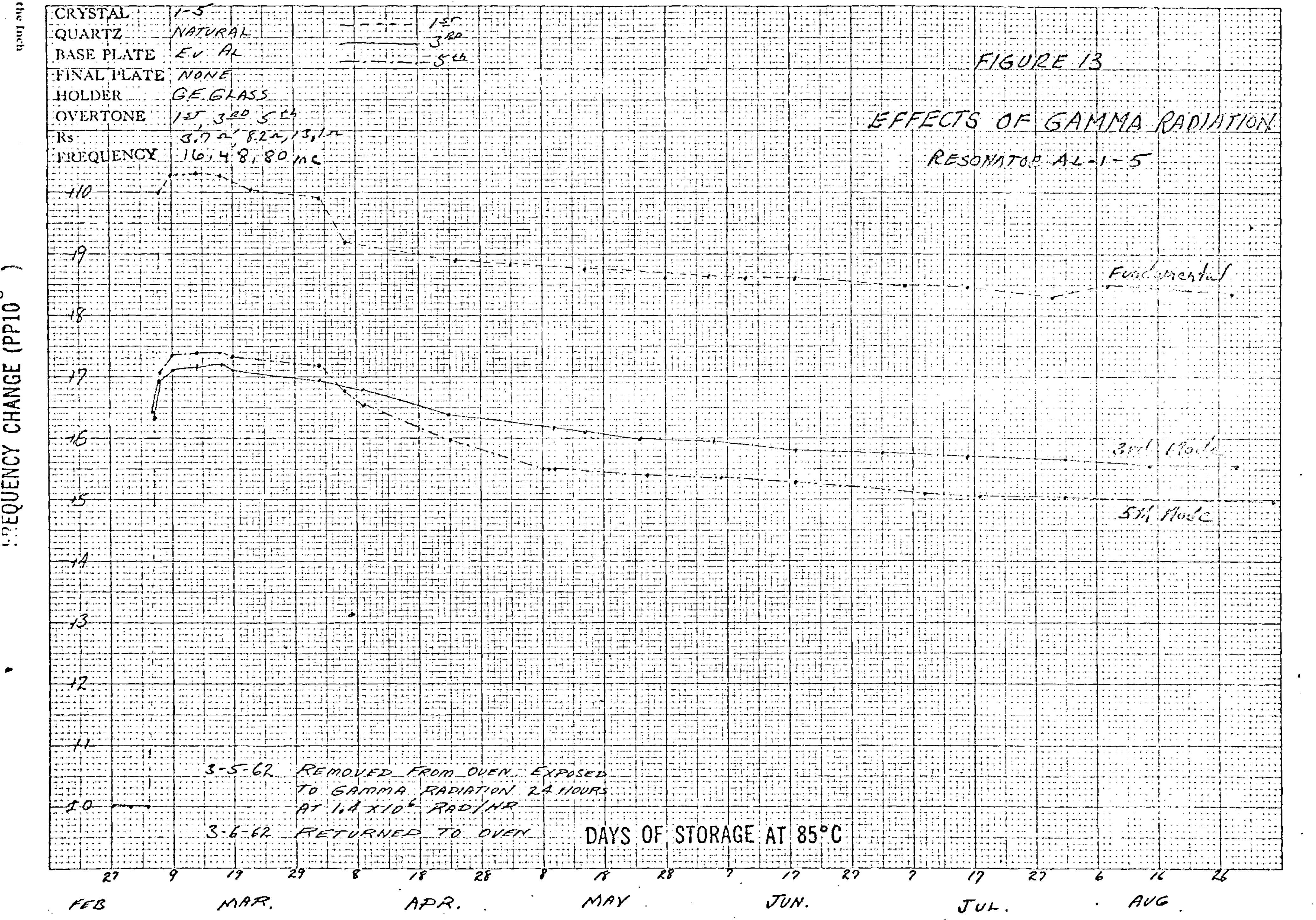
Figure 11 Frequency changes with gamma irradiation time for a 20 Mc, silver plated resonator.

FIG 12



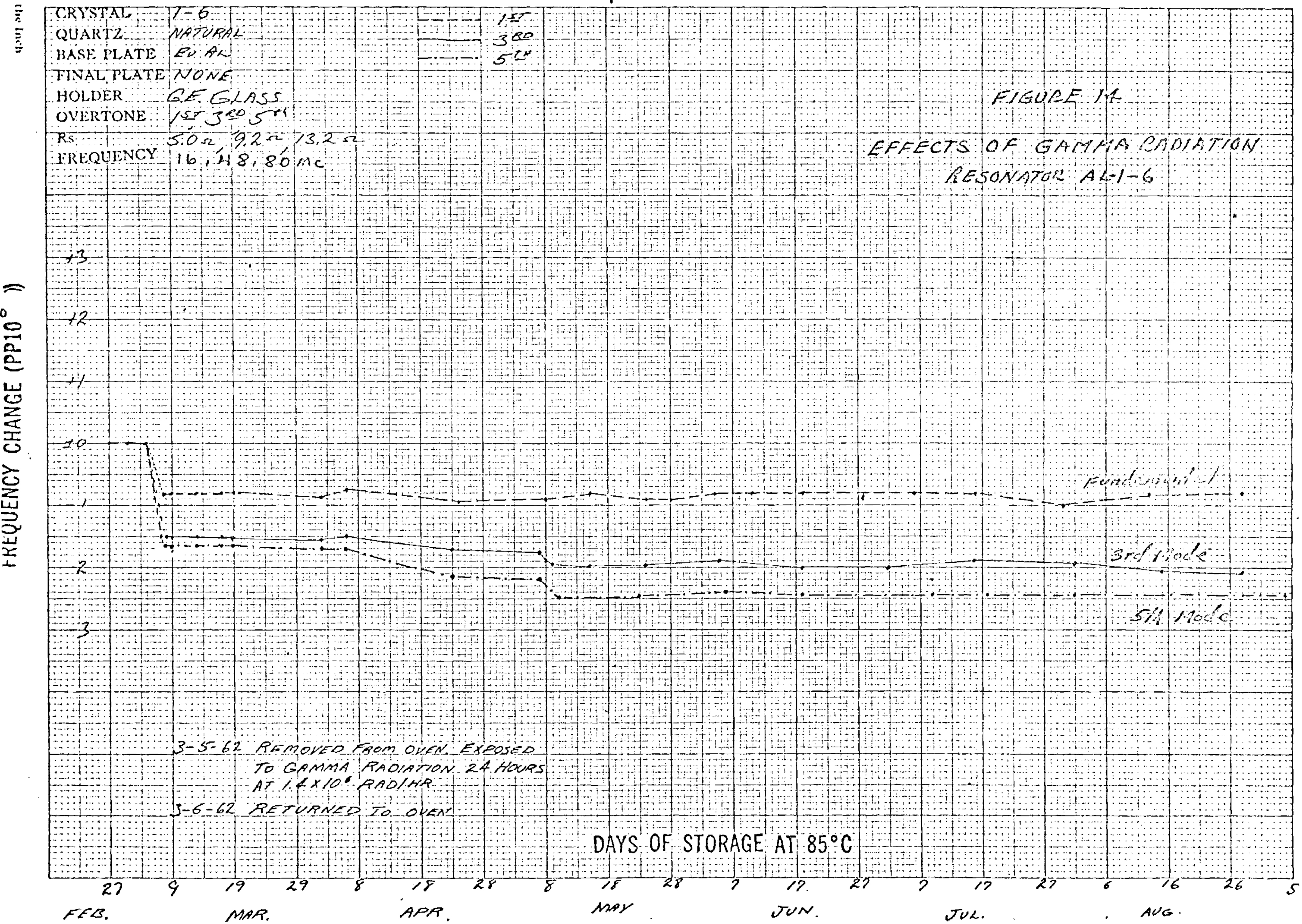
CRYSTAL 1-2
QUARTZ NATURAL
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1st, 3rd, & 5th
Rs 7.1Ω, 11.4Ω, 16.2Ω
FREQUENCY 16, 48, 80 mc
1st
3rd
5th
FIGURE 12
EFFECTS OF GAMMA RADIATION
RESONATOR AL-1-2
Fundamental
3rd Mode
5th Mode
FREQUENCY CHANGE (PP10⁶)
14
13
12
11
10
1
2
3
4
3-5-62 REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION 24 HR AT 1.4 x 10⁶ RAD/HR
3-6-62 RETURNED TO OVEN
DAYS OF STORAGE AT 85°C
27 9 19 29 8 18 28 8 18 28 7 17 27 7 17 27 6 16 26
FEB MARCH APR. MAY JUNE JULY AUG

FIG. ~~FD~~ 13



CRYSTAL 1-5
QUARTZ NATURAL
BASE PLATE Ev Al
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1ST 3RD 5TH
Rs 3.7Ω, 8.2Ω, 13.1Ω
FREQUENCY 16, 48, 80 mc
1ST
3RD
5TH
FIGURE 13
EFFECTS OF GAMMA RADIATION
RESONATOR AL-1-5
Fundamental
3rd Mode
5th Mode
FREQUENCY CHANGE (PP10
+10
+9
+8
+7
+6
+5
+4
+3
+2
+1
+0
3-5-62 REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION 24 HOURS AT 1.4 X10^6 RAD/HR
3-6-62 RETURNED TO OVEN
DAYS OF STORAGE AT 85°C
27
9
19
29
8
18
28
8
18
28
7
17
27
7
17
27
6
16
26
FEB
MAR.
APR.
MAY
JUN.
JUL.
AUG

FIG. # 14


CRYSTAL 1-6
QUARTZ NATURAL
BASE PLATE Ev. AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1ST 3RD 5TH
Rs 5.0Ω 9.2Ω 13.2Ω
FREQUENCY 16, 48, 80 mc
1ST
3RD
5TH
FIGURE 14
EFFECTS OF GAMMA RADIATION
RESONATOR AL-1-6
Fundamental
3rd Mode
5th Mode
FREQUENCY CHANGE (PP10⁸)
3-5-62 REMOVED FROM OVEN. EXPOSED TO GAMMA RADIATION 24 HOURS AT 1.4X10⁶ RAD/HR
3-6-62 RETURNED TO OVEN
DAYS OF STORAGE AT 85°C
FEB.
MAR.
APR.
MAY
JUN.
JUL.
AUG.

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

1 November 1962

Headquarters
U.S. Army Electronics Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. G. K. Guttwein
Solid State and Frequency Control Division
Piezoelectric Crystal and Circuitry Branch

Subject: Progress Letter No. 17
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 October to 1 November 1962

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

During the month of November Progress Letter No. 16 was prepared and forwarded to USAERDL. On 15 October the approved copy of Quarterly Report No. 6 was received and sent to reproduction. It was completed and sent to the Security Officer for distribution on 31 October 1962.

Three groups of crystals were fabricated during the month; the pertinent parameters of these are listed in Table I attached.

Thirty resonator units were fabricated during the month. These consisted of ten aluminum plated natural quartz resonators in which getters were flashed after seal off and 20 gold plated units fabricated of natural, swept natural, cultured, and swept cultured quartz. The total yield of units was 26 giving four or five each of the latter four categories of units. More complete details concerning fabrication parameters are listed in the Table I attached.

It is planned to measure the frequency versus time data for these resonators by utilizing the Rohde and Schwarz frequency synthesizer as the RF generator and the necessary accessory equipment. This will give accuracies up to $\pm$ 1 cycle and will allow ready measurement at the fundamental, third and fifth modes. However, the gold plated resonators exhibit a relatively high resistance at the fifth mode and will not be measured at this mode. The gold was employed because, in this particular case, the types of quartz in the blanks is the principal interest and gold has proven to be the most reliable and reproducible plating material for minimum aging ascribable to fabrication.

On 15 October 1962 three cultured and three swept, cultured quartz units, mounted in HC-27/U holders, and not previously irradiated, were removed from an 85°C oven, exposed to gamma irradiation of a cesium Ce 137 source for 24 hours and returned to the oven. The dose level was approximately 1.4×10^6 Rad./Hr.

The frequency changes produced by the irradiation are given in Table II which is attached. It will be noted that the cultured quartz blanks underwent large (about 28 ppm) frequency shifts whereas the swept cultured quartz underwent only small ones (< 2 ppm).

The apparent superiority of the swept quartz from the standpoint of its ability to withstand damage due to radiation effects is thus dramatically illustrated. However additional information similar to that which has already been reported for natural quartz, must be obtained in order to define the expected behavior of resonators made from the different kinds of quartz. The position with respect to total frequency change of the various types of units on an irradiation time vs frequency curve will probably allow prediction of aging to be expected.

The subsequent aging data on the gamma irradiated units is only limited in nature. The frequency changes obtained for the swept cultured units have been slightly positive whereas three of the readings of the unswept units have been negative. All are small, of the order of one half ppm. Due to the limited measurements completed thus far and the possibility of effects due to temperature cycling on removal and replacement, no prediction as to future aging can be made at this time.

Frequency measurements of units for routine aging studies at the fundamental, 3rd and 5th modes have been continued. No unusual developments have been noted.

Measurements of the resonators exposed to high intensity pulsed neutron radiation were continued. It is evident from the data that the radiation received by the resonators produced no damage that would lead to subsequent frequency changes, resistance changes, or other changes affecting appreciably the aging rates of the resonators.

The program for the month of November includes:

1. Continued frequency and other electrical measurements of all units presently stored at 85°C;
2. Fabrication of a group of swept, natural quartz units in HC-27/U holders for continued gamma radiation studies; and

3. Fabrication of one group of special units for measurements in the Marconi high precision temperature control oven.

Respectfully submitted,

Richard B. Belser
Project Director

RBB:md

Addressee: 5

Enclosures: Tables I and II

TABLE I

Parameters of Resonators Fabricated in October, 1962

Group	No. of Units	Yield (o/o)	Quartz	Base Plate	Support	Bonding Cement	Holder	Remarks
G	8	80	Natural	Al	0.006" Springs	DuPont 5504A	T/5 1/2	Holder Vac. Baked and Gettered
14	9	90	4-Natural 5-Swpt. Nat.	Au	0.006" Springs	DuPont 5504A	T/5 1/2	Holder Vac. Baked Only
15	9	90	4-Cultured 5-Swpt. Cult.	Au	0.006" Springs	DuPont 5504A	T/5 1/2	Holder Vac. Baked Only

TABLE II

Frequency Changes Experienced by Resonators Exposed to Gamma Radiation from Ce 137 Source for 24 hours*

Unit	Quartz	AF(PPM) 1st. Mode	AF(PPM) 3rd. Mode	ΔZ* 1st. Mode	ΔZ* 3rd. Mode
Al-3-7	Cultured	+28.2	+27.3	-5.5	±0.0
Al-3-8	Cultured	+28.4	+28.8	+2.0	±1.5
Al-3-9	Cultured	+29.2	+29.8	- -	+0.5
Al-5-1	Swpt. Cultured	-0.6	-0.3	-5.5	-2.0
Al-5-3	Swpt. Cultured	±1.1	-0.5	-1.5	±0.0
Al-5-4	Swpt. Cultured	-0.4	-0.3	±0.0	±0.0

- - - - -

Z is a direct function of R_s and is obtained from the calibration dial of an impedance bridge.

*Total Dose: Approximated 1.4 Rad./Hr. for approximately 24 hours.

GEORGIA INSTITUTE OF TECHNOLOGY

ENGINEERING EXPERIMENT STATION

ATLANTA 13, GEORGIA

1 January 1963

Headquarters
U. S. Army Electronics Research and Development Laboratory
Fort Monmouth, New Jersey

Attention: Dr. G. K. Guttwein
Solid State and Frequency Control Division
Piezoelectric Crystal and Circuitry Branch

Subject: Progress Letter No. 18
Contract No. DA-36-039-SC-87407
Georgia Tech Project No. A-552
Period: 1 December 1962 to 1 January 1963

Dear Sir:

The purpose of this project is to delineate the effects of materials and fabrication techniques on stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes and a comparison between the stabilities of resonators fabricated of natural, synthetic, and swept synthetic quartz. A frequency measurement accuracy of a few parts in 10^9 is desired.

During the month of December Quarterly Report No. 7 was completed. Approved copies were sent to USAERDL. No monthly progress letter was submitted for November since Report No. 7 was being prepared.

Work on the project during the month was limited principally to frequency measurements since sufficient resonators have already been fabricated to meet the principal objectives of the current program.

The most recently fabricated units (groups 14 through 20 and group G) have been stored at 85°C for thirty days or more. As the units mature, behavior patterns for the different groups and for certain units of the same group can be detected.

Groups 14 and 15 were intended to be identical except for the types of quartz used. Group 14 units were fabricated using swept and unswept natural quartz. Group 15 units were fabricated of swept and unswept cultured quartz.

Figure 1 illustrates the data for a gold plated unit of group 14. This resonator was fabricated of unswept, natural quartz. The data for a similar unit of swept, natural quartz are shown in Figure 2.

FIGURE 1

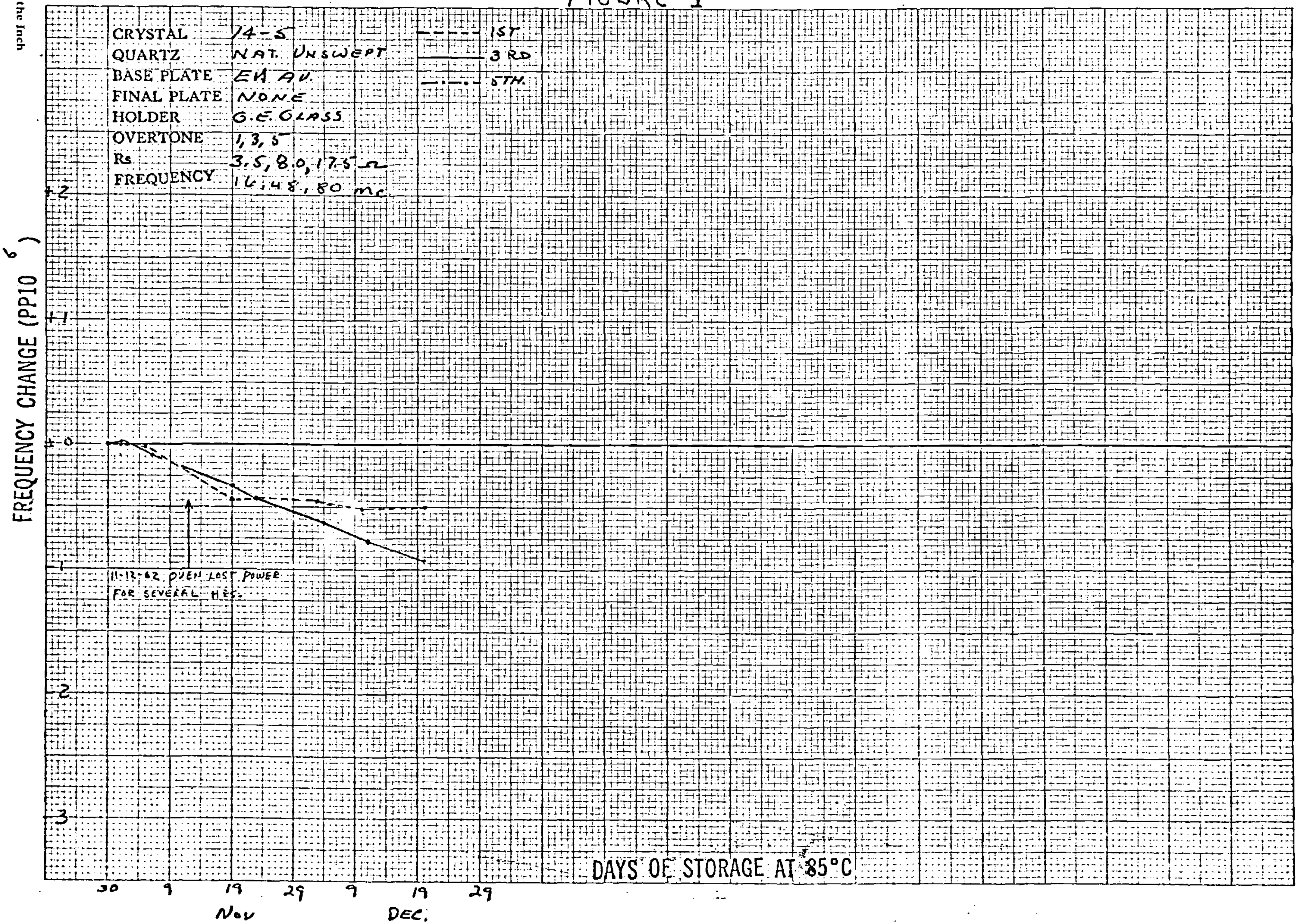

CRYSTAL 74-5
QUARTZ NAT. UNSWEPT
BASE PLATE EH AU.
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1, 3, 5
Rs 3.5, 8.0, 17.5 Ω
FREQUENCY 16, 48, 80 mc
1ST
3RD
5TH.
FREQUENCY CHANGE (PP10 6)
+2
+1
0
1
2
3
11-12-62 OVEN LOST POWER
FOR SEVERAL HRS.
DAYS OF STORAGE AT 85°C
30
9
19
29
9
19
29
Nov
DEC.

FIGURE 2

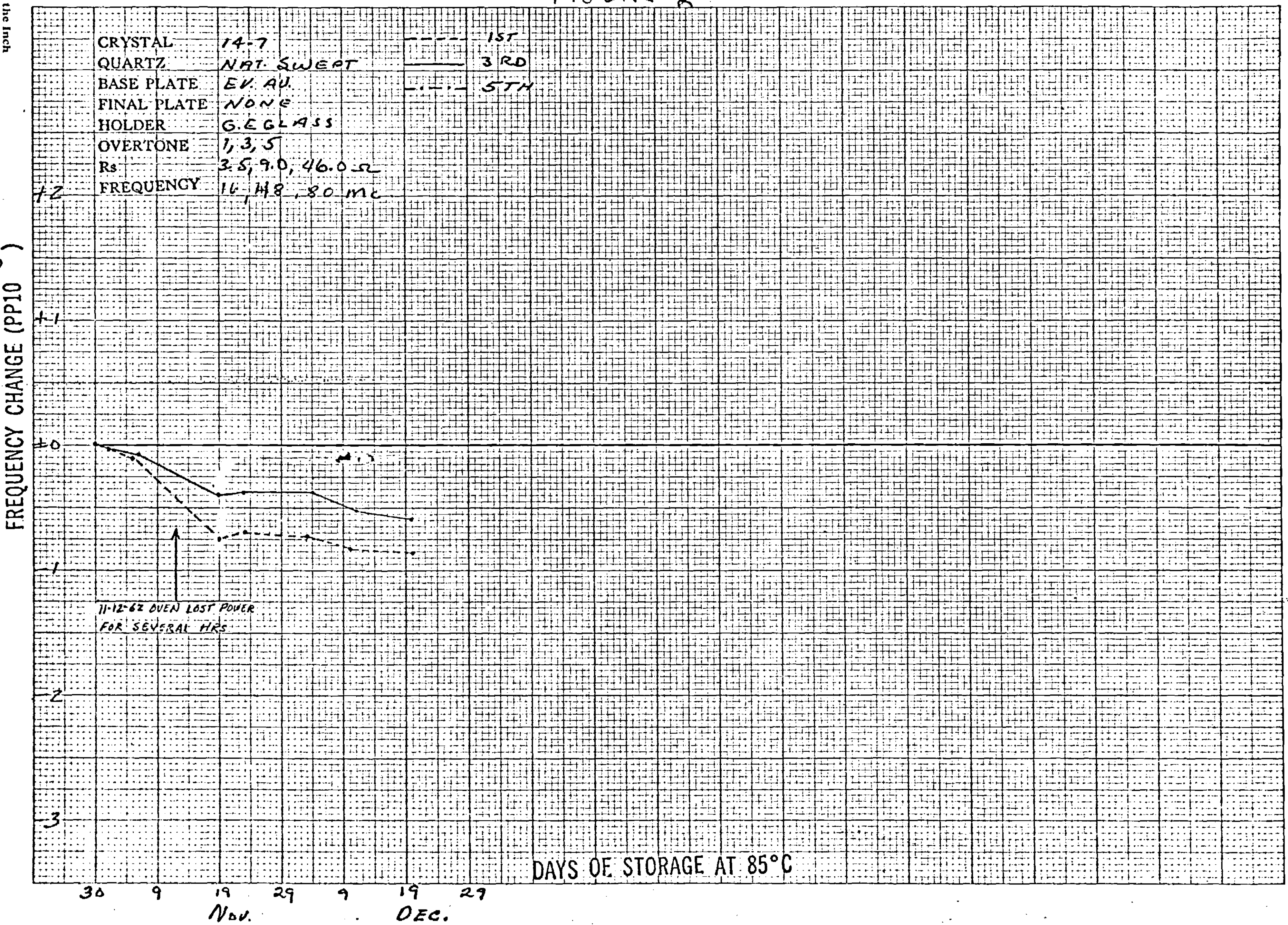
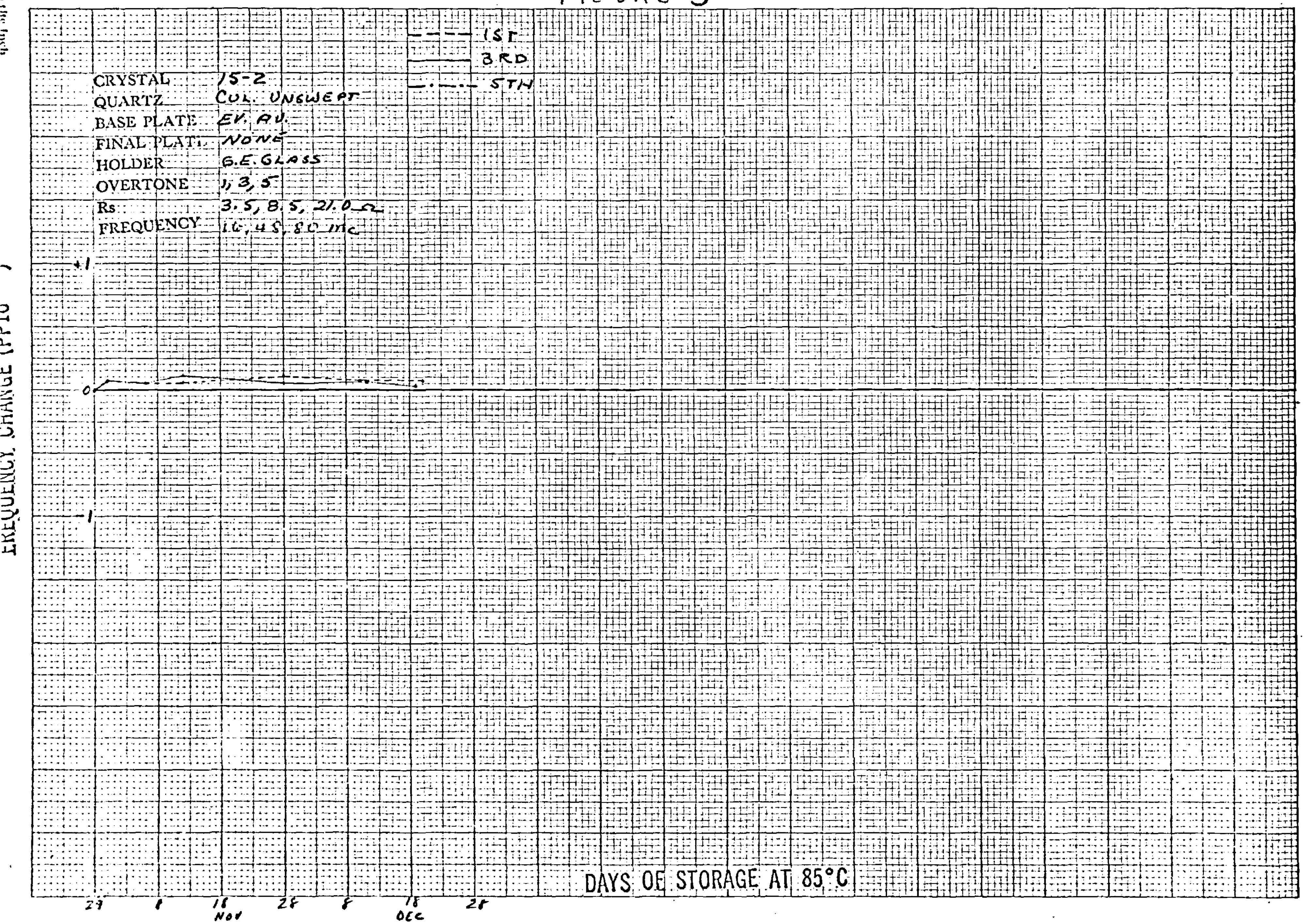
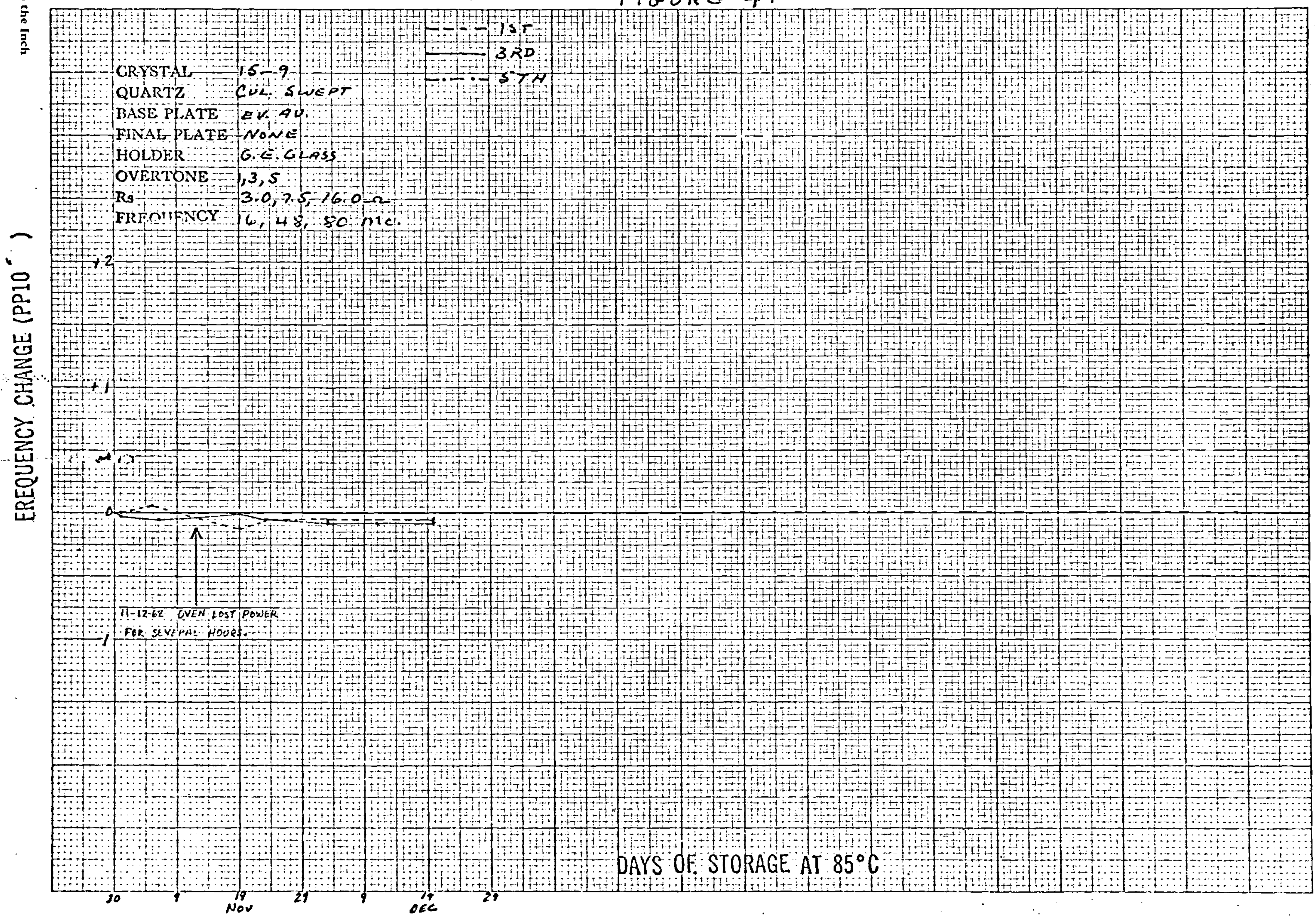

CRYSTAL 14-7
QUARTZ NAT. SWEPT
BASE PLATE EV. AU.
FINAL PLATE NONE
HOLDER G.E GLASS
OVERTONE 1, 3, 5
Rs 3.5, 9.0, 46.0 Ω
FREQUENCY 16, 48, 80 mc
1ST
3 RD
5TH
FREQUENCY CHANGE (PP10 6)
+2
+1
±0
-1
-2
-3
11-12-62 OVEN LOST POWER
FOR SEVERAL HRS
DAYS OF STORAGE AT 85°C
30
9
19
29
9
19
29
NOV.
DEC.

FIGURE 3



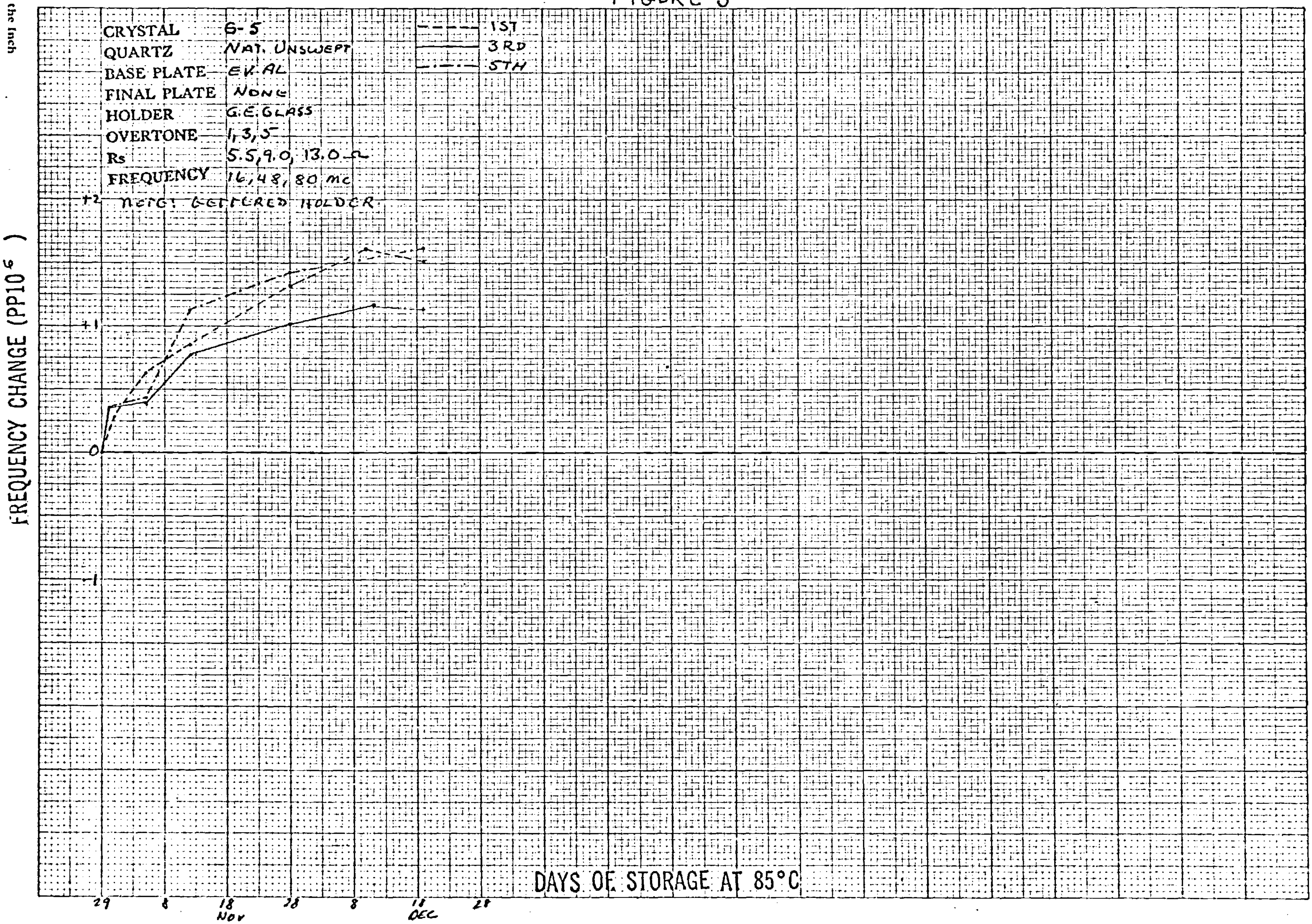
12-282

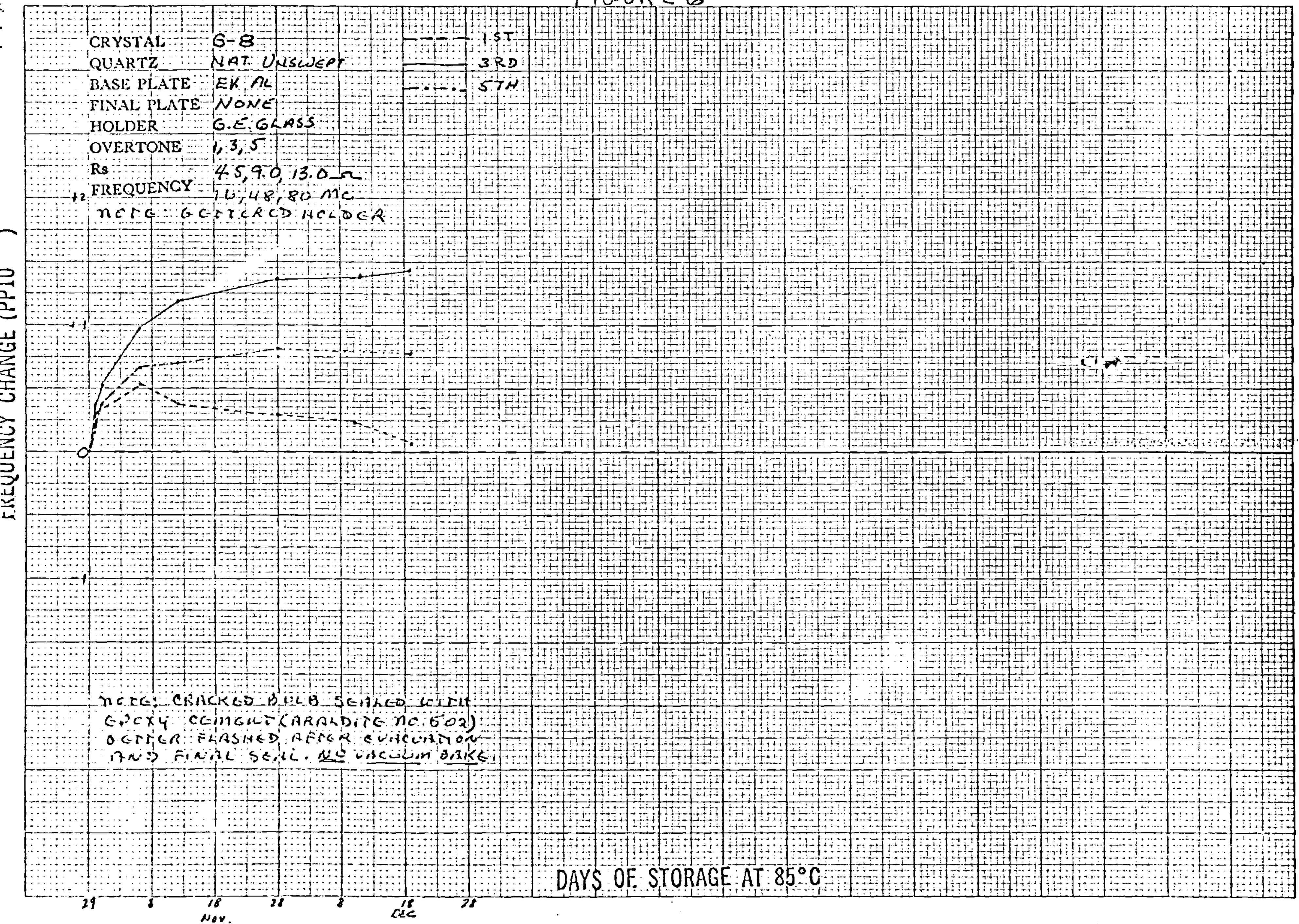
FIGURE 4.



1ST
3RD
5TH
CRYSTAL 15-9
QUARTZ CUL. SWEPT
BASE PLATE EV. AU.
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1,3,5
Rs 3.0, 7.5, 16.0 Ω
FREQUENCY 16, 48, 80 MC.
+2
+1
0
-1
11-12-62 OVEN LOST POWER FOR SEVERAL HOURS.
FREQUENCY CHANGE (PP10⁶)
DAYS OF STORAGE AT 85°C
30
9
19 NOV
29
9
19 DEC
29

FIGURE 5

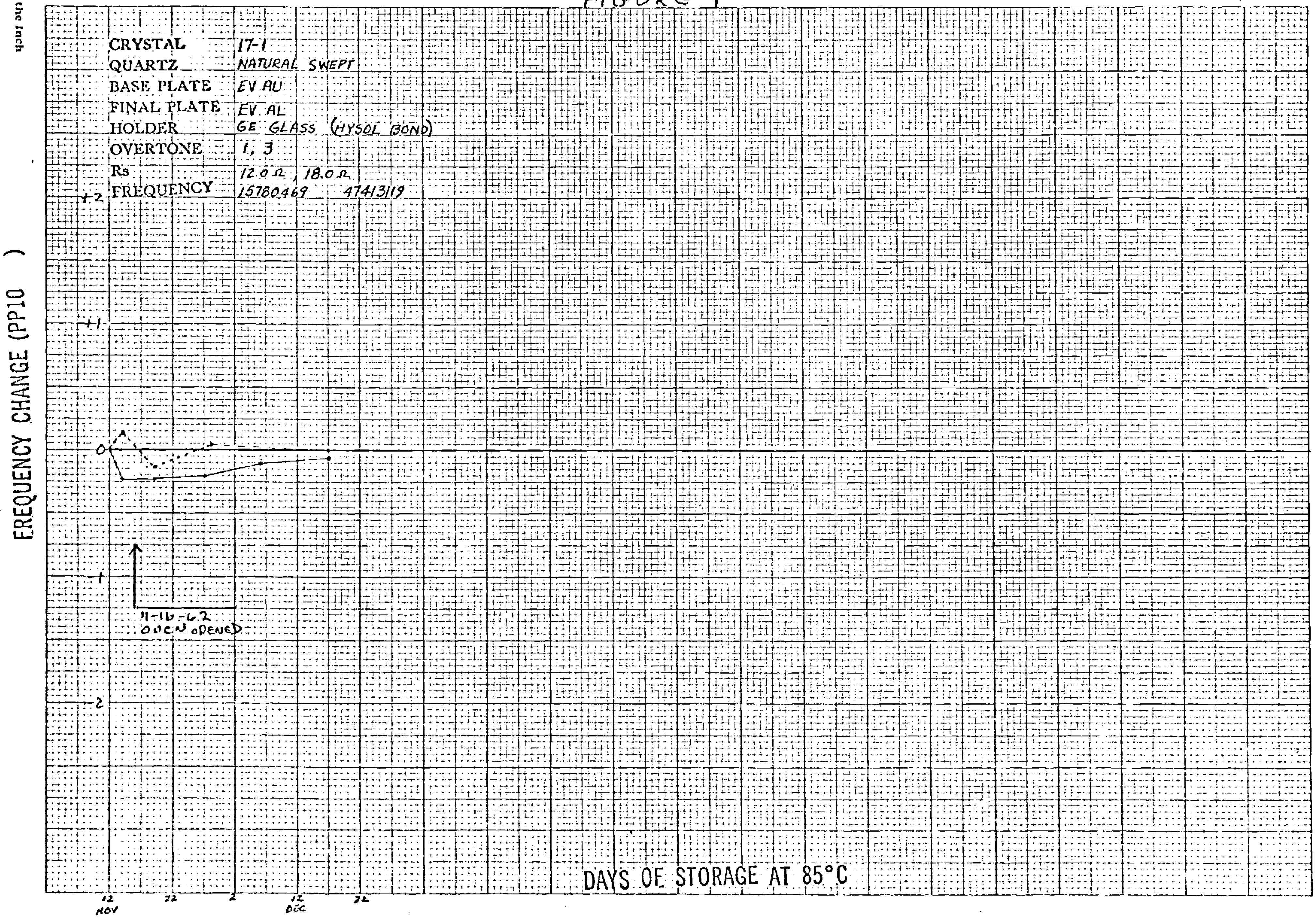

CRYSTAL 6-5
QUARTZ NAT. UNSWEPT
BASE PLATE EV. AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1, 3, 5
Rs 5.5, 9.0, 13.0 Ω
FREQUENCY 16, 48, 80 mc
1ST
3RD
5TH
+2
+1
0
-1
FREQUENCY CHANGE (PP10⁶)
DAYS OF STORAGE AT 85°C
29
8
18
NOV
28
8
18
DEC
28



CRYSTAL 6-8
QUARTZ NAT. UNSWEPT
BASE PLATE EK AL
FINAL PLATE NONE
HOLDER G.E. GLASS
OVERTONE 1, 3, 5
Rs 4.5, 9.0, 13.0 Ω
FREQUENCY 16, 48, 80 MC
NOTE: GETTERED HOLDER
1ST
3RD
5TH
+2
+1
-1
FREQUENCY CHANGE (PP10)
NOTE: CRACKED BULB SEALED WITH EPOXY CEMENT (ARALDITE NO. 502) GETTER FLASHED AFTER EVACUATION AND FINAL SEAL. NO VACUUM BAKE.
DAYS OF STORAGE AT 85°C
29
8
18
28
8
18
28
NOV.
DEC

FIGURE 6

FIGURE 7



12-282

FIGURE 8

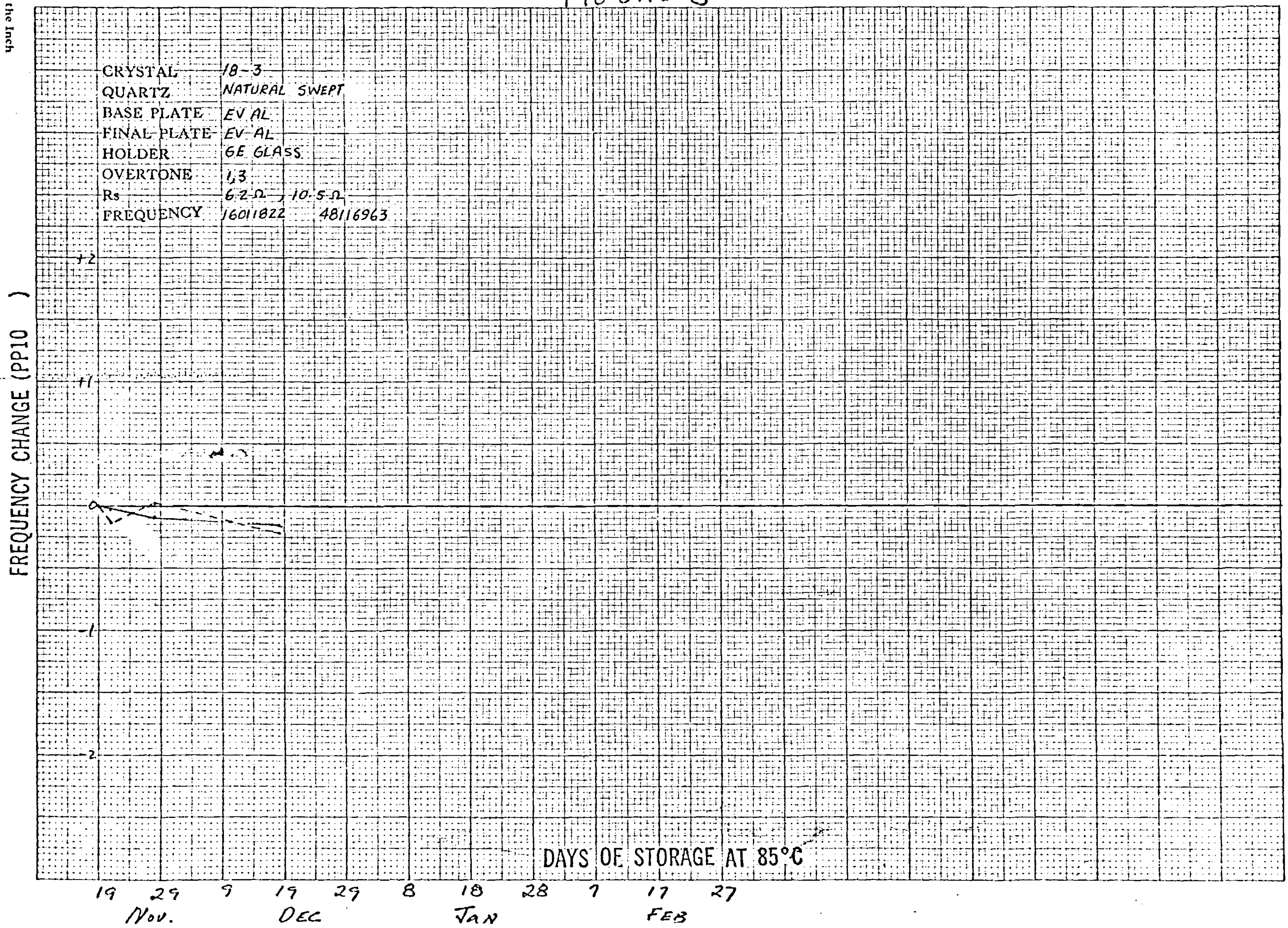

CRYSTAL 18-3
QUARTZ NATURAL SWEPT
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER GE GLASS
OVERTONE 1,3
Rs 6.2 Ω , 10.5 Ω
FREQUENCY 16011822 48116963
FREQUENCY CHANGE (PP10)
+2
+1
-1
-2
DAYS OF STORAGE AT 85°C
19 29 9 19 29 8 18 28 7 17 27
Nov. Dec Jan Feb

FIGURE 9

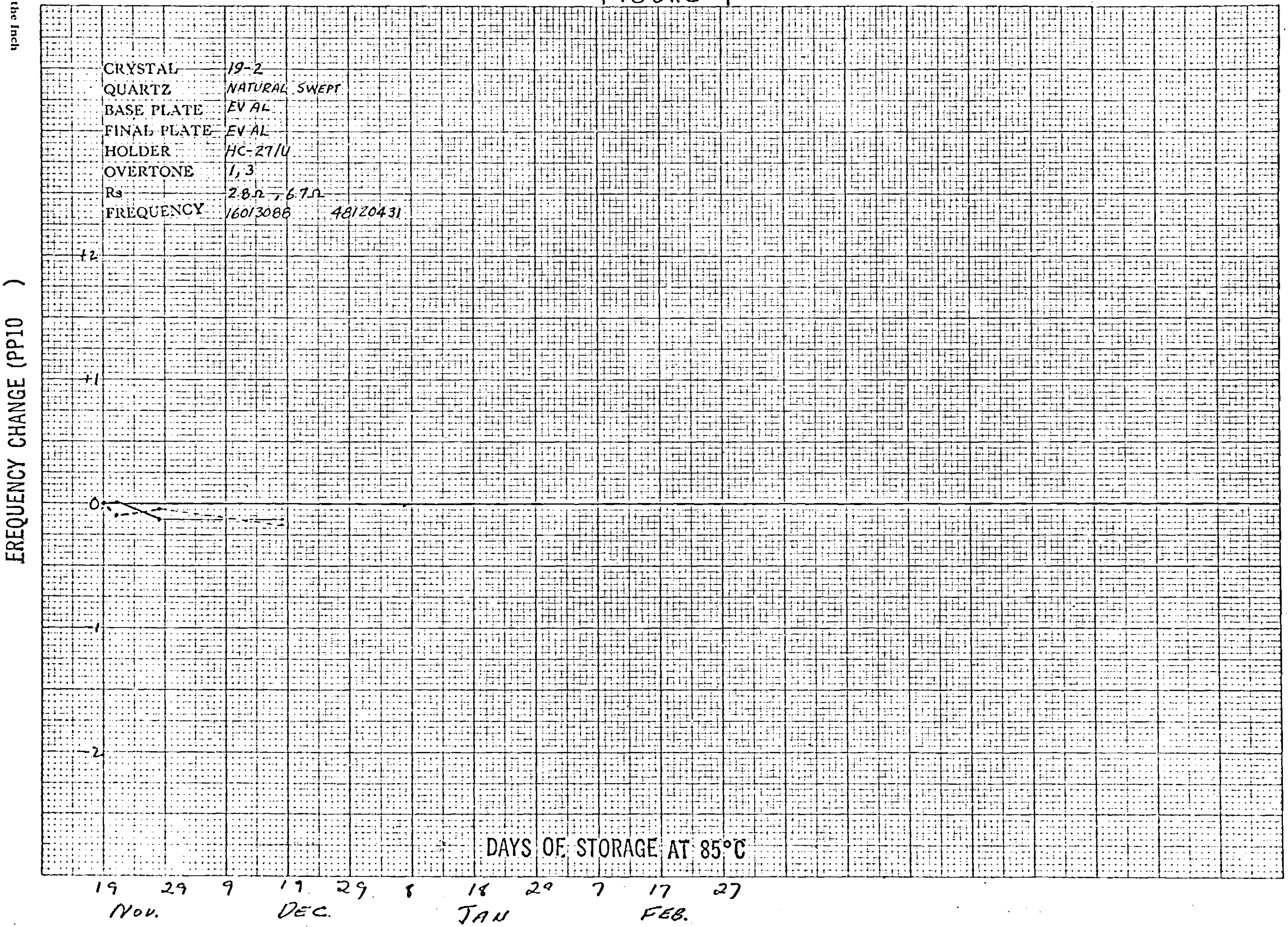
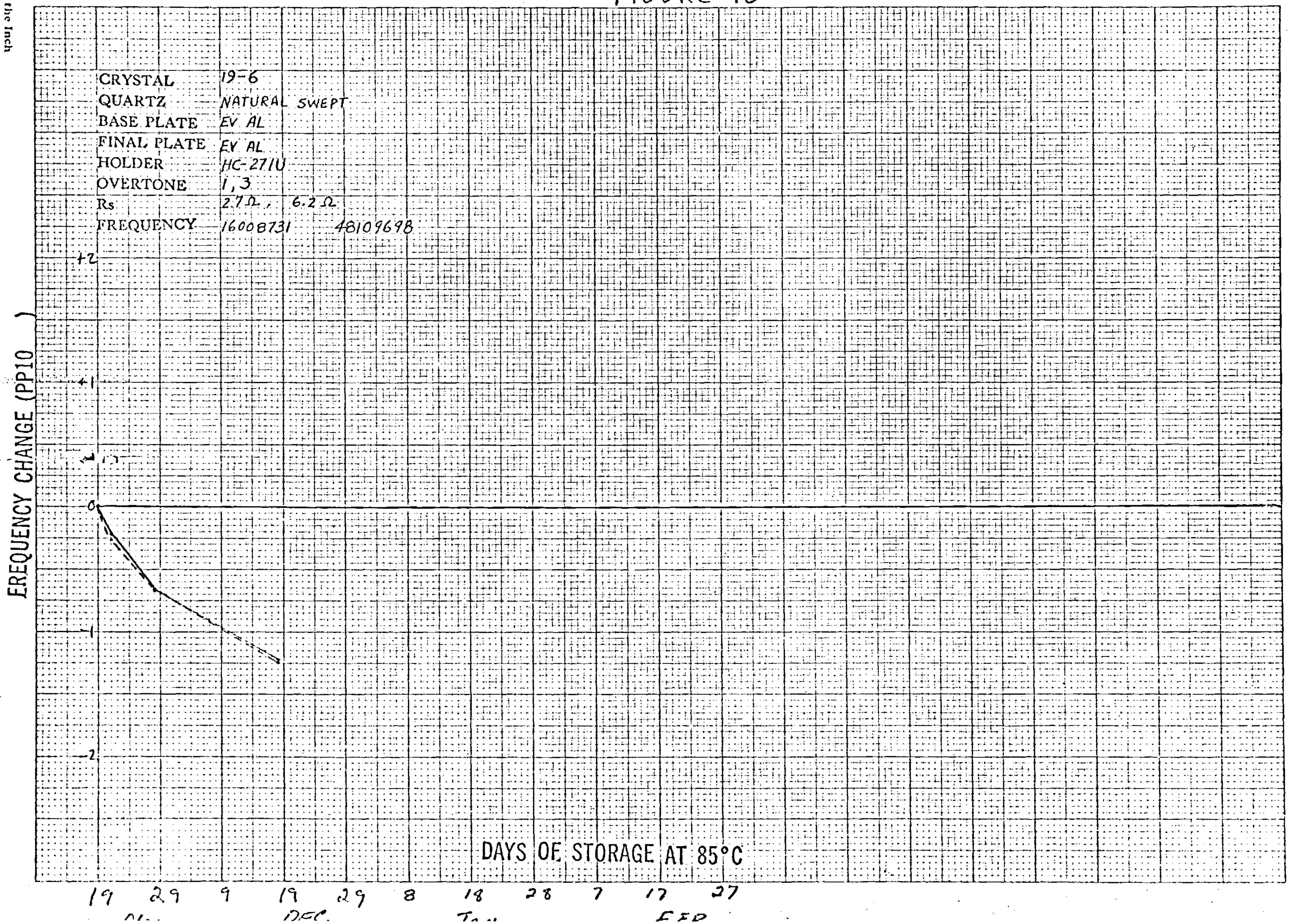

CRYSTAL 19-2
QUARTZ NATURAL SWEPT
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER HC-27/U
OVERTONE 1, 3
Rs 2.8Ω, 6.7Ω
FREQUENCY 16013088 48120431
FREQUENCY CHANGE (PP10)
+2
+1
0
-1
-2
DAYS OF STORAGE AT 85°C
19
29
9
19
29
8
18
29
7
17
27
NOV.
DEC.
JAN
FEB.

FIGURE 10



CRYSTAL 19-6
QUARTZ NATURAL SWEPT
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER HC-27U
OVERTONE 1, 3
Rs 2.7Ω, 6.2Ω
FREQUENCY 16008731 48109698
FREQUENCY CHANGE (PP10)
+2
+1
0
-1
-2
DAYS OF STORAGE AT 85°C
19
29
9
19
29
8
18
28
7
17
27

It is noteworthy that again the principal shifts observed were at the fundamental whereas those occurring at the overtone modes were less or inappreciable except as exhibited in Figures 5 and 6. This data has been summarized more thoroughly by making a tabulation of all the shifts occurring in the six groups under discussion. This data is exhibited in Table I. The larger change in frequency at the fundamental than at the overtone is easily noted even for units of groups 19 and 20 although there was an appreciable change at the 3rd overtone mode also; however, the latter amounted to only one-half that at the fundamental.

A second point which is brought out by the data in the table is that changes that occurred for groups 17, 18, 19 and 20 were decidedly larger than those for groups S and 16. The former groups are characterized by being plated with two metal layers, Au + Al, Al + Al or Al + Au, whereas the latter two groups are plated only with a single layer of gold.

In cases where the metal films were alloyed by heating during sealing, as for three units of group #20 (20-1, -2, -3), the frequency change was the same order of magnitude as for groups S and 16 at the fundamental and virtually zero at the third overtone. For group 17, partially alloyed during sealing, the frequency changes at the fundamental and at the third overtone were less than for the remaining bilayer films. It thus appears that the effect of stress applied by the bimetal layers during a temperature change is sufficient to exhibit frequency changes measurable in parts in 10^7. This effect may be the result of layers of two different metals or of two layers of the same metals applied at a temperature different from that at which the base coating was applied. Furthermore, diffusion of the two layers into a single layer reduced or removed the observed frequency shift. The frequency changes of group 18 at the fundamental were very large (Figure 4). They appear to be the result of a stress effect caused by the application of the second aluminum layer at a temperature of about 350°C. Perhaps this in turn caused the presence of an oxide interface between the two layers or oxide contamination of the second layer. However, this particular behavior needs further investigation for better interpretation.

Of particular interest to the current stability studies is the fact that bilayer films, whether of single or different metals, continue to exhibit undesirable aging behavior in contrast to single layer films. This fact argues that bilayer films should be excluded as electrodes for AT-Cut resonators of which the highest stability is required.

The remainder of the contract time is to be spent principally in finishing up measurements for the Technical Report covering the research completed in the last two years. Additional continuous drive and gamma radiation studies are to be conducted if time permits. Work on the Technical Report will begin.

Respectfully submitted,

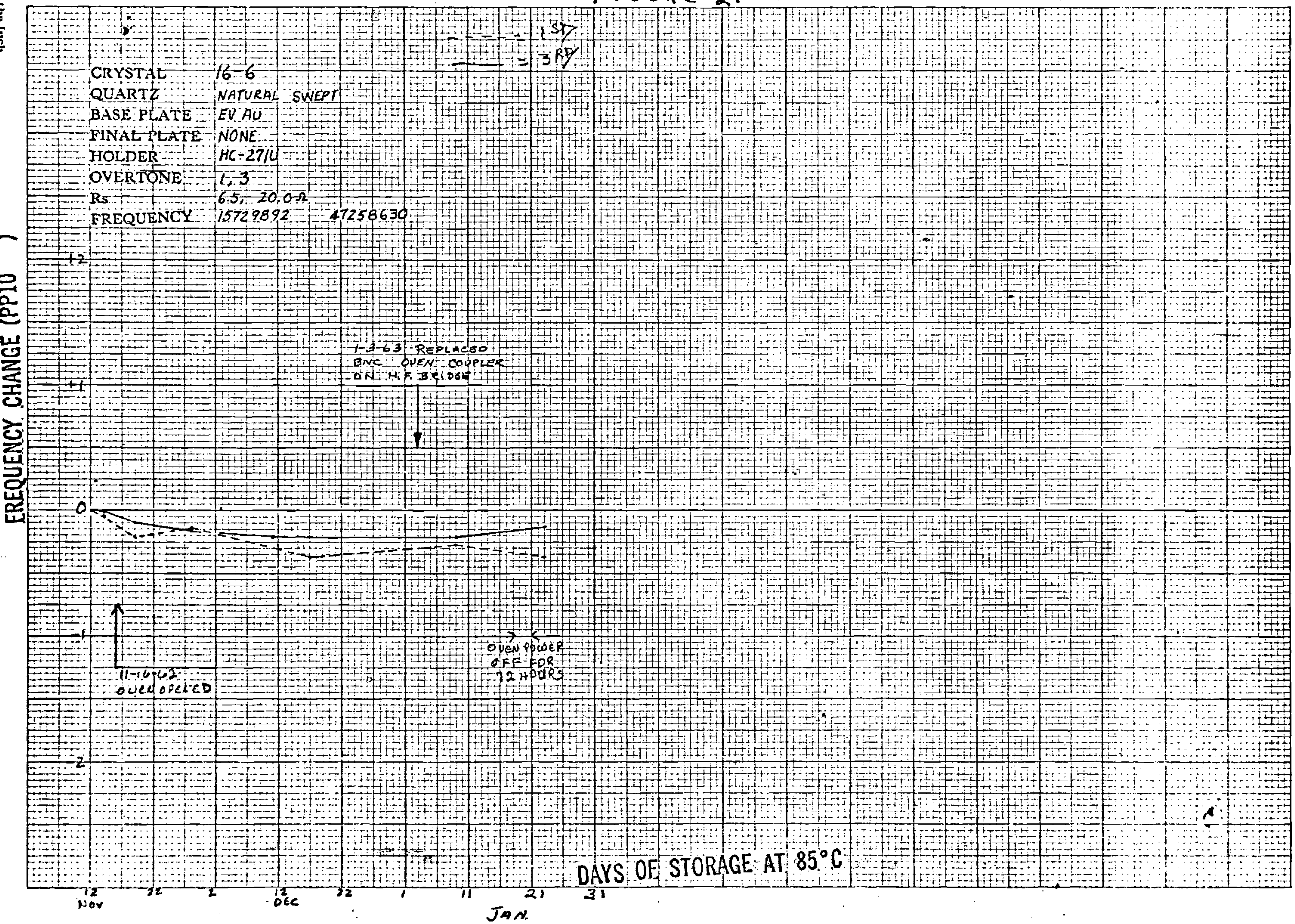
Richard B. Belser
Project Director

RBB:md

Addressee: 5

Enclosures: Table I, Figures 1-6

FIGURE 2.



- - - - = 1ST
—— = 3RD
CRYSTAL 16-6
QUARTZ NATURAL SWEPT
BASE PLATE EV AU
FINAL PLATE NONE
HOLDER HC-27/U
OVERTONE 1, 3
Rs 6.5, 20.0 Ω
FREQUENCY 15729892 47258630
FREQUENCY CHANGE (PP10^6)
+2
+1
0
-1
-2
1-3-63 REPLACED BNC OVEN COUPLER ON H.F. BRIDGE
11-16-62 OVEN OPENED
OVEN POWER OFF FOR 72 HOURS
DAYS OF STORAGE AT 85°C
12
NOV
22
2
12
DEC
22
1
11
21
31
JAN.

FIGURE 4

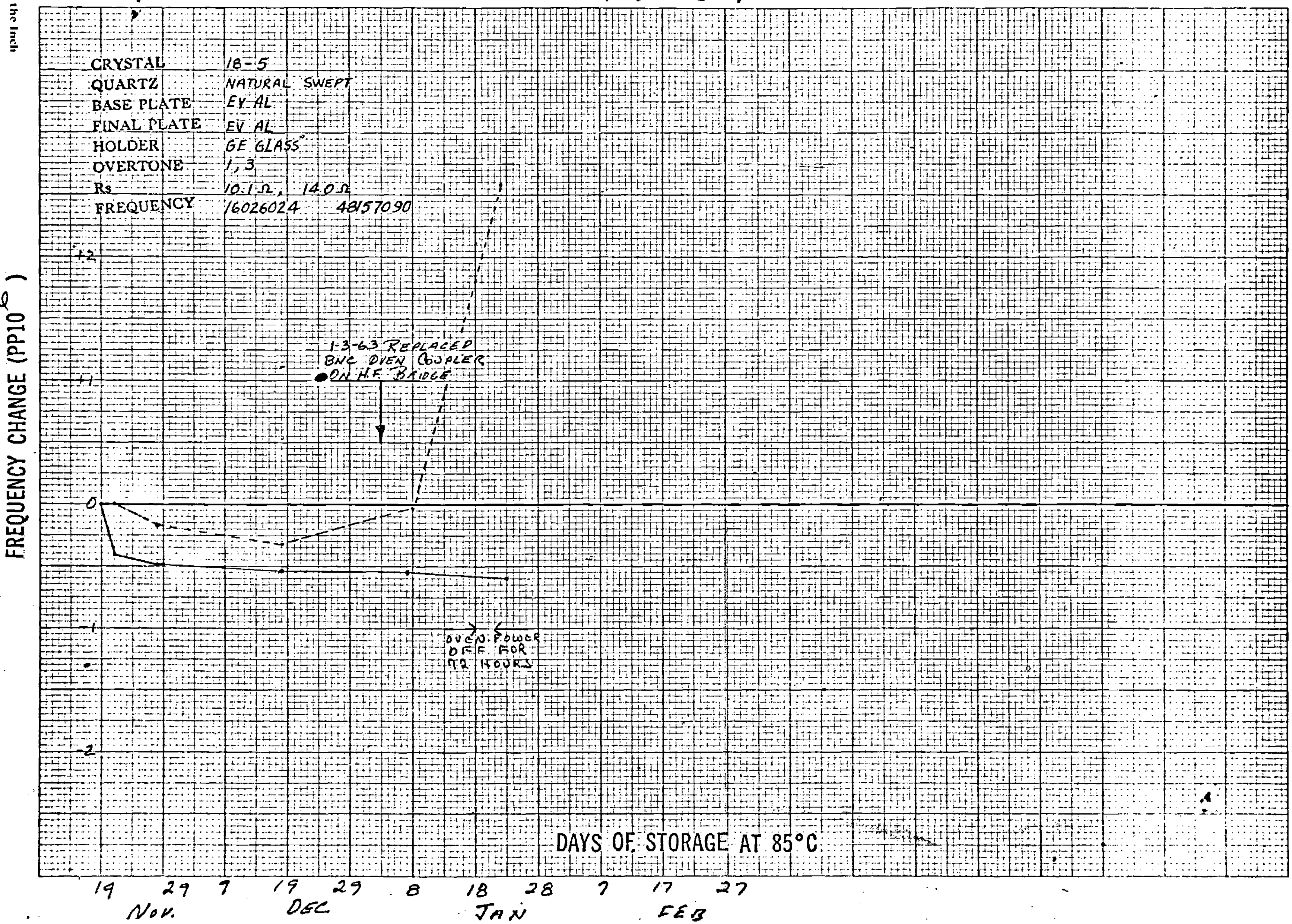
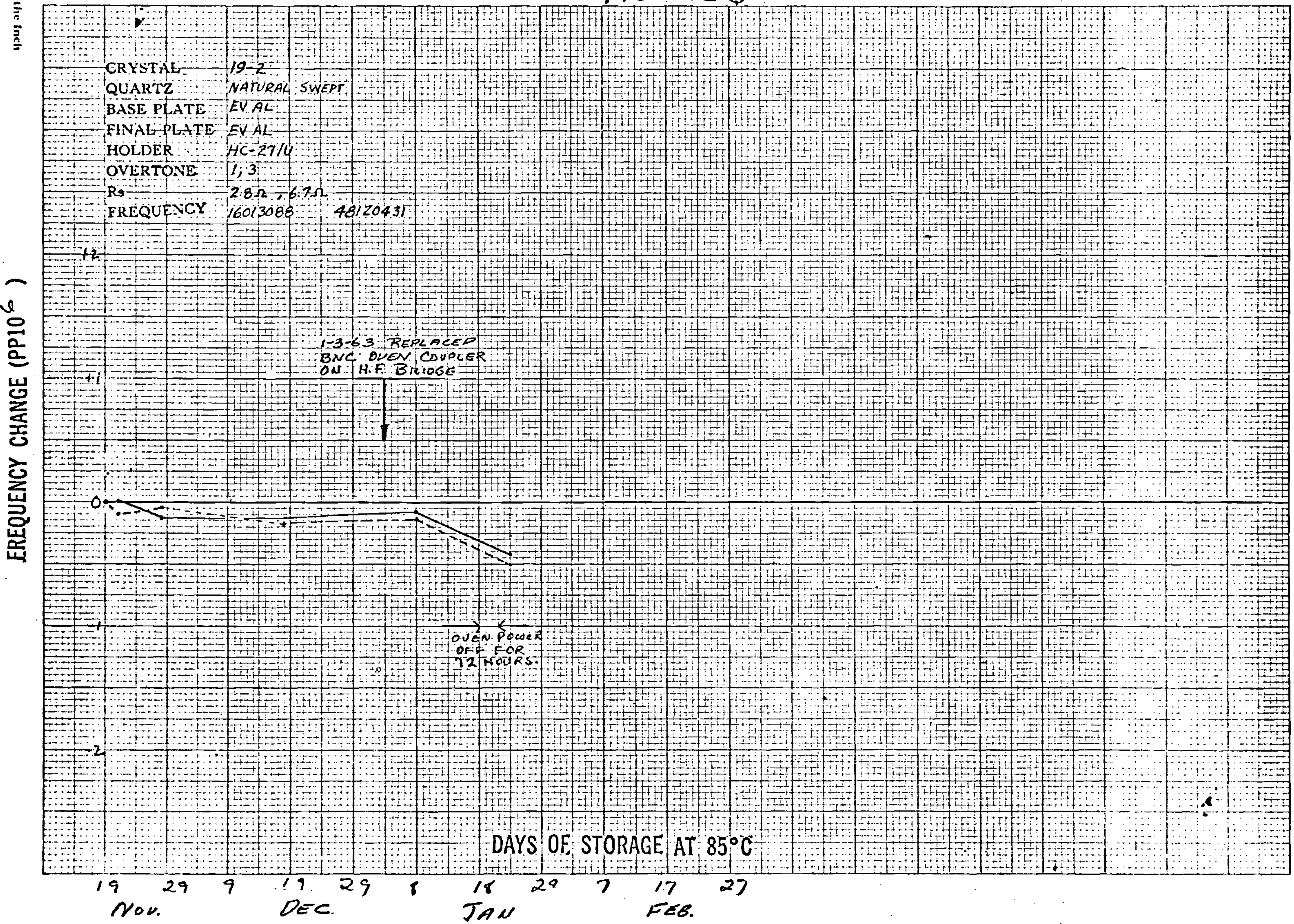

CRYSTAL 18-5
QUARTZ NATURAL SWEPT
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER GE GLASS
OVERTONE 1, 3
Rs 10.1 Ω, 14.0 Ω
FREQUENCY 16026024 48157090
1-3-63 REPLACED BNC OVEN COUPLER ON H.F. BRIDGE
OVEN POWER OFF FOR 72 HOURS
FREQUENCY CHANGE (PP10^6)
+2
+1
0
-1
-2
19 29 7 19 29 8 18 28 7 17 27
NOV. DEC JAN FEB
DAYS OF STORAGE AT 85°C

FIGURE 5



CRYSTAL 19-2
QUARTZ NATURAL SWEPT
BASE PLATE EV AL
FINAL PLATE EV AL
HOLDER HC-27/U
OVERTONE 1, 3
Rs 2.8Ω, 6.7Ω
FREQUENCY 16013088 48120431
1-3-63 REPLACED BNC OVEN COUPLER ON H.F. BRIDGE
OVEN POWER OFF FOR 72 HOURS.
FREQUENCY CHANGE (PP10^6)
+2
+1
0
-1
-2
DAYS OF STORAGE AT 85°C
19 29 9 19 29 8 18 29 7 17 27
NOV. DEC. JAN FEB.

AD ______________________ Accession No. ______________
Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia. AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS, R. B. Belser and W. H. Hicklin.

Report No. 1 (First Quarterly), 15 February 1961 to 15 May 1961, 17 pp., 4 Illus. Signal Corps Contract No. DA-36-039-SC-87407, Unclassified Report.

Vacuum equipment for fabrication of resonators of frequencies of 16, 48 and 80 mc has been modified to incorporate improved pumping and cold trapping in order to perform processing steps at pressures of 10^{-6} to 10^{-7} mm of mercury. A 200-unit constant temperature oven has been likewise improved by incorporation into it of coaxial leads and BNC terminations. These improvements facilitate measurements at frequencies above 16 mc.

The frequency measurement system, based on a single-ended bridge and counter method, has been modified to incorporate automatic gain control of the Crystal Impedance Meter Oscillator and automatic nulling of the bridge. These improvements are expected to bring the frequency measurement accuracy to a few parts in 10^9.

Polished quartz crystal blanks of 16 mc fundamental frequency for operation at the fundamental, the third and fifth overtones have been procured. A portion of these are of natural quartz and a portion of cultured quartz. Arrangements have also been made for procurement of blanks of "swept" natural and cultured quartz.

Twenty aluminum plated resonators have been fabricated and measured. Initial aging measurements of these units have indicated excellent stabilities.

UNCLASSIFIED

1. Aging Characteristics of Quartz Crystal Resonators
2. Signal Corps Contract No. DA-36-039-SC-87407

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Twenty aluminum plated resonators have been fabricated and measured. Initial aging measurements of these units have indicated excellent stabilities.

UNCLASSIFIED

1. Aging Characteristics of Quartz Crystal Resonators
2. Signal Corps Contract No. DA-36-039-SC-87407

filament and substrate heater assembly. The lower section contains only the lower filament and heater assembly.

The crystal mask is held horizontally in the center section of the chamber between the filaments and heaters. The chamber pressure may be reduced to the 10^{-7} mm Hg range through the use of cryogenic and getter pumping in addition to conventional pumping technique. Automatic controls on the substrate heaters allow prolonged degassing at elevated temperatures. Viton* O-rings are used for sealing the header and base plates. Electrical and thermocouple circuits enter the chamber through sealed packing glands.

b. Final Plating

This apparatus has been redesigned to include a liquid nitrogen trap which serves both as a baffle and cryogenic pump. The arrangement of the valves as shown in Figure 3 permits the trap in the lower chamber to remain charged while the upper chamber is opened for loading.

The upper chamber where the evaporations are performed may be pumped to pressures in the 10^{-7} mm Hg range in the time formerly required to pump to 10^{-5} mm Hg, about 20 minutes. Getter pumping in the lower chamber is available if desired.

c. Vacuum Baking

A combination of diffusion, cryogenic and getter pumping reduces the pressure in the main chamber to about 3×10^{-7} mm Hg during vacuum baking of the crystals at temperatures up to 250°C. The units to be evacuated and baked enter the main chamber by means of sealed packing glands. A demount-

*Viton is the duPont trade name for a linear copolymer of vinylindene fluoride and hexafluoropropylene and has a lower vapor pressure than neoprene rings.

VII. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

Name	Position	Time (Hours)
Richard B. Belser	Project Director	178
W. Bruce Warren	Research Engineer	89
Robert E. Meeks	Research Engineer	46
Walter H. Hicklin	Assistant Research Engineer	288
James O. Darnell	Research Assistant	92
Carroll M. Shirley	Technician	344
Walter C. Knapp	Technician	240
Charles S. Wilson	Electronic Technician	92

Respectfully submitted:

Richard B. Belser
Project Director

Approved:

Vernon Crawford
Head, Physics Branch
Physical Sciences Division

REPORT NO. 2 (SECOND QUARTERLY REPORT)
GEORGIA TECH PROJECT NO. A-552

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

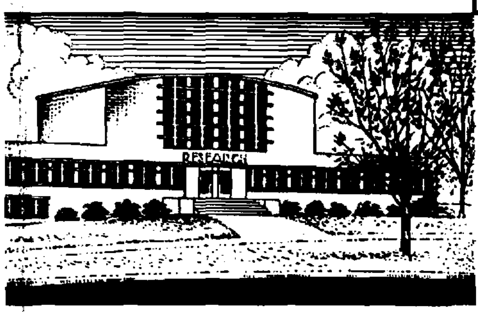
By

R. B. BELSER and W. H. HICKLIN

CONTRACT NO. DA-36-039-SC-87407
DA Task No. 3A 99 15 004

15 MAY 1961 to 15 AUGUST 1961

PLACED BY THE U. S. ARMY
SIGNAL RESEARCH AND DEVELOPMENT LABORATORIES
FORT MONMOUTH, NEW JERSEY



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

QUARTERLY REPORT NO. 2

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser
W. H. Hicklin

Contract No. DA-36-039-SC-87407
DA Task No. 3A 99 15 004
Georgia Tech Project No. A-552

15 May 1961 to 15 August 1961

Placed by the U. S. Army
Signal Research and Development Laboratories
Fort Monmouth, New Jersey

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

- - - - -

*"Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500 to 574°C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

Work has been continued on the AGC-AFC frequency measuring system and it is now ready for its final check-out. Present equipment is suitable for measurement to a part in 10^8 at 80 Mc; the modification is expected to increase accuracy of measurement to a few parts in 10^9 and to extend the accuracy range of the measuring equipment to measurements made at the fundamental and third overtone.

The source of temperature variations in the storage ovens during the early portion of the work was traced to modifications necessary for the installation of coaxial leads to each resonator position. The temperature was stabilized by increasing the external thermal insulation and placing a curtain about the base of the oven to reduce drafts. Upon completion of these modifications frequency measurement data were greatly improved.

Sixty resonators have been fabricated during the quarter. These consisted of forty units fabricated of natural quartz, ten of cultured unswept quartz, and ten of cultured swept quartz. Platings utilized were Al only, Al + Al, and Al + Au.

Measurements have not been underway for a sufficient time to interpret data fully. However, initial measurements indicated little difference in the stabilities of resonators fabricated of the different types of quartz or with the various types of plating. Differences observed were in the range of a few parts in 10^8 and indications are that the differences ascribable to the quartz itself will be less than those ascribable to fabrication variables.

III. PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

During the reporting period three monthly letters (Nos. 3, 4, and 5) were completed and submitted. Report No. 1 (First Quarterly Report) was distributed.

Conferences between Dr. G. K. Guttwein and Mr. P. E. Mulvihill of USASRADL and Mr. R. B. Belser and Mr. W. H. Hicklin of the Georgia Institute of Technology were held during the 15th Annual Frequency Control Symposium at Atlantic City, New Jersey, 31 May, 1-2 June 1961. Progress and plans of the project were discussed.

IV. FACTUAL DATA

A. Introduction

The principle effort during the second quarter has been the fabrication and measuring of resonator units fabricated of natural quartz and synthetic quartz, both swept and unswept. Refinements of the measurement technique, oven temperature control, and measurement equipment temperature control were made in order to improve the precision of frequency measurement.

B. Apparatus

1. Frequency Measurement System

The AGC-AFC frequency measuring system has been built in final assembly form and has been rack mounted.

Figure 1, a block diagram of the final system, reveals some changes in the original design discussed in Report No. 1. Modulation of the i.f. voltage in the null signal channel by a 10-kc voltage was employed to overcome the stability problem associated with the necessary dc amplification of the phase detector output to give sufficient AFC voltage. The output of the synchronous detector in the above figure is now a 10-kc signal of which the phase and amplitude are proportional to the phase and amplitude of the bridge null output. Their output is amplified to produce adequate AFC voltage in an ac coupled amplifier. The latter was chosen because it is inherently more stable than a conventional dc coupled amplifier.

Trouble shooting of the whole system is now in progress. Some problems exist with regard to CI-meter signal leakage through the null-signal channel. This leakage masks the null indication and has deteriorated

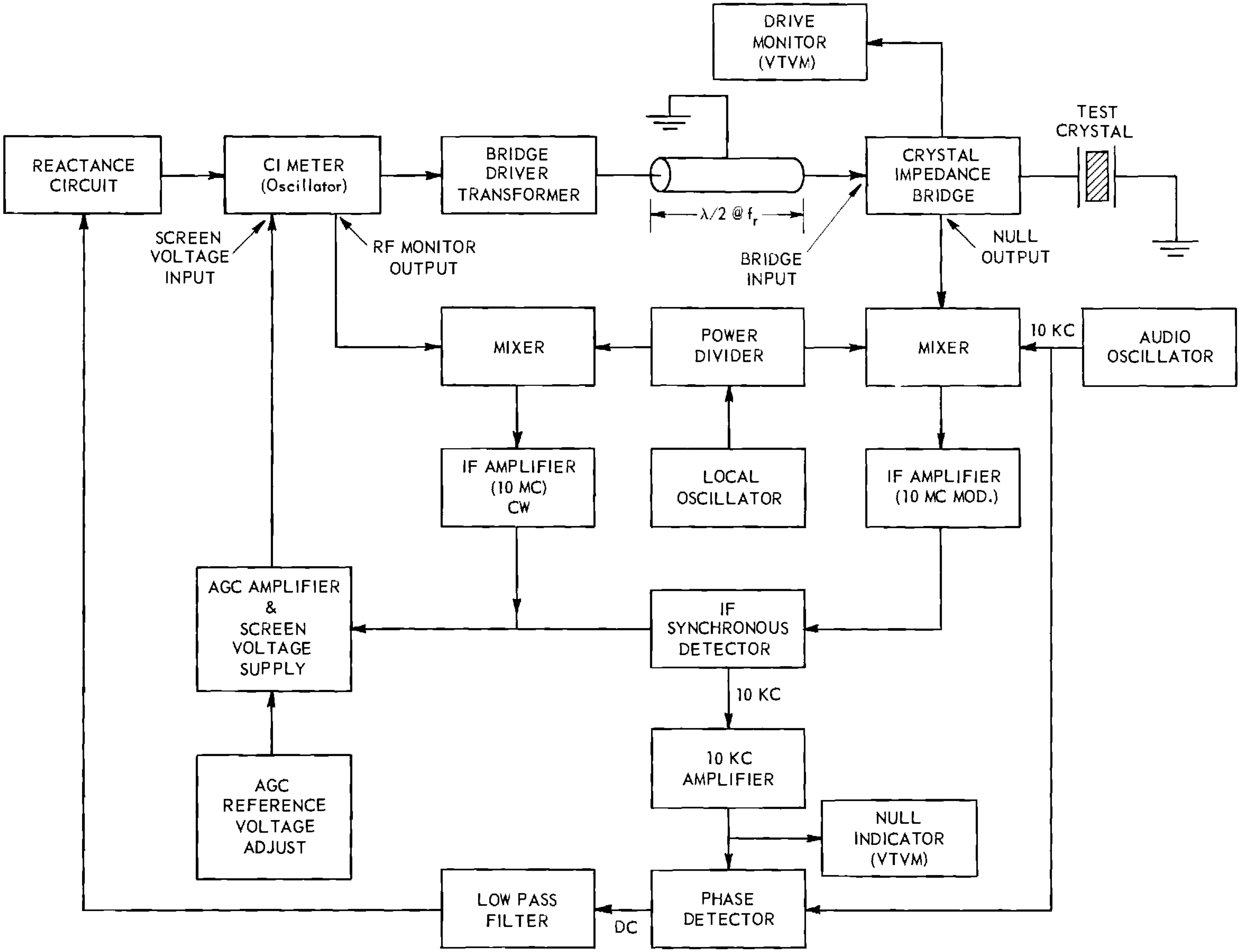

Figure 1. Block diagram of crystal frequency measuring system showing latest modification of AGC and frequency tracking system.

the frequency resolution obtainable with this system. These problems can be remedied with little difficulty. The AGC portion of the system appears to be satisfactory. The equipment is expected to be in operation within 15 days.

2. Vacuum Equipment

Both vacuum systems and the vacuum chambers for base plating, final plating, and vacuum baking have been operated without repair or modification during the quarter.

One more vacuum chamber will be required for this project for the sealing of glass, HC-6/U crystal holders. The design of the chamber will be completed when the bulbs and headers, now on order, are received.

3. Aging Oven Modifications

Considerable improvement in the temperature stability of the 200 unit, 85°C oven was achieved by the following modifications:

a. Covering the sides and top of the oven with styrofoam, the top being removable to permit loading of the oven, and

b. Enclosing the area beneath the oven with a styrofoam housing and a plastic curtain. The latter allowed access to the BNC connectors for engagement by the bridge assembly.

Improvement in the ability to maintain a null reading on the bridge galvanometer of the frequency measurement system was achieved by enclosing the bridge-driving oscillator in a styrofoam housing. Access to the CI-meter controls is accomplished through a plastic curtain at the front of the enclosure.

C. Experimental Work

Sixty resonators were fabricated during the period of this report. Parameters of the resonators and details of their fabrication are outlined in Table I.

TABLE I

DESCRIPTIVE DETAILS OF 80 Mc RESONATORS
FABRICATED AND EXAMINED IN THE FIRST AND SECOND QUARTERS

Group Number	Type Quartz	Base Plate Metal	Base Plate Temp. (°C)	Base Plate P(MM Hg)	Final Plate Metal	Final Plate P(MM Hg)	Bonding Cement	Bonding Cure (°C)	Bonding Time (Hrs)
1	Natural	Al	300	4×10^{-6}			5504 A	150	3
2	Natural	Al	300	2×10^{-6}			5504 A	300	1
3	Cultured Unswept	Al	300	5×10^{-6}			5504 A	150	3
4	Cultured Swept	Al	300	4×10^{-6}			5504 A	150	3
5	Natural	Al	300	4×10^{-6}	Au	2×10^{-6}	5504 A	150	3
6	Natural	Al	300	6×10^{-6}	Al	3×10^{-6}	5504 A	150	3
7	Natural	Al	300	2×10^{-6}	Au	5×10^{-6}	5504 A	150	3
8	Natural	Al	300	3×10^{-6}	Al	1×10^{-5}	5504 A	150	3

(Continued Below)

(Continuation)

Group Number	Type Quartz	Mounting Type	Mounting Resonator Holder	Vacuum Bake Time (Hrs)	Vacuum Bake Temp. (°C)	Vacuum Bake P(MM Hg)	Percent Yield
1	Natural	GE Glass	.006" Springs	3	175	2×10^{-7}	100
2	Natural	GE Glass	.006" Springs	3	175	2×10^{-7}	90
3	Cultured Unswept	GE Glass	.006" Springs	3	175	2×10^{-7}	100
4	Cultured Swept	GE Glass	.006" Springs	3	175	3×10^{-7}	100
5	Natural	GE Glass	.006" Springs	3	175	2×10^{-7}	100
6	Natural	GE Glass	.006" Springs	3	175	2×10^{-7}	50
7	Natural	GE Glass	.006" Springs	3	175	2×10^{-7}	60
8	Natural	GE Glass	.006" Springs	3	175	3×10^{-7}	100

It will be noted that the sixty resonators were comprised of six groups of ten each. The first two groups (groups 3 and 4) were base plated only to furnish control specimens. Groups 5 and 7 were overplated to frequency with gold, and groups 6 and 8 were overplated to frequency with aluminum.

Two procedures for overplating were used. The first was to base plate the resonator blanks with aluminum, open the system to air, evacuate and replate the resonator blanks with an overplate of gold or aluminum. This was the method used respectively for groups 5 and 6.

The second method was to base plate the resonator blanks with aluminum, mount the resonator blanks, then overplate the resonators to frequency individually with the desired metals. This is the normal method of overcoating and was used for groups 7 and 8 for overcoating with gold and aluminum respectively.

The series resistances of the resonators fabricated during the Quarter and measured in the aging oven at the 5th overtone are given in Table II.

Figures 2, 3, 4, 5, 6, and 7 depict typical frequency changes with storage time at 85°C for resonators of each of the six groups fabricated during the period. In Figures 8 and 9 are given data for typical specimens fabricated during the preceding period and unreported previously because of measurement difficulties encountered during the First Quarter.

An analysis of the data displayed reveals that some measurement difficulty continued to be encountered during the first month of the current quarter. This difficulty was due to poor thermal control of the ovens brought on by modifications necessary to install coaxial connectors

TABLE II

SERIES RESISTANCE OF OPERABLE RESONATORS
FABRICATED DURING THE SECOND QUARTER*

Unit	R_s (Ω)	Unit	R_s (Ω)
	Plating, Al Only		
3-1-Al	33.5	4-1-Al	53.0
3-2-Al	21.5	4-2-Al	26.0
3-3-Al	37.0	4-3-Al	20.0
3-4-Al	41.5	4-4-Al	15.0
3-5-Al	15.0	4-5-Al	15.0
3-6-Al	16.5	4-6-Al	52.0
3-7-Al	20.0	4-7-Al	18.0
3-8-Al	15.0	4-8-Al	17.5
3-9-Al	16.5	4-9-Al	10.5
3-10-Al	21.0	4-10-Al	11.5
AVERAGE VALUE	23.8		23.9
	Plating, Al + Al		
6-1-Al+Al	16.5	8-1-Al+Al	21.5
6-2-Al+Al	14.0	8-2-Al+Al	20.0
6-3-Al+Al	18.5	8-3-Al+Al	45.0
6-4-Al+Al	13.0	8-4-Al+Al	15.0
6-6-Al+Al	15.0	8-5-Al+Al	21.5
		8-6-Al+Al	52.0
		8-7-Al+Al	50.0
		8-8-Al+Al	21.5
		8-9-Al+Al	26.5
		8-10-Al+Al	33.5
AVERAGE VALUE	15.4		30.7
	Plating, Al + Au		
5-1-Al+Au	15.0	7-1-Al+Au	25.0
5-2-Al+Au	16.5	7-6-Al+Au	46.0
5-3-Al+Au	38.5	7-7-Al+Au	17.5
5-4-Al+Au	20.0	7-8-Al+Au	21.5
5-5-Al+Au	17.5	7-9-Al+Au	22.5
5-6-Al+Au	> 100	7-10-Al+Au	24.0
5-7-Al+Au	24.0		
5-8-Al+Au	14.0		
5-9-Al+Au	13.0		
5-10-Al+Au	38.5		
AVERAGE VALUE	21.9		26.1

- - - - -

* Average R_s values for Groups 1 and 2 (Al only), 17.9 ohms and 19.8 ohms respectively.

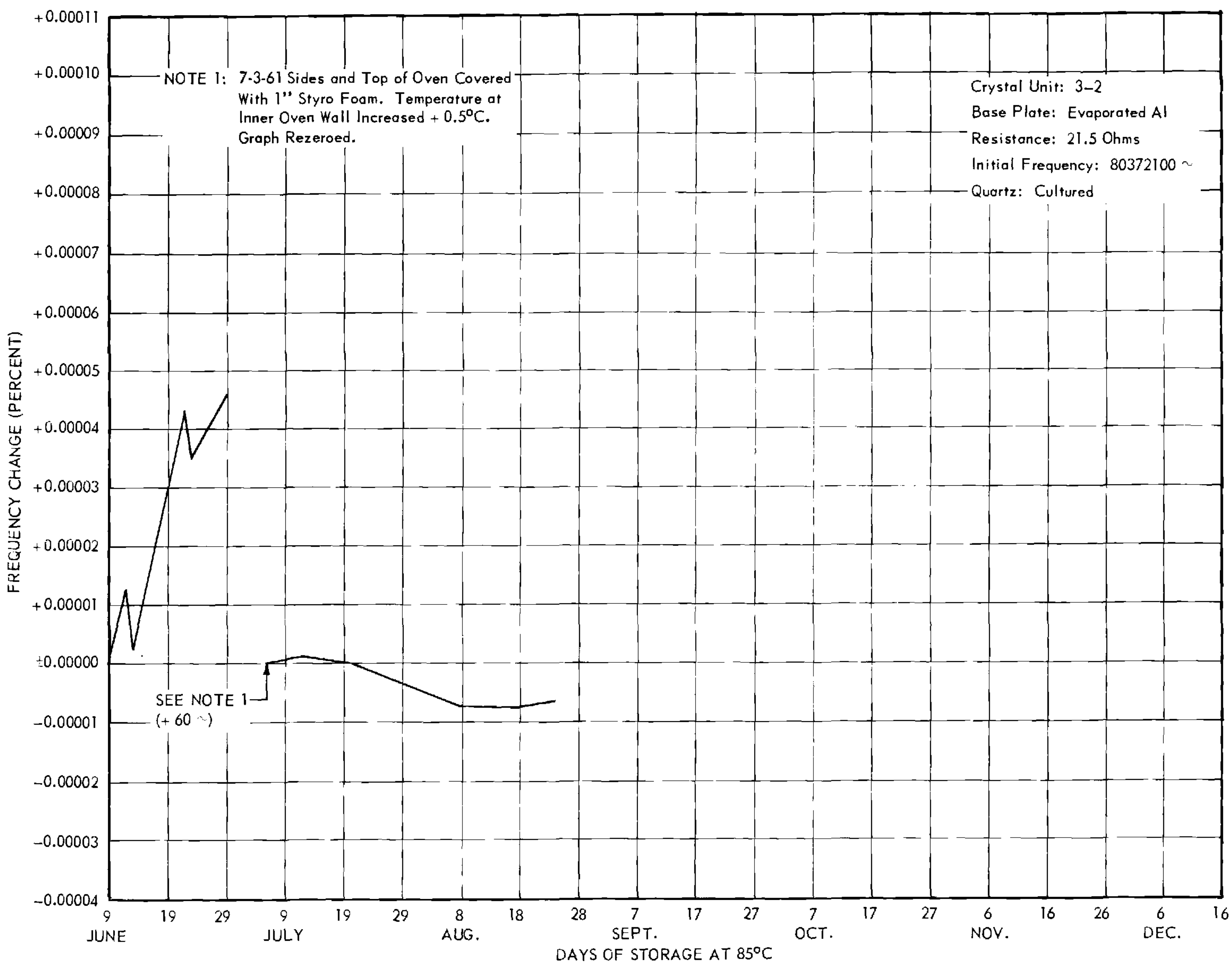

Figure 2. Plot of frequency data for resonator 3-2-Al.

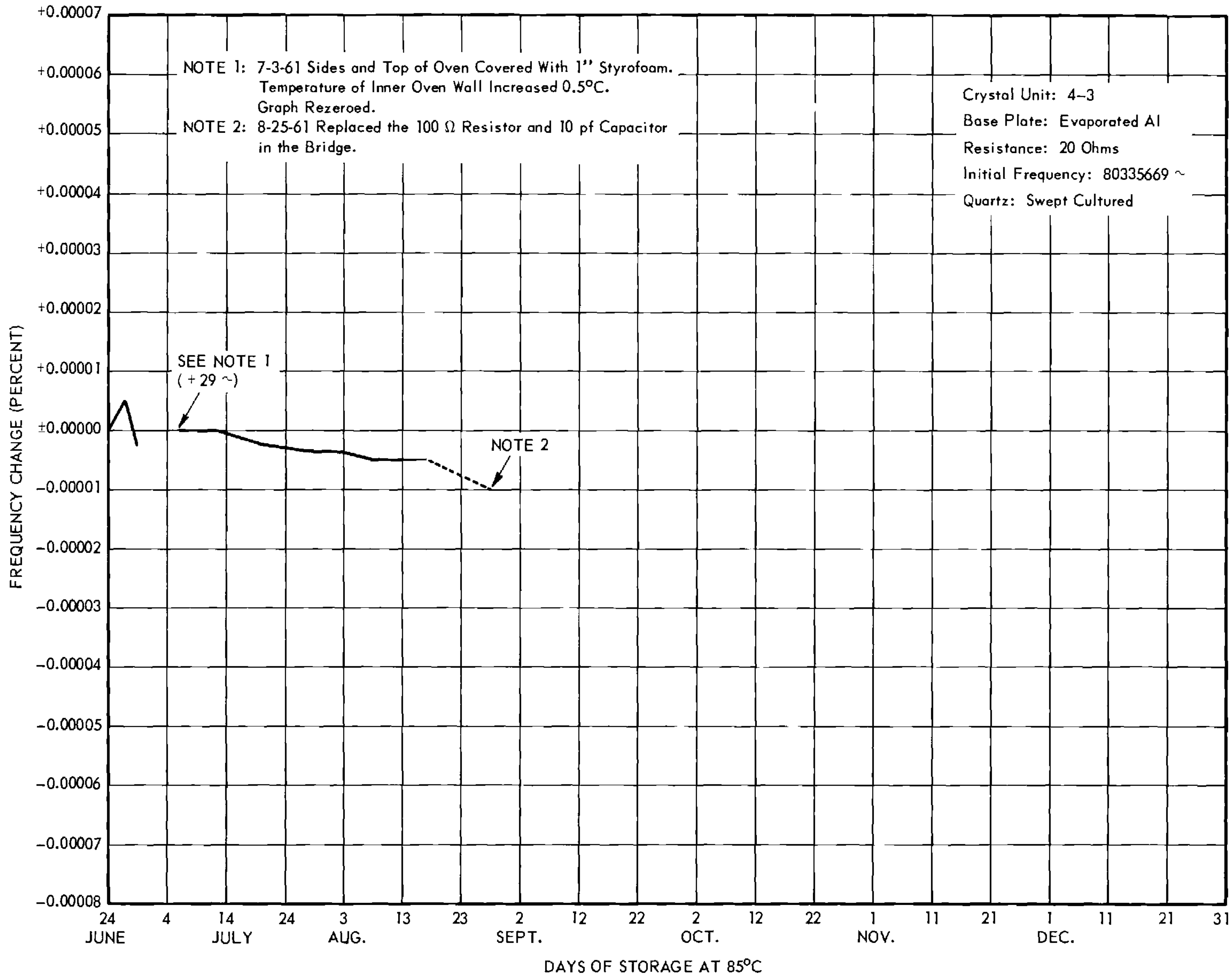

Figure 3. Plot of frequency data for resonator 4-3-Al.

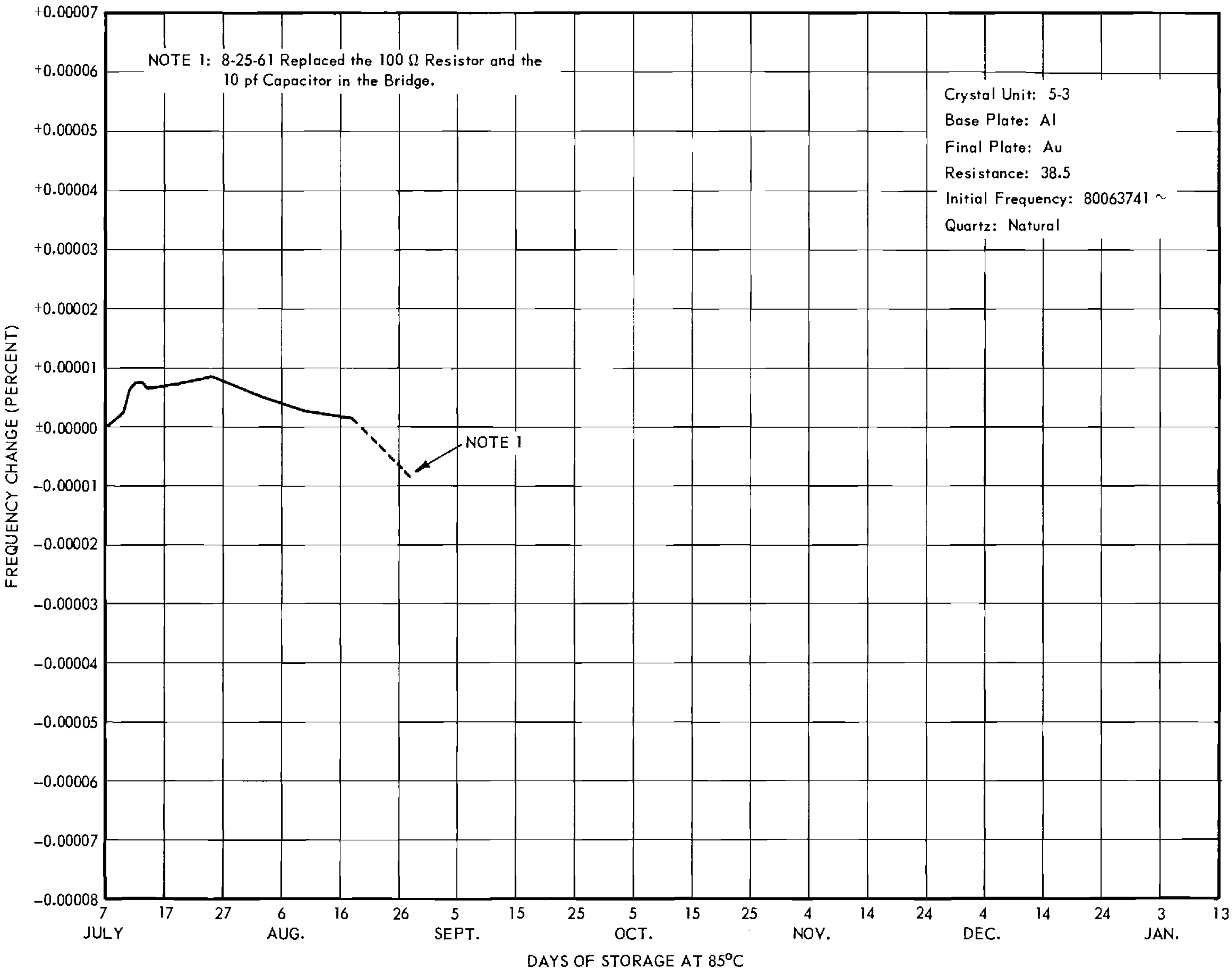

Figure 4. Plot of frequency data for resonator 5-3-Al + Au.

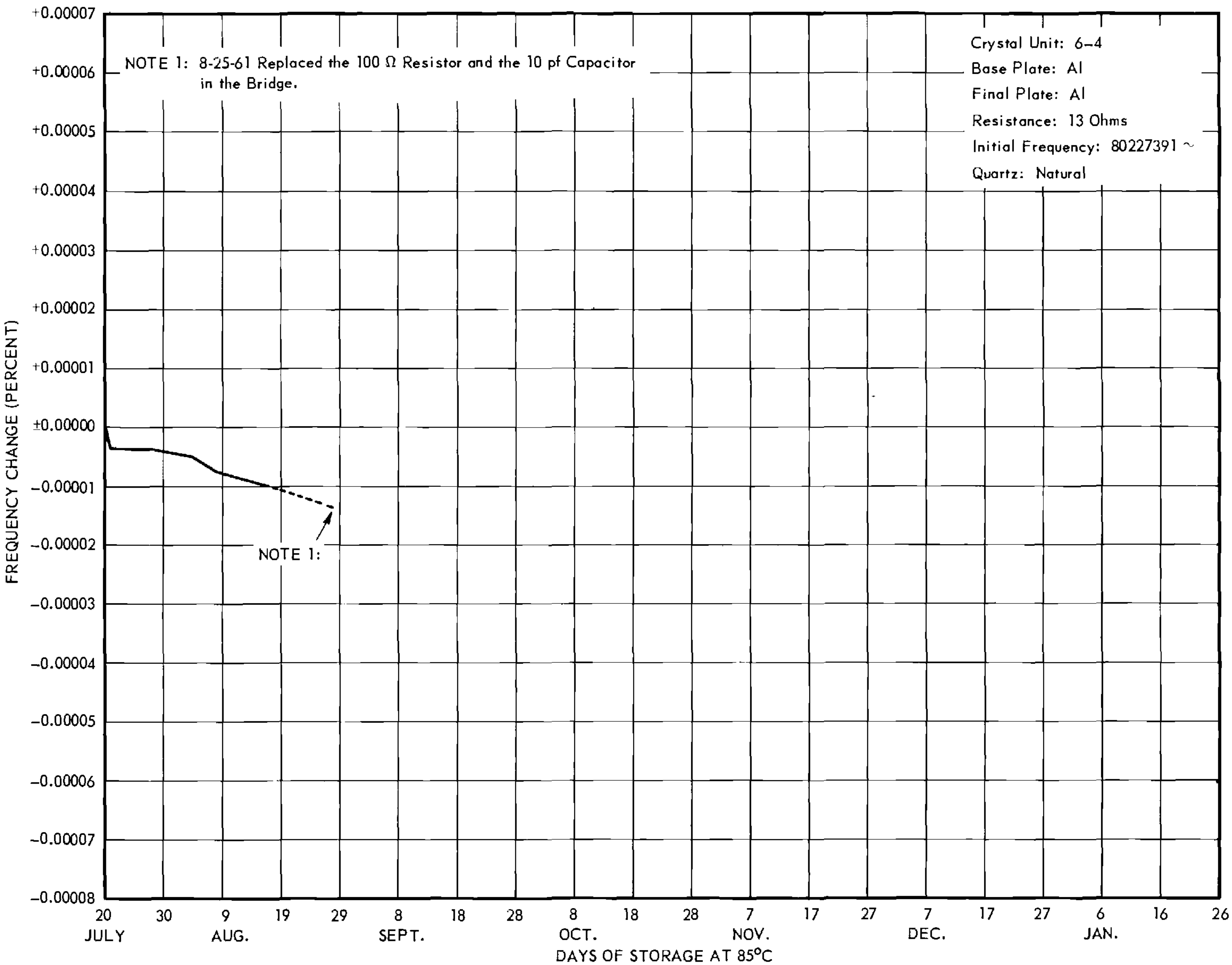

Figure 5. Plot of frequency data for resonator 6-4-Al + Al.

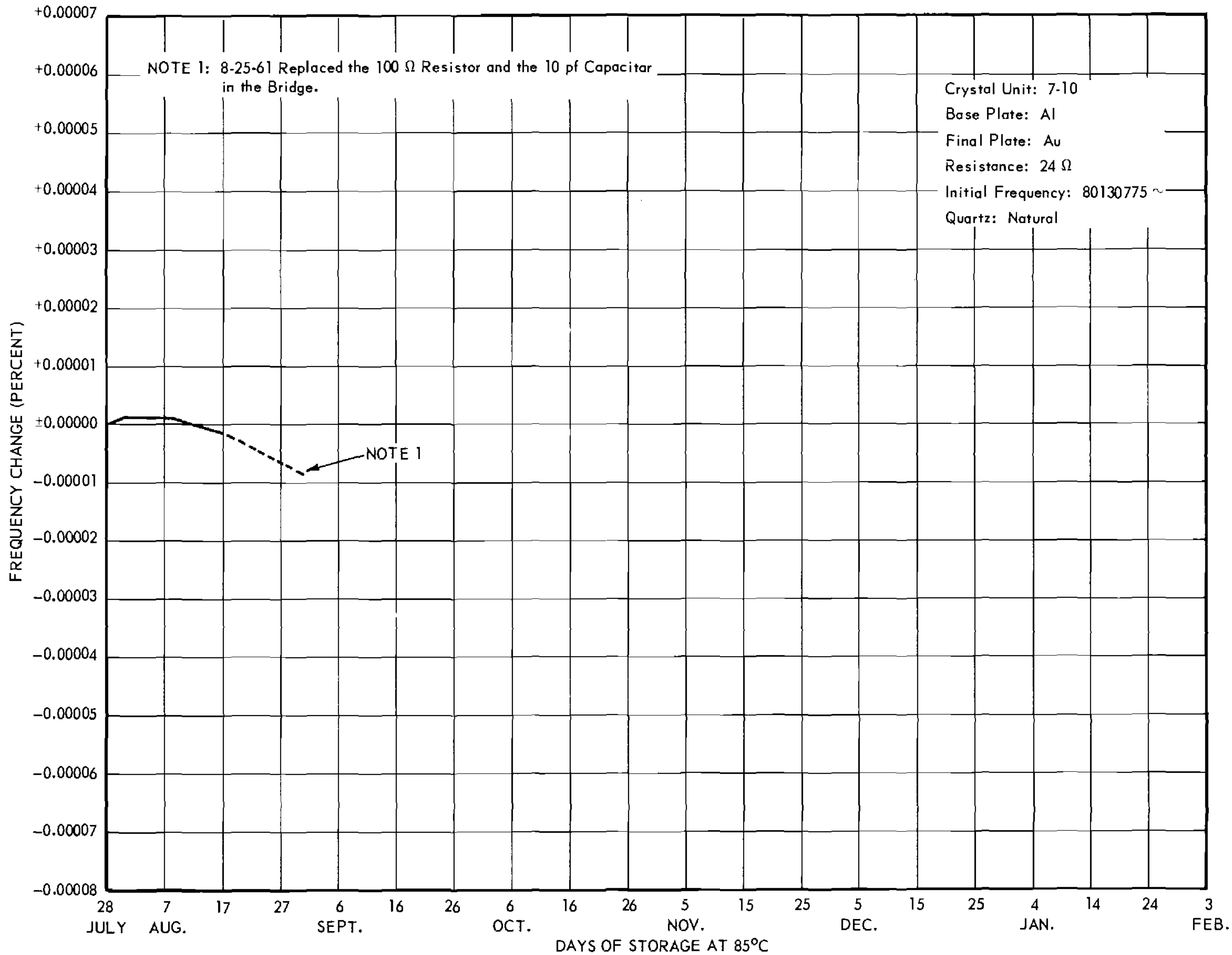

Figure 6. Plot of frequency data for resonator 7-10-Al + Au.

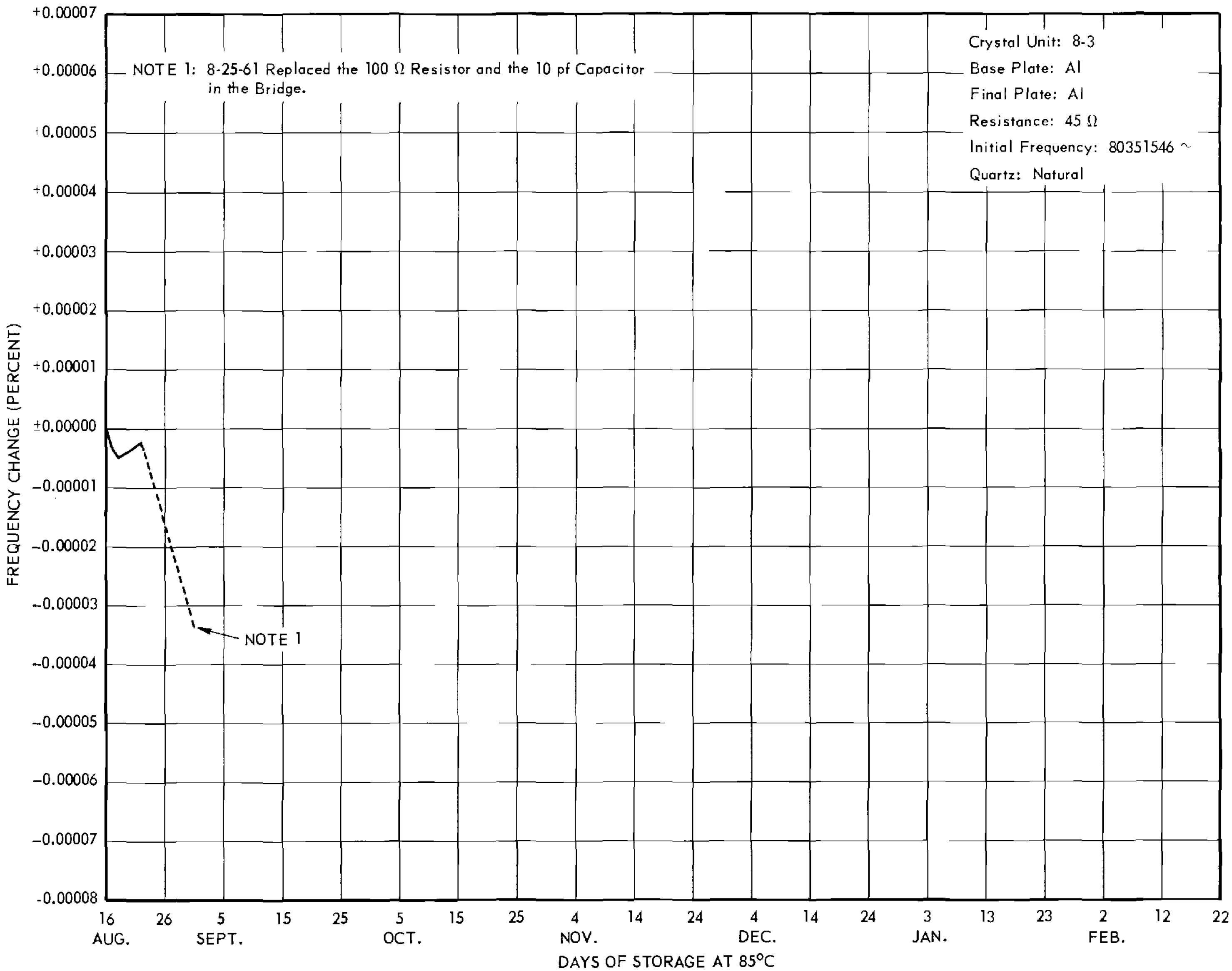

Figure 7. Plot of frequency data for resonator 8-3-Al + Al.

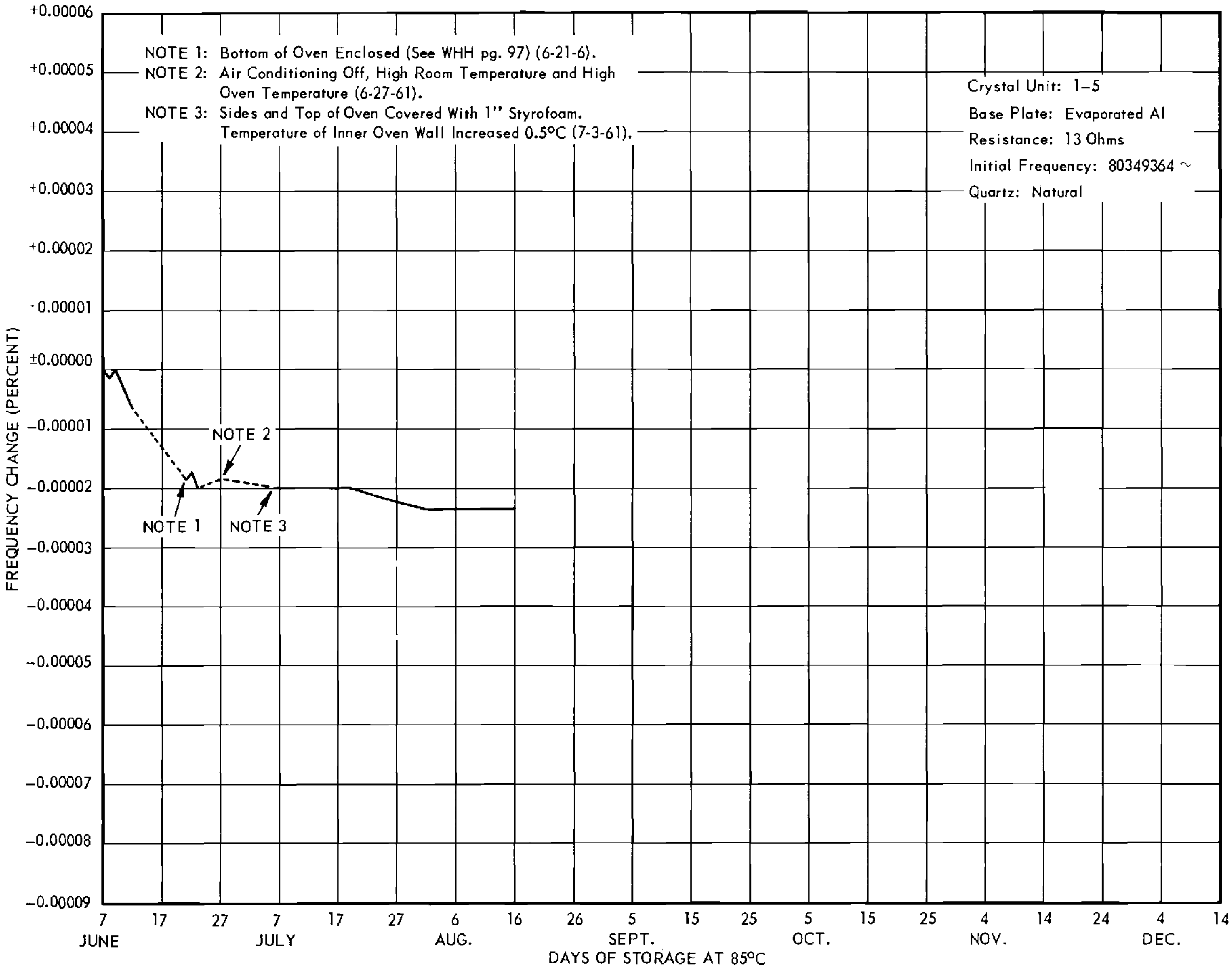

Figure 8. Plot of frequency data for resonator 1-5-Al.

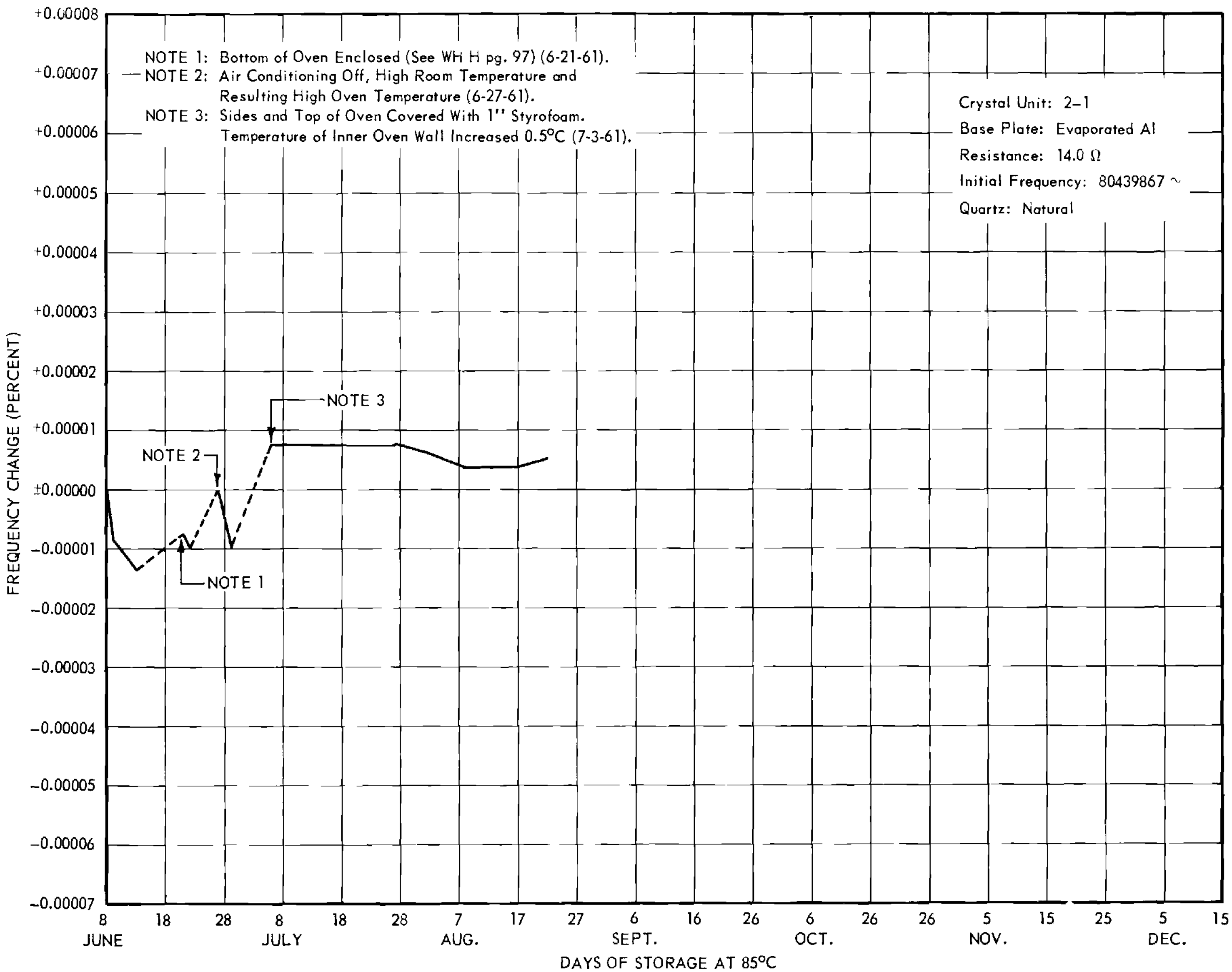

Figure 9. Plot of frequency data for resonator 2-1-Al.

to each position. The improved insulation of the ovens, described in Section B.3. above, overcame these difficulties. Typical resonators displayed drifts of less than 5 parts in 10^8 in 60 days.

The period and accuracy of measurement have not yet established a clear pattern of behavior and differences between resonators due to the variables examined will be more clearly delineated during the next 90 days.

It will be noted that quartz blanks of all groups except 3 and 4 were natural quartz whereas the latter were of cultured unswept and cultured swept quartz, respectively. Differences in behavior due to the use of these respective types of quartz are not yet defined. However, it cannot be large since no particularly different behavior for these units has been observed on a scale of a part in 10^8.

Units base plated with aluminum and overplated with gold exhibited a peculiar behavior after a period of two or three weeks in the 85°C oven. The units tended to drop out of oscillation while the bridge was being balanced. Such behavior could be partially eliminated by increasing the drive level. A number of Group 5 units were removed from the oven for inspection. No visible reason for such action was seen with a binocular microscope. It was noted that the units would suddenly drop out of oscillation in a CI meter as the drive level was slowly reduced. The threshold power level for stable operation varied somewhat for the different units. Units base plated only with aluminum or final plated with aluminum did not exhibit this peculiarity. The behavior was observed only at 5th overtone operation since no measurements were made at the fundamental or 3rd overtone modes.

Measurements of the values of Q for the resonators were not made during the period but are on the agenda for the next Quarter.

D. Comments

When the initial supply of duPont No. 5504-A thermosetting conductive cement was received the following alternate curing schedules were recommended in the duPont Ceramic Products Bulletin No. CP 2-960.

Temperature (°C)	Curing Time Minimum	Curing Time Maximum
110	48 hr	Unlimited
130	10 hr	Unlimited
150	3 hr	Unlimited
170	80 min	Unlimited
190	45 min	Unlimited
220	1 hr	2 hr
280	30 min	1 hr

The curing schedule used for most of the units fabricated was three hours at 150°C. Recently a duPont Ceramic Products Bulletin No. CP 2-361 was obtained which gives the following schedules for curing duPont No. 5504-A cement:

Operation	Time (Hours)	Temperature (°C)
Drying	1	150 - 160
Curing	16	160
Curing	1	260

The considerable difference in the recommended curing schedules was noted and clarification was requested from the duPont Company. They advised that Bulletin CP 2-960 was obsolete and that the latter curing schedule should be used. Future units bonded with 5504-A cement will be dried for one hour at 150°C and cured for one hour at 260°C. The curing oven will be designed so that an inert atmosphere can be used to prevent damage to the resonator plating or mounting assembly during curing.

V. CONCLUSIONS

Differences in stabilities and R_s values of resonators fabricated of natural, cultured, and cultured swept quartz, on the basis of limited evidence, are quite small and are probably overshadowed by variables in fabrication. Differences that may occur are in the range of a few parts in 10^8 or less.

VI. PROGRAM FOR THE NEXT INTERVAL

Fabrication and measurement of resonators in accordance with the planned program will be continued. A larger number of resonators will be fabricated of the synthetic and synthetic swept quartz blanks. A portion of the resonators will be bonded with the Pyroceram formula suggested by Dr. G. K. Guttwein.

Procurement of glass HC-6/U bases and envelopes is currently underway, and a supply of these is expected in the near future. The design of a suitable sealing chamber for these units has been initiated and will be completed on arrival of the glass containers.

VII. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

The following persons have been employed on this project during its second quarter for the time indicated.

Name	Position	Time (Hours)
Richard B. Belser	Project Director	106
W. Bruce Warren	Research Engineer	114
Robert E. Meek	Research Engineer	60
Walter H. Hicklin	Ass't. Research Engineer	196
James O. Darnell	Research Assistant	211
Carroll M. Shirley	Technician	275
Walter C. Knapp	Technician	319
Charles S. Wilson	Electronic Technician	379

Mr. R. B. Belser, Research Associate Professor of Physics and Project Director, has been associated with resonator aging studies sponsored by USASRADL for over eleven years and has directed a number of other projects concurrently dealing with the structure, properties and applications of thin metal films for electrical and optical purposes. Mr. W. H. Hicklin, Assistant Research Engineer, has been active in quartz resonator fabrication and measurement and other electronic component studies as a principal assistant to Mr. Belser for approximately ten years.

Mr. W. B. Warren is an electrical engineering graduate of the Georgia Institute of Technology with an M.S. degree and has had eight years experience in electronic circuit design and instrumentation. He has directed a number of projects under U.S. Air Force sponsorship in related fields over this period.

Mr. R. E. Meek is an electrical engineering graduate of the University of Kentucky with two years graduate study additional. He has had ten years experience in electronic circuit design and instrumentation and has directed a number of projects in associated fields sponsored by USASRADL and by the U.S. Air Force.

Mr. W. C. Knapp received a B.S. degree in physics from the Georgia Institute of Technology in 1961 and has had approximately ten years experience in electronic circuitry design, construction, and maintenance.

Messrs. J. O. Darnell, C. M. Shirley, and C. S. Wilson are technical school graduates or equivalent with training in the fields of chemistry, mechanical engineering, and electrical engineering, respectively. They have worked directly under Mr. Hicklin in the fabrication and maintenance of high vacuum equipment, the design, construction and maintenance of electronic instrumentation, and the fabrication and measurement of quartz resonators for periods of from 1 to 5 years.

Respectfully submitted:

Richard B. Belser
Project Director

Approved:

Arthur L. Bennett
Chief, Physical Sciences Division

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REPORT NO. 3 (THIRD QUARTERLY REPORT)
GEORGIA TECH PROJECT NO. A-552

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

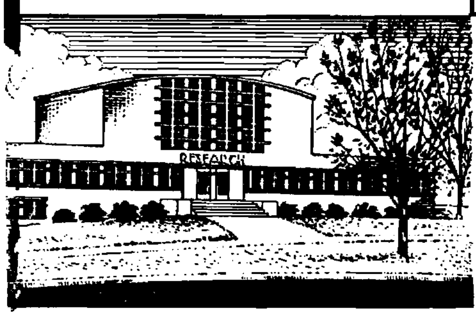
By

R. B. BELSER and W. H. HICKLIN

CONTRACT NO. DA-36-039-SC-87407
DA Task No. 3A 99 15 004

15 AUGUST 1961 to 15 NOVEMBER 1961

PLACED BY THE U. S. ARMY
SIGNAL RESEARCH AND DEVELOPMENT LABORATORIES
FORT MONMOUTH, NEW JERSEY



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

- - - - -

*"Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500 to 574°C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

The AGC-AFC frequency-measurement system designed with the intent to measure frequency to a few parts in 10^9 ran into difficulty because of phase shifts occurring in the signals from two IF amplifiers supplying reference signals from the input of the crystal impedance bridge and the null output of the bridge respectively. Adjustments to compensate for this shift led to inaccurate frequency measurements. Although these difficulties were overcome subsequently, the probability of the completion of a successful measurements system in a limited time based on this approach appeared small, and further development was arranged to be carried out on equipment which would not interfere with aging measurements.

A return was made to the original bridge measurement system. However, a basic fault with the single ended bridge, the transformer coupling through which the crystal controlled the CI meter, could only be removed by adopting a passive measurement system in which the CI meter was directly controlled by a second crystal or in which a high precision frequency synthesizer supplied the signal. The measurement system was converted to the passive system and initial accuracies appear excellent.

An apparatus for sealing the glass HC-6/U containers was developed. The container and base held in mated position in a jig in vacuo were preheated by a gas ring burner around the pyrex tube vacuum chamber. The Kovar ring in the base was heated by induction and the envelope and base compressed under the action of a spring. A dial gauge measured the relative motion between the parts. A relative movement of 0.020" was found to give consistently leakproof seals.

Approximately 75 resonators previously fabricated remained on storage at a temperature of 85°C during the period. However, measurements were largely interrupted due to the extensive equipment modifications during the period.

III. PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

During the reporting period three monthly letters (Nos. 6, 7, and 8) were completed and submitted. Report No. 2 (Second Quarterly Report) was distributed.

Dr. G. K. Guttwein visited the Georgia Institute of Technology on 2 November 1961. Discussions concerning the frequency-measurement problem and general progress on the project were conducted. It was agreed that aging studies of groups of resonators would be made at the fundamental, 3rd, and 5th overtones concurrently in order that aging at the various overtones could be compared with each other and with the fundamental. Some resonators were to be operated continuously during the aging period.

Progress in sealing the HC-6/U glass units was demonstrated and the advisability of continuing studies of radiation-saturation effects on subsequent frequency was discussed.

In attendance at the discussions were:

Dr. G. K. Guttwein of the Signal Research and Development Laboratories and

Dr. A. L. Bennett, Messrs. R. B. Belser, S. N. Witt, R. E. Meek, W. B. Warren, W. H. Hicklin, C. M. Shirley, C. S. Wilson, and Dr. D. S. Harmer of the Georgia Institute of Technology.

IV. FACTUAL DATA

A. Introduction

Work during the third quarter has been primarily directed toward a solution to the measurement problem of obtaining an accuracy of a few parts in 10^9 for resonators operated at 16, 48, and 80 Mc. In the initial stages a single-ended bridge with automatic gain control and automatic frequency control incorporated into the driving oscillator and nulling system respectively appeared to be a probable solution. However, the farther the work progressed the more complex appeared the problem, and the likelihood of a quick solution diminished.

The necessity that measurements be made without further interruption and to the highest accuracy possible suggested a return to the former bridge system. However, the work on the AGC-AFC system had revealed that poor control of the Crystal Impedance Meter was obtained due to isolation of the crystal from the oscillator by a transformer. A method whereby the oscillator could be directly controlled by a crystal and the crystal to be measured remained a passive element was investigated. This arrangement proved to be the best solution to the measurement problem yet obtained. More complete details of this technique are discussed subsequently.

Concurrent with the measurement problem a method of sealing the HC-6/U glass container was investigated and solved. Resonators previously fabricated were continued on storage.

B. Apparatus Modification and Construction

1. AGC-AFC Frequency Measurement System

Unexpected difficulties were encountered in the application of the frequency measuring system discussed in Quarterly Report No. 2. Repeat measurements of the crystal frequency of a resonator failed to agree to the desired accuracy. Upon consideration of the nature of this difficulty, it was determined that the primary cause of the error in successive measurements was due to a differential phase shift between the two 10-Mc IF amplifiers. One of the IF signals is a reference signal derived from the CI meter oscillator, while the other IF signal is an error signal derived from the modulated null output of the crystal impedance bridge. These two IF signals are combined in a synchronous detector to obtain the 10-kc low frequency error signal, so that any differential phase shift between the outputs of the two IF amplifiers causes a change in the phase of the 10-kc signal from the synchronous detector. This change in phase requires that the frequency of oscillation of the CI meter be slightly changed in order to produce a null condition at the output of the 10-kc phase detector.

Though careful attention was given to maintaining very similar construction in the two IF amplifier channels, the necessity for manual gain control of the null channel introduced in this IF channel a phase shift which was a function of the setting of the gain control. As a result the measured value of the crystal resonant frequency was a function of the gain setting. Another system was devised which combined the reference IF and the null output IF signal in a common IF channel to eliminate the differential phase shift. Figure 1 illustrates the method by which this single IF amplifier system has been applied. From this figure it is seen

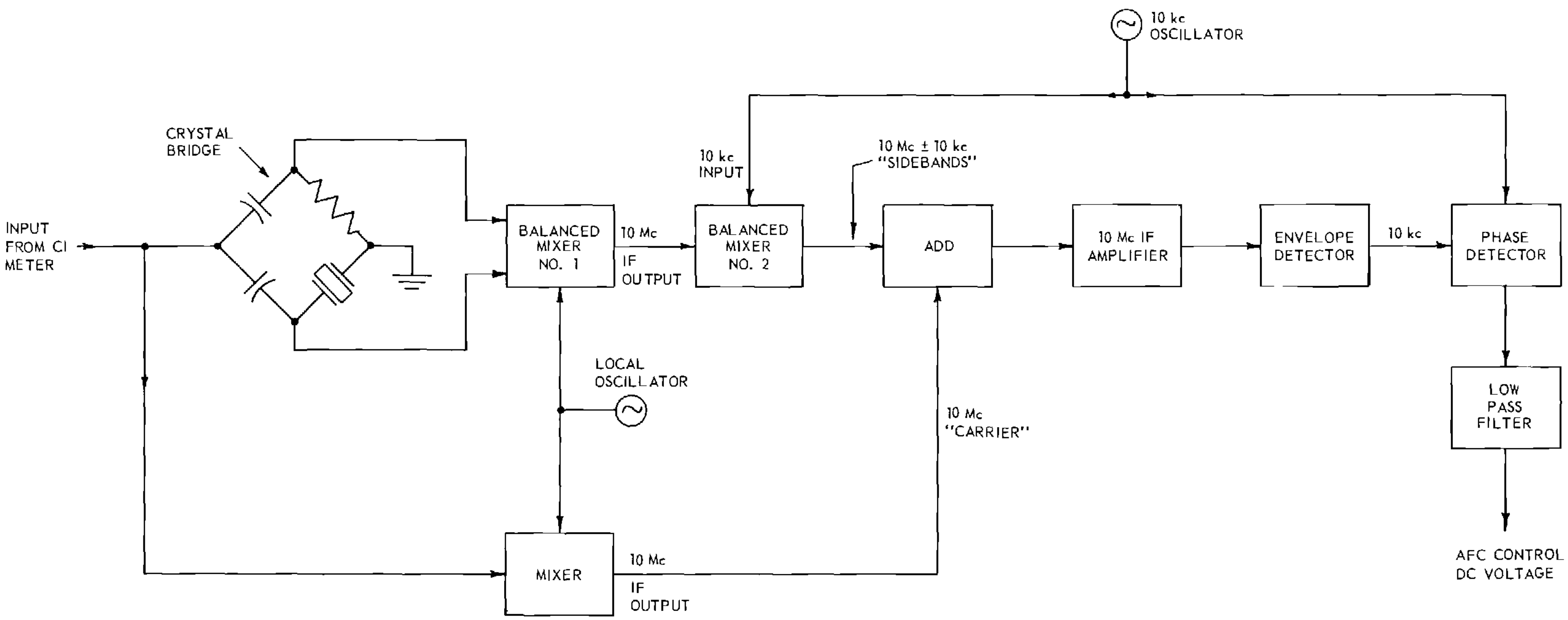


Figure 1. AFC system for measurement of crystal frequency

that the null output signal is heterodyned in the local oscillator in the first balanced mixer to produce an IF signal which is used as the carrier signal for a second balanced mixer. The other input to this second mixer is the 10 kc modulation, which heterodynes in this mixer with the IF output of the first mixer to produce a pair of sidebands which are spaced 10 kc on either side of the IF center frequency. Since this mixer is a balanced one, none of the IF center frequency appears in the output. The output of the second mixer is linearly added to a signal at the IF center frequency, which is derived by heterodyning the drive signal to the crystal bridge with the local oscillator signal.

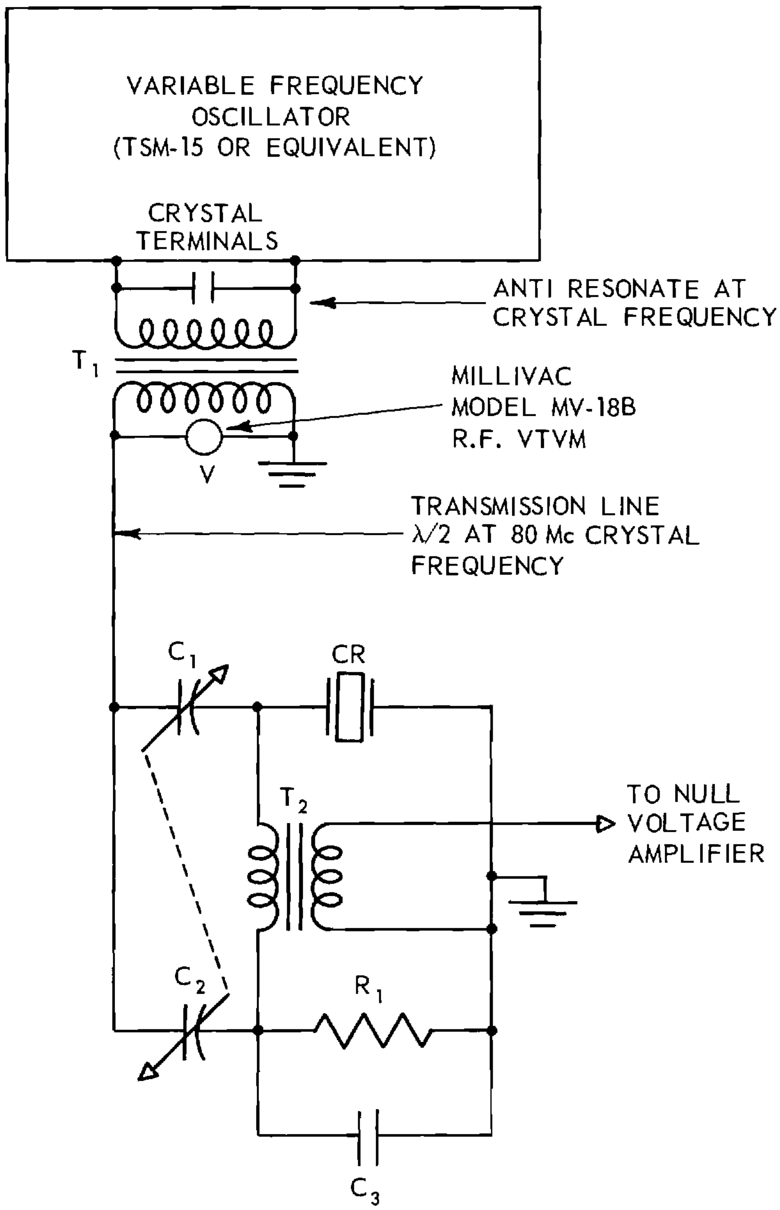
This composite output signal then consists of a carrier component at the IF center frequency, whose phase is independent of the condition of balance of the crystal bridge. The phase angles of the two sidebands, appearing 10 kc either side of the carrier, change with respect to this carrier by 180° whenever the sense of the crystal bridge null signal reverses. The amplitudes of these sideband components are directly proportional to the amplitude of the null output of the crystal bridge. Since the amplitude of the carrier component is adjusted to be large in respect to the amplitude of the sideband components, this composite signal is a conventional amplitude modulated signal with a 10 kc modulation. This signal can be amplified in a conventional IF amplifier whose bandwidth is in the neighborhood of 100 to 200 kc. The use of this bandwidth then permits the elimination of the differential phase shift between the carrier and the sidebands over the relatively narrow region of 10 kc either side of the center frequency. The output of this IF amplifier is supplied to an envelope detector the output of which is the 10 kc modulation riding on the IF carrier. When the sense of the crystal bridge balance is reversed, the phase of this demodulated 10 kc component is also reversed so that comparison of this 10 kc component in a phase detector with the original 10 kc modulation signal as a reference will result in a dc output of magnitude proportional to the null output of the crystal bridge. The polarity of this signal is reversed whenever the balance condition of the bridge is reversed. This output signal may be used to control the frequency of the CI meter to force it automatically to the point of bridge balance.

Some initial work was performed on this system but work was halted before any conclusive results were obtained. This action was taken because of the great need for immediate data in some form which would allow necessary aging information to be obtained. The work on this particular AFC measurement system was therefore curtailed in order that the measurement equipment might be returned to its original state so as to obtain aging data as rapidly as possible.

Future work on this system will be performed as a parallel development and in such a way as not to interfere with the data acquisition by the currently used frequency measurement system described in the subsequent section.

2. Passive Bridge Frequency Measurement System

The frequency measuring system displayed in Figure 2 was used first for 100 Mc and later for 80 Mc frequency measurements. The transformer T_1 must be a theoretically perfect transformer if the oscillator is to "see" at the crystal terminals an exact duplicate of the bridge impedance both in phase and magnitude. This condition cannot be obtained practically. Factors such as leakage inductance and stray capacitance (in addition to small variations in the transmission line characteristics)



T_1 – FERRITE TRANSFORMER (UNITY TURNS RATIO)
T_2 – FERRITE CORE COUPLING TRANSFORMER
C_1, C_2 – DIFFERENTIAL CAPACITOR (3–20 $\mu\mu f$)
R_1 – RESISTOR (100Ω)
CR – CRYSTAL RESONATOR
C_3 – COMPENSATING CAPACITOR (ABOUT 10 $\mu\mu f$)

Figure 2. Single-ended bridge for improved measurement accuracy at high frequencies

modify the bridge impedance as seen by the oscillator. Thus the net effect is to reduce further the effective Q of the crystal which has already been reduced somewhat by the degradation of Q intrinsic to operation in a bridge circuit.

It was found that transformer T_1 could be eliminated by the passive bridge frequency measurement system shown in Figure 3. The system requires a stable source of R.F. voltage at the crystal frequency to drive the bridge. At present a crystal controlled CI meter is being used, and a large number of crystals are required to cover the range of frequencies to be measured since each unit represents a very limited bandwidth of satisfactory operation. A more convenient arrangement would be to substitute a frequency synthesizer* for the crystal-controlled CI meter. The use of such an instrument would improve the accuracy of measurement as much as one full order of magnitude.

Two new crystal bridges are being constructed for use with the passive bridge system. The circuits are shown in Figure 4. The network composed of C_2, R_2, and D_1 in each bridge rectifies the R.F. voltage across the bridge input terminals, then returns the D.C. voltage back through the transmission line where it is removed from the line and displayed on the R.F. VTVM (item G in Figure 3).

Since 10 mv is the lowest voltage which may be conveniently read with the particular R.F. VTVM used, that value of voltage will be used as the input voltage to the bridge at all frequencies.

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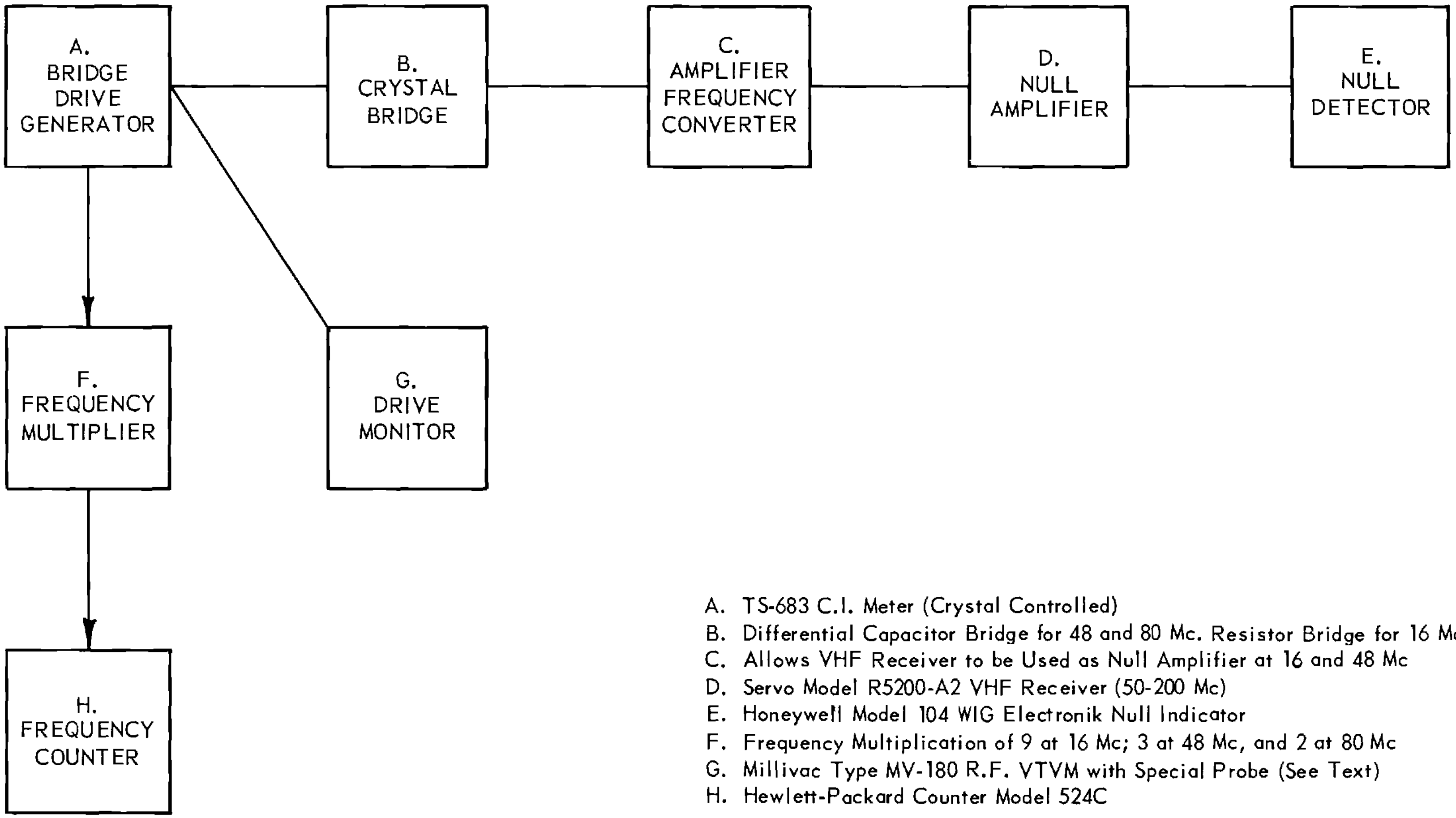
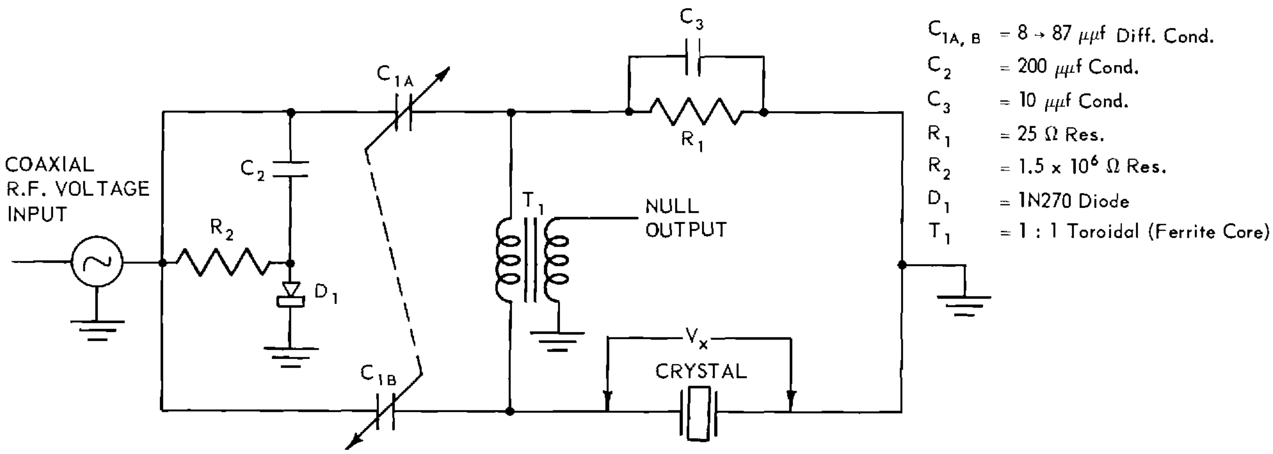
*Rohde and Schwarz, Model XU8.

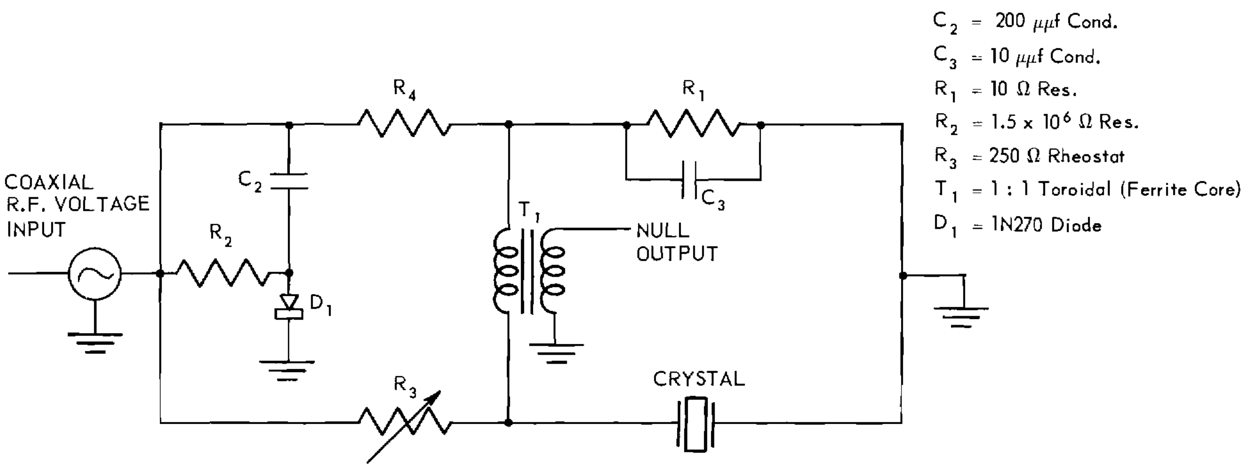


A. TS-683 C.I. Meter (Crystal Controlled)
B. Differential Capacitor Bridge for 48 and 80 Mc. Resistor Bridge for 16 Mc.
C. Allows VHF Receiver to be Used as Null Amplifier at 16 and 48 Mc
D. Servo Model R5200-A2 VHF Receiver (50-200 Mc)
E. Honeywell Model 104 WIG Electronik Null Indicator
F. Frequency Multiplication of 9 at 16 Mc; 3 at 48 Mc, and 2 at 80 Mc
G. Millivac Type MV-180 R.F. VTVM with Special Probe (See Text)
H. Hewlett-Packard Counter Model 524C

Figure 3. Passive bridge frequency measurement system



A. CRYSTAL BRIDGE FOR 48 AND 80 Mc



B. CRYSTAL BRIDGE FOR 16 Mc

Figure 4. Crystal bridge circuits for passive bridge frequency measuring system

The balanced condition of the bridge for 48 and 80 Mc can be shown to be:

$$R_s = \frac{C_{1A}}{C_{1B}} R_1 \qquad \text{(provided } R_1C_3 = R_sC_o\text{)}. \tag{1}$$

For the particular condenser used, the balance equation is satisfied for R_s values of 2.3 ohms minimum and 272 ohms maximum.

The theoretical value of drive level at 80 Mc was determined for an average crystal resistance of 23 ohms*.

$$V_x = V_B \left[\frac{\dfrac{R_s}{1 + j\omega R_s C_o}}{\dfrac{R_s}{1 + j\omega R_s C_o} + \dfrac{1}{j\omega C_{1B}}} \right] = V_B \left[\frac{j\omega C_{1B} R_s}{1 + j\omega R_s (C_{1B} + C_o)} \right] \tag{2}$$

$$P_x = \frac{|V_x|^2}{R_s} = \frac{(V_B)^2}{R_s} \left[\frac{\omega^2 \, C_{1B}{}^2 \, R_s{}^2}{1 + \omega^2 R_s{}^2 \, (C_{1B} + C_o)^2} \right] = \frac{\omega^2 C_{1B}{}^2 \, R_s \, (V_B)^2}{1 + \omega^2 R_s{}^2 \, (C_{1B} + C_o)^2} \tag{3}$$

Now determine the value of C_{1B}:

Since the capacitor is a differential type: $C_{1A} + C_{1B} = 8 + 87 = 95$ μμf

or: $C_{1A} = 95 - C_{1B}$

At the bridge null,

$$\frac{C_{1A}}{C_{1B}} = \frac{\left(\dfrac{R_s}{1 + j\omega C_o R_s}\right)}{\left(\dfrac{R_1}{1 + j\omega C_3 R_1}\right)} = \left(\frac{R_s}{R_1}\right) \left(\frac{1 + j\omega C_3 R_1}{1 + j\omega C_o R_s}\right) \tag{4}$$

But $C_{1A} = 95 - C_{1B}$

$$\frac{95 - C_{1B}}{C_{1B}} = \left(\frac{R_s}{R_1}\right) \left(\frac{1 + j\omega C_3 R_1}{1 + j\omega C_o R_s}\right) \tag{5}$$

---

* An average of 75 crystal units.

$$C_{1B}\left[1+\left(\frac{R_s}{R_1}\right)\left(\frac{1+j\omega C_3R_1}{1+j\omega C_oR_s}\right)\right]=95 \qquad (6)$$

$$C_{1B}=\frac{95}{\left[1+\left(\frac{R_s}{R_1}\right)\left(\frac{1+j\omega C_3R_1}{1+j\omega C_oR_s}\right)\right]} \qquad (7)$$

If: $\left\{\begin{array}{l} R_s = 23\Omega \\ R_1 = 25\Omega \\ R_sC_o = R_1C_3 \\ \omega = (2\pi)\ (80)\ (10^6) \\ C_o = 7\ \mu\mu f \end{array}\right\}$ Then:

$$C_{1B}=\frac{95}{1+\frac{23}{25}} = 49.5\ \mu\mu f \qquad (8)$$

$$P_x=\left(V_B{}^2\right)\left(\frac{\omega^2 C_{1B}{}^2\ R_s}{1+\omega^2R_s^2\ (C_{1B}+C_o)^2}\right) \qquad (9)$$

$$P_x=\left[(10^{-2})\right]^2\left[\frac{4\pi^2\ (80)^2\ (10^{12})\ (49.5)^2\ (10^{-24})\ 23}{1+4\pi^2\ (80^2)\ (10^{12})\ (23)^2\ (56.5)^2\ (10^{-24})}\right] \qquad (10)$$

$$P_x=\left(10^{-6}\right)\left(\frac{1.43}{1.43}\right)=10^{-6}\ \text{watts.}$$

An average value of crystal resistance of 15 ohms is found for the 3rd mode (48 Mc) crystal. Similar calculations give a value of 3.9×10^{-7} watts for the crystal power. The voltage division ratio for the 16 Mc bridge was calculated to give a crystal power of 8.1×10^{-7} watts for an assumed value of 7 ohms for R_s. This latter bridge has a balance range of 0.2 ohms to 50 ohms.

The circuit for the frequency converter (item C, Figure 3) is shown in Figure 5. The signal from the unit oscillator is 64 Mc when measuring 16-Mc units; 128 Mc when measuring 48-Mc units. An 80-Mc signal from the bridge is not heterodyned.

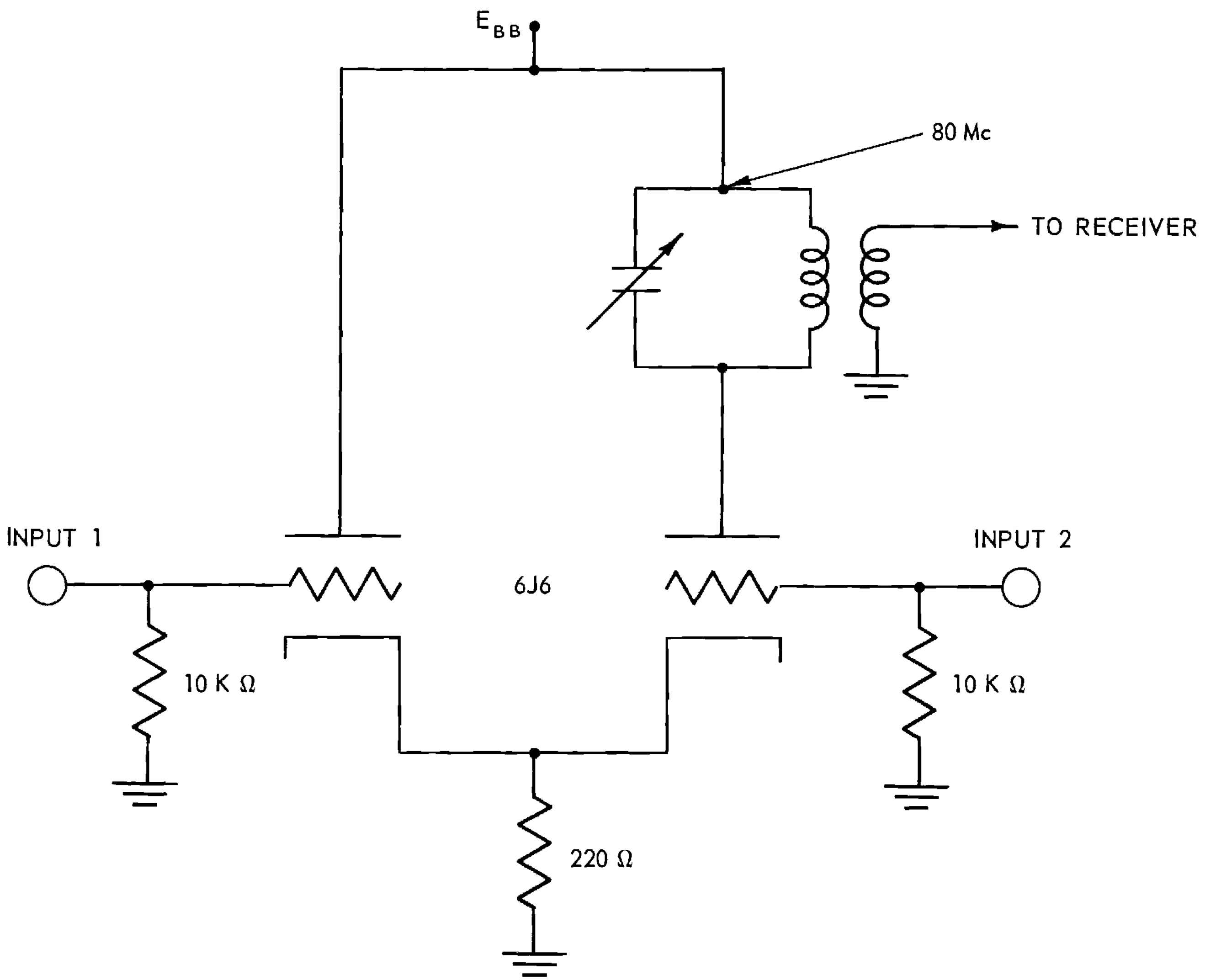
The frequency multiplier (item F, Figure 3) is of conventional design and serves to multiply the frequency of the bridge-drive signal source so that the $\pm$ 1 count intrinsic to all counting equipment is not an important measurement error. For example, the measurement error introduced at 16 Mc by the $\pm$ 1 count error is 6.25×10^{-8}. If the 16-Mc signal is multiplied by 9 and counted at 144 Mc this error reduces to 6.95×10^{-9}. Multiplications are 9 at 16 Mc, 3 at 48 Mc, and 2 at 80 Mc.

Preliminary measurements with the system discussed indicate excellent sensitivity and a measurement accuracy of a few parts in 10^{8}. Accuracy is expected to become an order of magnitude better with gradual refinement. The acquisition of a frequency synthesizer of high quality should give an immediate improvement in accuracy near the maximum potential to the system.

3. Vacuum Equipment

The HC-6/U glass holders were received during the quarter and the design and fabrication of a satisfactory sealing system was completed. A photograph of the sealing equipment is reproduced in Figure 6. The important features of the system are:

1. A vacuum tube furnace which may be quickly evacuated to about 2×10^{-5} mm Hg;
2. A gas-fired burner for pre-heating and annealing the parts to be joined (essentially eliminating the need for a programmed inducation heating cycle);



INPUT 1. R.F. Signal from General Radio Unit Oscillator (50 to 250 Mc)

INPUT 2. From Null Output of Crystal Bridge (16, 48, or 80 Mc)

Figure 5. Frequency converter to permit use of VHF receiver as the null amplifier at 16 and 48 mc crystal frequencies

3. An induction-heater* coil for heating the Kovar ring imbedded in the frit on the base;
4. A spring-loaded jig containing the envelope and base in mated position (when the frit is melted by the application of heat the spring loaded rod** forces the base and cover together to a distance adjustable by a stop on the rod); and
5. A dial-gauge which measures the distance traveled by the rod during sealing.

The dial-gauge measurement was found to be the most important control parameter for the production of uniform seals which will pass the vacuum-oil leak test. Initially, seals were made with the parts mated and under pressure by induction heating the Kovar ring to a selected temperature for a prescribed time. The times and temperatures were varied over a wide range to determine the most suitable values for these parameters. The resulting seals, however, were non-uniform and frequently leaked. The use of the dial-gauge permits continuous monitoring of the relative motion between the base and envelope during the melting of the frit and this distance appears to be more critical than any time-current combination used to obtain it. The travel of 0.020 inches has been found to give consistently leak-proof seals of excellent appearance. This amount could probably be increased to about 0.030 inches without degradation of the seal. For an induction current of one ampere, the time required for the spring-loaded rod to compress the mated junction 0.020 inches is in the range 30 to 45 seconds.

- - - - -

*Lepel Model CB-2.

**The rod may be moved vertically and rotated if needed. A double O-ring provides vacuum tight seal.

C. Other Work

The work during the quarter has been primarily directed to the development of the frequency measurement system and the glass HC-6/U sealing apparatus. These phases have been reported in detail under Section B preceding.

Approximately 75 resonators in the ovens were continued on storage at 85°C but, because of the interference with frequency measurements caused by the extensive measurement equipment modifications, no measurements were made in the period 7 September to 15 November 1961.

Likewise, since the primary effort in the project was directed to the solution of these two problems no resonators were fabricated after 10 August 1961. Complete reports on resonators remaining on storage will be available in the next report.

VI. PROGRAM FOR THE NEXT INTERVAL

During the third Quarter fabrication and measurement of resonators with selected metal plating materials will be undertaken according to the previously arranged schedule for inclusion of natural, synthetic, and swept synthetic blanks in the measurements.

Of particular interest will be:

(1) The planned use of pyroceram-silver bonding cement for selected resonators:

(2) The mounting of resonators in the glass HC-6/U containers;

(3) The commencement of aging studies of continuously operated resonators; and

(4) "Q" measurements of resonators previously fabricated.

VII. PERSONNEL

The persons employed on this project and the hours devoted to it during the period of this report by each are:

		Hours
R. B. Belser	Project Director	100
W. H. Hicklin	Ass't. Research Engineer	263
W. B. Warren	Research Engineer	16
S. N. Witt	Research Engineer	52
C. S. Wilson	Electronic Technician	508
J. O. Darnell	Research Assistant	176
C. M. Shirley	Technician	40

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Arthur L. Bennett, Chief
Physical Sciences Division

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Motorola, Inc. Comm. and Electronics Division 4501 Augusta Boulevard Chicago 51, Illinois	1
Systems Incorporated 2400 Diversified Way Orlando, Florida ATTN: Dr. W. Horton	1

This contract is supervised by the Solid State and Frequency Control Division, Electronic Components Department, USASRDL, Fort Monmouth, New Jersey. For further technical information contact Mr. P. E. Mulvihill, Project Engineer, Telephone: 535 2475.

REPORT NO. 4 (FOURTH QUARTERLY REPORT)
GEORGIA TECH PROJECT NO. A-552

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. BELSER and W. H. HICKLIN

CONTRACT NO. DA-36-039-SC-87407
DA Task No. 3A 99 15 004

15 NOVEMBER 1961 to 15 FEBRUARY 1962

PLACED BY THE U. S. ARMY
SIGNAL RESEARCH AND DEVELOPMENT LABORATORIES
FORT MONMOUTH, NEW JERSEY

Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

QUARTERLY REPORT NO. 4

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser
W. H. Hicklin

Contract No. DA-36-039-SC-87407
DA Task No. 3A 99 15 004
Georgia Tech Project No. A-552

15 NOVEMBER 1961 TO 15 FEBRUARY 1962

Placed by the U. S. Army
Signal Research and Development Laboratories
Fort Monmouth, New Jersey

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

* "Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500 to 574° C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

The passive bridge frequency measuring system is capable of determining crystal frequencies with a precision of a few parts in 10^9. The crystal controlled CI meter is not entirely satisfactory as the RF generator, and some loss of precision results from the instability of the RF voltages applied to the bridge, especially when the reference crystal must be "pulled" off of its resonant frequency.

The 200 position, $85^{\circ}C$ crystal oven temperature cycling of about $\pm$ $0.03^{\circ}C$ has given some measurement errors since the crystals are measured when possible at the first, third, and fifth modes and can have a zero temperature coefficient of frequency at but one of the modes. In some cases, units fabricated of cultured quartz appear to have a turn-over temperature of other than $85^{\circ}C$ at all three modes of operation.

A proportional control system for this oven has been designed. The system is based on thermistor bridge control of the output voltage of a magnetic amplifier. Preliminary studies indicate that the temperature cycling can be reduced to $\pm$ $0.01^{\circ}C$.

The crystal bonding cement composed of five parts Pyroceram 95 plus one part silver flake by volume does not appear to be suitable for high precision, high-frequency crystal resonators. The lack of compatibility between the thermal expansion coefficients of the Pyroceram and quartz appears to cause intermittent or "noisy" bonds. A more suitable mixture is one part Pyroceram plus two parts silver by volume. The cement is fired for five minutes at $450^{\circ}C$. Neither of the above cements is considered to be as effective as the duPont No. 5504A cement within its temperature limitations provided the bond is properly cured and vacuum baked before sealing.

III. PUBLICATIONS, LECTURES, REPORTS, AND CONFERENCES

During this reporting period, two monthly letters (Nos. 9 and 10) were submitted. Report No. 3 (Third Quarterly Report) was distributed.

An abstract of the paper to be presented at the Sixteenth Annual Frequency Control Symposium was submitted.

IV. FACTUAL DATA

A. Introduction

Work during the fourth quarter has been directed toward refinements of the frequency measuring system and the fabrication of crystal units.

Attention has been directed to the improvement of the temperature stability of the 200-position, 85°C oven. The control of the oven temperature is considered to be a basic factor in the measuring system and oven temperature deviation is now one of the major sources of measurement error.

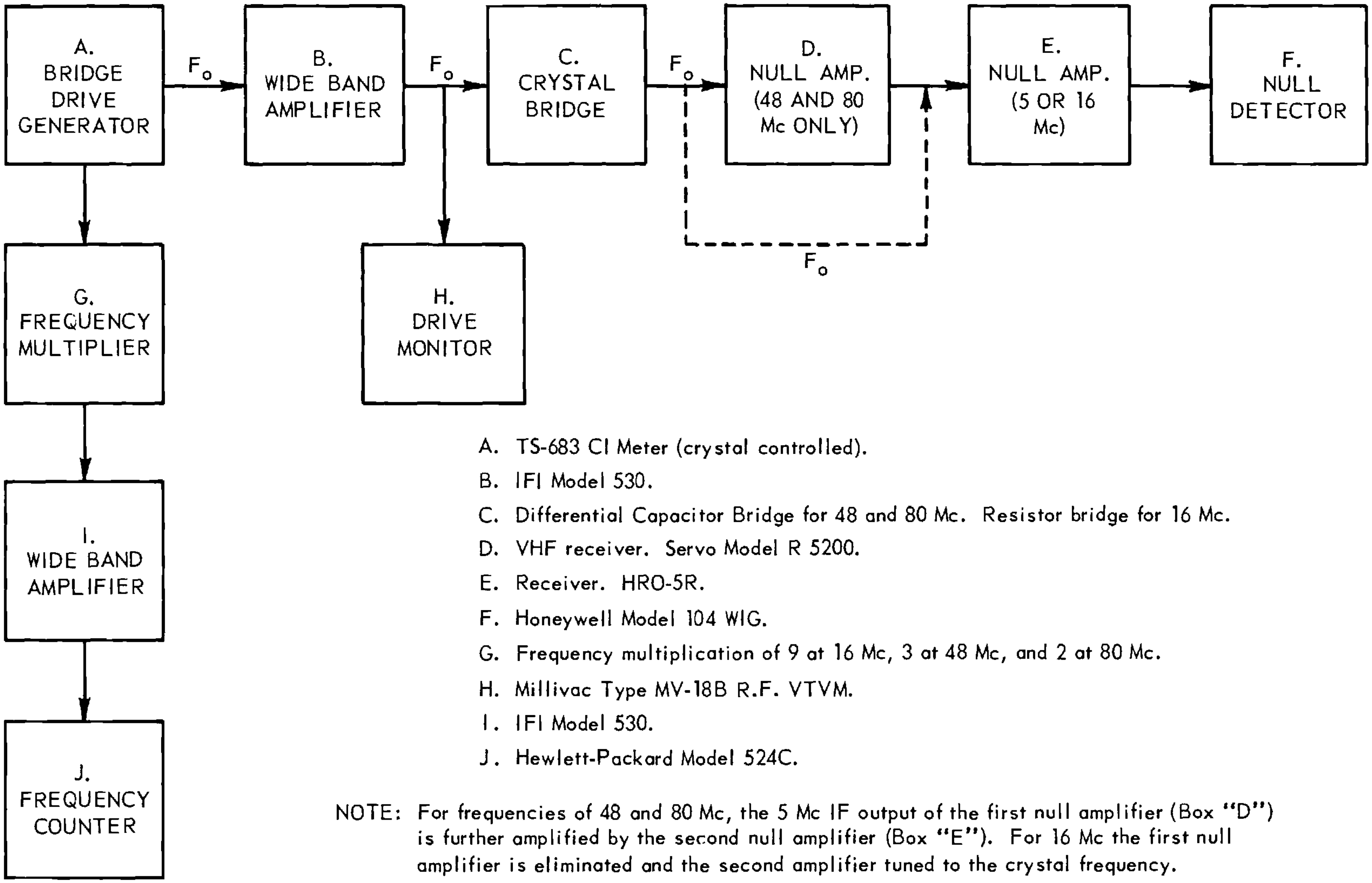
A second 85°C oven providing 36 additional positions was placed in service. One hundred and thirty six (136) oven positions were available for use by the end of the fourth quarter. This number will be soon increased to 172 by the installation of a second 36-position oven.

B. Apparatus Modification and Construction

1. Frequency Measuring System

The passive bridge frequency measuring system described in the Third Quarterly Report was modified to eliminate the frequency converter in the null amplification chain. This action eliminated some loss of sensitivity in the chain due to the presence of the converter. The subsequent addition of an HRO-5R receiver in the null amplification chain allowed some reduction in the system bandwidth and thus a better signal to noise ratio for improved sensitivity. The system in its final form is illustrated in Figure 1.

The basic weakness of the frequency measuring system is the necessity of maintaining a large number of reference crystals for controlling the frequency of the CI meter. For a number of measurements, the refer-



A. TS-683 CI Meter (crystal controlled).

B. IFI Model 530.

C. Differential Capacitor Bridge for 48 and 80 Mc. Resistor bridge for 16 Mc.

D. VHF receiver. Servo Model R 5200.

E. Receiver. HRO-5R.

F. Honeywell Model 104 WIG.

G. Frequency multiplication of 9 at 16 Mc, 3 at 48 Mc, and 2 at 80 Mc.

H. Millivac Type MV-18B R.F. VTVM.

I. IFI Model 530.

J. Hewlett-Packard Model 524C.

NOTE: For frequencies of 48 and 80 Mc, the 5 Mc IF output of the first null amplifier (Box "D") is further amplified by the second null amplifier (Box "E"). For 16 Mc the first null amplifier is eliminated and the second amplifier tuned to the crystal frequency.

Figure 1. Passive-bridge frequency measuring system for frequency measurements in the range of 16 to 80 Mc.

ence crystal must be "pulled" off of its normal resonant frequency in order to make a measurement. The result of this latter action is to degrade the stability of the frequency applied to the impedance bridge. However, when a good frequency match between the reference crystal and the crystal being measured is obtained, the measurements are accurate to within a few parts in 10^9.

Standard frequency signals for the frequency counter are provided by an O-76U 100 kc oscillator. The frequency of this oscillator is maintained at 14 ± 2 pp 10^9 above the frequency of WWVL. A continuous recording of the beat frequency between the two signals is made and displayed at the frequency measuring position. In addition, a second O-76/U oscillator is monitored continuously by plotting the beat frequency of the two 100 kc oscillators. This latter unit serves as a stand-by.

2. Crystal Storage Ovens

Presently two 85°C ovens are in operation. One provides positions for 36 units and has very good temperature stability with the modified proportional control system used at Tech for several years. The second oven provides positions for 200 units and has a temperature deviation of about ± 0.03°C. This temperature deviation is too large for the current measurement program. The crystals are being measured at three overtone modes and have, at best, a "frequency turnover point" at but one of the modes. Some of the units, especially those fabricated from the synthetic quartz, appear to have turnover temperatures at other than 85°C on all of the three modes of operation.

Time does not permit the oven to be rebuilt. Thus, the probable solution appears to be the substitution of a 100 per cent proportional temperature control system for the modified proportional control system. A design based on the control of a magnetic amplifier output voltage by means of a thermistor bridge was constructed and used for controlling the oven temperature. The temperature stability of the oven at 85°C is now about ± 0.01°C. However, an unreliable chopper amplifier has restricted use of this system to periods when performance can be monitored (i.e., when measurements are being made). The proportional temperature control system is illustrated in Figure 2. With refinements, this system should be adequate for all frequency measurements.

3. Vacuum Equipment

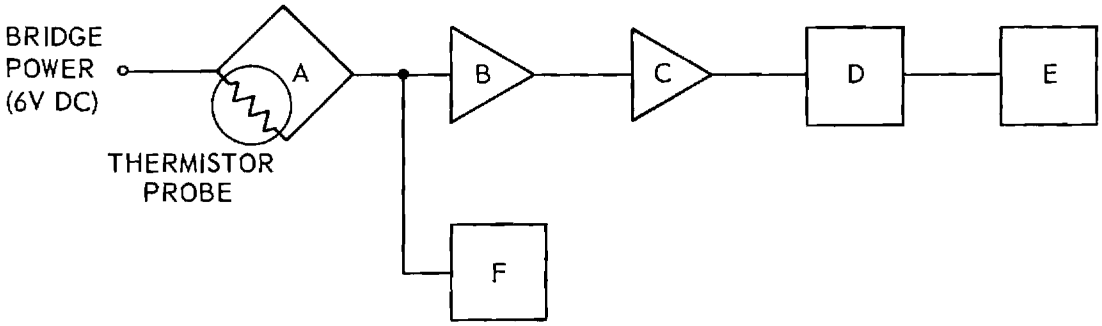
No major modifications or repairs have been made on the vacuum equipment during this reporting period. Some changes on the HC-6/U glass sealing equipment is anticipated. For a discussion of these changes, see Section IV.C of this report.

C. Crystal Resonator Fabrication and Measurement

Two groups of crystal resonators were fabricated during this quarter. Group 9 was base plated with aluminum, mounted in tab-clips, spot-welded to HC-6/U glass bases, bonded with Pyroceram-silver cement* and sealed in HC-6/U glass holders. The sealing apparatus described in Quarterly Report No. 3 was used for the sealing.

Considerable difficulty was encountered with the bonding of the crystals. Some of the units were "bonded" several times before operation was obtained. The cement appeared to crack from the plated quartz upon cooling. Such action was very likely due to the poor match of the thermal

* Five parts Pyroceram No. 95 to one part silver powder by volume.



A = Impedance Bridge: Brown Electro-Measurements Corporation, Model 250-CA.

B = DC Micro Volt-Ammeter: Hewlett Packard Model 425A.

C = Magnetic Amplifier: Freed Transformer Company Model MAO-3.

D = Matching Transformer, step-down 2:1.

E = Oven heater winding, 15 ohms.

F = Monitor null detector: Honeywell Model 104 WIG.

NOTE: The thermistor probe above is located at the oven wall. A second thermistor bridge monitors the resistance of a thermistor in an evacuated bulb located at a crystal position.

Figure 2. Proportional oven temperature control system with thermistor bridge control of a magnetic amplifier.

expansions of the quartz and cement. During the bonding of group 9, the following bonding technique was developed and used subsequently on group 10:

1. Dry mix 5 parts Pyroceram 95 and 1 part silver flake (by volume).
2. Add the vehicle* until the mixture has the consistency of cream.
3. Apply a thin coat to the mounted crystal at the clip and allow to dry.
4. Apply a second coat and dry.
5. Fire for 5 minutes in an oven pre-set to 450°C.

All but one of the group 10 units operated after the first bonding.

Aging of group 9 units were generally very poor. The behavior suggested that the units were leaking although vacuum oil leak tests indicated no definite leaks. The history of bonding trouble and multiple firing of the cement could have contributed to the poor aging. Also, one could conjecture that when the HC-6/U glass seal is made <u>in vacuo</u>, an outgassing of the sealing glass covering the Kovar ring could contaminate the resonator and holder.

When units mounted in HC-6/U glass holders are next fabricated, the sealing apparatus will be modified to <u>reduce</u> the pressure forcing the parts to be sealed together. This pressing,if too high, could compress the sealing glass before it was soft enough to make an air tight seal.

Group 10 crystals were completed exactly like group 9 with the bonding technique previously described. These units, however, were mounted

---

* Anyl acetate plus about 3% nitrocellulose by weight.

in the normal manner and given the regular vacuum bake of 3 hours at 175°C. The purpose of group 10 was to check the aging rate of units bonded with Pyroceram 95 silver cement when other variables had been reduced to a minimum. The aging rates for some of the group 10 units were excellent as shown in Figures 3 and 4. As a group, the units tended to be noisy. A noisy unit can be easily detected at null because the residual noise level is considerably higher than normal. This noise is considered to be due to small resistance changes in the bond. One unit of the group (No. 10-3) became too noisy to measure. It should be added that several units of group 9 failed after a short period in the oven. Again the bonding cement was suspect.

Figures 5, 6, and 7 illustrate the aging of selected units when measured at two or more modes of operation. All of these units will operate at the fifth overtone but reference crystals are available for but one unit (7-9 in Figure 7C).

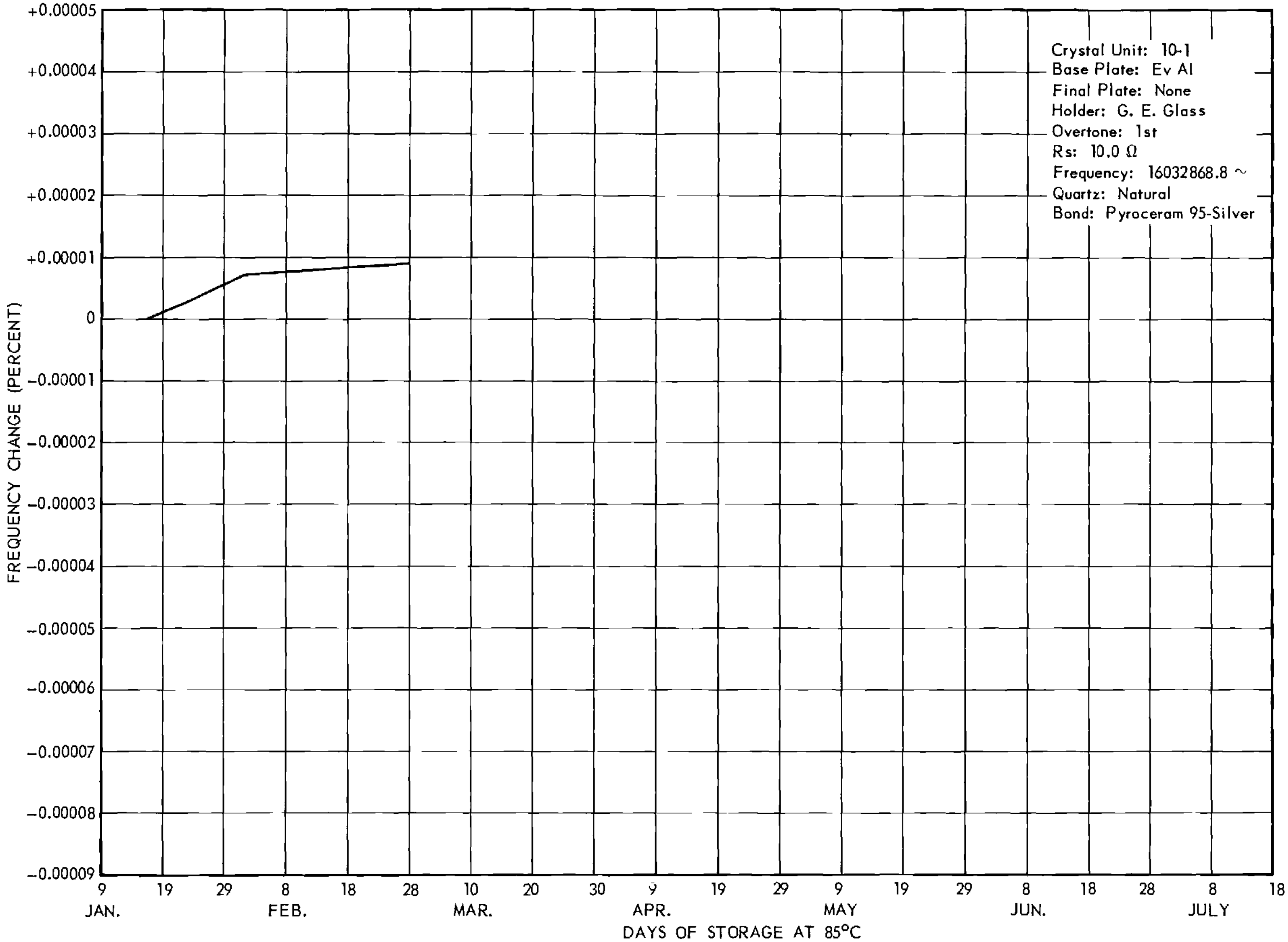


Figure 3a. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

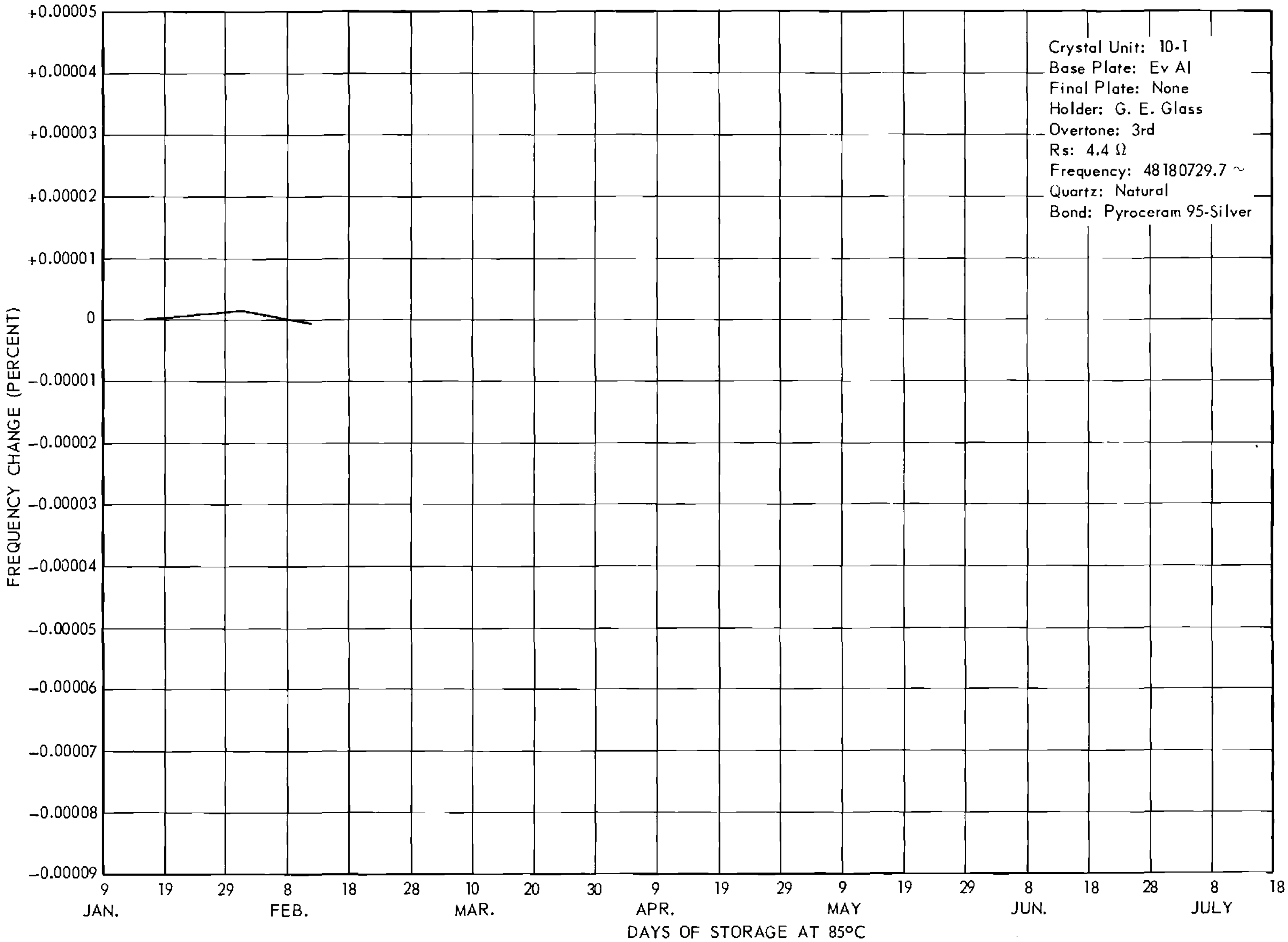


Figure 3b. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

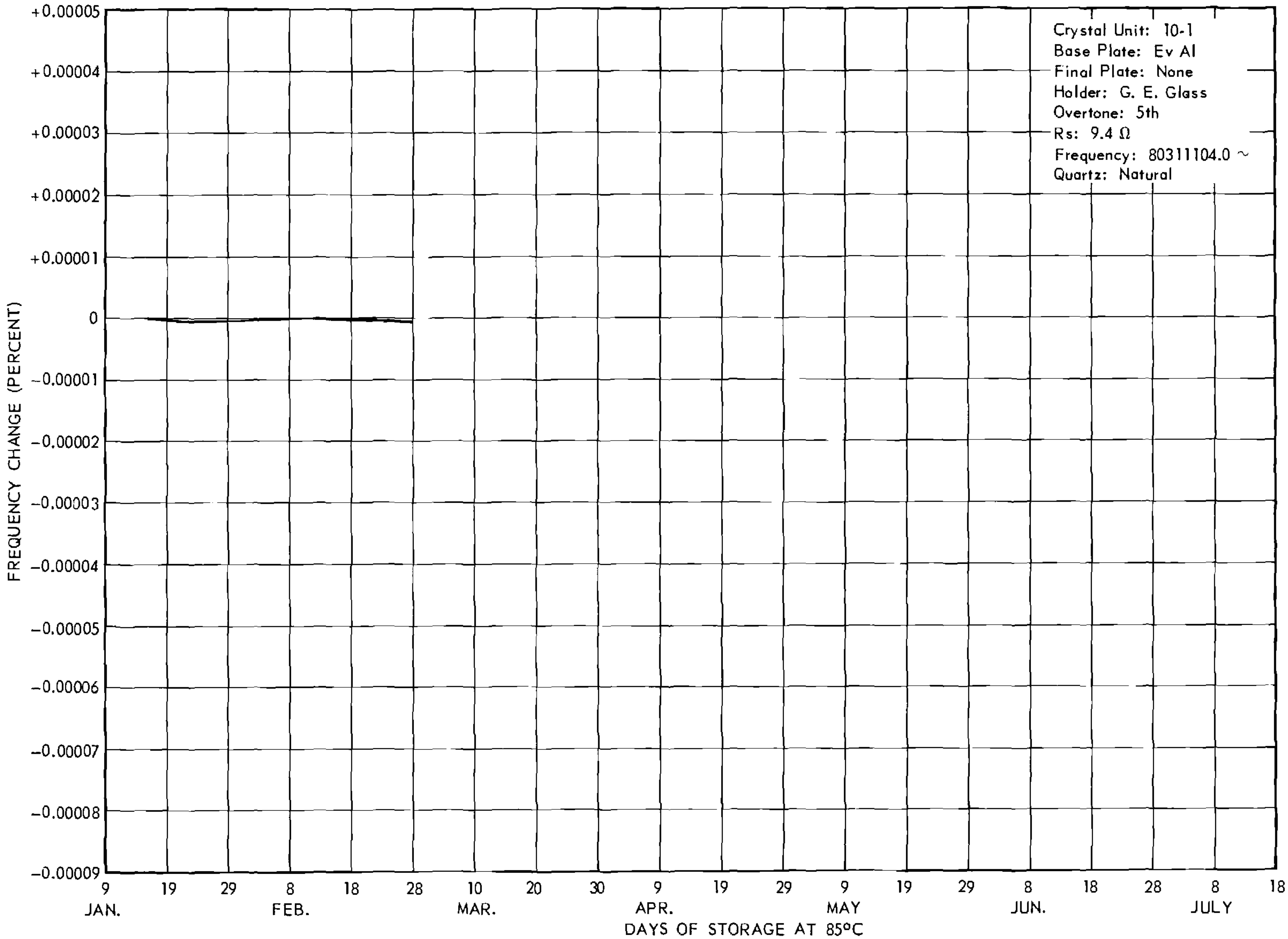


Figure 3c. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

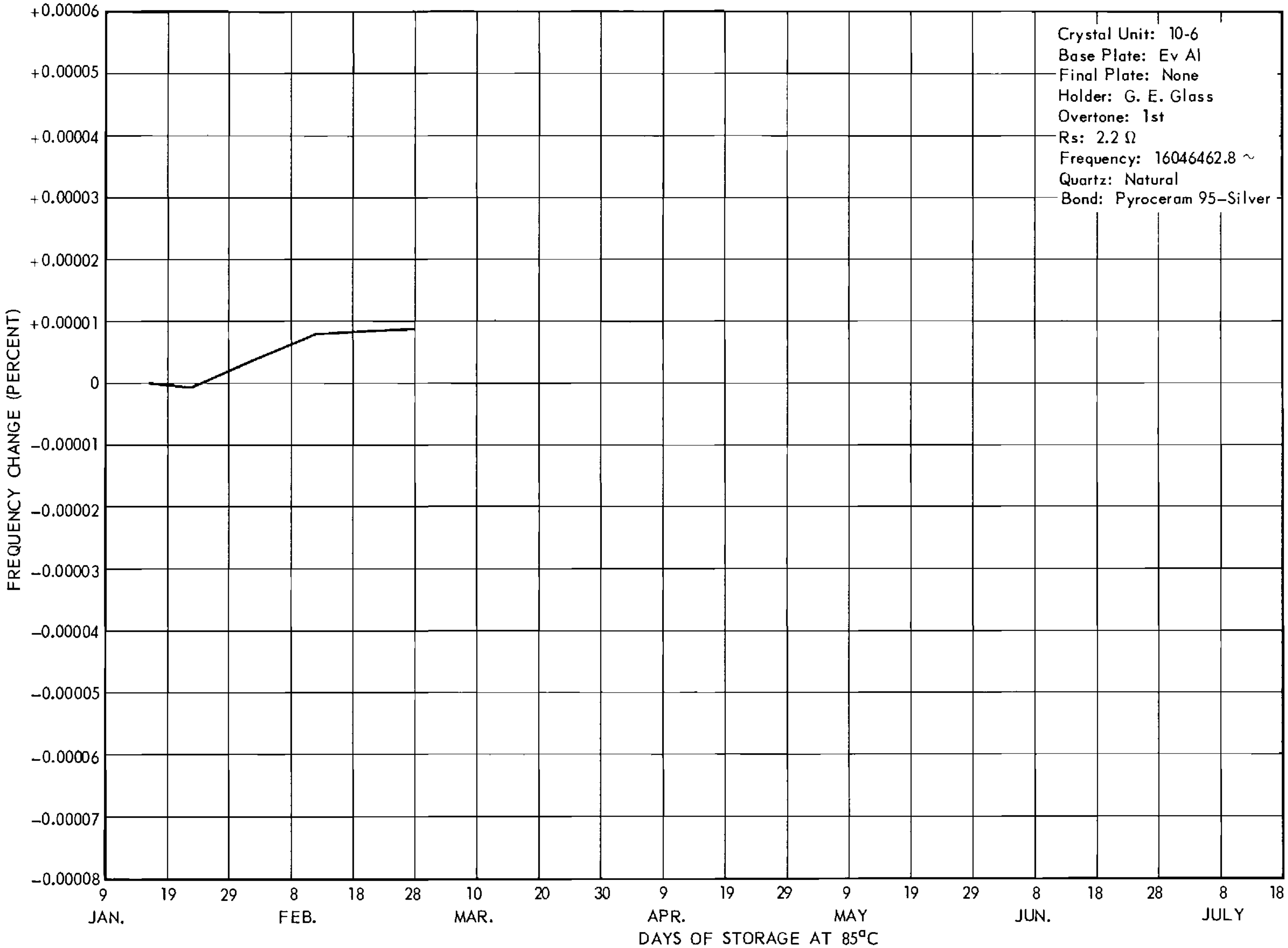


Figure 4a. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

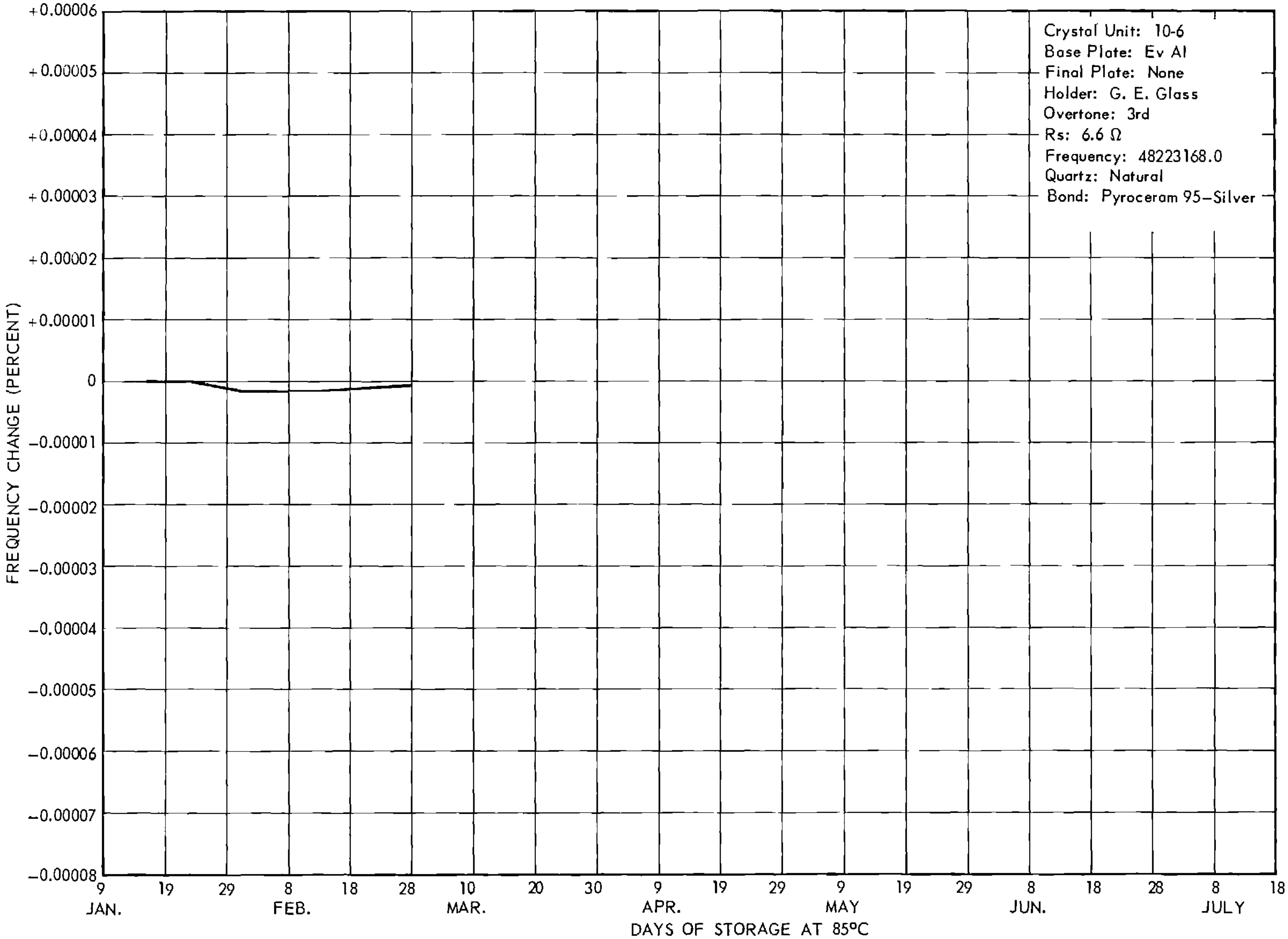


Figure 4b. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

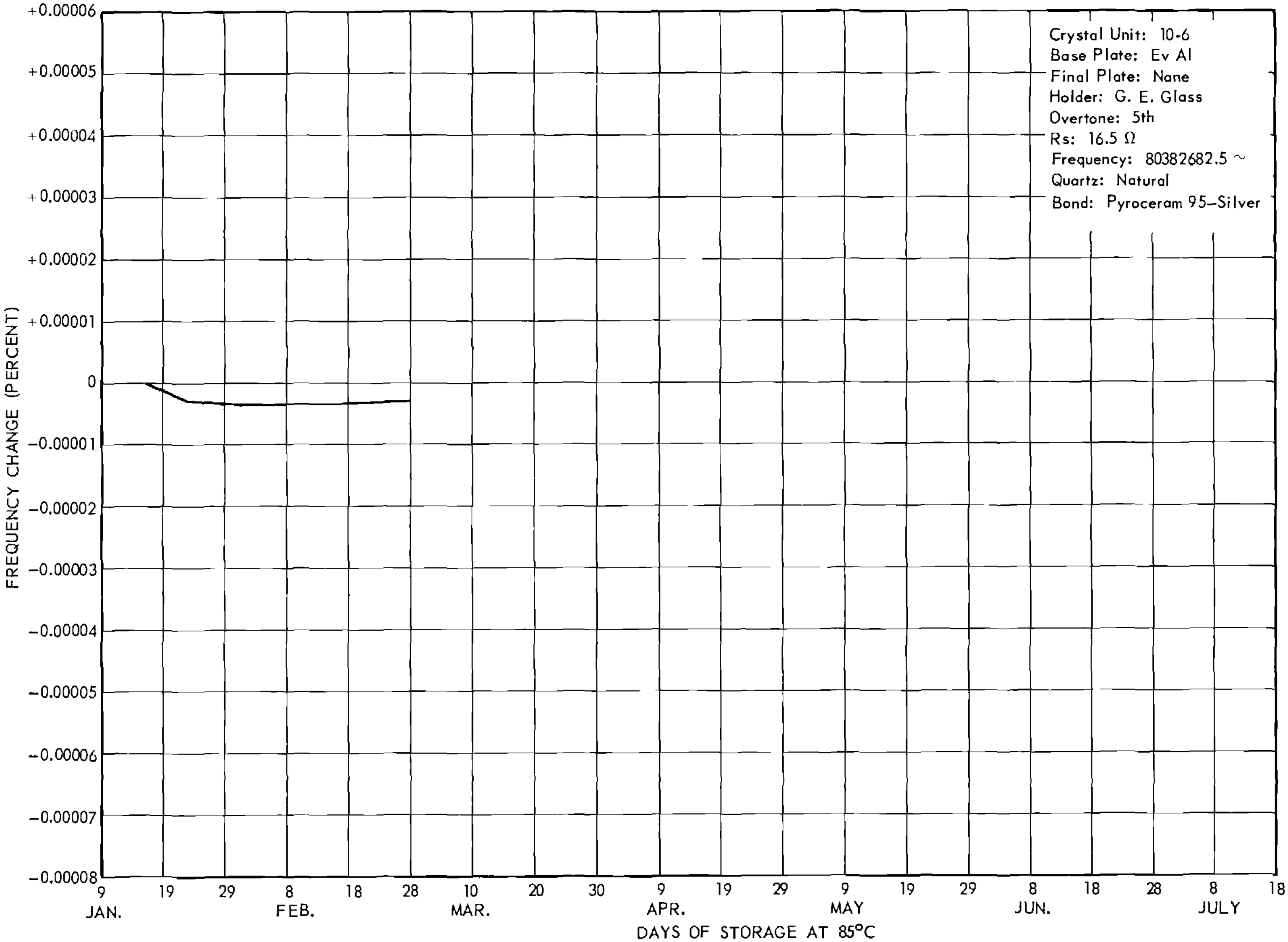


Figure 4c. Frequency versus temperature characteristics of an aluminum plated resonator bonded with pyroceram plus silver cement.

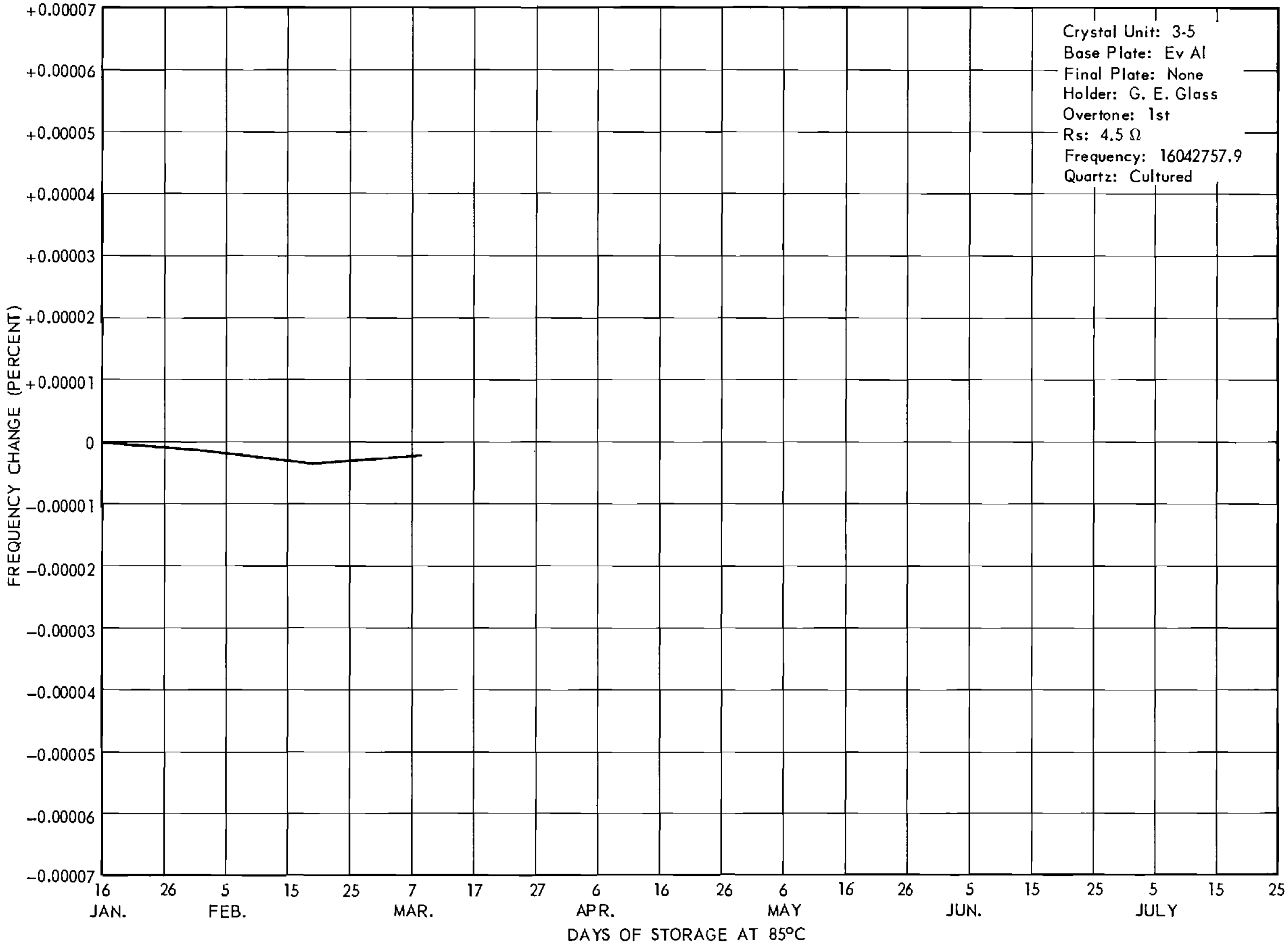


Figure 5a. Frequency versus temperature characteristics of an aluminum plated resonator of cultured quartz.

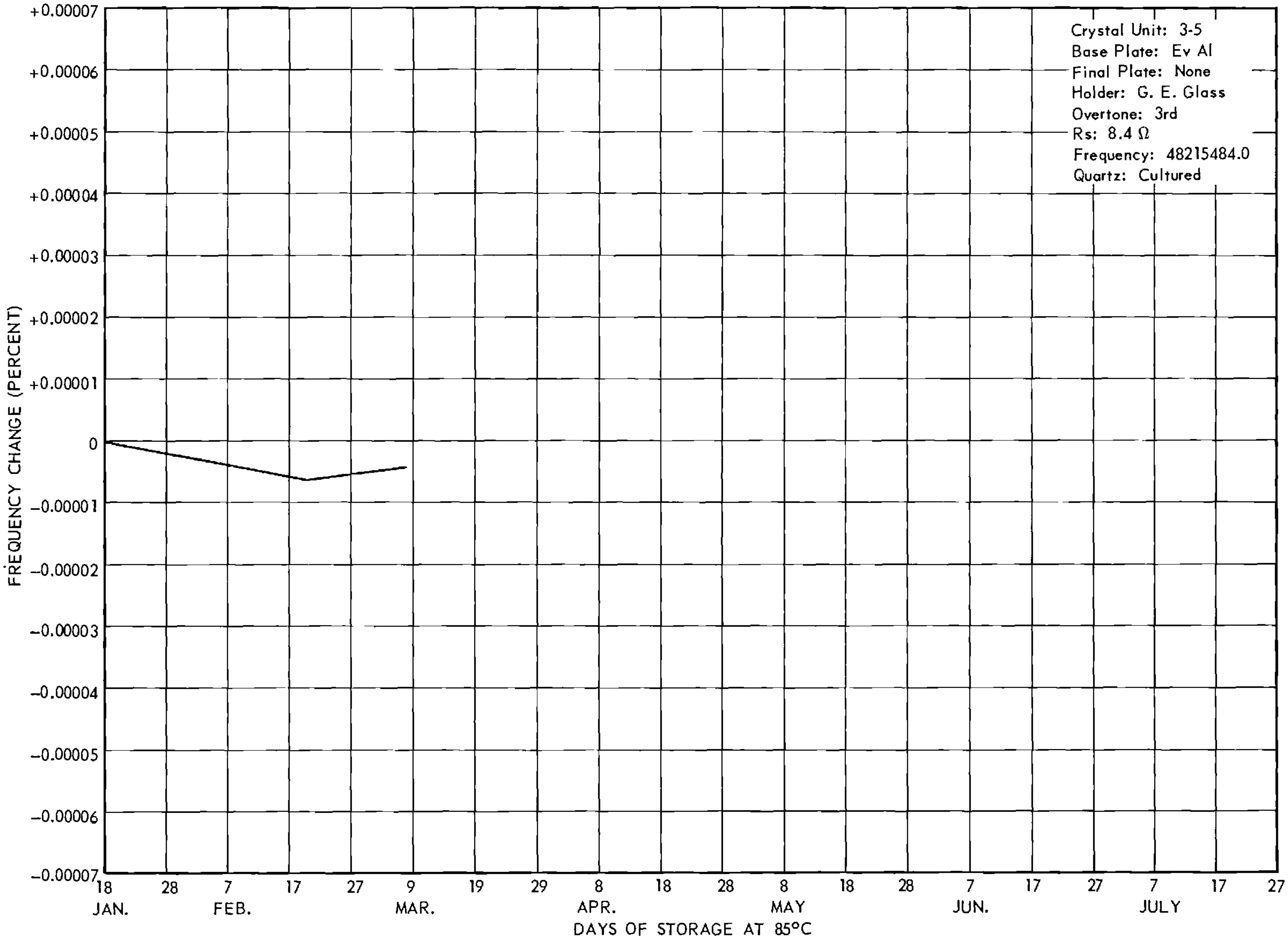


Figure 5b. Frequency versus temperature characteristics of an aluminum plated resonator of cultured quartz.

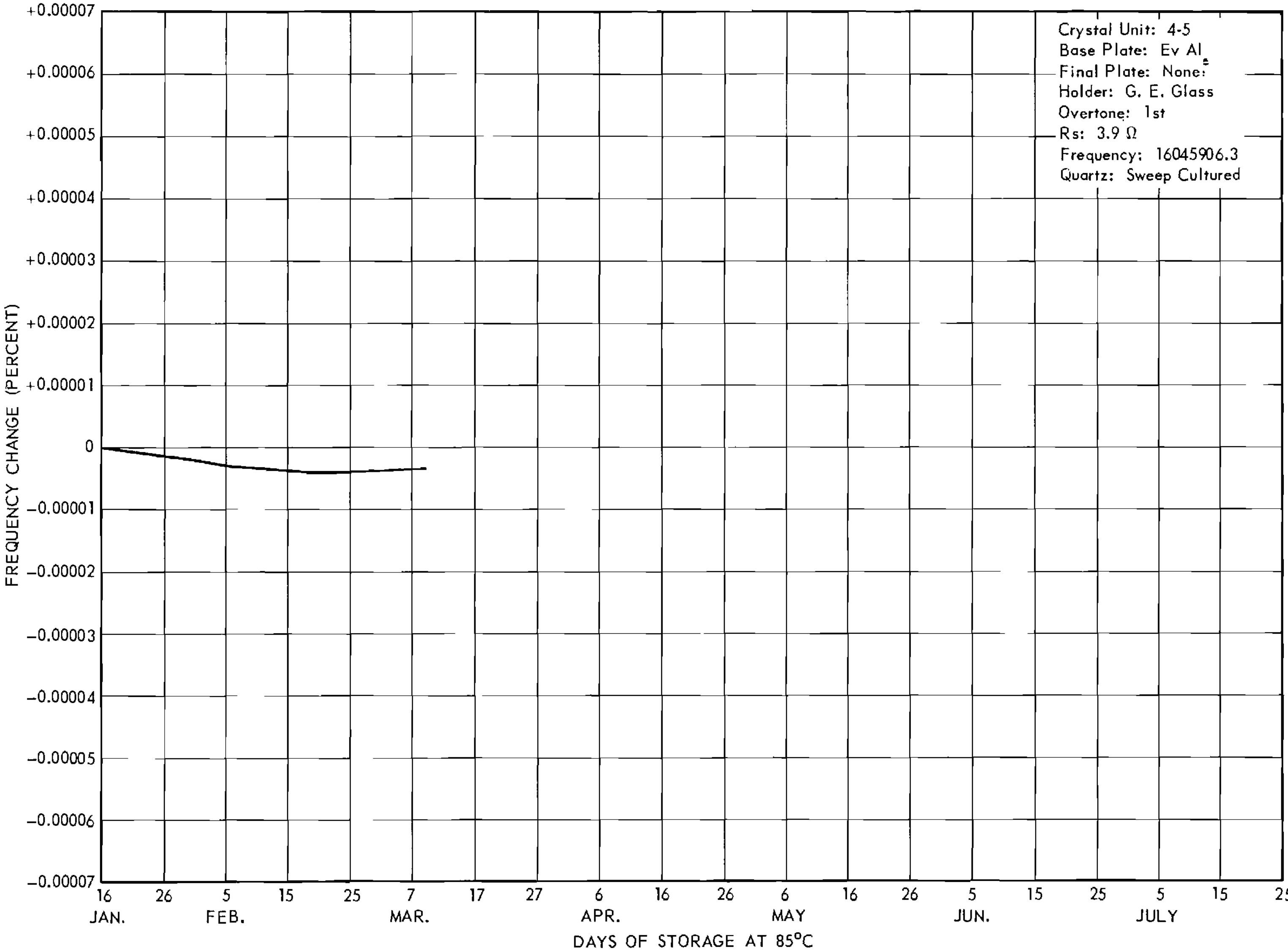


Figure 6a. Frequency versus temperature characteristics of an aluminum plated resonator of swept, cultured quartz.

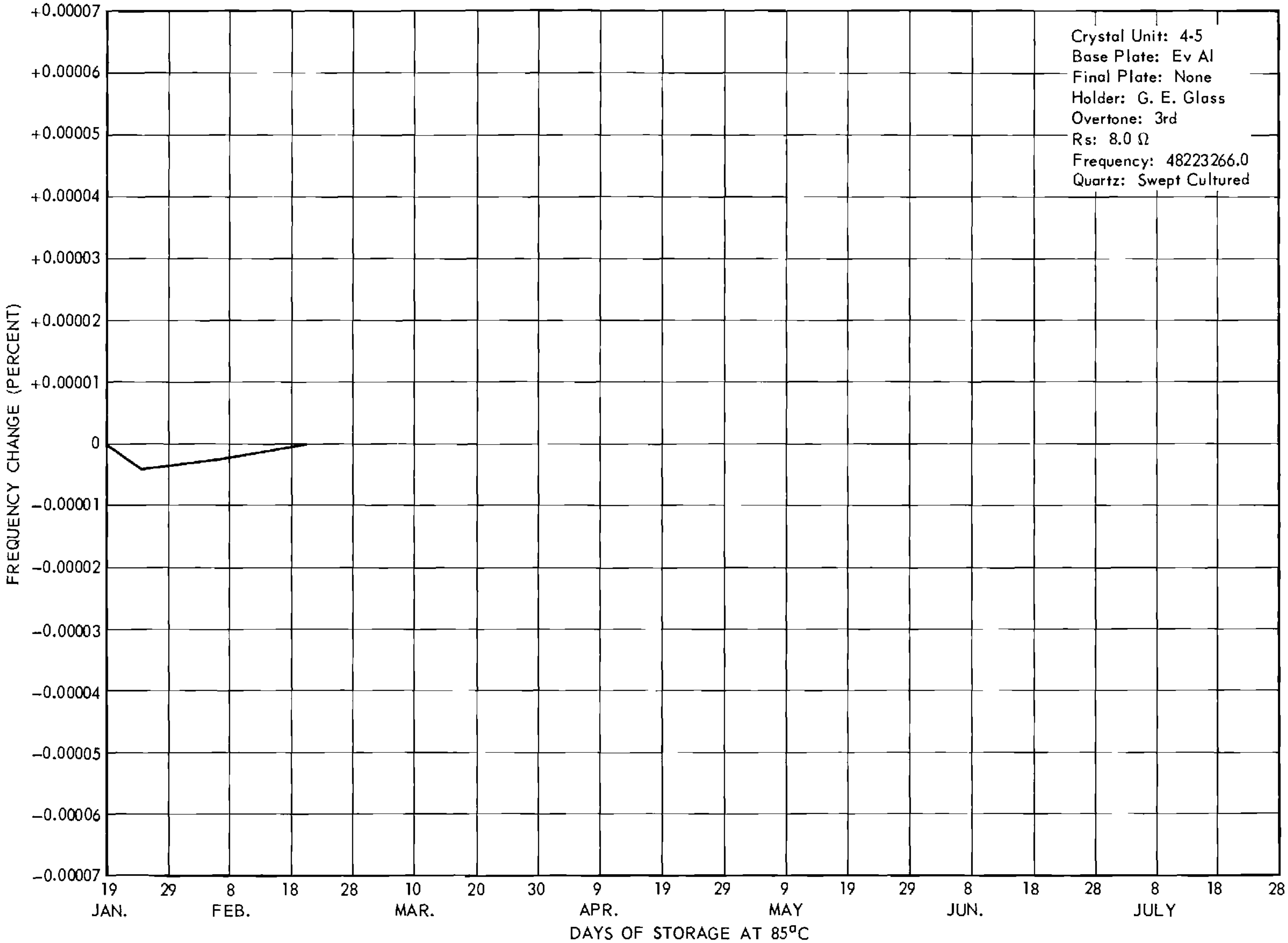


Figure 6b. Frequency versus temperature characteristics of an aluminum plated resonator of swept, cultured quartz.

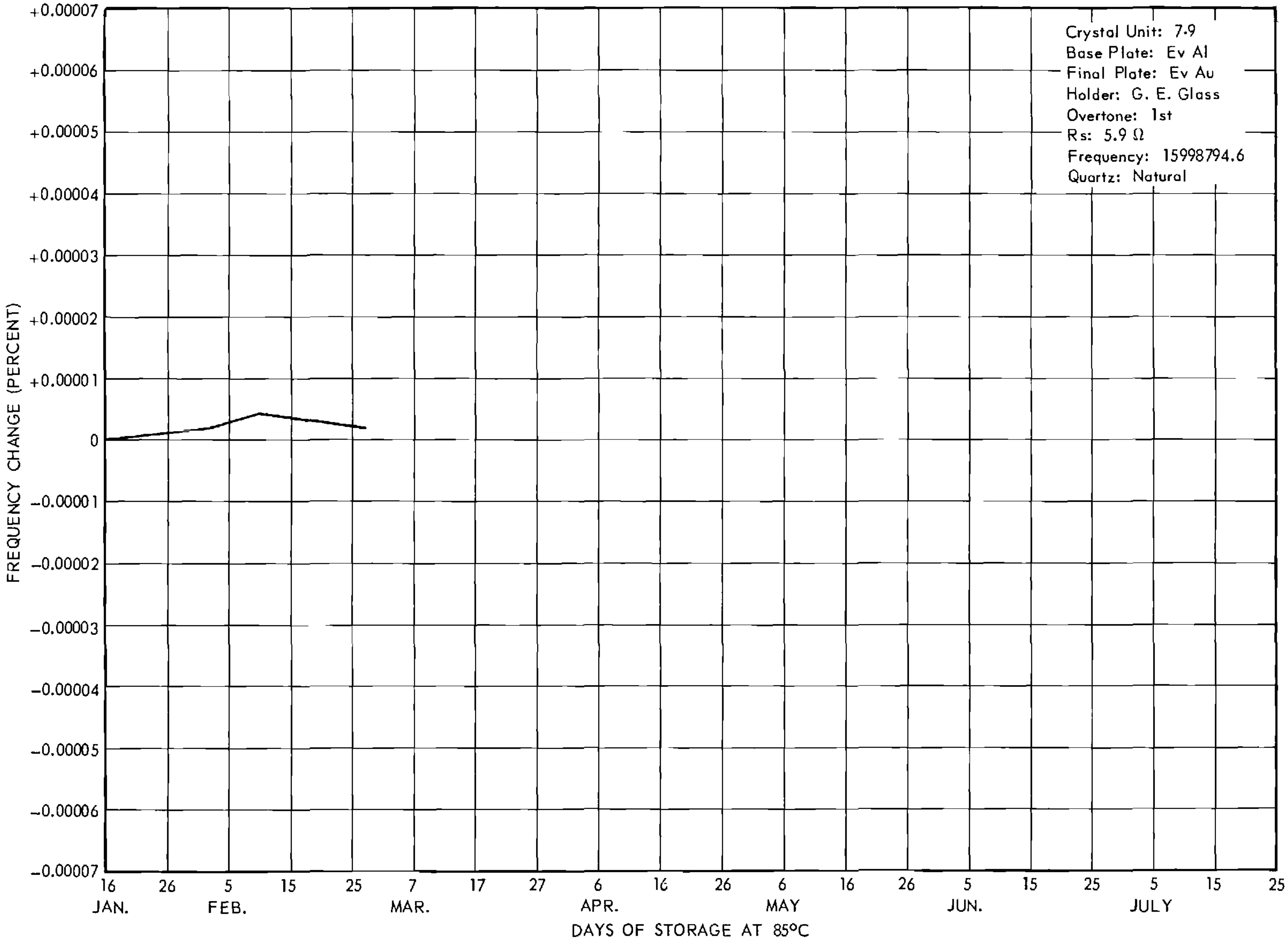


Figure 7a. Frequency versus temperature characteristics of an aluminum plus gold plated resonator.

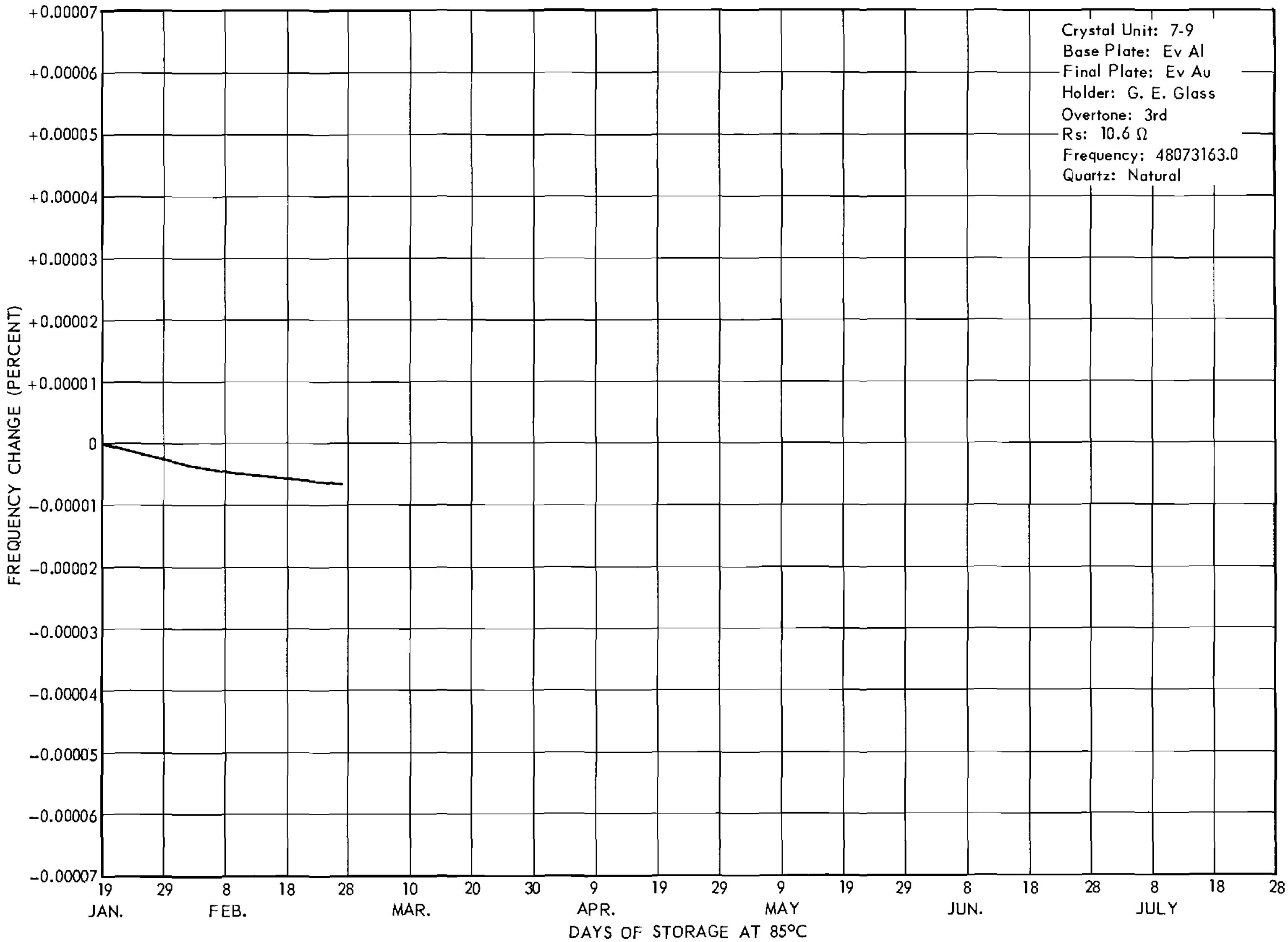


Figure 7b. Frequency versus temperature characteristics of an aluminum plus gold plated resonator.

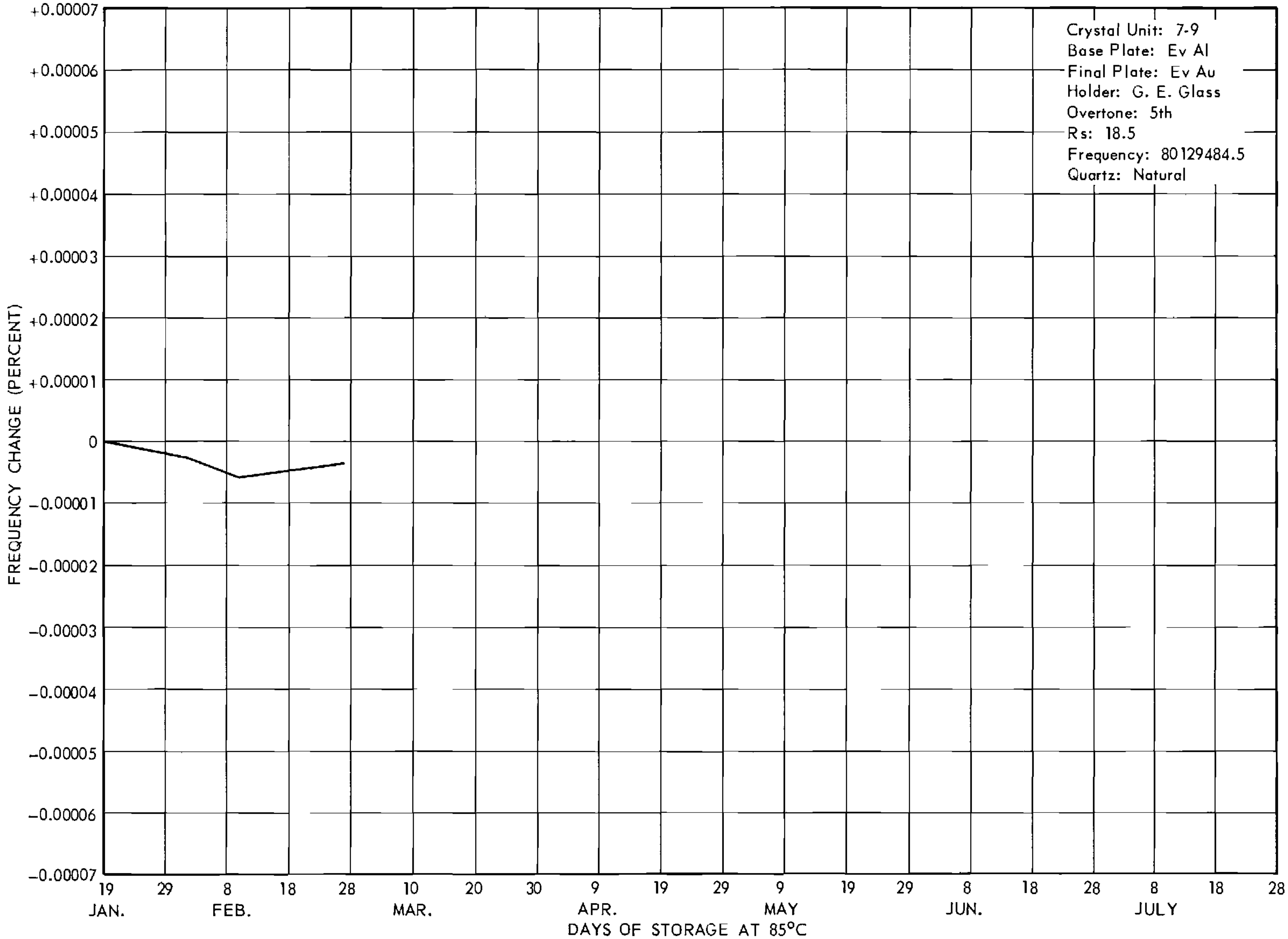


Figure 7c. Frequency versus temperature characteristics of an aluminum plus gold plated resonator.

V. CONCLUSIONS

The passive bridge measuring system is capable of making measurements of the desired accuracy of a few parts in 10^9. The use of a crystal controlled CI meter as the RF generator, however, is not entirely adequate. It is anticipated that a frequency synthesizer will be available shortly to replace the crystal controlled CI meter and that the system will then reach its full potential.

One of the major sources of measurement error is the oven temperature deviation of $\pm$ 0.03°C. This deviation is especially troublesome since each crystal is measured when possible at the fundamental frequency and at the third and fifth overtones. The temperature coefficient of frequency can be zero for but one of the modes of operation. Full-proportional oven temperature control now being installed will, it appears, reduce the temperature deviation to a maximum of $\pm$ 0.01°C.

The bonding cement composed of Pyroceram 95 and silver powder does not appear to be entirely suitable for use on high precision crystal units. The incompatibility of the thermal expansion coefficients of the Pyroceram and quartz may cause the bond to be noisy or, in some cases, to fail completely. A cement having one part Pyroceram to two parts silver by volume has given results superior to the mixture composed of five parts Pyroceram to one part silver recommended by some users. The epoxy-silver cement, duPont No. 5504A (within its temperature limitations) has superior bonding properties and does not cause undesirable aging when properly cured and vacuum baked before sealing.

VI. PROGRAM FOR THE NEXT INTERVAL

During the fifth quarter, the following tasks will be undertaken:

1. Continued frequency measurements of resonators on storage.

2. Fabrication and measurement of about 50 crystal resonators.

3. Improvements on crystal oven temperature stability.

4. Studies of the effects of gamma irradiation on the aging of crystal resonators.

5. Aging studies of continuously operated units.

VII. PERSONNEL

The persons employed on this project and the hours devoted to it during the period of this report by each are:

		Hours
R. B. Belser	Project Director	181
W. H. Hicklin	Ass't. Research Engineer	422
J. O. Darnell	Research Assistant	205
C. M. Shirley	Technician	264
C. S. Wilson	Electronic Technician	437

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Arthur L. Bennett, Chief
Physical Sciences Division

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Commaner Air Force Cambridge Research Center ATTN: CROTR L. G. Hanscom Field Bedford, Massachusetts	1

REPORT NO. 5 (FIFTH QUARTERLY REPORT)
GEORGIA TECH PROJECT NO. A-552

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

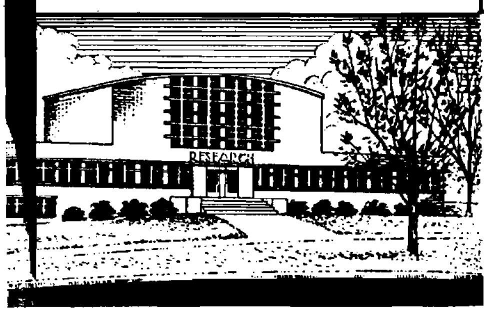
By

R. B. Belser and W. H. Hicklin

CONTRACT NO. DA-36-039-SC-87407
DA TASK NO. 3A 99 15 004

15 February 1962 to 15 May 1962

PLACED BY THE U. S. ARMY
SIGNAL RESEARCH AND DEVELOPMENT LABORATORIES
FORT MONMOUTH, NEW JERSEY



Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

QUARTERLY REPORT NO. 5

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser
W. H. Hicklin

Contract No. DA-36-039-SC-87407
DA Task No. 3A 99 15 004
Georgia Tech Project No. A-552

15 February 1962 to 15 May 1962

Placed by the U. S. Army
Signal Research and Development Laboratories
Fort Monmouth, New Jersey

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

- - - - -

* "Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500° to 574°C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

Approximately 70 quartz resonators have been continued on storage and measurement, and 94 new units have been fabricated. The acquisition of a Rohde and Schwarz frequency synthesizer, after some necessary maintenance, has facilitated frequency measurement.

The measurement accuracy and resonator stabilities obtained have directed attention to oven temperature control and oven design as the principal remaining areas wherein improvements must be made for attainment in this work of maximum resonator stabilities. The problems encountered are associated with large ovens where heat losses, entry recovery, and frequency versus position differences cause significant variations in frequency measurements for a given resonator. In addition, these conditions limit periods in which accurate measurements may be made.

Measurements of Q for resonators fabricated, made for the series mode of operation, have given values in the range 100,000 to 300,000.

Resonators previously fabricated have continued to exhibit excellent stabilities within the limitations of the measurement and temperature control facilities. Mounting of resonators in the HC-27/U glass container is now giving excellent yield (about 90%). Silver plated units did not survive heat requirements for sealing.

Three resonators were subjected to irradiation by the cesium 137 source at a rate of 1.4×10^6 rad/hour for a period of 24 hours. All units cycled through a minimum in frequency of >5 ppm below the original value

and returned near the original value. For a unit terminating about 1 ppm below its original value the aging, upon subsequent storage at 85°C, was very small < 1 pp 10^7 per month. Shifts in frequency and aging rates were somewhat different for the same unit operated at the fundamental, third, and fifth modes.

Resonators for exposure to pulsed neutron radiation have been fabricated and stored at 85°C. These are ready for initial aging studies before exposure. Twelve resonators of known history have been forwarded for exposure in the vicinity of an atomic burst. These are to be returned for aging studies subsequent to exposure to the radiation. Arrangements are also underway for exposure of 60 units to pulsed neutron radiation at a reactor site.

III. PUBLICATIONS, LECTURES, AND REPORTS

During this reporting period three monthly letters (Nos. 11, 12, and 13) were submitted and Report No. 4 (Fourth Quarterly Report) was reproduced and distributed.

Mr. W. H. Hicklin and Mr. C. M. Shirley attended the 16th Annual Frequency Control Symposium at Atlantic City, New Jersey, April 25-27, where Mr. Hicklin presented the paper, "Aging of Quartz Resonators at Fundamental and Overtone Modes with Comments on Radiation Effects."

While present at the symposium, Mr. Hicklin discussed problems related to the course of the work with Dr. G. K. Guttwein, technical representative of the U. S. Army Research and Development Laboratories on the project.

IV. FACTUAL DATA

A. Introduction

The primary work on the project during the course of the Quarter has been directed to refinement of the oven storage and frequency measurement system and the fabrication of 84 resonators to be used in studies of the effects of pulsed radiation on the aging of resonators. Concurrently, studies of the aging of resonators stored at 85°C and of units continuously operated have been carried out.

B. Apparatus and Procedures

1. Resonator Storage Ovens

The crystal units stored in the 100-unit oven were removed and installed in the two 36-unit ovens. The 100-unit oven was thus made available for the crystals for the pulsed radiation studies. While the 100-unit oven was out of service, the coaxial lines into the 100 previously but now unused crystal positions were removed and the remaining lines were thermally insulated from the outer shell of the nested oven. The heat losses through these lines were thus reduced. Studies have indicated the oven temperature variation after modification is about ± 0.015°C instead of the previous value of ± 0.03°C. Hence, the variation has been reduced by approximately 50 per cent.

2. Vacuum and Sealing Equipment

Both vacuum systems available to the project have operated without repair or modification during the quarter. Operating pressures were in the low 10^{-7} Torr range for both base plating and vacuum baking.

The HC-27/U sealing apparatus was modified to provide:

a. Reduced pressure forcing the base and bulb together during sealing; and

b. Improved gasket sealing of the upper header to the fused quartz vacuum sealing tube.

These modifications have increased the yield of acceptable seals from 50% to 90%.

A technique was developed which allowed the HC-27/U seals to be made in vacuo and the bulbs subsequently filled with air in order to test the seal with the vacuum oil leak test. This technique is as follows:

(1) Drill a hole in the bulb with a tungsten wire (0.010 to 0.020 inches in diameter). This is done at very high rpm (25,000) and the friction generated melts a hole through the glass.

(2) Make the base seal in vacuo at a pressure of about 10^{-5} Torr.

(3) Remove the holder, thus sealed at the base, from the chamber. The holder fills with gas when air or argon is admitted to the vacuum chamber.

(4) Remove the container from the chamber and plug the small hole in the envelope with vacuum wax (Apiezon or Dekhotinsky).

(5) Using the newly sealed specimen, make a vacuum oil leak test in the manner described in previous reports.

3. Frequency Measurements

The Rohde and Schwarz Type XUA Frequency Synthesizer and Type XMC Indicator Unit were received from USASRDL during the quarter. It was quickly determined that the unit would not serve as a source of R.F. voltage for driving the crystal impedance bridges without repair. The spurious signals from the synthesizer masked the amplified null response so that the precision of the null adjustment was obscured.*

All of the tubes in the synthesizer and the indicator unit were checked except the types EF 800 for which there was no information or equipment available for testing. About 90% of the tubes had mutual conductances below the acceptable minimum. One new tube of each type (except the EF 800) was purchased to check the method of testing the tubes. The new tubes were better than the acceptable minimums whereas the older ones continued to give values below the minimum acceptable ones.

The Rohde and Schwarz Sales Company was contacted for futher servicing information related to realignment procedures which may be necessary when a large number of tubes is replaced. It was stated that none was necessary except for a few critical tube elements. New tubes were ordered and several switches of weak tubes in critical positions to less critical ones were made. These changes improved the instrument somewhat and further improvements are expected in the near future.

During the quarter it became necessary to replace the BNC oven coupler (UG-1104A/U) on the high frequency bridge. Some trouble was encountered with the first coupler installed. A second coupler was installed before acceptable operation was obtained. Some aging data were lost as a result of these changes.

- - - - -

* A technique of locating the null by interpolation rather than by direct indication has been tried and may provide accuracies of $\pm$ 1 cycle at 48 Mc. This method permits the null loop gain to be reduced and, since the galvanometer readings are taken off null, the signal to noise ratio is improved.

TABLE I

Gold Base Plated Units for Pulsed Radiation* Studies
(3rd Mode Only)

Unit	$R_s(\Omega)$	$F_s(\sim)$	$R_a(\Omega)$	$F_a(\sim)$**	ΔF (F_a-F_s)	$\frac{C_o}{\mu\mu f}$	Q
Au-1-2	6.8	47328832	9.8	47330332	1500	6.1	202200
Au-1-4	7.4	47294893	10.0	47296366	1473	6.1	192000
Au-1-5	10.0	47341642	14.0	47343243	1601	6.1	130000
Au-1-7	10.5	47379920	15.5	47381450	1530	6.1	130000
Au-1-8	10.3	47415630	14.0	47417150	1520	6.1	133500
Au-1-9	9.7	47342936	16.0	47344387	1451	6.1	148500
Au-2-1	8.8	47580880	13.5	47581190	390?	6.1	
Au-2-4	6.8	47537450	11.5	47538730	1280	6.1	240000
Au-2-7	8.2	47540156	12.7	47541393	1237	6.1	206200
Au-2-8	8.2	47491025	12.0	47492268	1243	6.1	205500
Au-2-10	6.6	47533480	10.5	47534840	1360	6.1	233000
Au-2-12	10.5	47565198	15.5	47566350	1152	6.1	172800
Au-2-13	7.2	47682186	11.0	47683603	1417	6.1	205000
Au-2-15	11.3	47491114	18.0	47492204	1090	6.1	169000
Au-2-17	7.0	47407040	11.3	47408450	1410	6.1	211000
Au-2-20	11.2	47290070	15.5	47291476	1406	6.1	132800
Au-2-21	8.2	47417185	10.0	47418590	1405	6.1	181400
Au-2-22	7.1	47598425	11.5	47599585	1160	6.1	253800
Au-3-1	6.8	47235520	9.4	47237014	1494	6.1	205500
Au-3-2	6.3	47395230	10.5	47396750	1520	6.1	218400
Au-3-16	7.0	47338431	11.0	47339870	1439	6.1	205500
Au-3-19	9.0	47604772	11.0	47605850	1078	6.1	215500

* Quartz: Natural; Holder: HC-27/U; Bond: 1 part pyroceram + 2 parts silver (by volume) fired 5 hours at 450°C.

** R_a + F_a obtained using a series load condenser of 32 μμf.

TABLE I (Continued)

Unit	$R_s(\Omega)$	$F_s(\sim)$	$R_a(\Omega)$	$F_a(\sim)$**	ΔF $(F_a - F_s)$	$\frac{C_o}{\mu\mu f}$	Q
Au-4-1	7.2	47279475	8.5	47280722	1247	6.1	233000
Au-4-2	5.8	47289371	9.0	47290605	1234	6.1	292000
Au-4-5	7.0	47210612	10.5	47211771	1159	6.1	257500
Au-4-6	6.0	47263608	11.3	47264839	1231	6.1	282500
Au-4-7	8.4	47273495	12.2	47274683	1188	6.1	209000
Au-4-8	6.7	47173198	8.9	47174586	1388	6.1	225000
Au-4-9	6.6	47207566	10.0	47208733	1167	6.1	272000
Au-4-10	6.8	47231838	10.7	47232940	1102	6.1	281000

TABLE II

Silver Plated Units for Pulsed Radiation* Studies
(3rd Mode Only)

Unit	$R_s(\Omega)$	$F_s(\sim)$	$R_a(\Omega)$	$F_a(\sim)$**	ΔF $(F_a - F_s)$	C_o / $\mu\mu f$	Q
Ag-1-1	9.5	49209678	13.8	49211025	1347	8.0	153800
Ag-1-2	10.5	49348614	16.0	49349860	1246	8.0	152400
Ag-1-3	12.5	48985592	17.5	48986995	1403	8.0	113200
Ag-1-4	16.0	48998740	26.0	49000077	1337	8.0	93000
Ag-1-5	10.5	48986986	13.0	48988459	1474	8.0	128800
Ag-1-6	10.5	49190650	15.5	49191852	1202	8.0	157800
Ag-1-7	9.2	49505251	15.0	49506630	1379	8.0	157000
Ag-1-8	9.2	49111317	13.5	49112570	1255	8.0	172200
Ag-1-9	17.5	49193350	28.0	49193930	580?	8.0	
Ag-1-10	10.0	49052491	13.0	49053990	1509	8.0	132000
Ag-1-11	9.0	49127018	13.0	49128260	1242	8.0	177500
Ag-1-12	9.5	49341631	15.5	49342834	1203	8.0	173000
Ag-1-13	8.0	49147207	13.5	49148387	1180	8.0	212000
Ag-1-14	10.5	49145985	14.5	49147238	1253	8.0	151200
Ag-1-15	20.0	49186157	28.0	49187500	1343	8.0	74200
Ag-1-16	9.7	49072261	15.0	49073723	1462	8.0	140000
Ag-1-17	11.2	49345871	16.5	49347000	1129	8.0	157700
Ag-1-18	10.5	49357900	15.5	49359018	1118	8.0	164000
Ag-1-19	9.3	49424508	16.0	49425773	1265	8.0	169000
Ag-1-20	32.0	49264307	38.0	49264903	596?	8.0	
Ag-2-1	10.5	49276940	--	--	Unable to measure R_a and F_a		
Ag-2-2	7.2	49129666	10.0	49131150	1484	8.0	186200
Ag-2-3	10.5	49307200	13.5	49308622	1422	8.0	133200
Ag-2-4	10.0	49154316	17.0	49155680	1364	8.0	145900
Ag-2-5	6.5	49200915	13.0	49202312	1397	8.0	219000
Ag-2-6	7.1	49246870	13.0	49248245	1275	8.0	220000
Ag-2-7	7.5	49141919	13.5	49143157	1238	8.0	214000
Ag-2-8	8.5	49142550	11.5	49144007	1457	8.0	160900
Ag-2-9	9.5	49209678	13.8	49211025	1347	8.0	155200

* Quartz: Natural; Holder: GE glass; Bond: DuPont 5504A cement cured 3 hours at 150°C.

** R_a and F_a obtained using a series load condenser of 32 $\mu\mu f$.

TABLE III

Aluminum Plated Units for Pulsed Radiation* Studies
(3rd Mode Only)

Unit	$R_s(\Omega)$	$F_s(\sim)$	$F_a(\Omega)$	$F_a(\sim)$**	ΔF (F_a-F_s)	$\frac{C_o}{\mu\mu f}$	Q
Al-1-1	5.7	48158239	9.5	48160114	1875	6.1	196000
Al-1-2	8.5	48137273	12.0	48139080	1807	6.1	136000
Al-1-3	8.8	48216026	16.2	48217831	1805	6.1	133000
Al-1-4	6.8	48185190	10.0	48187116	1926	6.1	159800
Al-1-5	6.6	48139128	10.5	48141021	1893	6.1	160000
Al-1-6	8.3	48169790	12.2	48171610	1820	6.1	138200
Al-1-7	5.7	48132751	8.7	48134744	1993	6.1	183000
Al-1-8	6.8	48142280	11.0	48144053	1773	6.1	174000
+Al-1-9							
Al-1-11	9.5	48188519	14.0	48190588	2069	6.1	80300
Al-1-12	7.5	48140224	11.1	48142273	2049	6.1	137500
Al-1-13	46.0	48213494				6.1	
Al-1-15	6.8	48146102	10.5	48148123	2021	6.1	152200
+Al-1-16							
+Al-1-17							
+Al-1-18							
+Al-1-19							
+Al-1-20							
Al-2-1	11.0	48021085	13.5	48023072	1987	6.1	95700
Al-2-2	6.5	47997834	9.5	47999712	1878	6.1	171500
Al-2-3	48.0	48042522					
Al-2-4	6.0	48009756	8.7	48011838	2082	6.1	167000
Al-2-5	46.0	48086230					
Al-2-6	5.5	48006867	7.6	48008903	2036	6.1	187200
Al-2-7	32.5	48080153					
Al-2-8	5.0	48033294	8.0	48035239	1945	6.1	216000
Al-2-9	4.9	48018517	7.6	48020643	2126	6.1	212000
+Al-2-10							
+Al-2-11							
+Al-2-12							
Al-2-13	5.7	48030826	8.0	48032852	2026	6.1	181000
Al-2-14	6.6	48028774	9.0	48030810	2036	6.1	156200
+Al-2-15							
Al-2-16	5.0	48019870	8.0	48021989	2119	6.1	197000
Al-2-17	8.0	48039024	11.0	48041023	1999	6.1	131000

* Quartz: Natural; Holder: HC-27/U; Bond: 1 part pyroceram + 2 parts silver (by volume) fired 5 hours at 450°C.

** R_a and F_a obtained using a series load condenser of 32 μμf.

\+ High frequency. Possibly "twinned."

C. Crystal Resonator Fabrication and Measurement

1. Units Fabricated

Approximately 84 resonators were fabricated during the Quarter. These consisted of 30 gold-plated units, 29 silver-plated units, and 25 aluminum-plated units. All units were base plated only. The gold-plated and aluminum-plated resonators were bonded with pyroceram cement composed of 2 parts silver flake and 1 part pyroceram 95 by volume and mounted in the HC-27/U glass container. The silver-plated units could not be thus mounted because of agglomeration of the films induced by high temperatures encountered in the bonding and sealing procedures. The silver units were therefore bonded with duPont #5504 cement and mounted in the T 5-1/2 glass envelope.

Quartz plates prepared for these experiments were all of natural quartz. Pertinent parameters of each resonator are listed in Tables I, II, and III.

2. Resonator Storage and Measurements

The resonators fabricated during the Quarter were designed principally for studies of the effects of pulsed radiation exposure on the aging of the resonators. Upon completion of fabrication and measurement of the parameters listed the units were stored in the 85°C ovens to await the beginning of the aging measurements. Due to some difficulty with the measurement apparatus, and the measuring load already incurred with the routine aging measurements of previously fabricated resonators, aging measurements of these units were delayed until about 1 June, this time coming within the 30-day prestorage time.

Routine frequency measurements were continued on about 70 resonators fabricated during previous quarters. A continuation of frequency data for representative specimens covered in the previous report is exhibited in Figures 1 through 6.

4. Measurements of Resonators Exposed to Conditions of Continuous Drive

Among the assignments of the project was a study of the aging behavior of resonators subjected to continuous drive at a level of approximately 2 milliwatts. The aging behavior of the units had previously been examined under the usual measurement condition of 85°C and operation at a power level of a few microwatts only during warm up and the period of measurement. Three units were studied.

After a period of aging in the 85°C ovens for a period of 60 or more days the resonators were removed and driven in a CI meter for a period of 7 days at room temperature (25°C). The power level was adjusted to 2 mw by measuring the crystal resistance (R_s) and the voltage across the crystal (E_c). Drive level (P_c) is then:

$$P_c = (E_c)^2/R_s$$

On completion of the period of continuous drive the resonators were returned to the 85°C ovens where aging measurements were continued at the fundamental, third, and fifth overtones.

The behavior observed for two units is depicted in Figures 7, 8, 9, and 10.

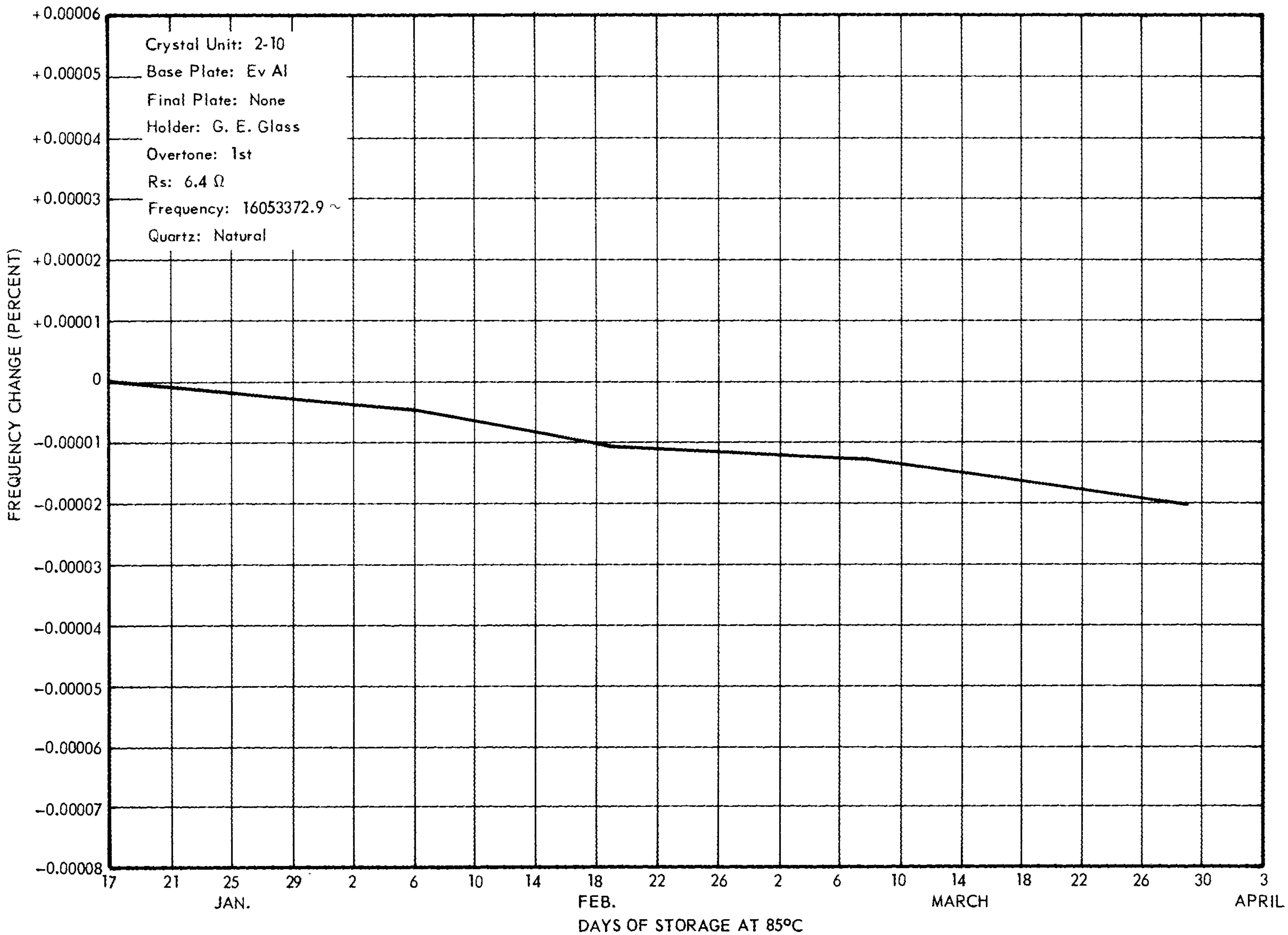

Figure 1a. Frequency versus time data for a natural quartz resonator base plated with aluminum.

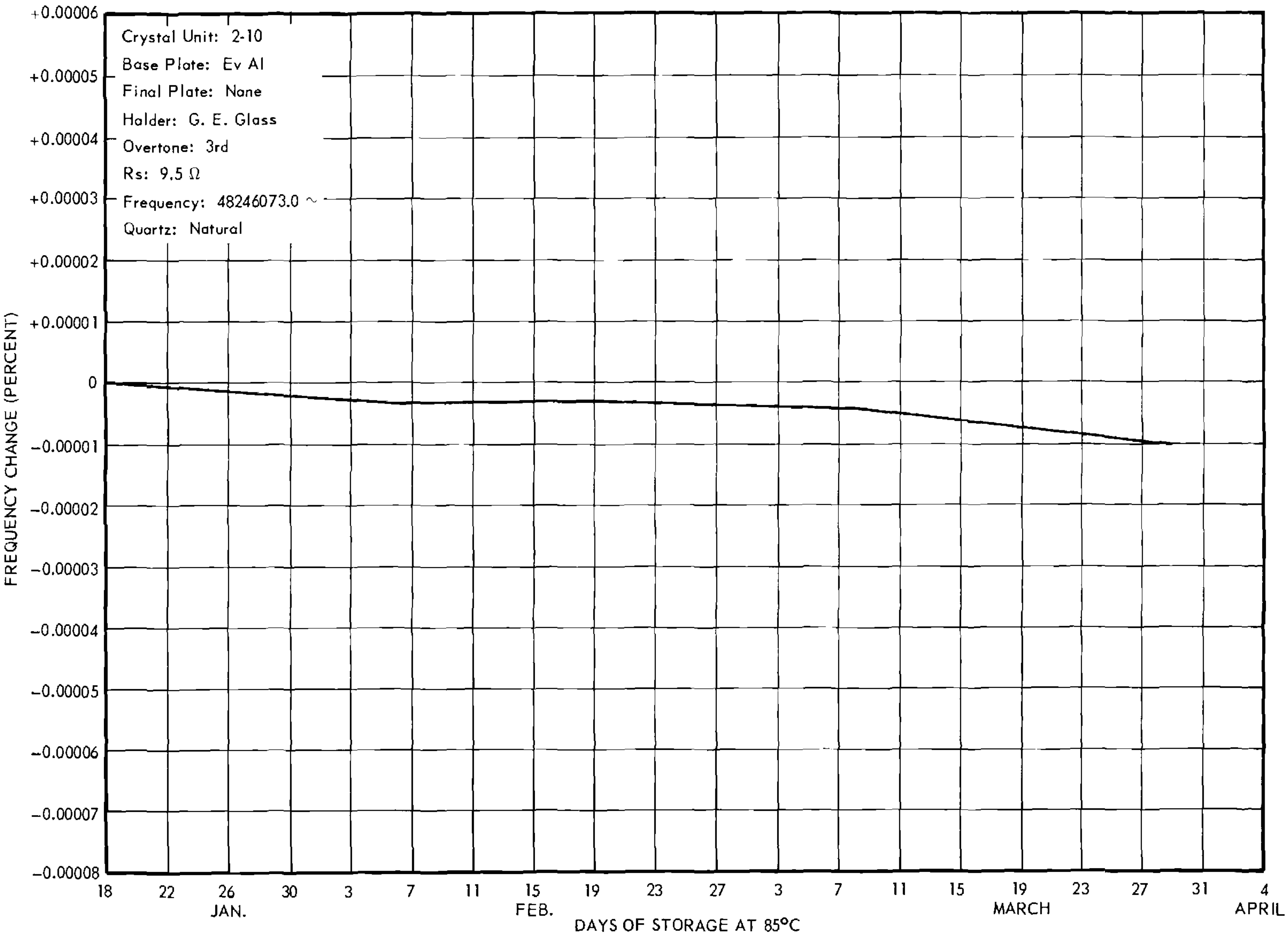

Figure 1b. Frequency versus time data for a natural quartz resonator base plated with aluminum.

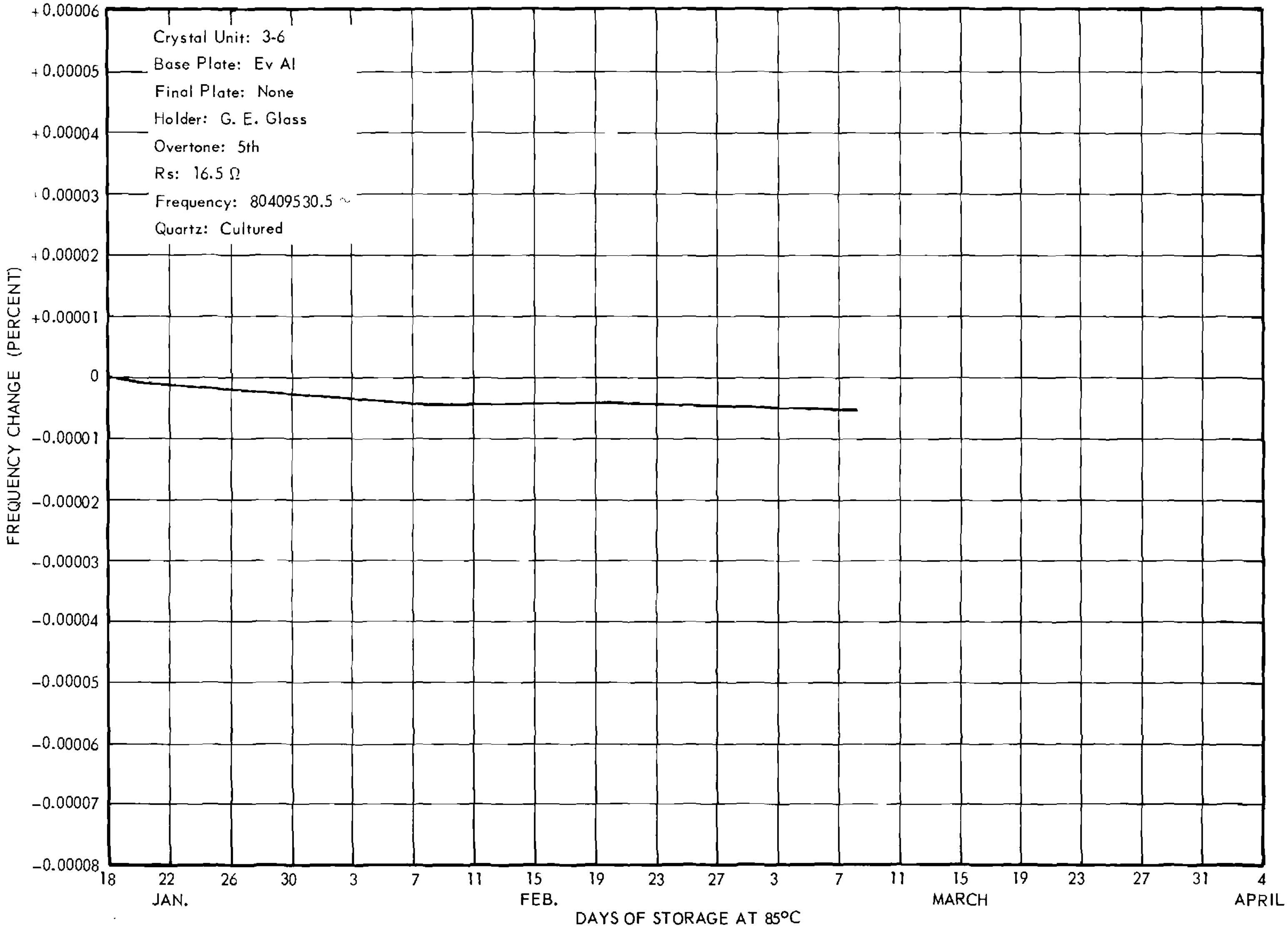

Figure 2a. Frequency versus time data for a cultured quartz resonator base plated with aluminum.

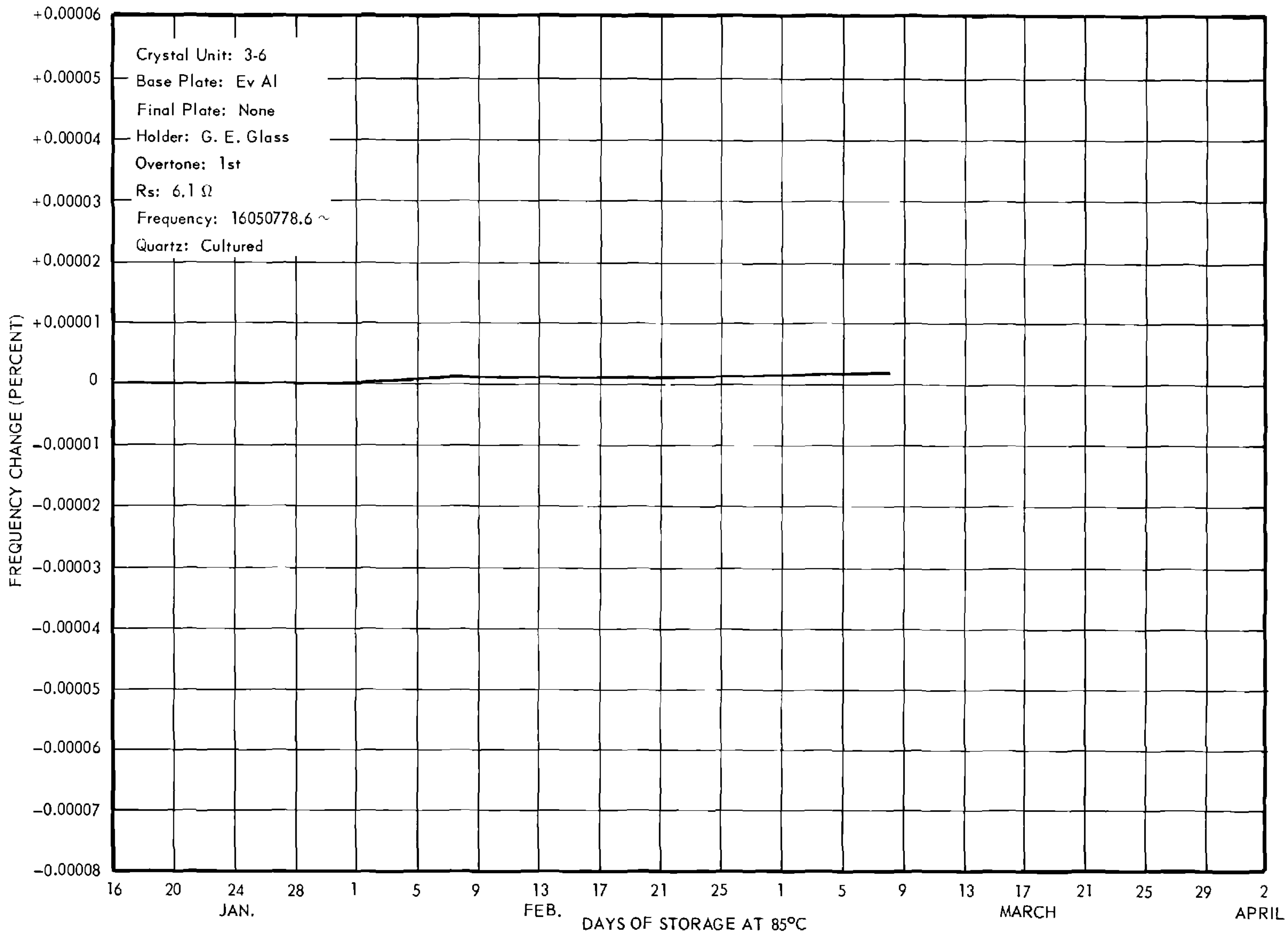

Figure 2b. Frequency versus time data for a cultured quartz resonator base plated with aluminum.

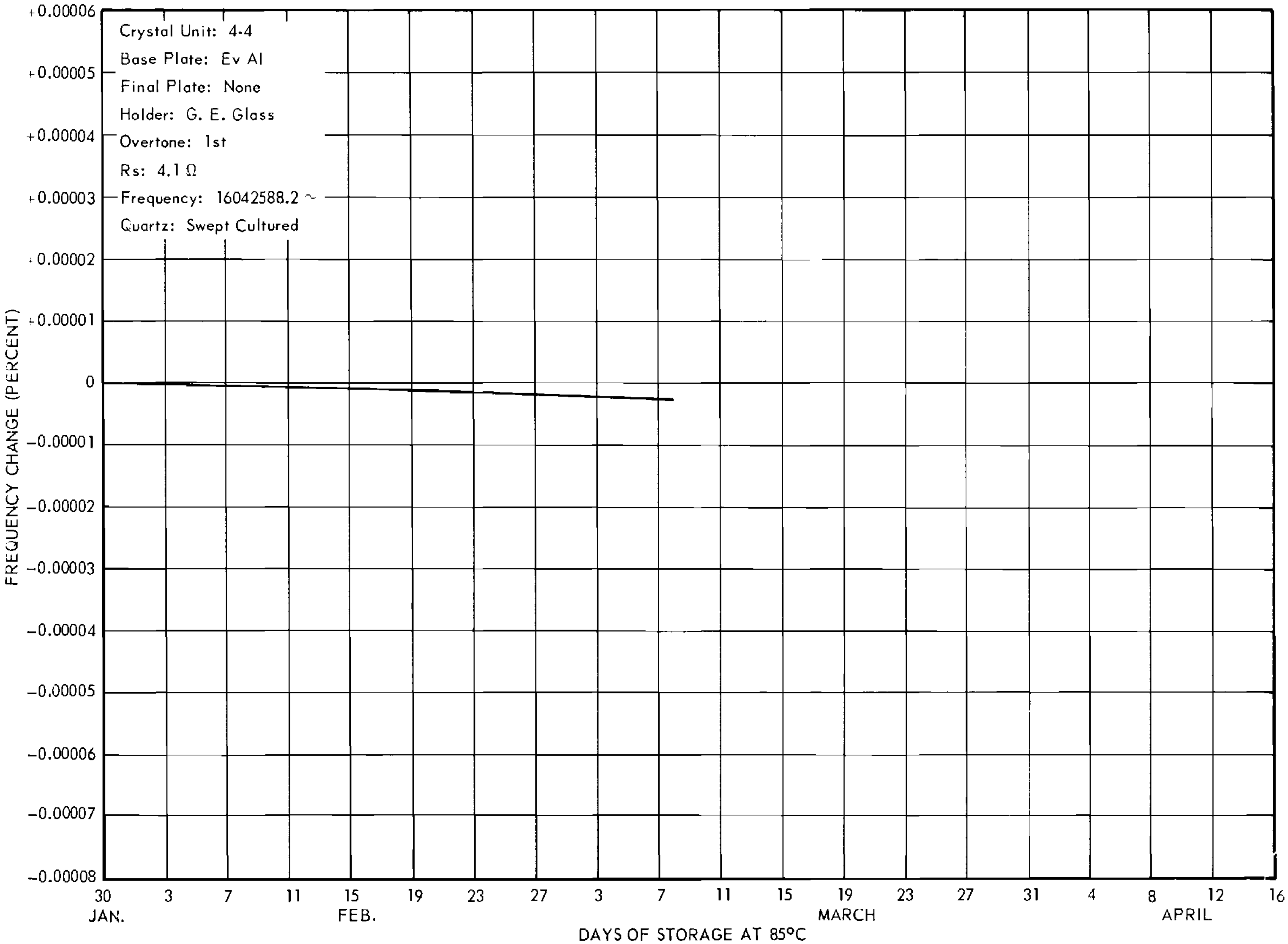

Figure 3a. Frequency versus time data for a swept, cultured quartz resonator base plated with aluminum.

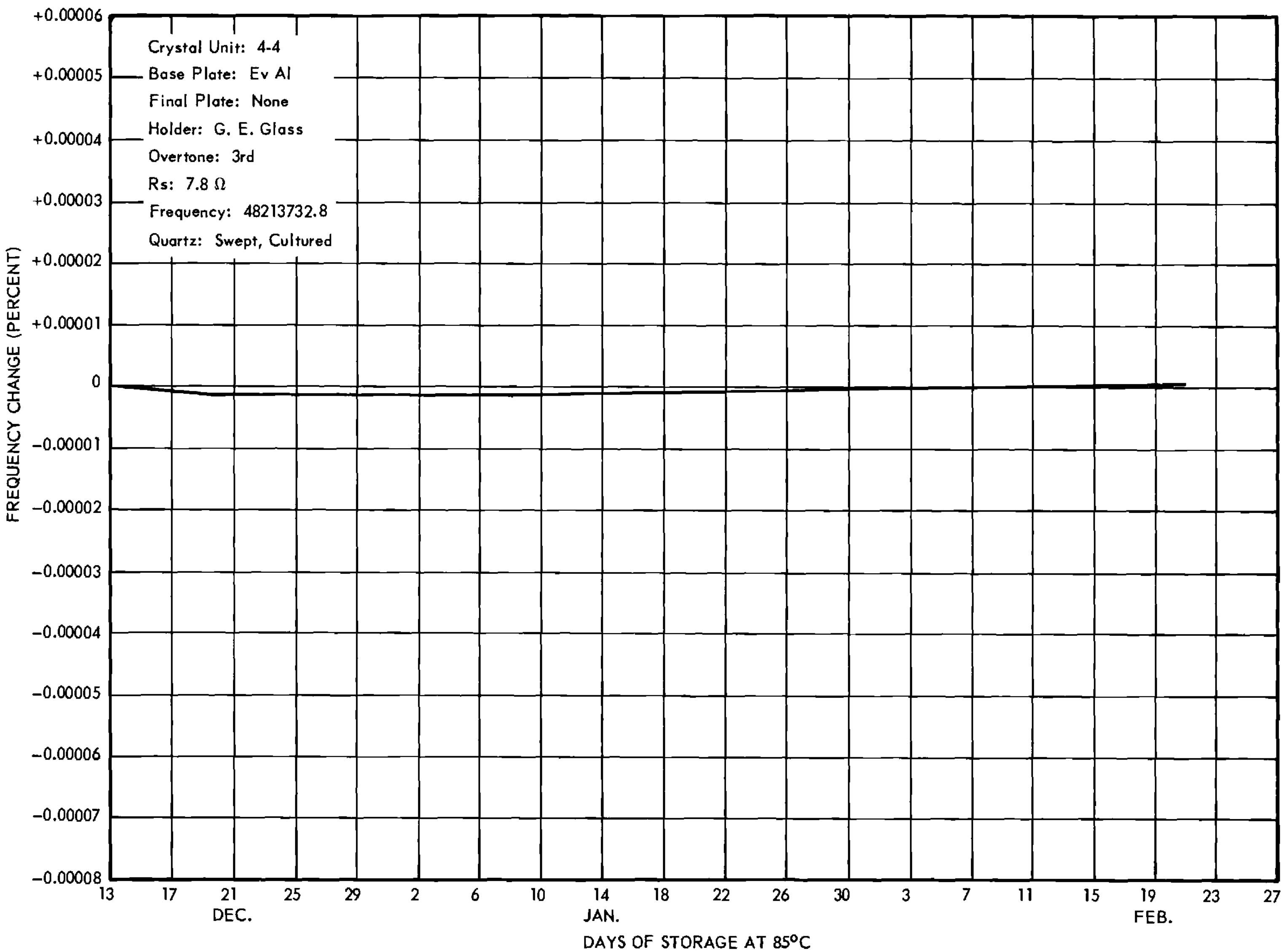

Figure 3b. Frequency versus time data for a swept, cultured quartz resonator base plated with aluminum.

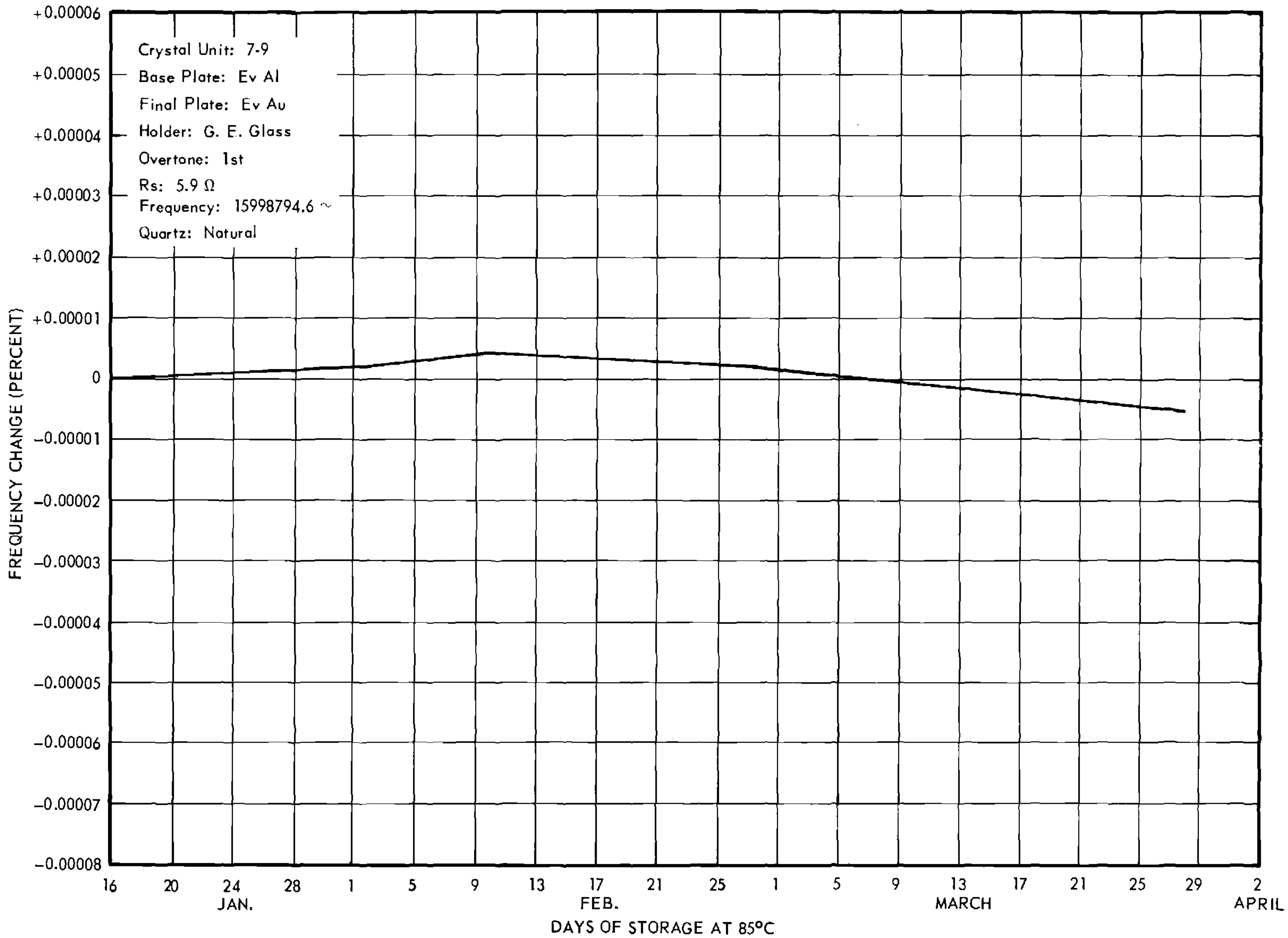

Figure 4a. Frequency versus time data for a natural quartz resonator base plated with aluminum and final plated with gold.

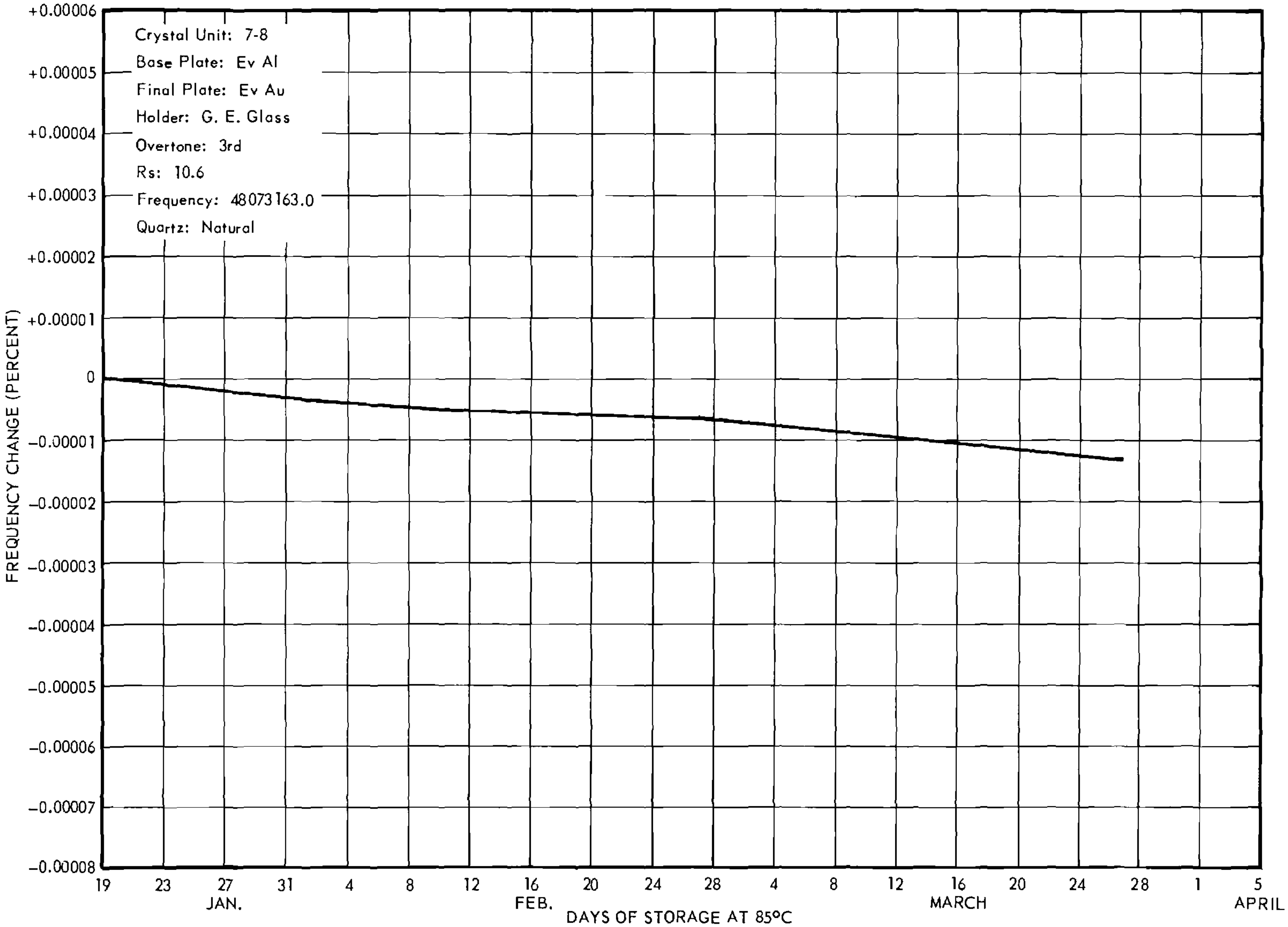

Figure 4b. Frequency versus time data for a natural quartz resonator base plated with aluminum and final plated with gold.

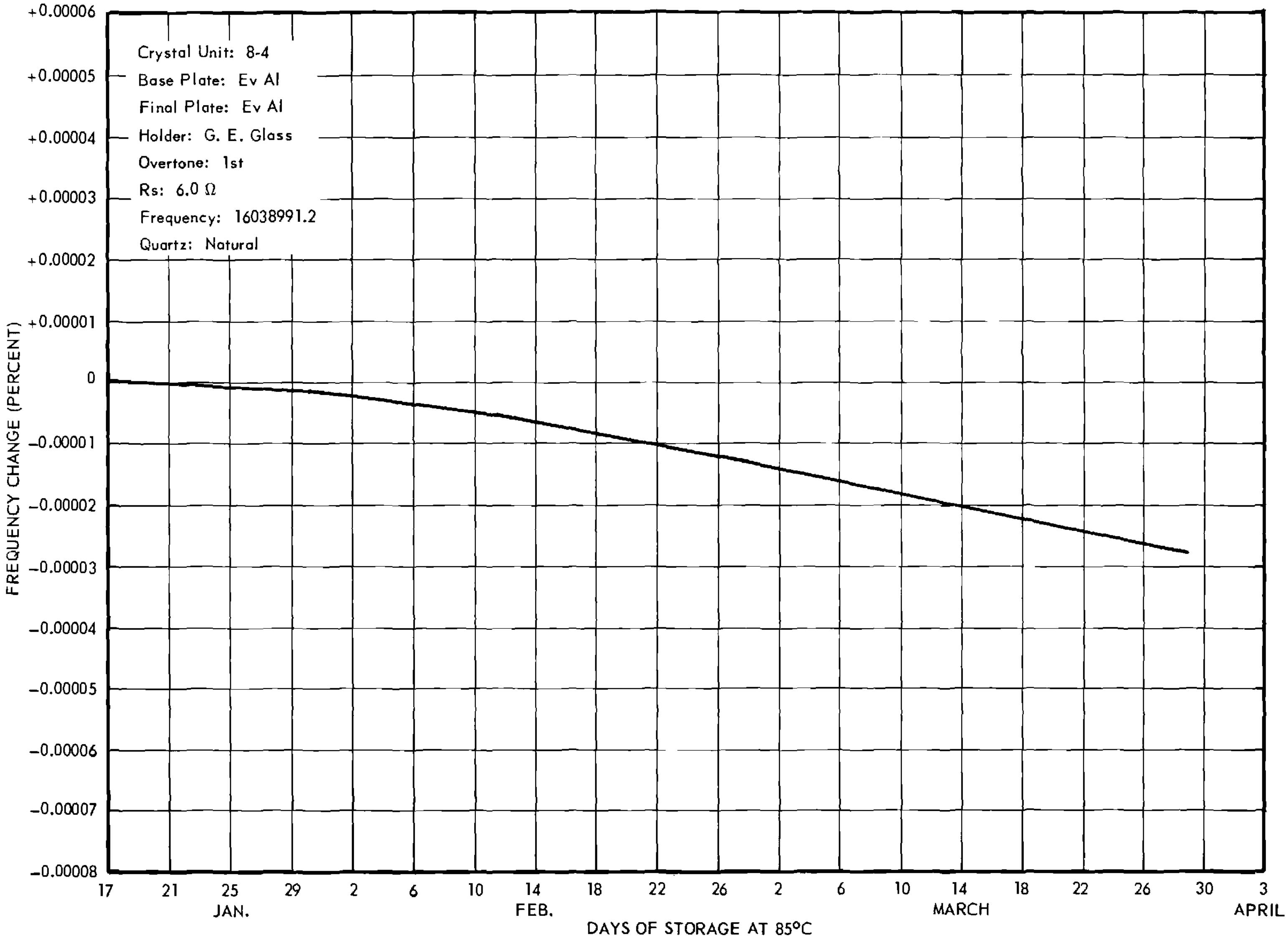

Figure 5a. Frequency versus time data for a natural quartz resonator base plated with aluminum and final plated with aluminum.

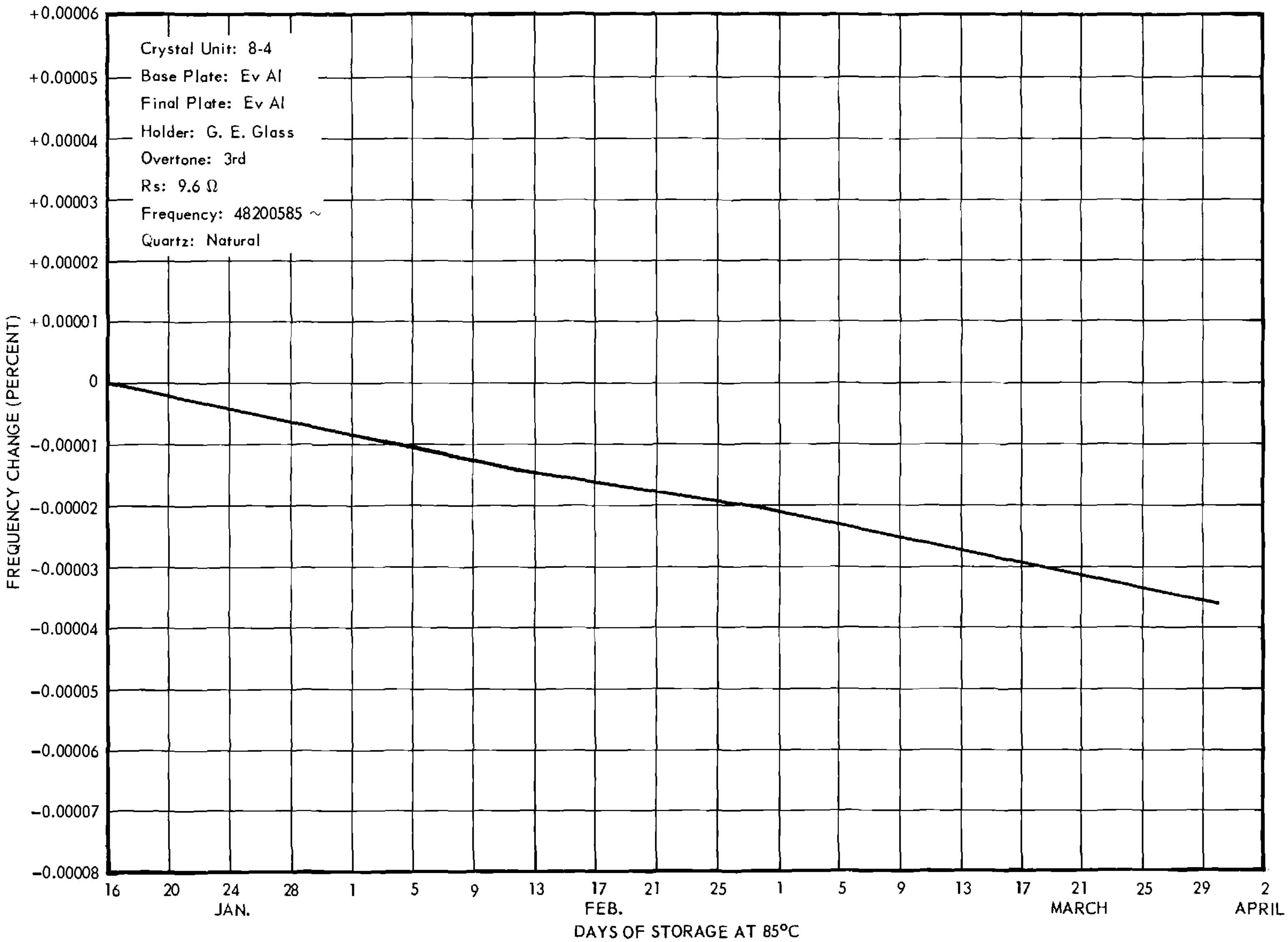

Figure 5b. Frequency versus time data for a natural quartz resonator base plated with aluminum and final plated with aluminum.

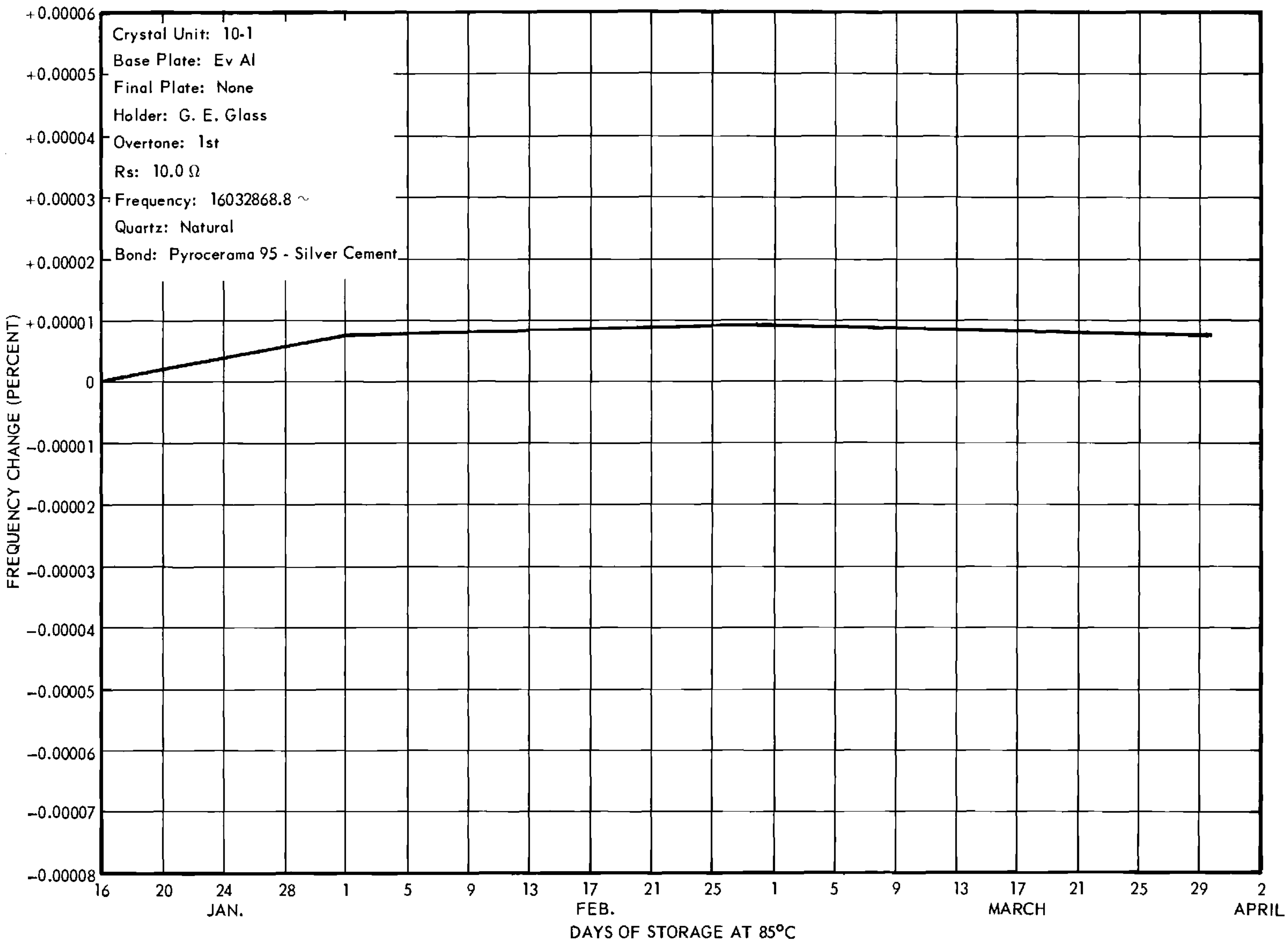

Figure 6a. Frequency versus time data for a natural quartz resonator base plated with aluminum and bonded with pyroceram 95-silver cement.

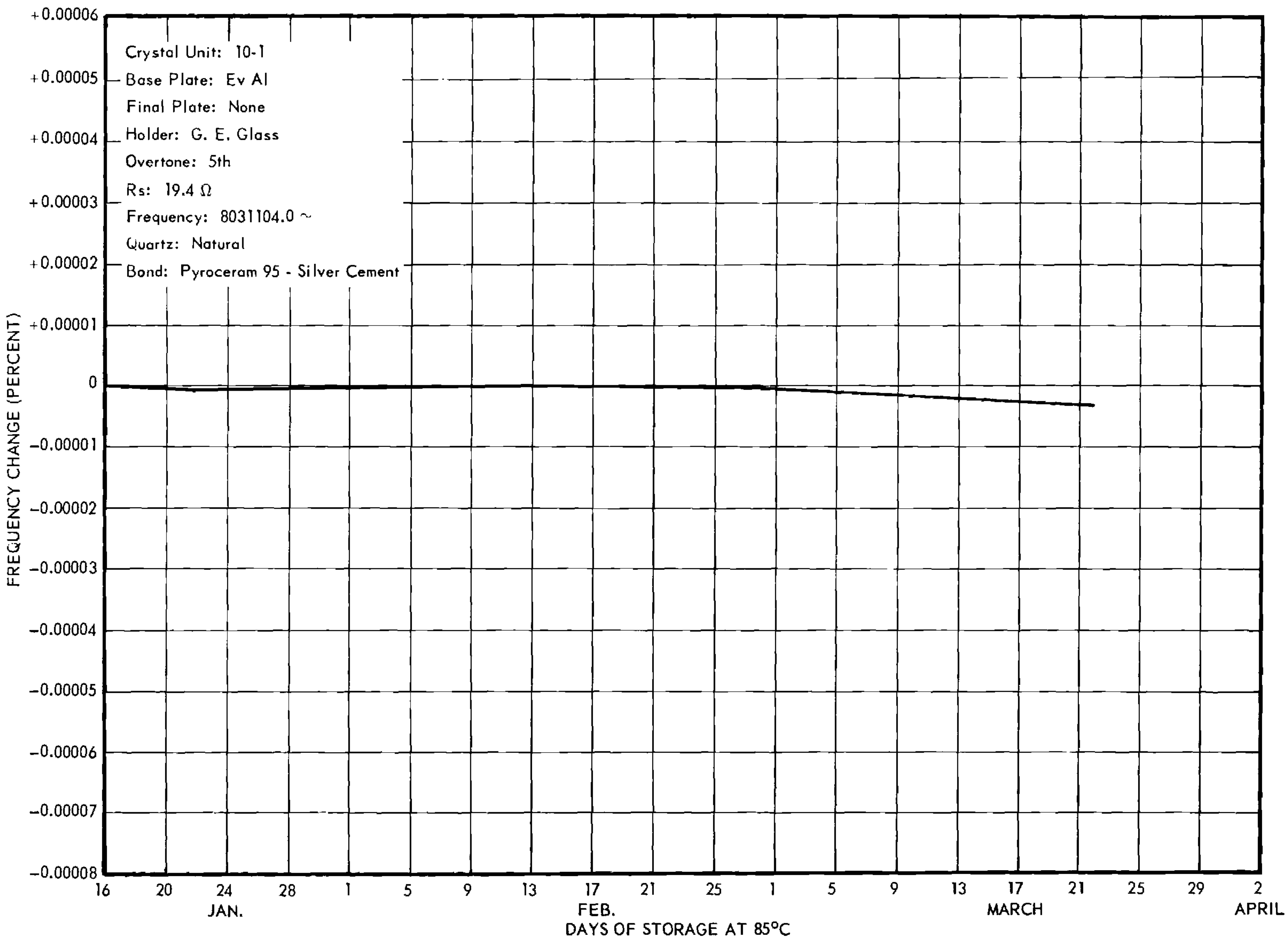

Figure 6b. Frequency versus time data for a natural quartz resonator base plated with aluminum and bonded with pyroceram 95-silver cement.

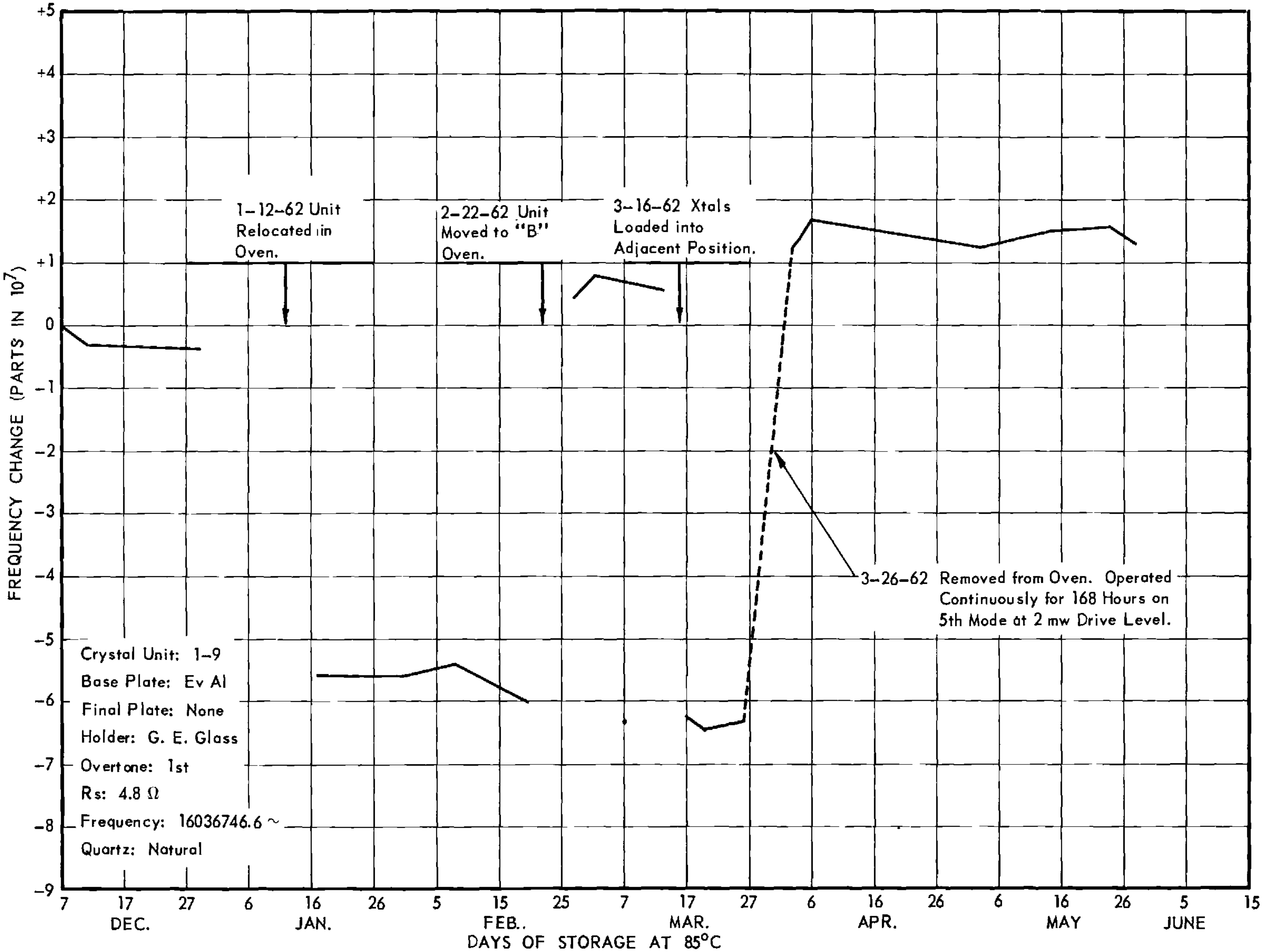

Figure 7. Frequency shift and aging of resonator 1-9 Al before and after operation at high drive level, 2 mw for 7 days, fundamental mode.

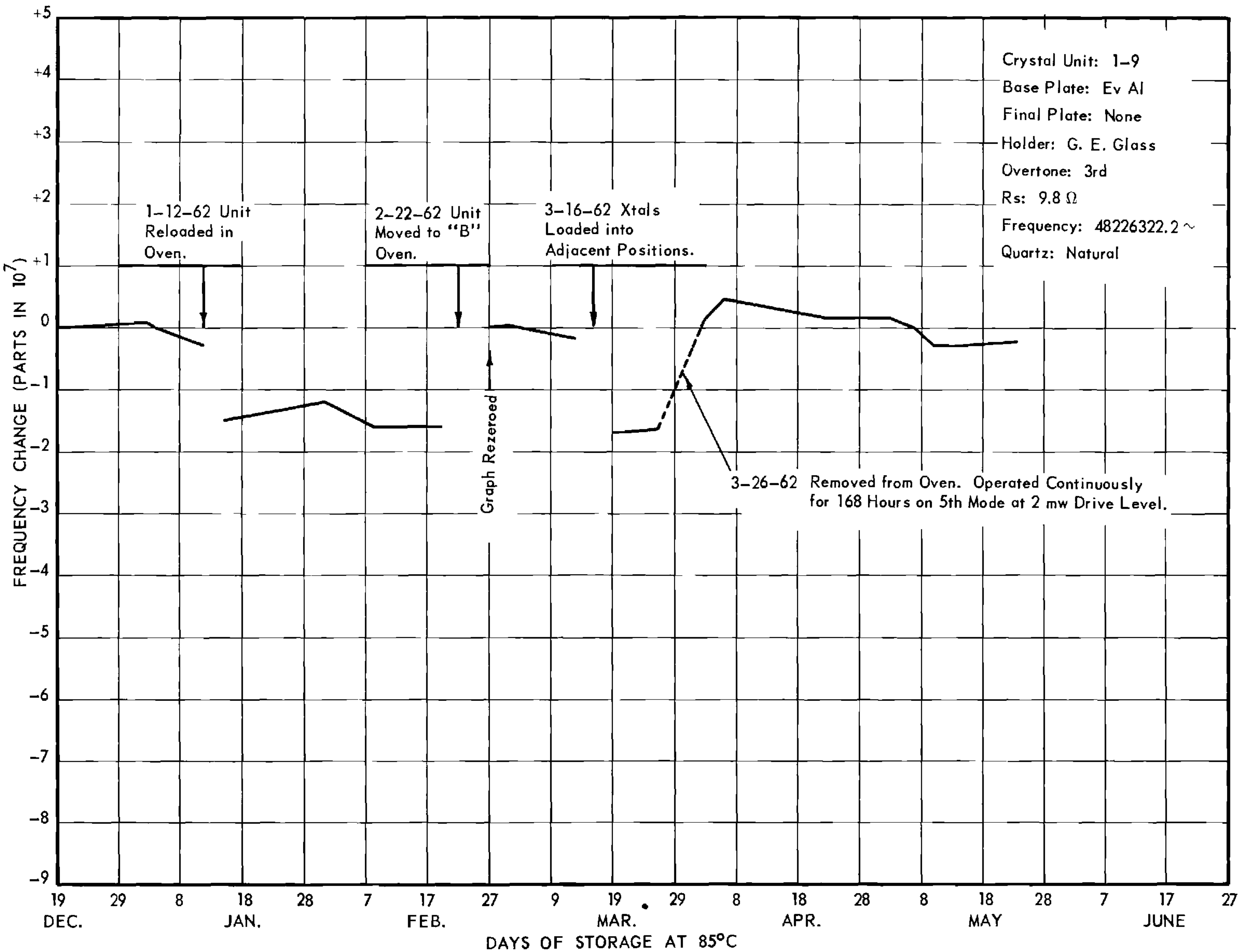

Figure 8. Frequency shift and aging of resonator 1-9 Al before and after operation at high drive level, 2 mw for 7 days, 3rd overtone mode.

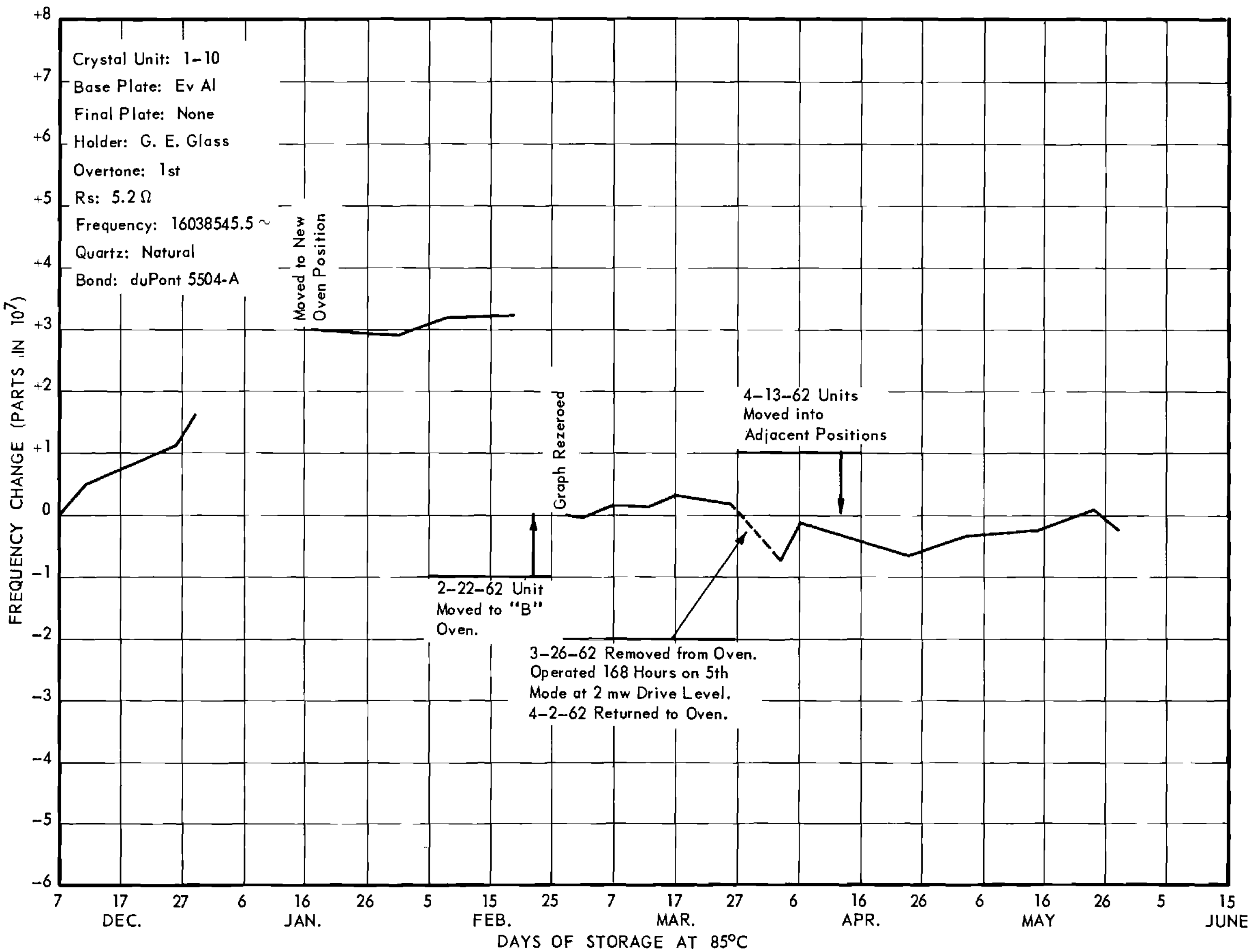

Figure 9. Frequency shift and aging of resonator 1-10 Al before and after operation at high drive level, 2 mw for 7 days, fundamental mode.

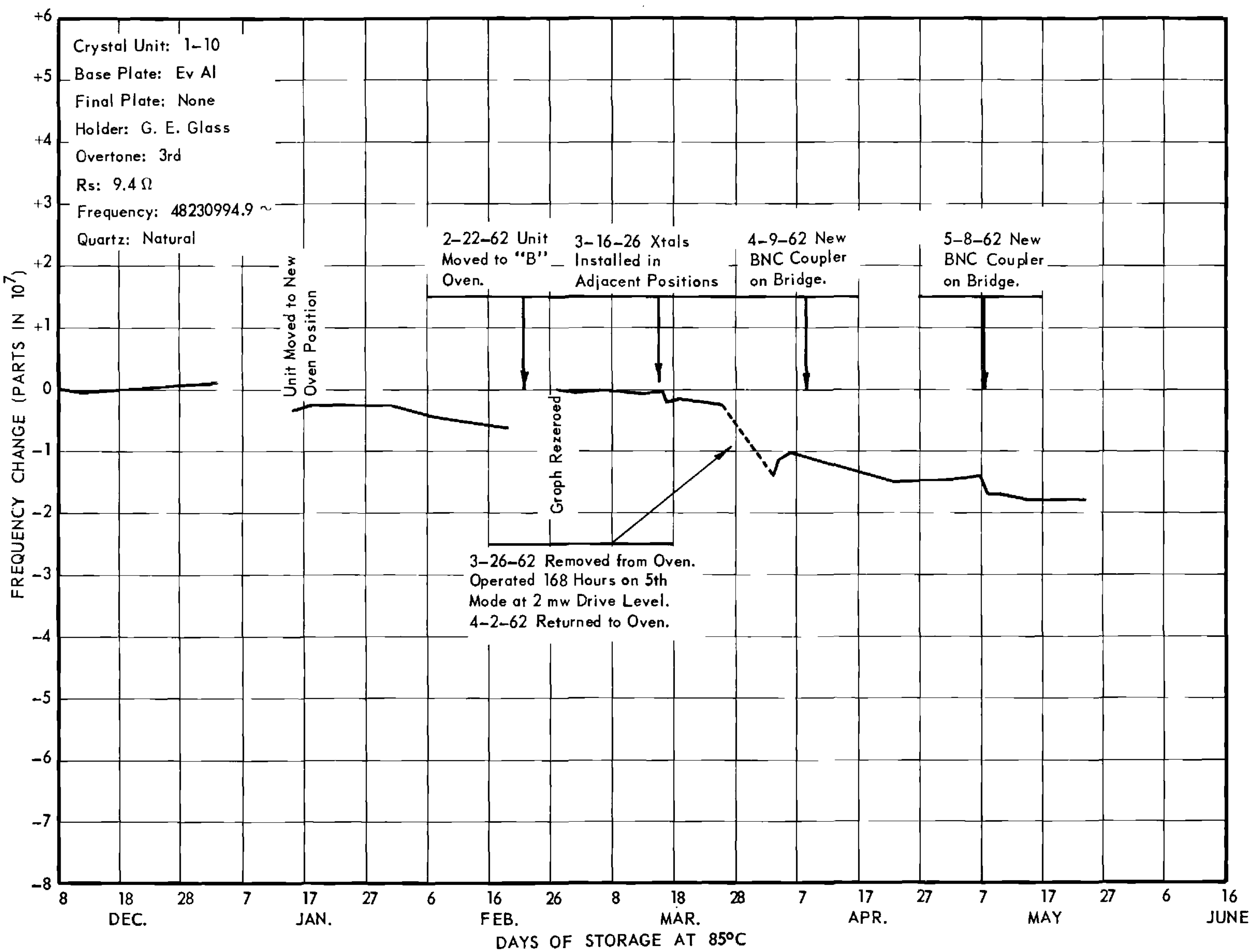

Figure 10. Frequency shift and aging of resonator 1-10 Al before and after operation at high drive level, 2 mw for 7 days, 3rd overtone mode.

5. Effects of Gamma Radiation on the Stability of Resonators

Under Contract No. DA-36-039-sc-85363 the effect of gamma irradiation from a cesium 137 source on quartz resonators was described and found to be generally in agreement with work reported earlier by Frondel* for irradiation of quartz plates with x-rays. Results of the exposure of the resonators to a proton beam were also described. Specimens of 100 Mc frequency exposed to gamma irradiation at a dosage rate of 1.4×10^6 rad/hour for periods 10 to 60 minutes exhibited large downward frequency shifts of 300 to 1000 cycles per second. Subsequent aging of the resonators at 85°C revealed gradual upward drifts in frequency and leveling off at a plateau, perhaps 100 cycles above the minimum point. Hence recovery was only partial. A typical pattern is shown in Figure 11.

If, however, the resonator was exposed for greater periods of time at this intensity the pattern of behavior similar to that in Figure 12 was observed. As may be seen, the frequency begins a positive shift at about five hours irradiation at 1.4×10^6 rad/hour and continues upward until it may overshoot the original value. Since Contract No. DA-36-039-sc-85363 terminated during the period of this particular study aging measurements after 24 hour exposures were not obtained.

More recently such data have been obtained and are reported herein. Three units were exposed in the cesium 137 well at an intensity 1.4×10^6 rad/hour for 24 hours. The resonators were retrieved and returned to the normal 85°C storage ovens for aging measurements at the fundamental, third,

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* Frondel, Clifford, "Effects of Radiation on the Elasticity of Quartz," American Mineralogist 30, Nos. 1 and 2, 432 (1945).

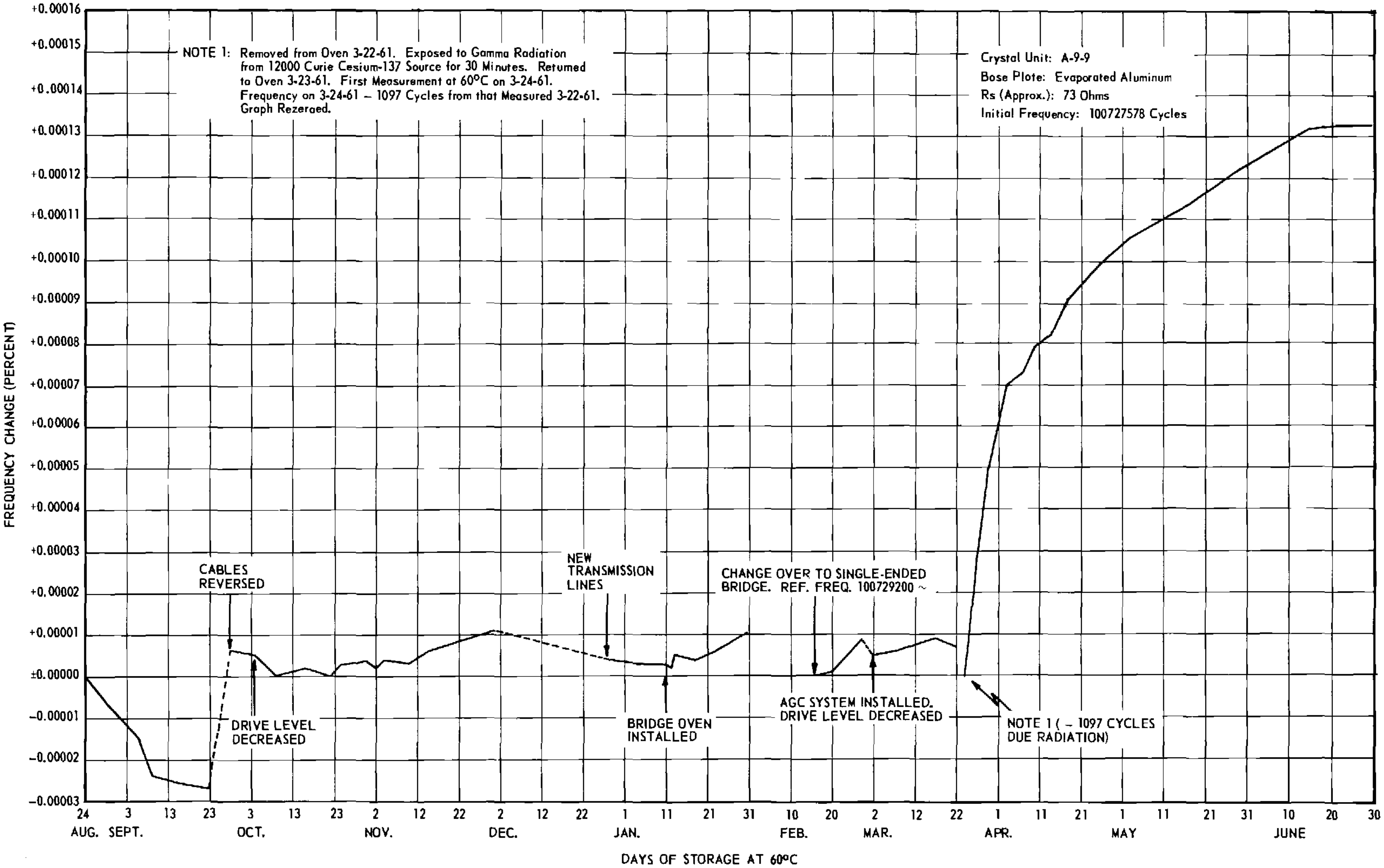

Figure 11. Frequency versus time data for resonator A-9-9-A1, a ninth overtone unit plated with evaporated aluminum and stored at 60°C.

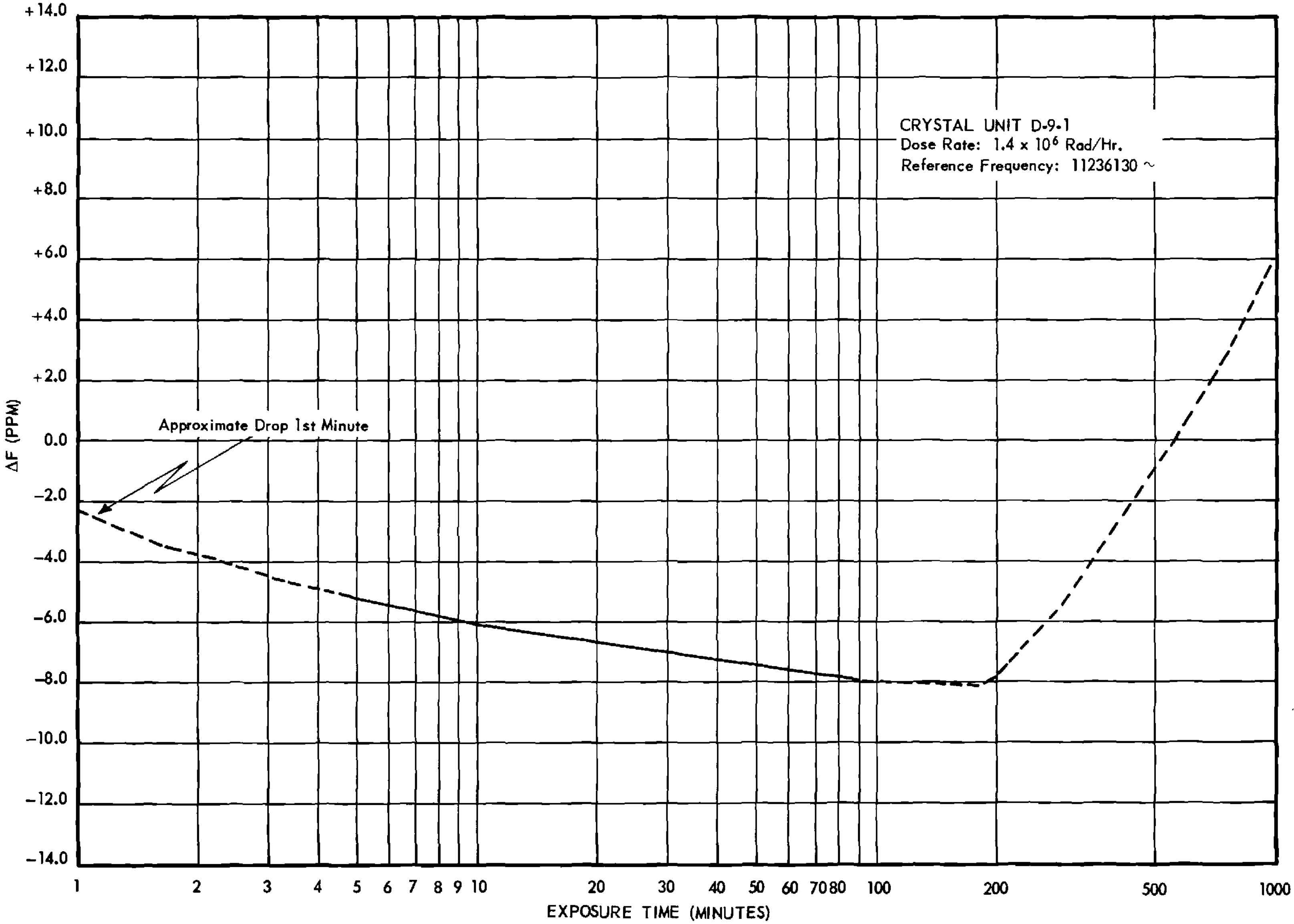

Figure 12. Typical frequency variation with Cesium-137 irradiation for resonator D-9-Ag. Note positive frequency shift after about five hours irradiation.

and fifth modes. Patterns of behavior are exhibited in Figures 13, 14, 15, 16, and 17. Figures 13 to 15 exhibit the pattern of unit 1-2 Al at each mode of operation whereas Figures 16 and 17 exhibit only the fundamental modes of units 1-5 Al and 1-6 Al. In general, the patterns of the three modes were similar although the total frequency shift at the overtone modes during exposure was somewhat less and the subsequent aging drifts appeared to be slightly more.

Of particular interest as may be noted in Figures 13, 16, and 17 was the fact that the units being exposed sufficiently to overshoot the initial frequency drifted downwards at an appreciable rate (> 1 ppm in 60 days) and the unit undershooting drifted very little (< 2 pp 10^7). The overtone modes of the latter aged downward slightly more.

6. Resonators for Exposure to Pulsed Radiation

Twelve resonators for which aging histories are known were transmitted to Mr. J. M. Stanley for exposure to the effects of an atomic explosion. These were as follows:

Unit No.	Plating Type	Quartz Blank Material
2-1	Aluminum only (no overcoat)	Natural quartz
2-4	"	"
2-7	"	"
2-9	"	"
3-1	"	Cultured quartz
3-2	"	"
3-3	"	"
3-5	"	"
4-2	"	Swept cultured quartz
4-3	"	"
4-4	"	"
4-6	"	"

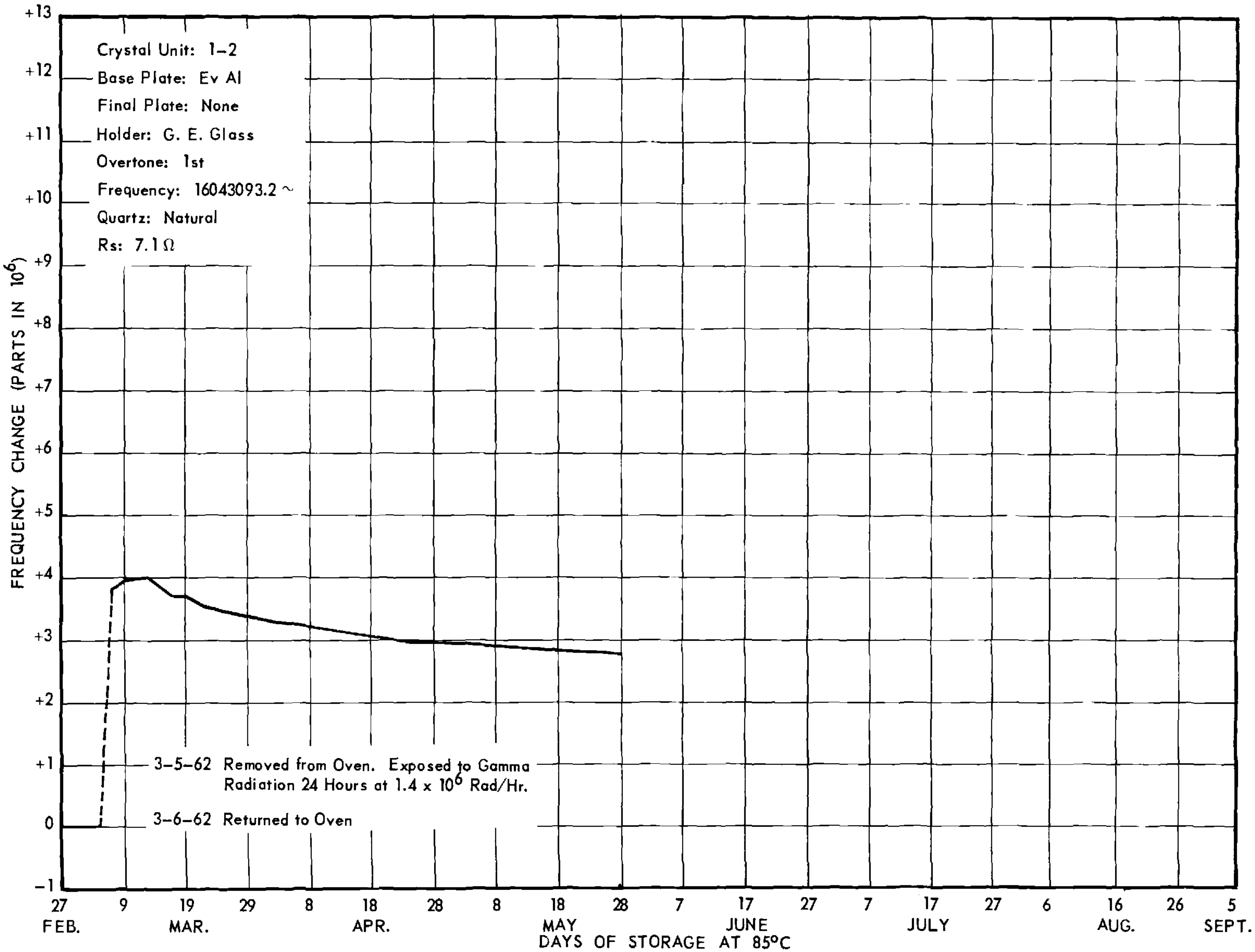

Figure 13. Frequency shift and aging of resonator 1-2 Al after 24 hour radiation exposure (1.4×10^6 rad/hour), fundamental mode, 16 Mc.

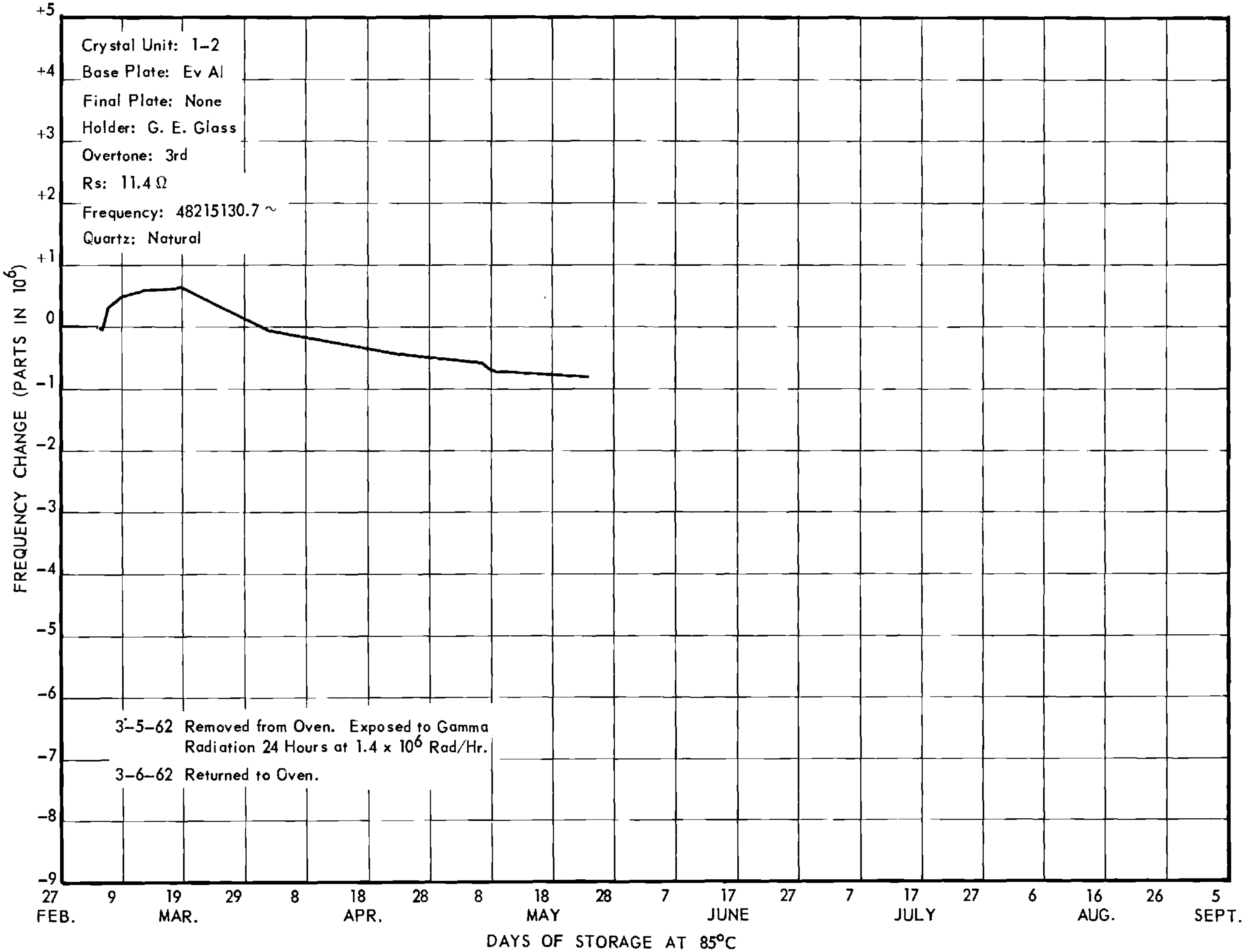

Figure 14. Frequency shift and aging of resonator 1-2 Al after 24 hour exposure to radiation (1.4×10^6 rad/hour), 3rd mode, 48 Mc.

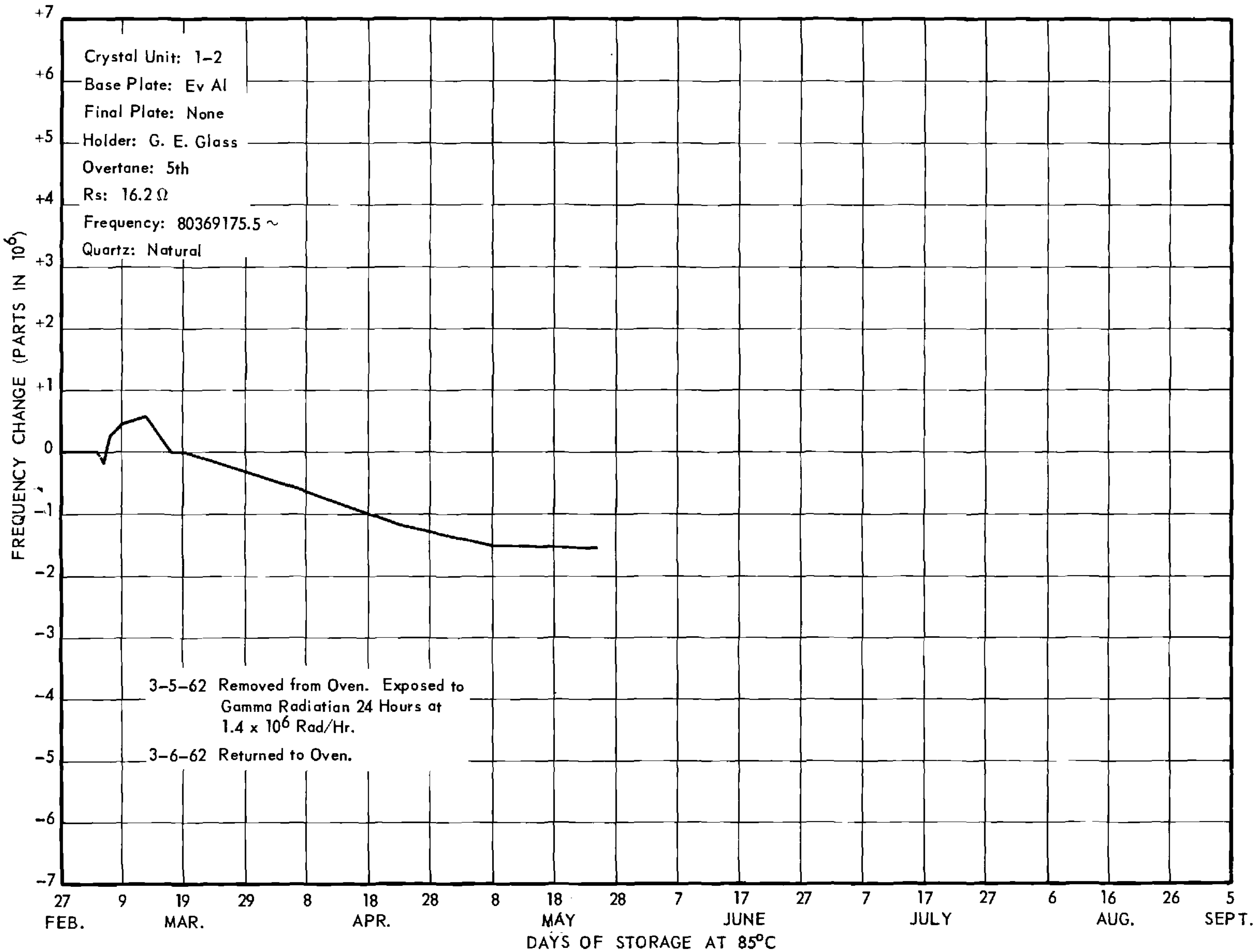

Figure 15. Frequency shift and aging of resonator 1-2 Al after 24 hour exposure to radiation (1.4×10^6 rad/hour), 5th mode, 80 Mc.

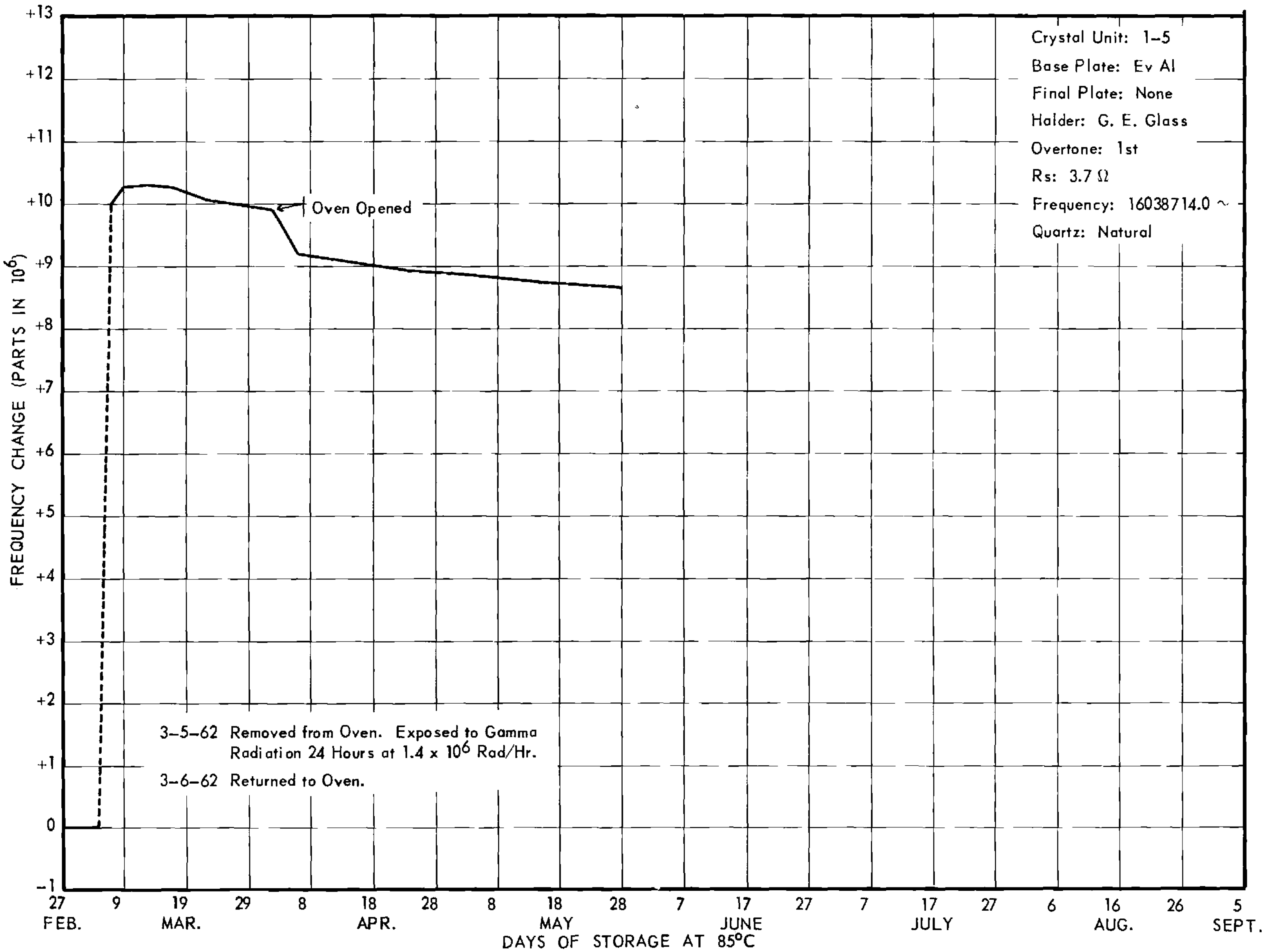

Figure 16. Frequency shift and aging of resonator 1-5 Al after 24 hour exposure to radiation (1.4×10^6 rad/hour), fundamental mode, 16 Mc.

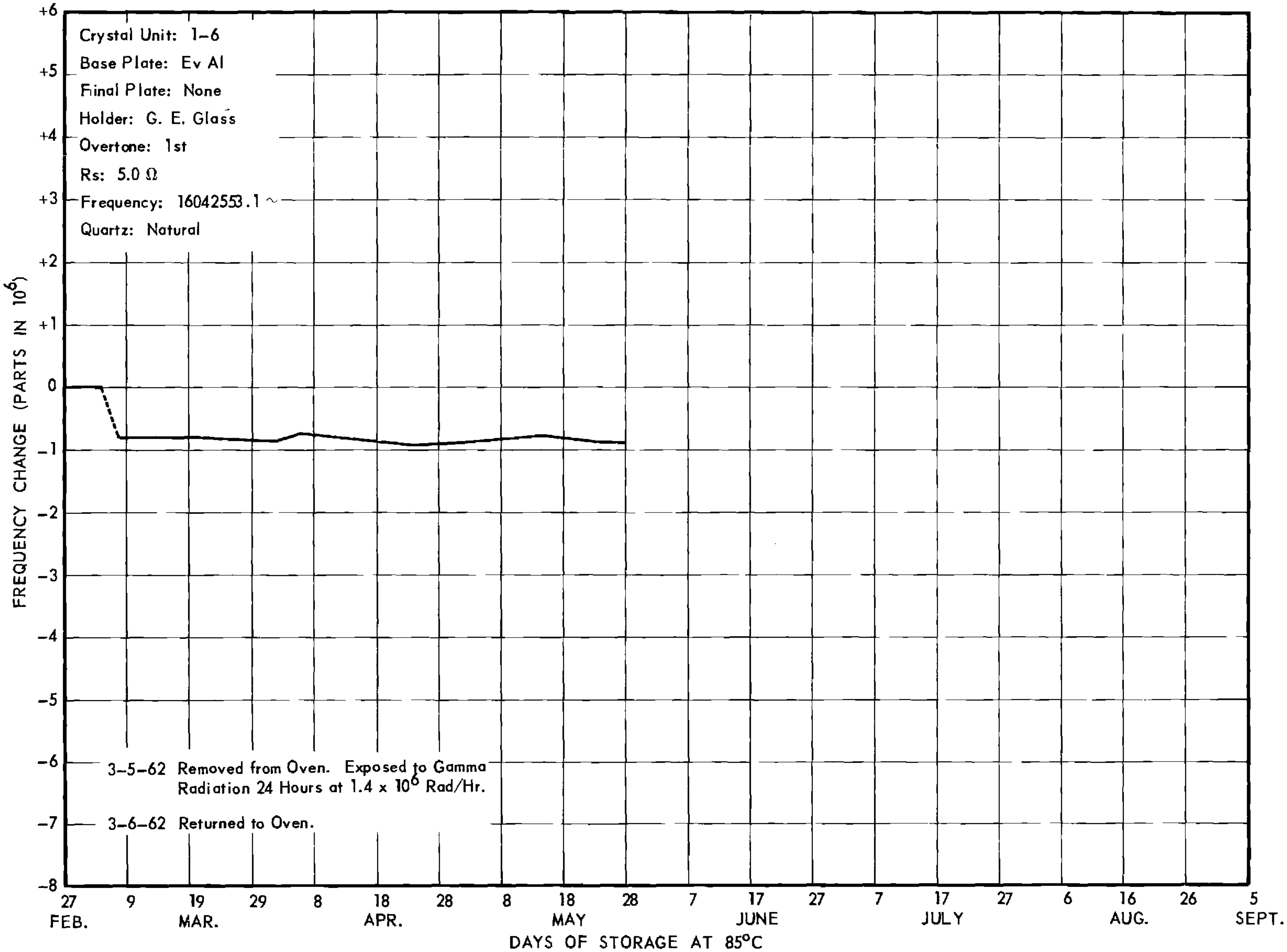

Figure 17. Frequency shift and aging of resonator 1-6 Al after 24 hour exposure to radiation (1.4 x 10^6 rad/hour), fundamental mode, 16 Mc.

Arrangements are being made for exposure of other units at a pulsed atomic reactor as soon as the prescribed aging period of 90 days at 85°C is completed.

7. Data Analyses

a. Resonators Fabricated Previously

Aging measurements continued for 16 Mc units fabricated in previous quarters, in spite of some measurement difficulties experienced during the period, have shown that units fabricated with meticulous care within rather varied material specifications will exhibit minimal aging. The data depicted in Figures 1-6 show that units made of natural or synthetic quartz, base plated with aluminum only, may age < 5 parts in 10^8 in 60 days and exhibit distinct differences in aging at the overtone mode or modes (Figures 1a and 1b). The data for an outstandingly stable example is depicted in Figure 3b. Here the aging is essentially zero for 100 days.

The addition of a final overplating of any type, aluminum plus aluminum or aluminum plus gold, degrades stability somewhat. Figures 4a and 4b for aluminum plus gold exhibit an aging slope of one part in 10^7 in about 60 days. For the resonator plated with aluminum plus aluminum the rate exhibited in Figures 5a and 5b was approximately double that for the aluminum plus gold specimen of the preceding Figures 4a and 4b.

b. Resonators Operated at High Drive Level

Resonators operated at high drive level (2 mw) exhibited shifts in frequency upon stabilization and remeasurement at 85°C. Shifts for the few units measured were up or down < 10 parts in 10^7 and the shift observed was different at the various modes of operation for the same unit. Aging of resonators after exposure to the high drive level experiment was not markedly directional although it appeared to be somewhat more erratic. Measurement difficulties encountered during the period, however, appear to be superimposed upon the curve contributing in part to random frequency shifts of small magnitude.

c. Aging of Resonators Exposed to Gamma Radiation

Resonators of 100 Mc frequency exposed to gamma radiation at an intensity of 1.4×10^6 rad/hour for periods less than five hours exhibited marked negative frequency shifts of 5 to 10 ppm. Aging thereafter was upward until a plateau was reached a few ppm above the minimum frequency reached. Exposure for longer periods of time resulted in a partial, complete, or overshoot return to the initial frequency level. Aging, after the 24-hour exposure, was downward. The rate of aging appeared to be dependent on whether the frequency established was over or under the frequency before exposure to gamma radiation. A slight undershoot resulted in a minimal aging for one specimen. This point needs further investigation.

V. DISCUSSION

A. Frequency Measurement Technique

The frequency measurement technique, with the aid of the Rohde and Schwarz synthesizer, has now progressed until the rate and accuracy of measurement are satisfactory. The synthesizer still needs some of its weaker tubes replaced but the swapping of several stronger tubes of similar types to critical sites reduced the noise level of the instrument until its performance has reached a useful level. Further improvements are expected upon the arrival and substitution of new tubes.

B. Oven Temperature Control Effects

The improvement in frequency measurement accuracy and reliability pointed up other major causes of resonator instability. These were the limits of oven temperature control accuracy, a capacitative or inductive effect due to position of any given resonator within the oven, and the necessity of entering the ovens at relatively frequent intervals. Each of these operations is associated with shifts in frequency that are easily discernible by present measurement techniques and will undoubtedly require rectification before greatly improved stabilities are obtained.

The ovens as now constructed have up to 100 coaxial connectors leading through the bottom layers of the oven nest. These, having a significant cross section area, establish a large heat conduction path to the external room temperature. Large variations in the ambient may result in small diurnal shifts in the oven temperature. Although these may appear to be insignificant ($\pm$ 0.015°C), and are for most purposes, they may be quite significant when measurements are made to an accuracy of a few parts in 10^9. Furthermore, the angle of cut of a crystal for its fundamental may not be the best for operation at the higher overtones of the unit; as a result, some units display excessive shifts due to temperature variation when measurements are made at the third and fifth modes.

Another disadvantage of large capacity ovens is the loss of measuring time encountered on entry of an oven for insertion or extraction of resonators. Such interruptions may required 24 or more hours for the return of stable temperature conditions and serious time losses may develop as a result by entry and retrieval of units for various special studies.

The unsatisfactory temperature control of the larger ovens and the entry and retrieval problems of the current design indicate a definite need for ovens of smaller unit capacity for aging studies such as the current one.

C. Position Effects

In addition to temperature problems induced by opening and closing the oven, the very act of inserting or removing a resonator may change the frequencies of nearby units. Even though spare units are employed in all spaces at all times, small shifts in frequency may occur. These vary from 10 to 100 cycles in the present 100 unit oven.

D. Summary and Recommendations

The problems associated with large ovens for aging studies, i.e., temperature control, entry perturbations, and position effects, indicate the need for smaller oven units to be employed in aging studies. Ovens holding not more than 10 to 20 units are envisioned and a few ovens should be provided that hold only single units.

VI. CONCLUSIONS

Present oven design and temperature control limitations establish the stabilities obtainable for many resonators currently being fabricated and measured. Improved ovens will result in improved measurements and more useful aging studies. Seventy resonators previously fabricated and continued on storage and measurement at constant temperature have continued to show excellent stabilities or aging changes ascribable to known parameters. Differences in the material of the blank, i.e., natural, synthetic, or swept, did not give significant differences in stability. Differences in plating metal, i.e., gold, silver, or aluminum, have not resulted in appreciable differences in aging rates where meticulous known fabrication procedures were used. Overcoating aluminum with aluminum or with gold resulted in greater aging rates than for non-overcoated units. Overcoating with gold in several instances resulted in smaller aging rates than upon overcoating similar units with aluminum.

Values of Q for resonators fabricated, operated in the series mode, are in the range 100,000 to 300,000.

Resonators exposed to cesium source gamma radiation at a rate of 1.4×10^6 rad/hour for 24 hours, upon subsequent storage at 85°C, exhibited small downward drifts in frequency. The amount of this drift appeared to be dependent on the relative position of the frequency after exposure to that before exposure. For resonators with a final frequency very near the original one the drift rate was small, < 1 pp 10^7 per month.

Frequency shifts resulting from irradiation were different for the same unit operated at its various modes and aging rates also varied somewhat.

Resonators for pulsed radiation studies have been fabricated and negotiations for proper exposures are progressing satisfactorily.

VII. PROGRAM FOR THE NEXT INTERVAL

The following tasks will be accomplished during the next quarter:

1. Continued frequency measurements of units stored at 85°C;

2. Initial aging measurements of the units completed for the pulsed radiation study; and

3. Fabrication of one crystal group for routine aging measurements.

VIII. PERSONNEL

The persons employed and the approximate hours worked by each upon the project are listed below.

		Hours
Richard B. Belser	Project Director	193
W. H. Hicklin	Assistant Research Engineer	589
J. O. Darnell	Research Assistant	443
C. M. Shirley	Technician	412
T. L. Spradling	Student Assistant	141

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Arthur L. Bennett, Chief
Physical Sciences Division

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This contract is supervised by the Solid State and Frequency Control Division, Electronic Components Department, USASRDL, Fort Monmouth, New Jersey. For further technical information contact Mr. P. E. Mulvihill, Project Engineer, Telephone: 535 2475.

REPORT NO. 6 (SIXTH QUARTERLY REPORT)
GEORGIA TECH PROJECT NO. A-552

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser and W. H. Hicklin

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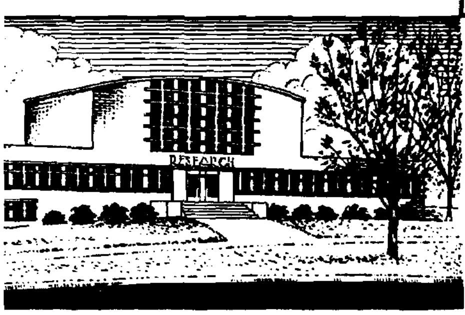
15 May 1962 to 15 August 1962

PLACED BY THE U. S. ARMY
ELECTRONICS RESEARCH AND DEVELOPMENT LABORATORY
FORT MONMOUTH, NEW JERSEY



Engineering Experiment Station
Georgia Institute of Technology
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GEORGIA INSTITUTE OF TECHNOLOGY
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QUARTERLY REPORT NO. 6

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser
W. H. Hicklin

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Fort Monmouth, New Jersey

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

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* "Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500° to 574°C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

During the quarter approximately 140 resonators have been maintained in oven storage at 85°C and measured periodically for frequency and R_s. Of these approximately 56 were units prepared for long term aging study and the remainder were undergoing measurements preliminary to exposure to high intensity pulsed radiation (10^{13}nvt).

Thirty new resonators, with aluminum electrodes, were fabricated and mounted in the HC 27/U glass container. Heat effects during sealing resulted in major frequency shifts for 12 of these units, from 16 Mc to the vicinity of 22 Mc, with no significant change in R_s. Frequency versus temperature data and R_s values indicated characteristics resembling an AC-cut more than an AT-cut resonator. An investigation of changes in these resonators by the method of X-ray diffraction topography indicated extensive electrical twinning in the units exhibiting the frequency shift. It was also shown that information concerning strains produced in the quartz by mounting clips and cements could be obtained by X-ray diffraction topography and that this method holds promise as a means of further study of this problem.

Aging studies have continued to show that many units have high stability but definite differences in aging rates at the fundamental and overtone modes of the same unit have been observed. Also, overcoated units have displayed greater aging rates than units coated only with a base coat. For the base-coated units a typical change in frequency has been $< \pm$ 1 part in 10^7 in 150 days whereas the overtone modes of the same unit have shown a more definite negative frequency trend of about 2 parts in 10^7 in the same period. Some of the overcoated units have exhibited shifts at the overtone modes as large as 6 parts in 10^7 in about 120 days.

The fundamental mode has exhibited somewhat greater frequency shift spikes about the base frequency than have the overtone modes. This behavior has thus far been ascribed to a greater sensitivity to the effects of strains resulting from temperature changes; the precise control of temperature appears to be one of the yet unsolved problems for large volume resonator storage.

Preliminary measurements of resonators prepared for exposure to intense pulsed radiation have been completed and the units are scheduled for exposure in early September.

III. PUBLICATIONS, LECTURES, AND REPORTS

During this reporting period two monthly letters (No. 14 and 15) were submitted. Report No. 5 (Fifth Quarterly Report) was reproduced and distributed.

Dr. G. K. Guttwein, technical representative of the U. S. Army Electronics Research and Development Laboratory, visited Georgia Tech on 18 August 1962. The progress of the work on the present contract was discussed, and a preliminary outline of a continuation of the current program was formulated.

IV. FACTUAL DATA

A. Introduction

The principal work of the project during the current quarter has been devoted to the fabrication of quartz resonators and a continuation of aging measurements of two categories of resonators. The units of one set, containing approximately 56 resonators were fabricated for a study of long term aging effects and were measured in frequency to an accuracy of about 5 parts in 10^9 at the 1st, 3rd and 5th overtones. The resonators of the remaining category, containing about 84 units, were fabricated for the specific purpose of measuring the effects of intensive pulsed radiation on the aging of quartz resonators. The latter units were measured only at the third overtone to an accuracy of about 5 parts in 10^8. Secondary studies of oven temperature control, sealing of HC 27/U glass units, and damage inflicted on the quartz resonator during sealing were undertaken.

B. Apparatus and Procedures

1. General

Vacuum equipment, frequency measuring apparatus, constant temperature resonator storage ovens, and resonator sealing equipment were operated with a minimum of difficulty during the period of this report. No modifications of the ovens or vacuum systems were made.

2. New Equipment

A Marconi, F 3006 solid state, unit oven has been purchased and is awaiting installation. A Manson model RD 180-A, Ultra High

Stability Oscillator was purchased and installed for use as a frequency standard. A number of new tubes for the Rohde and Schwarz frequency synthesizer were received and installed.

3. Frequency Measurements

The replacement of a number of tubes in the Rohde and Schwarz Frequency Synthesizer has made possible its use as a signal generator for frequency measurements to a precision of about $\pm$ 5 parts in 10^8. The synthesizer is being used for all measurements of the special units for the pulsed radiation studies and for certain other measurements at the first, third and fifth overtone modes when crystals for controlling the CI meter are unavailable.

During the quarter a Manson model RD 180A Ultra High Stability Oscillator was purchased and calibrated for use as a standard frequency source. The calibration is maintained at + 14 parts in 10^9 $\pm$ 2 parts in 10^9 by comparison with the standard frequency transmission from WWVL.

In addition, a Western Electric company model O-76A/U oscillator is compared in frequency with the Manson oscillator using a RMS model CR-1 cosine phase plotter. The O-76A/U serves as a stand-by frequency standard and also furnishes standard frequency signals to other laboratory groups making precise frequency measurements.

The 100 Kc output of the Manson oscillator is used, in addition, to synchronize the Rohde and Schwarz synthesizer. The precision of measurement was improved by about 2 parts in 10^8 by this action. The improvement is apparently due to cleaner output signals from the synthesizer when using the Manson oscillator.

4. Comments

Both vacuum systems available to the project have operated without repair or modification during the quarter. Operating pressure was in the low 10^{-7} Torr range for both base plating and vacuum baking.

The HC-27/U sealing equipment has operated well. Only two of 68 units mounted in HC-27/U holders and stored at 85°C have shown to be definite leakers. Otherwise the aging rates for both gold and aluminum plated units has been very low, as will be illustrated subsequently.

No modifications were made on any of the three 85°C ovens in use during the quarter. Oven A, in which the units for pulsed radiation are stored, was opened once during the quarter (on 22 June 1962). Ovens B and C were not opened. Two unavoidable power failures (one for 2 1/2 hours and one for about 20 hours) occurred, however.

C. Experimental Work

1. Quartz Resonator Fabrication and Sealing

Three groups of crystal units comprising 30 resonators were fabricated during the quarter. Each group was base plated with aluminum, bonded with pyroceram, and sealed in an evacuated HC-27/U holder. Group Al-3 was fabricated of cultured quartz with a 100% yield. Group Al-4 and Al-5 were fabricated of swept, cultured quartz with a 30% and a 50% yield respectively. Pertinent parameters of each operable resonator (18) are given in Table I.

An investigation of the yield for groups Al 4 and 5 revealed that a number of the units had been damaged by heat occurring during the sealing phase. A similar behavior had been noted for a few previously fabricated units. The damaged units underwent a positive frequency change of about 7.5 Mc to approximately 22.5 Mc at the fundamental and a drastic change from the normal temperature - frequency behavior associated with

TABLE I

Aluminum Plated Crystal Units Fabricated for Pulsed Radiation Experiment

Unit	Quartz	$R_s(\Omega)$	$F_s(\sim)$	Q_s
Al-3-1	Cultured	9.5	48225766	95,500
3-2	"	22.2	48199401	62,600
3-3	"	16.0	48185702	75,800
3-4	"	43.0	48212283	30,400
3-5	"	20.0	48176125	67,700
3-6	"	12.5	48195792	76,500
3-7	"	11.5	48224353	84,200
3-8	"	15.5	48216342	59,400
3-9	"	21.5	48240396	56,300
3-10	"	17.0	48200704	62,200
Al-4-2	Swept Cultured	21.3	48226377	82,000
4-3	"	7.4	48240448	124,500
4-6	"	23.5	48252059	110.500
Al-5-1	"	5.5	48220484	172,000
5-3	"	6.5	48174740	151,500
5-4	"	5.9	48198143	168,000
5-5	"	17.0	48191730	52,500
5-6	"	16.5	48191365	104,500

*All units were mounted in the HC 27/U glass container and bonded with 1 part Pyroceram to 2 parts silver powder an AT-cut resonator as illustrated in Figure 1. This particular data plot resembles the frequency versus temperature behavior of an AC-cut quartz resonator rather than an AT-cut. The average series resistance of these units was however usually less than for similar but undamaged units, and this fact also supports the resemblance of the units to behavior typical of the AC-cut. An X-ray study of the quartz plates revealed twinning of the quartz over large areas and a more thorough discussion of the procedure and findings of this examination will be presented in the subsequent Section E.

2. Frequency Measurements

Resonator frequency aging studies conducted during the current quarter can be grouped into three general classifications;

a. routine frequency measurements of resonators fabricated for long term aging studies;

b. preliminary frequency measurements of units for pulsed radiation studies at only the third mode; and

c. short term, rapid sequence frequency measurements of selected units of group a. above at one or more modes. All measurements were made at 85°C.

Routine frequency measurements were continued on about 60 resonators fabricated previously to the current quarter. The frequency data for representative specimens are exhibited in Figures 2 through 7.

Representative frequency data for the series of 84 units prepared for the pulsed radiation series are illustrated in Figures 8, 9, 10 and 11. The plot of A1-5-5 (Figure 11) is included to exhibit the aging rate of a unit considered to be leaking in comparison with the non-leakers of Figures 8-10.

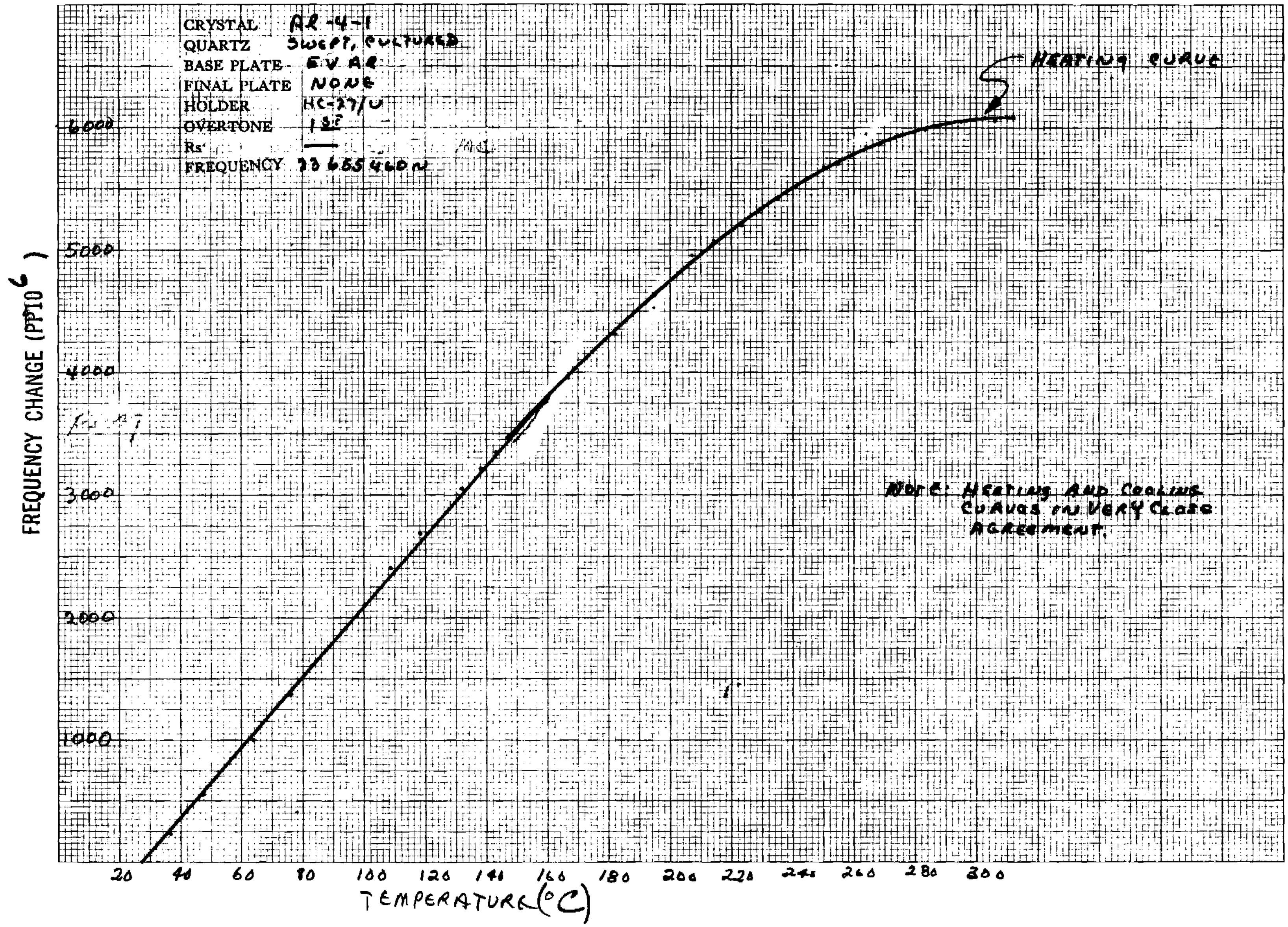

Figure 1. Frequency versus temperature characteristics of AT-cut resonator Al 4-1 twinned during sealing of the HC-27/U holder.

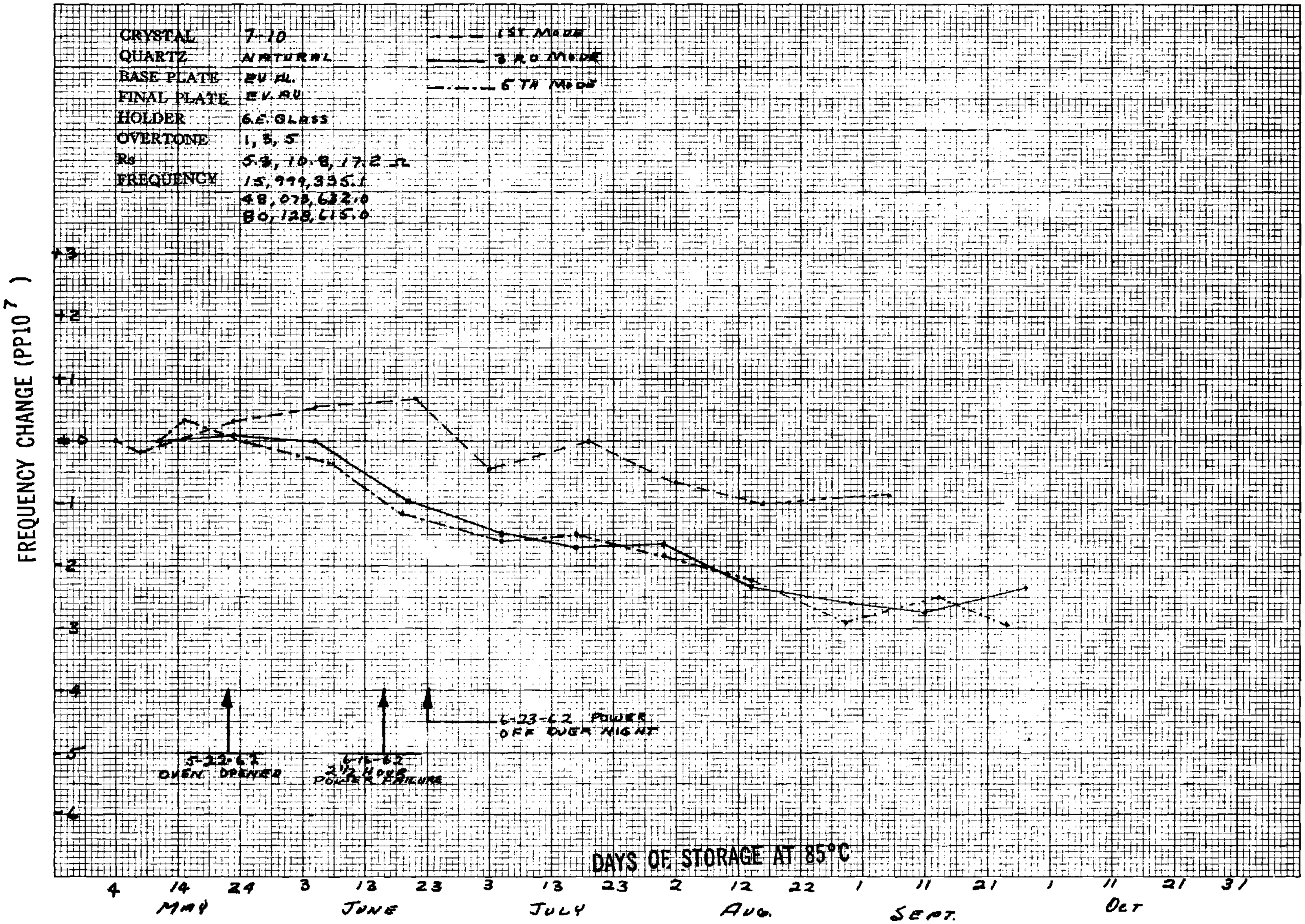

Figure 5. Frequency versus time data for natural quartz resonator Al + Au 7-10 base-plated with aluminum and overplated with gold.

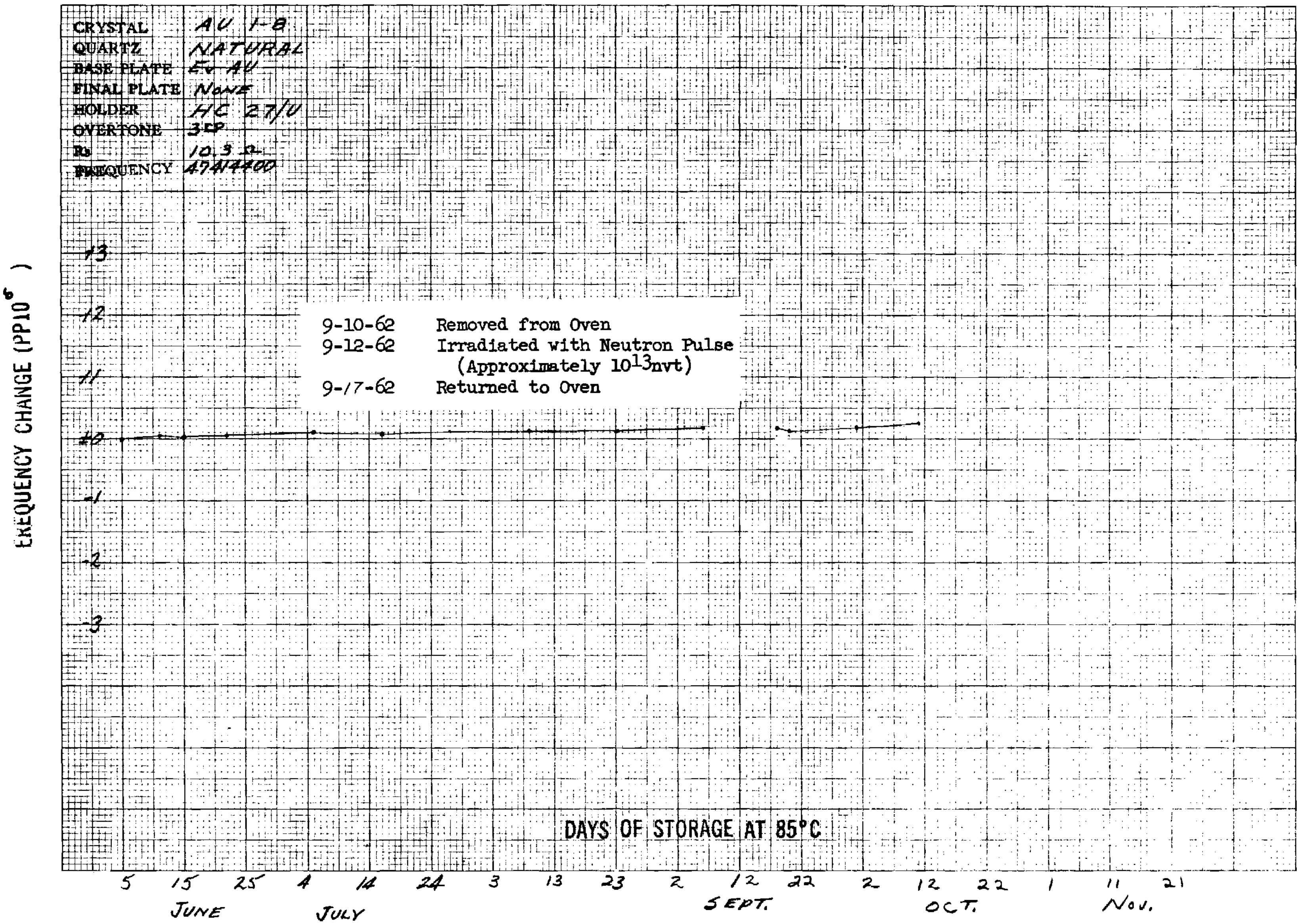

Figure 9. Frequency versus time data for natural quartz resonator Au 1-18 base-plated with gold.

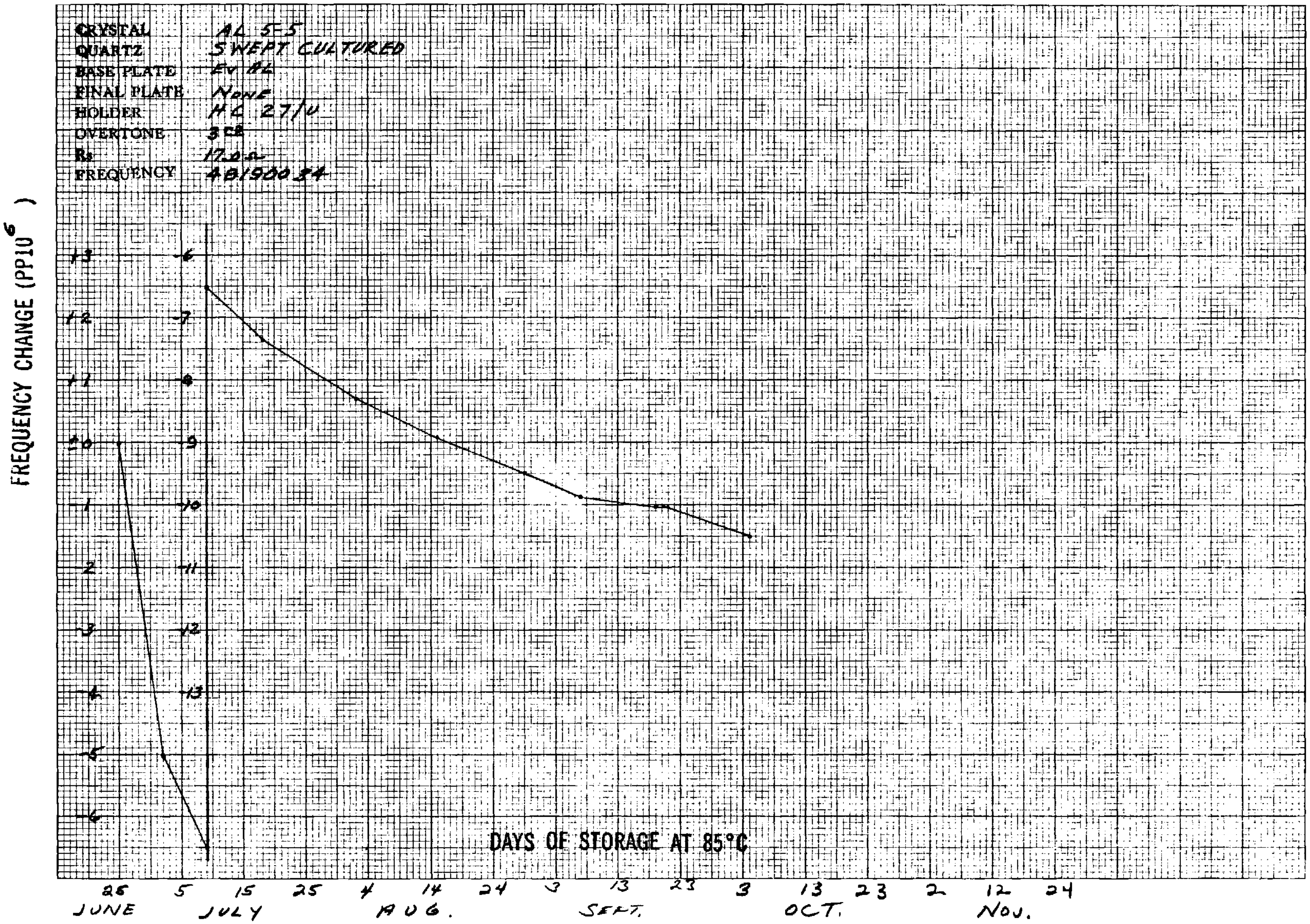

Figure 11. Frequency versus time data for swept, cultured quartz resonator Al 5-5 base-plated with aluminum showing the negative frequency change associated with a leaking envelope.

3. Equipment Capability Measurements

In addition to the principal aging measurements conducted during the quarter a series of equipment capability studies were made. These were designed primarily to detect temperature cycling in the ovens, both long and short term, which would effect resonator frequency measurements. In general these were conducted over periods of several hours up to 34 hours with a discontinuation of the measurements during the night hours. Data for representative studies are exhibited in Figures 12 and 13. The data indicate that changes of resistance of ± 30 ohms occurred in the value of the thermistors in the oven and, at 0.0003°C per ohm, this represents a change of ± 0.009°C (or approximately ± 0.01°C) over a period of 34 hours. The principal change, however, appears to be the one occurring in the morning of the second day, and consists of a temperature rise of the order of 0.01°C and a number of other lesser heating and cooling spikes. These spikes are in general also reflected in the frequency changes of highly stable resonators within the oven as shown in the two figures. These frequency changes reach a magnitude of a few parts in 10^8 and indicate that the true short term frequency stability obtainable for these units is dependent under present storage conditions, principally on the degree of temperature control obtained in these storage ovens. Long term aging exceeding a few parts in 10^8 should be readily discernible, however.

4. Data Analyses

a. Measurements at the Fundamental and Overtone Modes

(1) The aging rates of the third and fifth overtone modes agree very closely with each other;

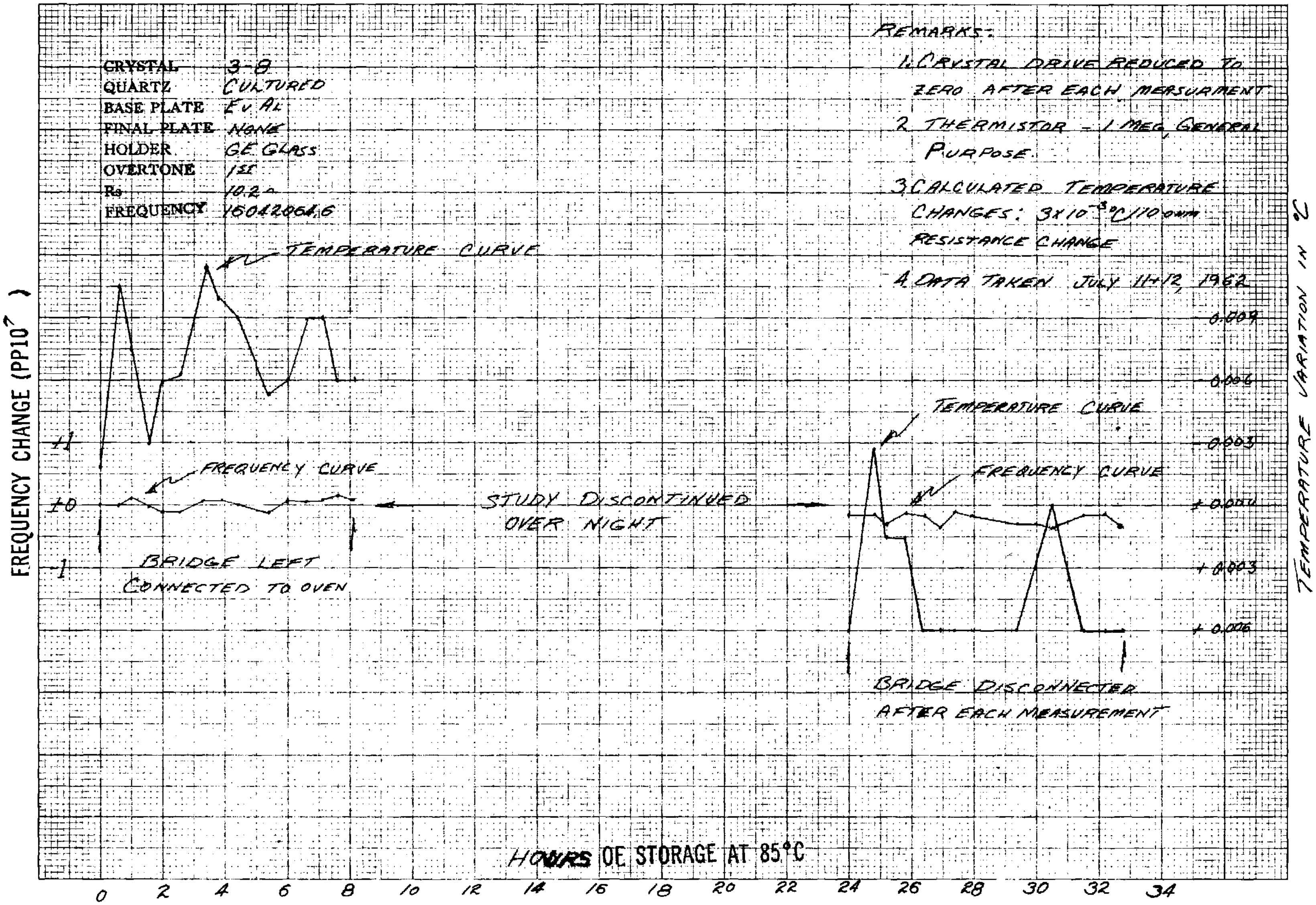

Figure 12. Equipment capability and short term aging study using resonator No. al 3-8 operated on the fundamental frequency.

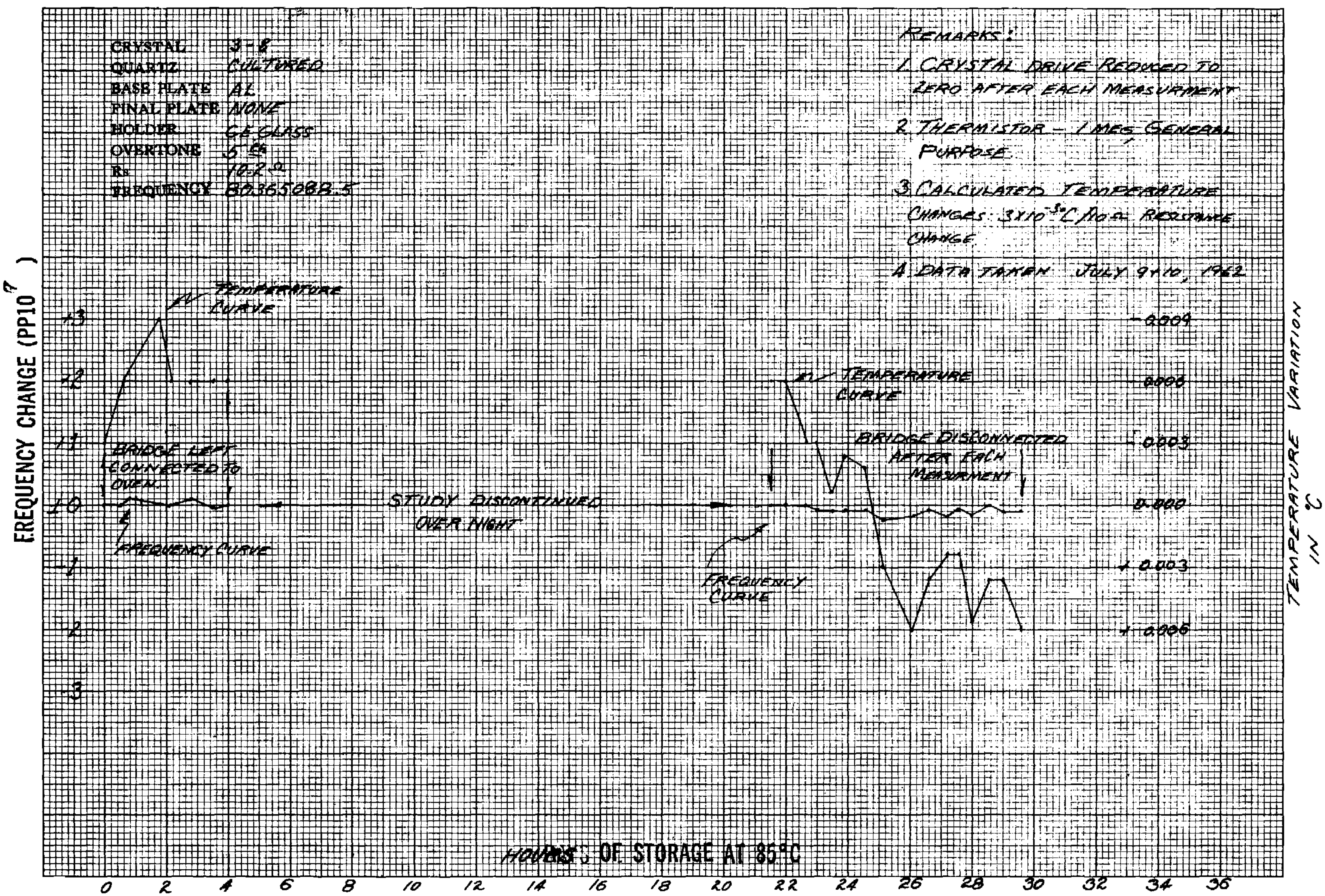

Figure 13. Equipment capability and short term aging study using resonator No. Al 3-8 operated on the fifth overtone.

(2) The frequency changes occurring at the fundamental frequency, as measured, are often erratic;

(3) Overplating with a second metal for frequency adjustment increases the frequency drift rate - especially at the third and fifth modes.

As noted in Figures 5-7, and as may be abundantly noted in graphs of many other units on file, the plot of the fundamental frequency exhibits many more excursions from a smooth aging curve then do plots of the overtone data for the same crystal. There appears to be an association of this behavior, in a number cases, with temperature variations of the oven caused by oven opening or power failure. These temperature variations in turn vary stresses applied to the quartz by the mounting and bonding system. In particular one may note that the unit of Figure 7 was bonded with Pyroceram 95-plus - silver cement. It thus appears that the fundamental mode may be more sensitive to stress then the overtone modes although an explanation of this behavior is not yet available.

Since the overcoating layer is evaporated onto a surface which can neither be cleaned or heated as well or as readily as the original substrate surface, it is deposited under conditions known to form less perfect films of higher surface areas. As a result the negative frequency change of the overplated units at the overtone modes is very likely due to loading of the overcoating metal film by gases or vapors in the sealed holder. An effort to improve the quality of the overcoating film insofar as possible appears to be a worthwhile future endeavor.

Many of the graphs show that some difficulty was encountered with the oven temperature control systems on 27 or 28 July 1962. Although complete records are kept of all power failures, oven openings, etc., no reason is presently known that accounts for the behavior of many units subsequent to 28 July.

D. Other Experiments

1. Resonators for Studies of the Effects of Pulsed Radiation on Aging of Quartz Resonators

As noted in preceding Section IV. C-2, approximately 84 resonators were fabricated and measured in preparation for the pulsed radiation effect experiment.

The silver plated units of this series were bonded with duPont No. 5504 cement and mounted in evacuated T-5 1/2 bulbs since, otherwise, the silver film agglomerated during the firing of the Pyroceram 95-silver cement normally required as the bonding agent in the HC-27/U holder. The gold and aluminum plated resonators, on the other hand, were bonded with the Pyroceram 95-silver cement and mounted in evacuated HC-27/U holders. The fact that many excellent units were obtained, in spite of the potentially significant variables introduced by use of the HC-27/U container, indicates that meticulous care during fabrication is probably the most important factor in the fabricating of resonators with highly stable frequency characteristics.

2. Short Term Aging and Equipment Capability Study

These studies were initiated to determine:

a. The precision of frequency measurements; and
b. The effect of oven temperature on the crystal frequencies.

Estimates based upon the data obtained and exhibited in Figures 12 and 13 indicate the precision of frequency measurement to be about 5 to 10 parts in 10^9. Such precision was obtained regardless of whether the bridge was left connected to the oven or removed after each measurement.

As outlined in paragraph IV. C-3 and Figures 12 and 13, short term aging studies of resonators measured periodically over a period of 34 hours revealed relatively high frequency stabilities on successive measurements with occasional excursions up to approximately 2 parts in 10^8. On the other hand, temperature excursions of the magnitude of 0.006 to 0.009°C were apparent and total drifts within the period of 0.018°C were observed. Although perfect correlation between frequency and temperature shifts is not displayed some correlation is indicated, more in the case of Unit Al 3-8 when operated at its fundamental (Figure 12) then when operated at its overtone Figure 13. This data is in agreement with other data exhibiting more extensive shifts with temperature and associated stresses of units operated at the fundamental mode. The frequency response appears to lag behind the temperature response and may be associated with the greater heat capacity of the resonator and its mounts in comparison with the thermistor.

The temperature control of an oven of large storage capacity to the degree necessary to achieve the maximum stability intrinsic to the quartz remains as a major problem.

E. Examination of Quartz Crystal Plates by X-ray Diffraction Topography*

As noted in Section C and Figure 1 a number of quartz crystal

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*This section was contributed principally by Dr. R. A. Young, Research Professor of Physics, and Mr. N. Kelly Hearn, Assistant Research Physicist of the Georgia Institute of Technology.

resonators suffered severe damage during sealing in the HC-27/U container. Both the frequencies and the temperature-frequency relation of the crystals underwent large changes. A search for a suitable method with which to determine the cause of these changes lead to discussions with Dr. R. A. Young, Head of the Solid State Branch and X-ray Diffraction Laboratories of the Engineering Experiment Station, who is well versed in the structure and behavior of quartz.*

Dr. Young and Dr. A. L. Bennett, Research Professor of Physics of the Engineering Experiment Station, were already undertaking some studies of quartz by the method of X-ray diffraction topography, a relatively recent development which appeared to hold promise in examination of the damaged units. Secondly, recent frequency measurements had suggested that strain effects in the quartz plates were responsible for otherwise unaccountable frequency deviations of certain resonators both during oven storage at constant temperature and, especially, when unavoidable temperature cycling was introduced by opening of ovens and, on two occasions, by unpredicted power failures. A method of examining units for strains was thus highly desirable. As a result, the method of X-ray diffraction topography was adopted for investigation of selected resonators for damage due to strain or to electrical twinning. The latter was suspected in the case of Unit Al 4-1 of Figure 1.

Two X-ray methods were actually used, one is the topographic method in which an image of the crystal is produced with a particular diffracted beam. Place to place variation in diffracting power due to

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*See: R. A. Young, "Mechanism of the Phase Transition in Quartz" Final Report Contract No. AF 49(638)-624, Solid State Sciences Division, Air Force Office of Scientific Research, Washington 25, D. C.

twinning, strains, dislocations, and other imperfections are thereby revealed in essentially true geometric shape in the resulting photograph. The Berg-Barrett, the Schulz, and the Lang techniques are some of the recognized forms of X-ray diffraction topography. Our use of the Lang technique will be discussed shortly.

In the topographic methods mentioned the data consist of the diffraction image of the specimen. In the second method used the data consist of the diffraction image of the X-ray source and information about the crystal comes from the distortion it produces in that image. As yet this second technique is unnamed.

A broad incident beam is used in which there is deliberately introduced recognizable character in the cross-sectional view of the beam. In the present case the character is a number of equally spaced parallel strips of zero intensity produced by the shadows of the sheets of a Soller slit. Figure 14 exhibits the general design of the apparatus. If the crystal is undistorted the source-image formed by a single diffracted beam contains equally spaced parallel stripes, as shown in Figure 15a. If the crystal is distorted, however, so that the Bragg planes themselves are effectively no longer exactly plane all over the specimen, the stripes are curved and their separation is changed, as is shown by Figure 15b. The greater is the crystal distortion, of course, the greater is the total distortion of the stripe pattern. Thus a photograph such as Figure 15b gives information about the variation of the distortion from place to place on the crystal. It would seem in principle possible to make quantitative interpretation of these patterns which would allow

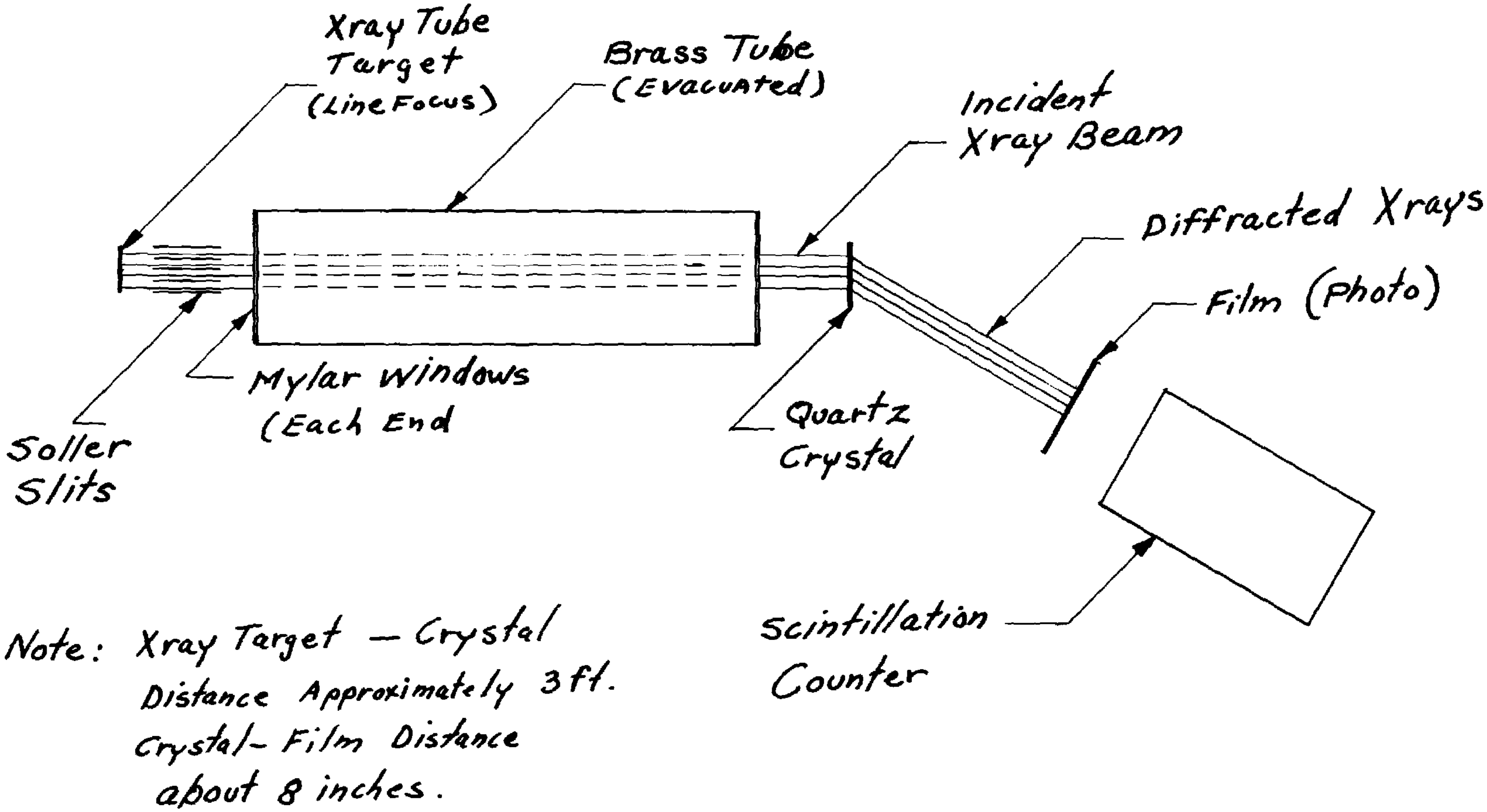

Figure 14. Sketch of X-ray topographic apparatus used to observe strain patterns in quartz plates.

determination of both direction and magnitude of the distortion-associated "tilt" of the Bragg planes as a function of position on the crystal. No quantitative approach has yet been undertaken.

On the other hand, purely qualitative comparisons have been quite informative. Various specimens differ considerably in regard to the amount of distortion they display in this manner. Our studies have so far shown that considerable observable strain is introduced by the mounting clamps and by the cements used to insure electrical contact between the clamps and the thin film electrodes. It is possible that the films, themselves, may also contribute to the observed strain; no experiments definitive on this point have yet been performed.

It has been of particular interest to note that the technique is equally applicable to the mounted and plated crystal as to the naked crystal, and therefore provides a fine non-destructive tool for following the increase in distortion throughout the several steps of fabrication up to, but not including, placement in the glass envelopes. It is also of special interest to note that preliminary studies show that various cements and mounting holders do differ markedly with respect to the amounts of distortion they introduce into the crystal specimens. Since the specimen can be examined by this method at each step of the fabrication process without demounting, a particular opportunity here exists for correlation of oscillator characteristics with strain. The work so far done is of a very preliminary nature; a great deal of work along these lines is anticipated.

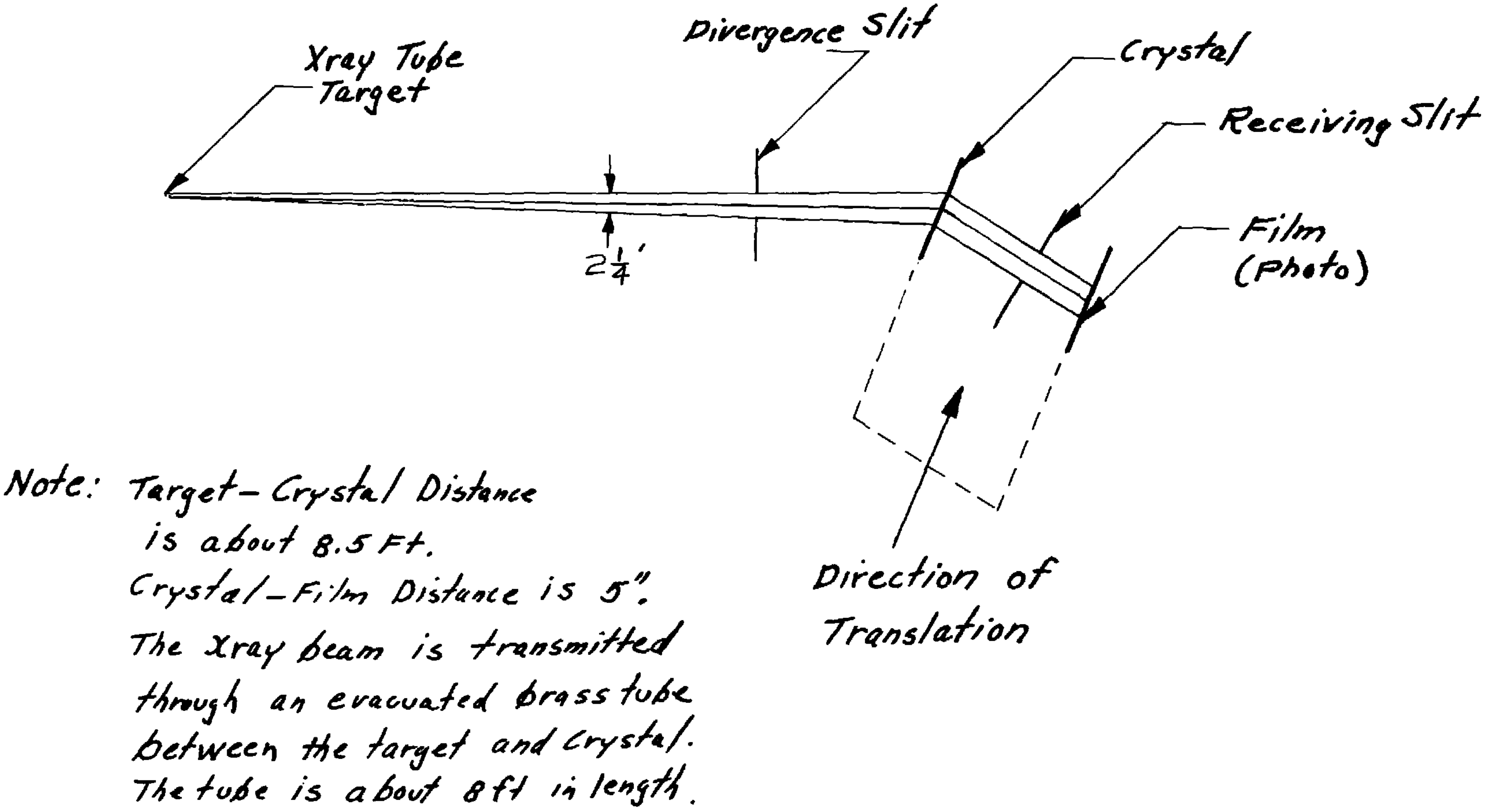

Figure 16. Sketch of X-ray topographic apparatus using Lang's technique.

The Lang method of X-ray diffraction topography is being employed in investigation of the causes of the large frequency changes which occur in many crystals when they are sealed into the HC-27/U containers. With this method a finely collimated X-ray beam with a minimum of divergence (2 1/4 minutes in our case) strikes a crystal in the transmission position and is diffracted through the crystal and a receiving slit to a photographic film. The crystal and film, which are placed parallel, are then translated along a line parallel to the crystal face so that a one to one correlation between crystal and topograph is preserved. This set up is shown in Figure 16.

A typical diffraction photograph, a "topograph", resulting from this method is shown in Figure 17. A diffraction image of the crystal appears and diffraction contrast effects make variations in the perfection and orientation visible. For example, an individual dislocation would appear as a single or multiply curved line if oriented favorably. The particular areas of interest are those indicated by "A". These are most probably Dauphiné (or electrically) twinned areas. A $(30.\bar{1})$ Bragg reflection was used in this diffraction topograph because of its sensitivity to Dauphiné twinning. There is a very large difference in the X-ray intensity in the $(30.\bar{1})$ and $(\bar{3}0.\bar{1})$ reflections, yet the $(30.\bar{1})$ of one region of the crystal occurs at the same angle as the $(\bar{3}0.\bar{1})$ of the adjacent Dauphiné twinned region. Consequently, the exposure in the areas "A" is small enough so that they appear to be complete voids in the crystal's diffraction image. As seen in the photograph a large portion of the plate (the more opaque section) is twinned with respect

to the remainder. The large amount of twinning occurring is undoubtedly responsible for the changes in frequency and temperature-frequency behavior of quartz resonator Al 4-1 and others in which large frequency shifts were observed. Dr. Young, in the reference cited on page 27, has discussed the occurrence of Dauphiné twinning at temperatures well below the α-β phase transition temperature of quartz. Twinning of this type must have occurred in this specimen during the sealing phase. One of the peculiarities of this twinning is that some quartz specimens are more susceptible to it than others. This susceptibility is probably related, in turn, to the entire history of the quartz of the particular plate from its time of original growth. This variation in susceptibility may account for the variation in twinning of resonators fabricated in a similar manner.

The experiments outlined have revealed a tool of considerable value in the further study of quartz as a frequency control element and the pursuit of more intensive work along the lines noted is recommended.

V. DISCUSSION

A. Frequency Measurement Techniques

The principal source of frequency measurement error appears to be the lack of precise temperature control allowing variation in temperature between successive measurements. In addition, a mismatch between oven temperature and crystal "turn-over" temperature exists for one or more frequency modes of the same quartz plate.

The principal cyclic temperature variations shown in Figures 12 and 13 are short term variations but, in addition there appear to be long term variations of temperature. The latter may be due to "aging" of the mercury, fixed-contact thermostats. The thermostats are protected from voltage surges by varistors. However, after many operations at 85°C, changes, especially at the surface of the mercury column, may occur which in turn may cause small changes in the operating temperature. Such changes would not be apparent over a period of a day or two, but would be apparent when measurements were compared over a period of several months.

B. The Effects and Analyses of Strains in Quartz Resonators

The introduction of the X-ray diffraction topographic technique as a method for examining quartz specimens brings to bear a new tool on the previously difficult subject of the effects of strains on frequency change. It has been apparent for some time, as reported in the Final Report of Contract No. DA-36-039-SC-74956 (July, 1958) and reports of subsequent contracts that stresses developed in plating and mounting procedures introduced frequency changes in the respective resonators with time. Normally, such strains appeared to be relieved with time with the result that a sharp or a gradual upward drift of the frequency of the particular resonator occurred.

Effects observed that appeared to be specifically tagged were increases in frequency where electroplated nickel films were used as an electrode material and occasions where tab clips were used in lieu of spring clips, the resonator being subsequently temperature cycled. Earlier positive frequency shifts had been observed with certain metal platings such as sputtered and electroplated rhodium and with certain bimetal pairs.

Still another experience in rapid upward aging was noted in the case of a number of commercially produced resonators examined for aging characteristics in the Final Report of Contract No. DA-36-039-SC-78910 (February, 1959). At this time the strong upward aging vector observed for resonators from a number of commercial sources was ascribed to the probability of highly stressed electroplated films used as electrodes. In any event the effects of strains and stress are undoubtedly of high significance in preparing resonators of high stability.

A tool of the suggested discrimination of the X-ray diffraction topographic technique will allow a thorough examination of the effect of strains including those introduced by bonding cements and mounting clips or other devices. A thorough study of this problem should give a keener understanding of procedures necessary for the fabrication of stable resonators on a mass production basis and may furnish a method of fabricating units of controlled aging drifts.

VI. CONCLUSIONS

Frequency measurements as now conducted allow precision of approximately 5 parts in 10^9 for 16 mc resonators operated at the fundamental, 3rd and 5th modes. A more rapid frequency measurement technique based on the Rohde and Schwarz frequency synthesiser allows a precision of about 5 parts in 10^8.

The principal source of deviation currently existing in the frequency measurements appears to be short and long term storage-oven temperature instabilities of a magnitude of approximately $\pm$ 0.01°C. Frequent entry into the ovens for specimen loading results in undesirable temperature cycling of already installed resonators and often results in undesired stresses in the resonators. The results of these are subsequently apparent in the frequency measurements of particular resonators.

Aging behavior at various modes of operation of the same resonator may be different. Part of this difference is ascribed to the fact that the cut of the crystal required for minimum temperature-frequency deviation at 85°C is particular to the mode of operation and part to the fact that the fundamental mode appears to be more strain sensitive than the overtone modes.

Resonators overcoated to frequency with a second metal coat exhibit larger aging vectors than units base-coated only. A part of this larger variation is due to the less perfect second film deposited on the substrate near room temperature after only restricted cleaning of the resonator.

Procedures for sealing the HC-27/U glass container have been perfected until very small losses from leakers have been suffered as a result of poor sealing technique. On the other hand, losses from quartz twinning during the sealing phase have been serious.

X-ray diffraction topography has proved to be a valuable tool for the examination of quartz plates for strain effects and twinning. It holds promise as a valuable tool for future studies and analyses of the effects of mounting and bonding procedures on the stabilities of quartz resonators.

Resonators scheduled for irradiation at a pulsed reactor facility have been completed and all necessary measurements and preparations have been made pending the scheduled conduct of the experiment on 12 September 1962.

VII. PROGRAM FOR THE NEXT INTERVAL

The following tasks will be accomplished during the next quarter:

1. Continued frequency measurements of units stored at 85°C.
2. Fast neutron pulse irradiation of selected units. Irradiation of 65 units is scheduled for 12 September 1962.
3. High (2mw) drive level studies of selected resonators for periods of 48 to 72 hours.

VIII. PERSONNEL

The persons employed and the approximate hours worked upon the project by each are listed below.

		Hours
Richard B. Belser	Project Director	195
W. H. Hicklin	Assistant Research Engineer	460
J. O. Darnell	Research Assistant	372
C. M. Shirley	Technician	371
T. L. Spradling	Student Assistant	298
J. C. Shaw	Student Assistant	237

Respectfully submitted,

Richard B. Belser
Project Director

Approved:

Edwin J. Scheibner, Chief
Physical Sciences Division

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This contract is supervised by the Solid State and Frequency Control Division, Electronic Components Department, USAERDL, Fort Monmouth, New Jersey. For further technical information, contact the Project Engineer, Mr. P. E. Mulvihill, Telephone: 535-2475.

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

QUARTERLY REPORT NO. 7

AGING CHARACTERISTICS OF QUARTZ CRYSTAL RESONATORS

By

R. B. Belser
W. H. Hicklin

Contract No. DA-36-039-SC-87407
DA Task No. 3A-99-15-004
Georgia Tech Project No. A-552

15 August 1962 to 15 November 1962

Placed by the U. S. Army
Electronics Research and Development Laboratory
Fort Monmouth, New Jersey

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I. PURPOSE

The purpose of this project is to delineate the effects of materials and fabrication techniques on the frequency stabilities of quartz crystal resonators. Of particular interest are resonators operated in the overtone modes. A comparison of the frequency stabilities of resonators fabricated of natural, synthetic, swept* natural, and swept synthetic quartz will be made.

The effect of the bonding cement and, in particular, the effects on the bonding cement of the high temperature reached during the sealing of the glass envelope will be investigated.

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*"Sweeping" is a method of purification of quartz. The process consists of heating the quartz to a temperature of 500° to 574°C and applying a potential gradient of a few thousand volts per centimeter. This results in the sweeping out of certain impurities.

II. ABSTRACT

Frequency measurements of 150 resonators stored in constant temperature ovens at 85°C have been continued during the Quarter. The resonators consisted of 55 units prepared for general studies of aging and 95 units prepared for study of the effects on aging of exposure to pulsed neutron radiation (10^{13}nvt). Ninety additional resonators were fabricated and the yield of 78 were examined for electrical parameters and aging by standard measurement procedures.

The general aging behavior observed continued to follow the previously defined trends, i.e., the frequency data plots of the fundamental mode were different and more erratic than those of the 3rd and 5th modes and the fundamental mode appeared to be more susceptible to the effects of stress. Aging of the better units plated with Al, Au or Al + Au continued to be small, < 3 parts in 10^8 per month. Units plated with Al + Al exhibited aging rates about 3 times this much.

The resonators exposed to a pulse of neutron irradiation at the Sandia Pulsed Reactor Facility (49 units) exhibited no appreciable frequency shift or aging effect as a result of this exposure.

A comparison of the effects of exposure of resonators of cultured and swept cultured quartz to gamma radiation from a Cs-137 source for 24 hours at a level of 1.4×10^6 Rad/hr indicated that the swept cultured quartz showed much less total frequency shift (< 1 ppm compared to about + 29 ppm) and subsequently exhibited somewhat less aging, although the aging of both types was relatively small in the time of measurement (30 days).

Some studies of the damage and resonator aging effects of continuous drive of resonators for about 60 hours at a 2 milliwatt level, as compared to the usual 1 microwatt level, were inconclusive.

A study by X-ray topography of stresses induced in resonators during the fabricating processes revealed that the principal stress was applied on mounting the unit in the spring clip. Removal of all mounting and fabrication components by suitable mechanical or chemical methods resulted in a return of the quartz blank to an essentially unstressed condition.

III. PUBLICATIONS, CONFERENCES AND REPORTS

During this reporting period two monthly letters (No. 16 and 17) were submitted. Report No. 6 (Sixth Quarterly Report) was written, reproduced and distributed.

On 26 September 1962 Dr. R. A. Young, Mr. R. B. Belser and Mr. W. H. Hicklin of Georgia Tech met with Dr. E. A. Gerber, Dr. G. K. Guttwein, Dr. E. Hafner, Mr. J. M. Stanley and Mr. P. E. Mulvihill of the U. S. Army Electronics Research and Development Laboratories at Fort Monmouth, New Jersey. Plans for the proposed continuation of the research program on aging studies of quartz resonators were established and the scope of the technical requirements was decided. A discussion of a technique of examining stresses, electrical twinning, and other faults in quartz resonators by X-ray diffraction topography was presented by Dr. Young.

IV. FACTUAL DATA

A. Introduction

The principal work of the project during the seventh quarter has been devoted to the completion of the studies of the effects of pulsed neutron radiation and of gamma radiation on the aging of quartz resonators and to the continuation of the primary aging studies related to the effects of materials and processing on the aging of the resonators. In addition, studies concerning the effects of continuous drive on the aging of resonators and the use of X-ray topography in examining strains induced in resonators by mounting procedures have been carried out.

B. Apparatus and Procedures

1. General

Apparatus and procedures have operated relatively well during the Quarter with the exception of a few difficulties which are noted below.

2. Quartz Resonator Fabrication

The base plating and sealing apparatus has operated well during the quarter. The equipment and techniques for sealing HC-27/U holders have been improved and the yield of successfully sealed units has now approached 100%.

3. Oven Operation

On 12 November one of the 36-position ovens lost power for several hours due to a blown fuse. The fuse was replaced and no further trouble was encountered. A severe electrical storm on the cited date may have caused the fuse to blow.

The Marconi solid state oven failed during the quarter and was returned for repair. A group of units, S group, comprising 9 units intended for use in the Marconi oven, was placed in a-100 position oven for storage and measurement.

4. Frequency Measurements

The frequency measuring system has required some maintenance during the quarter. The readout multiplier has caused the most trouble. The accuracy of the measuring system seems to have deteriorated slightly and the system will require overhaul in the near future.

The BNC oven connector (UG-1104/U)* on the HF crystal impedance bridge was replaced 29 October 1962. The frequency changes caused by the above action were about +0.65 parts per 10^7 at the third overtone and +1.4 parts per 10^7 at the fifth overtone.

C. Experimental Work

1. Resonator Fabrication

Eleven groups of crystal units comprising 90 resonators were fabricated during the quarter. The total number of operable units obtained was 78; the yield was thus 86.5%. Most of the losses occurred during sealing of either the T-5 1/2 or the HC-27/U glass containers. The pertinent parameters of each group are compiled in Table I.

As will be noted, one group of units is plated with Al only, 6 groups are plated with Au only, 2 groups are plated with Al + Al, one group is plated with Al + Au, and one group is plated with Au + Al. The type of quartz used in the gold plated units was varied in order to give a comparison among the behavior characteristics of the various types, i.e., natural and cultured, swept and unswept, respectively. Except for the Al only which is on natural unswept quartz, the remainder are on swept natural quartz blanks. There was also some variation in the type of bonding and container used. The principally used bonding agent was duPont 5504 A.

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*Gremar Part No. 91737.

TABLE 1

FABRICATION DETAILS FOR QUARTZ RESONATORS FABRICATED DURING PERIOD 15 AUGUST 1962 - 15 NOVEMBER 1962

SHEET 1

GROUP NUMBER	FABRICATION DATE	QUARTZ	BASE PLATE	FINAL PLATE	MOUNT	BOND	HOLDER	FINAL SEAL BAKE	FINAL SEAL PRESSURE* ATMOSPHERE	REMARKS
6	10-8-62	NATURAL UNSWEPT	AL	NONE	GE GLASS	5504A	.006" SPRINGS	3HRS - 175°C	4x10⁻⁷	TEFLON GETTER-SPLASH SHIELD USED. BARIUM GETTER FLASHED AFTER FINAL SEAL.
5	10-18-62	NATURAL UNSWEPT	Au	NONE	GE GLASS	5504 A PYROCERAM	.006" SPRINGS	3HRS - 175°C	3x10⁻⁷	STRAIN STUDIES MISALIGNED AND ANNEALED SPRINGS.
14	10-22-62	NATURAL UNSWEPT	Au	NONE	GE GLASS	5504A	.006" SPRINGS	3HRS - 175°C	2x10⁻⁷	
14	10-22-62	NATURAL SWEPT	Au	NONE	GE GLASS	5504A	.006" SPRINGS	3HRS - 175°C	2x10⁻⁷	
15	10-23-62	CULTURED UNSWEPT	Au	NONE	GE GLASS	5504A	.006" SPRINGS	3HRS - 175°C	2x10⁻⁷	
15	10-23-62	CULTURED SWEPT	Au	NONE	GE GLASS	5504 A	.006" SPRINGS	3HRS - 175°C	2x10⁻⁷	
16	10-29-62	NATURAL SWEPT	Au	NONE	HC-27/U	PYROCERAM	.006" SPRINGS	5MIN - 350°C	2x10⁻⁵	SPRINGS ATTACHED TO BASE W/ PYROCERAM + AG FLAKE.
17	11-2-62	NATURAL SWEPT	Au	AL	GE GLASS	HYSOL K16-081	.006" SPRINGS	3HRS - 175°C	4x10⁻⁷	ALLOY STUDIES.
18	11-6-62	NATURAL SWEPT	AL	AL	GE GLASS	5504 A	.006" SPRINGS	3HRS - 175°C	2x10⁻⁷	BASE PLATE DEGASED BY HEATING IN VACUO BEFORE EVAPORATION OF FINAL PLATE.
19	11-12-62	NATURAL SWEPT	AL	AL	HC-27/U	PYROCERAM	TAB CLIPS	5MIN - 350°C	2x10⁻⁵	
20	11-12-62	NATURAL SWEPT	AL	Au	HC-27/U	PYROCERAM	TAB CLIPS	5MIN - 160°C	2x10⁻⁵	FOUND 3 UNITS ALLOYING @ 300°C. DROP PREHEAT TEMP TO 150°C - NO VISIBLE ALLOYING AFTER PREHEAT TEMP DECREASED TO 150°C.

* Pressure in mm of Mercury

Eight groups are in GE T-5 1/2 containers and 3 are in HC-27/U glass containers. The Al + Au and Au + Al specimens were prepared to establish the extent of alloying occuring during and subsequent to fabrication and to examine the effect of this bimetal coat on the long term aging of resonators.

Table II gives the specific parameters determined to date for the individual resonators.

During the sealing of group No. 20 (Al + Au), the first three units sealed gave evidence, by color changes in the film, that the gold and aluminum were alloying.* The pre-heat temperature was reduced from 350°C to 200°C for unit No. 4 in this group and to 150°C for unit No. 5. The remaining five units were sealed at the 150°C pre-heat temperature. No visible alloying was obtained for units 20-4 to 20-10. The effect of the alloying on R_s is plainly visible in Table II. since the R_s values of 9 to 13 ohms were recorded for the first three specimens in the group and 1-6 ohms for the last seven. Similarly Group No. 17 (Au + Al) exhibited R_s values of 11 to 15 ohms compared with 4 to 8 ohms for group No. 1 (Al only) and 3 to 5 ohms for Groups 5, 14, and 15 (Au only). The R_s values for Groups 18 and 19 (Al + Al) were also relatively high with one or two specimens with very high R_s values. The Al overcoat on Group No. 18 was deposited on the quartz resonator at 300°C in contrast to 25°C for overcoats deposited heretofore.

Group 17 was plated with the combination gold base plate plus aluminum final plate. The thickness ratio of gold to aluminum was 3/1 (1500 Å/500 Å). The units were bonded with Hysol K-16-081 (A, B), an epoxy-silver cement that requires no high temperature baking for curing. The units were then mounted in T-5 1/2 bulbs and the frequency and resistance were measured for

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*The alloy formed in this case had a purple color similar to that described for the intermetallic compound Au_4 Al.

SHEET 2

TABLE 2 (Continued)

ELECTRICAL PARAMETERS OF QUARTZ RESONATORS FABRICATED

DURING PERIOD 15 AUGUST 1962 - 15 NOVEMBER 1962

	FUNDAMENTAL			THIRD OVERTONE			FIFTH OVERTONE			Q METER MEASUREMENTS						
UNIT	F_{s1}	R_{s1}	Q_1	F_{s3}	R_{s3}	Q_3	F_{s5}	R_{s5}	Q_5	ΔQ_1	ΔQ_3	ΔQ_5	C_{o1}	C_{o3}	C_{o5}	
15-1-Au	15760885	4.0	72200	47389500	19.0	61400	78943929	53.0	—	3.0	8.0	60.0	8.4	7.5	7.4	UNABLE TO MEASURE FA + RA
2	15756500	3.5	84000	47339960	8.5	109200	78912840	21.0	89500	3.0	8.0	57.0	8.1	7.2	7.4	
3	15742070	3.5	84300	47290720	16.0	73500	78823320	56.0	~~128300~~	2.0	8.0	63.0	8.8	7.3	7.4	UNABLE TO MEASURE FA + RA
4	15744600	3.5	83700	47304350	10.5	89500	78853790	21.0	128300	2.0	8.0	58.0	8.0	7.5	7.4	
5	15739680	3.5	85700	47286540	17.5	65000	78839480	32.0	—	2.0	8.0	55.0	8.0	7.1	7.2	UNABLE TO MEASURE FA + RA
7 ~~6~~	15764930	3.0	98700	47361850	8.0	126000	78946090	17.0	159000	2.0	8.0	60.0	8.6	7.1	7.2	
8 ~~7~~	15768975	3.0	110300	47377670	7.0	129500	78974650	15.5	99200	2.0	8.0	56.0	8.1	7.4	7.2	
9 ~~8~~	15763165	3.0	96300	47359990	7.5	136500	78945250	16.0	79000	2.0	8.0	59.0	8.7	7.7	7.2	
10 ~~9~~	15786670	3.0	98300	47431100	7.5	131000	79063180	15.0	184500	2.0	8.0	60.0	7.9	7.3	7.2	
~~10~~																
16-1-Au	15739250	3.8		47286045	9.5											SPRINGS BONDED TO HC-27/U HOLDER W/ PYROCERAM + AG- FOR GR. 16.
2	15744050	6.5		47289770	12.0											
3	15711360	11.0		47202410	31.0											
6	15730790	6.45		47259750	20.0											
8	15736620	7.8		47275880	33.0											
9	15747390	4.5		47310200	11.3											
(Au+Al) 17-1	15781480	13.3 (~~19~~)		47414761	19.0											AU + AL W/ SPECIAL BOND. HYSOL K18-061 FOR GR 17.
4	15796370	14.7		47457963	21.0											
5	15792230	14.7		47446234	20.0											
6	15803324	11.4		47480064	15.5											
7	15784503	13.1		47425050	17.5											
8	15784665	13.0		47425050	20.0											
9	15778960	13.0		47404981	20.5											

SHEET 3

TABLE 2 (Continued)

ELECTRICAL PARAMETERS OF QUARTZ RESONATORS FABRICATED

DURING PERIOD 15 AUGUST 1962 - 15 NOVEMBER 1962

	FUNDAMENTAL			THIRD OVERTONE			FIFTH OVERTONE			Q METER MEASUREMENTS						
UNIT	F_{s1}	R_{s1}	Q_1	F_{s3}	R_{s3}	Q_3	F_{s5}	R_{s5}	Q_5	ΔQ_1	ΔQ_3	ΔQ_5	C_{o1}	C_{o3}	C_{o5}	
(Al+Al) 18-1	16046570	5.8		48220993	10.2											
2	16016113	6.8		48131513	10.0											
3	16013089	6.2		48119161	10.5											
4	16024253	5.7		48152643	9.0											
5	16027357	10.1		48159370	14.0											
6	16060139	31.0		48259439	17.0											
7	16025043	9.0		48151232	12.5											
8	16045007	8.0		48213309	11.9											
9	16033284	8.5		48178288	14.5											
10	16021784	6.4		48141903	9.8											
(Al+Al) 19-1	16026342	10.0		48149633	15.2											
2	16014348	2.8			6.7											
3	16039856	3.8		48198041	7.5											
4	16016181	4.0		48128858	7.1											
5	16075676	5.3		48306452	10.7											
6	16009929	2.7		48111807	6.2											
7	16031554	11.8		48176040	12.0											
8	16026656	7.5		48154681	8.8											
9	16032707	6.4		48180341	11.0											
10	16034971	7.3		48142223	13.0											
(Al+Au) 20-1	15935209	9.2		47877237	18.5											FILM ALLOYED DURING SEALING
2	15925759	10.0		47835502	15.5											"
3	15930472	13.1		47860426	18.0											"
4	15936032	2.6		47880709	6.6											NO VISIBLE ALLOYING
5	15948653	1.2		47916890	8.5											"
6	15962190	1.7		47955931	7.2											"
7	15932106	1.5		47868123	7.0											"
8	15942228	6.0		47897878	24.0											"
9	15943766	2.7		47904003	7.5											"
10	15951713	2.8		47926793	8.0											"

the fundamental and third overtone modes. After vacuum baking at 175°C for three hours (chamber pressure 2 x 10^{-7} Torr), the parameters of the resonators were remeasured.* Table 3 indicates the changes in frequency and resistance due to vacuum baking and/or alloying of the plating.

Units of group 18 were base plated with aluminum and exposed to air. The units were then returned to the vacuum chamber, which was then evacuated to about 2 x 10^{-7} Torr. After the specimens were heated at 300°C, the final plate of Al was evaporated.

None of the units which were mounted in HC-27/U holders during this Quarter "twinned" during sealing. All of the units were fabricated of swept, natural quartz blanks. One unit of group 16 was found to be twinned before sealing, however.

2. Frequency Measurements

a. Long Term Aging Studies

Long term aging studies have been continued for approximately 56 units fabricated about 6-9 months ago. These units have been stored at 85°C in ovens having a total capacity of 36 units each. The frequency of each unit has been measured on the fundamental, third and fifth overtones at least twice a month during the elapsed time since storage.

Graphs of typical behavior patterns are shown in Figures 1-6. The order in which measurements have been made at the various modes seems to be of no significance. For example, a unit may be alternately measured on the third and fifth modes with excellent reproducibility.

b. Effects of Exposure to Neutron Pulse

On 10 September 1962 selected units were removed from the 100 unit oven for exposure to pulsed irradiation; about 30 specimens were

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*The plating was no longer in distinct layers. Instead the gold had disappeared and the color was that of aluminum.

TABLE 3

Frequency and Resistance Changes of Resonators Base Plated with Gold and Over Plated with Aluminum which Occurred during Vacuum Baking for 3 Hours at 175°C.

Unit	R_{s1} (Ω)	ΔR_{s1} Fund (Ω)	R_{s3} (Ω)	ΔR_{s3} Third Ov. (Ω)	ΔF_1 Fund (~)	ΔF_3 Third Ov. (~)
17-1	13.3	N.C.	19.0	-1.0	+39	-6
17-2*	- - -	+2.0	- - -	-3.0	-2622	-8422
17-4	14.7	+1.5	21.0	+0.5	+16	-756
17-5	14.7	+1.0	20.0	+2.5	+19	-197
17-6	11.4	-1.5	15.5	-4.0	+49	+43
17-7	13.1	-1.0	17.5	-1.0	+367	+899
17-8	13.0	+3.0	20.0	+0.5	+313	+888
17-9	13.0	+0.5	20.5	+1.0	+310	+1010

*Stem Damaged in Tip-Off Procedure

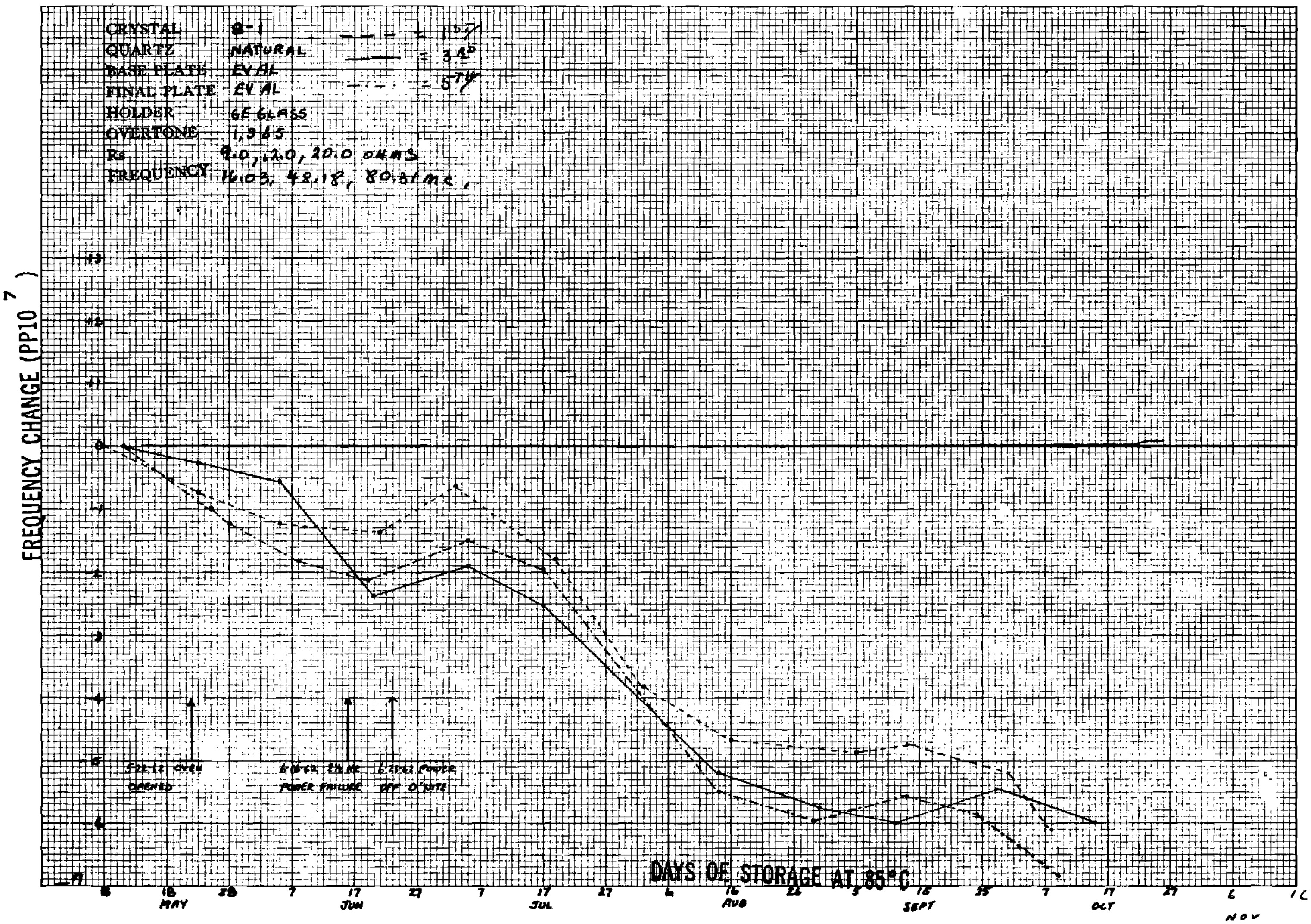

Figure 4. Frequency versus time data for quartz resonator Al + Al 8-1 (natural quartz).

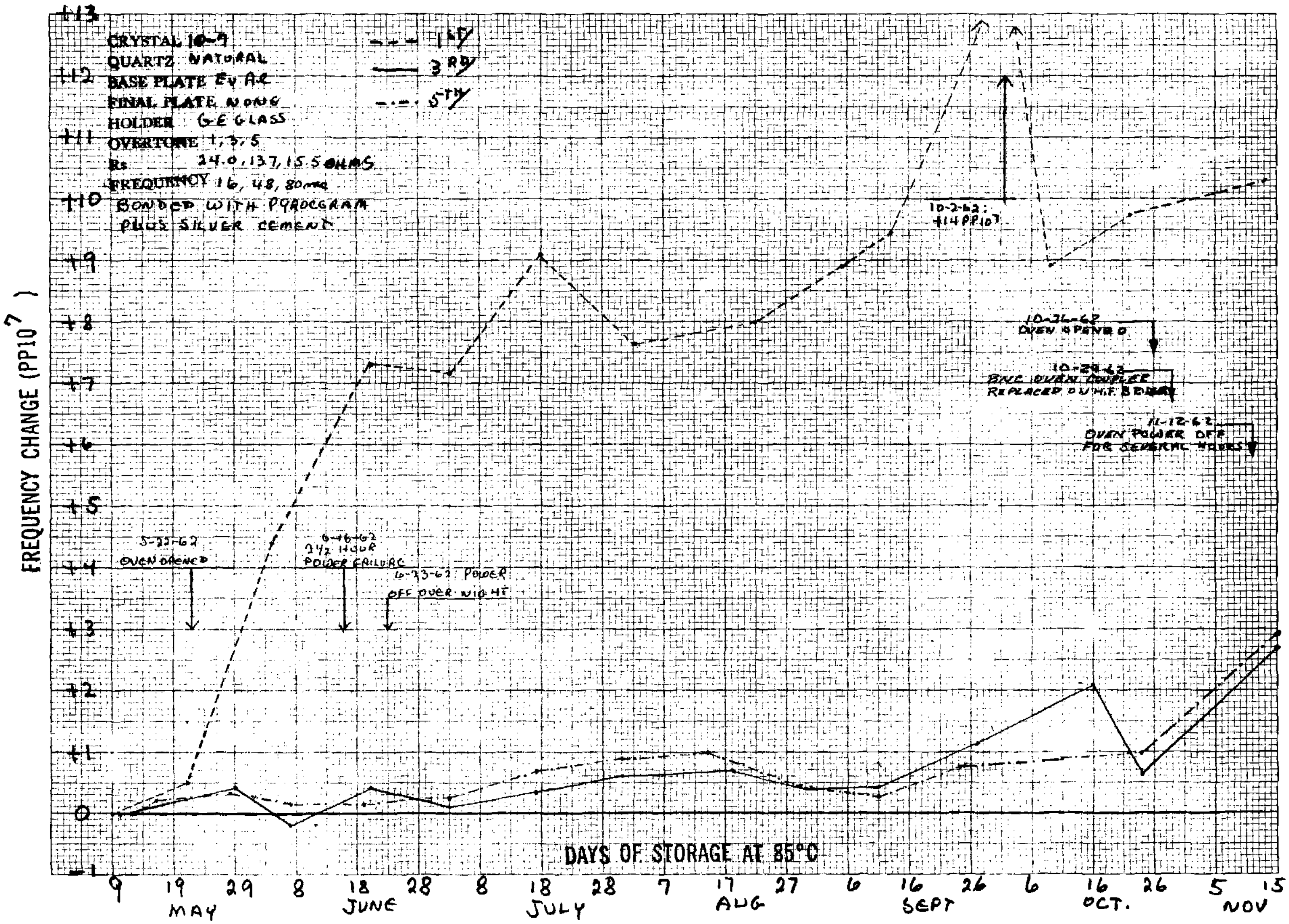

Figure 6. Frequency versus time data for quartz resonator Al 10-7 (natural quartz).

reserved as control specimens and kept in the laboratory at room temperature. The units to be irradiated were taken to the Sandia Pulsed Reactor Facility on 11 September and irradiated on 12 September.

These were arranged about the perimeter of the reactor with the plated faces of the quartz crystals perpendicular to radii of the reactor and at the position nearest possible to the reactor core, i.e., immediately adjacent to the core container. The units were supported in this position in a foamed plastic as suggested by operators of the reactor. After irradiation and a short cool-off period the units were retrieved and repacked for transportation back to Georgia Tech.

The irradiated units were returned to the laboratory on 14 September 1962, and nine of the irradiated units were immediately replaced in the oven. On 17 September the parameters of the nine units were measured; immediately afterwards the oven was opened again to return the balance of the units to their original test positions. The measurements of frequency changes experienced by the various resonators are summarized in Table 4. In general, frequency changes noted were only a few parts in 10^7 and of the same order of magnitude as that of the control units kept at room temperature in the laboratory. There appeared to be a slight negative change indicated for the aluminum plated resonators. The significance of this at this time has not been ascertained.

A test of the residual radioactivity of the resonators on return revealed that the red paint used to mark the containers of each unit for identification was the only part of the resonator giving off radiation at any appreciable level.

TABLE 4

Summary of Frequency Changes of Irradiated Resonators
(Sandia Pulsed Reactor Facility)

Base Plate	Quartz	Holder	Total Number Units	Number Irradiated	Average ΔF (PP 10^7)	Number Stored at Room Temp.	Average ΔF (PP 10^7)	Number Left in Oven	Average ΔF (PP 10^7)
AG	Natural	T-5 1/2	29	16	+0.125	6	-0.66	7	+0.71
AU	Natural	HC-27/U	29	16	-0.60	7	-1.78	6	±0.0
Al	Natural	HC-27/U	22	11	-3.96	3	-1.33	8	-0.25
Al	Cultured	HC-27/U	9	3	-3.0	1*	-3.00	5	-0.4
Al	Swept Cultured	HC-27/U	6	3	-5.83	---	------	3	±0.0
Totals			95	49		17		29	

*Unit taken to reactor but not irradiated.

Figures 7, 9 and 11 illustrate typical frequency stability measurements of these resonators before and after irradiation whereas Figures 8, 10 and 12 illustrate data for resonators removed from the ovens on the same date, stored at room temperature and returned to the oven along with the irradiated units. It will be noted that there is no appreciable difference in the behaviors of the irradiated and non irradiated units. The illustrations include silver plated units mounted in T-5 1/2 bulbs and gold and aluminum plated units mounted in HC-27/U holders. All of the units for which graphs are given were fabricated of natural quartz.

A few units fabricated of cultured and swept cultured quartz were included in the experiment. They showed no discernible differences in behavior that might be ascribed to the differences in the materials of the quartz blanks.

c. Effects of Gamma Irradiation

On 15 October 1962 several units not previously irradiated, three cultured and three swept cultured quartz units mounted in HC-27/U holders, were removed from the 100-unit oven, exposed to gamma-radiation from a cesium-137 source at a dose level of 1.4×10^6 RAD/hr. and then returned to the oven for continued aging measurements.

The results of these experiments are depicted in Figures 13 through 18. The large frequency changes for the cultured (not swept) quartz units required that a new reference frequency be chosen for the graphs. The magnitudes of the changes are noted on the graphs. The frequency changes due to irradiation were obtained from measurements made in the oven prior to and subsequent to the irradiation. Aging had not been established for the fundamental mode previous to exposure although data at the 3rd mode had been obtained.

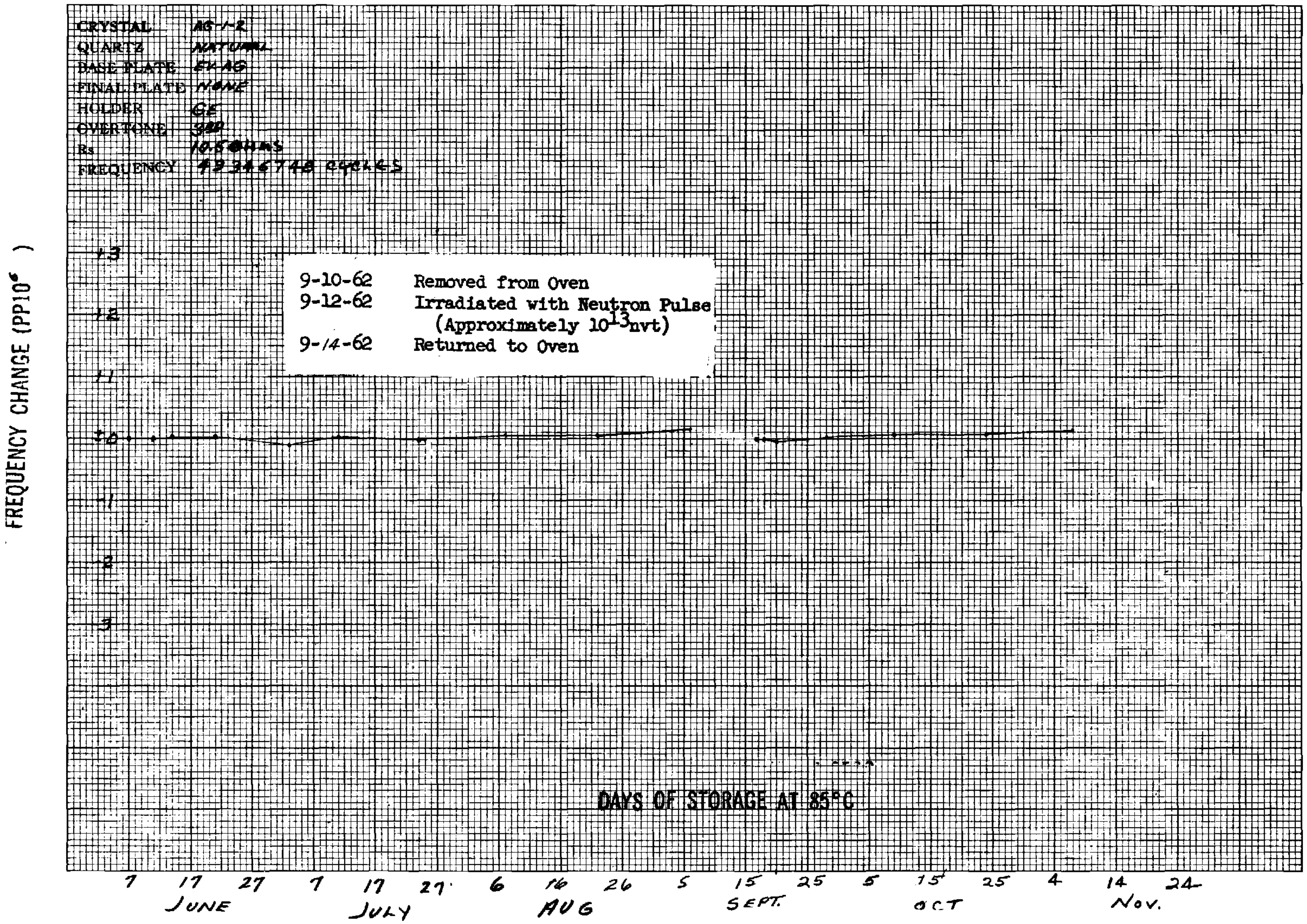

Figure 7. Frequency versus time data for quartz resonator Ag 1-2 (natural quartz), before and after irradiation with a neutron pulse of 10^{13} nvt.

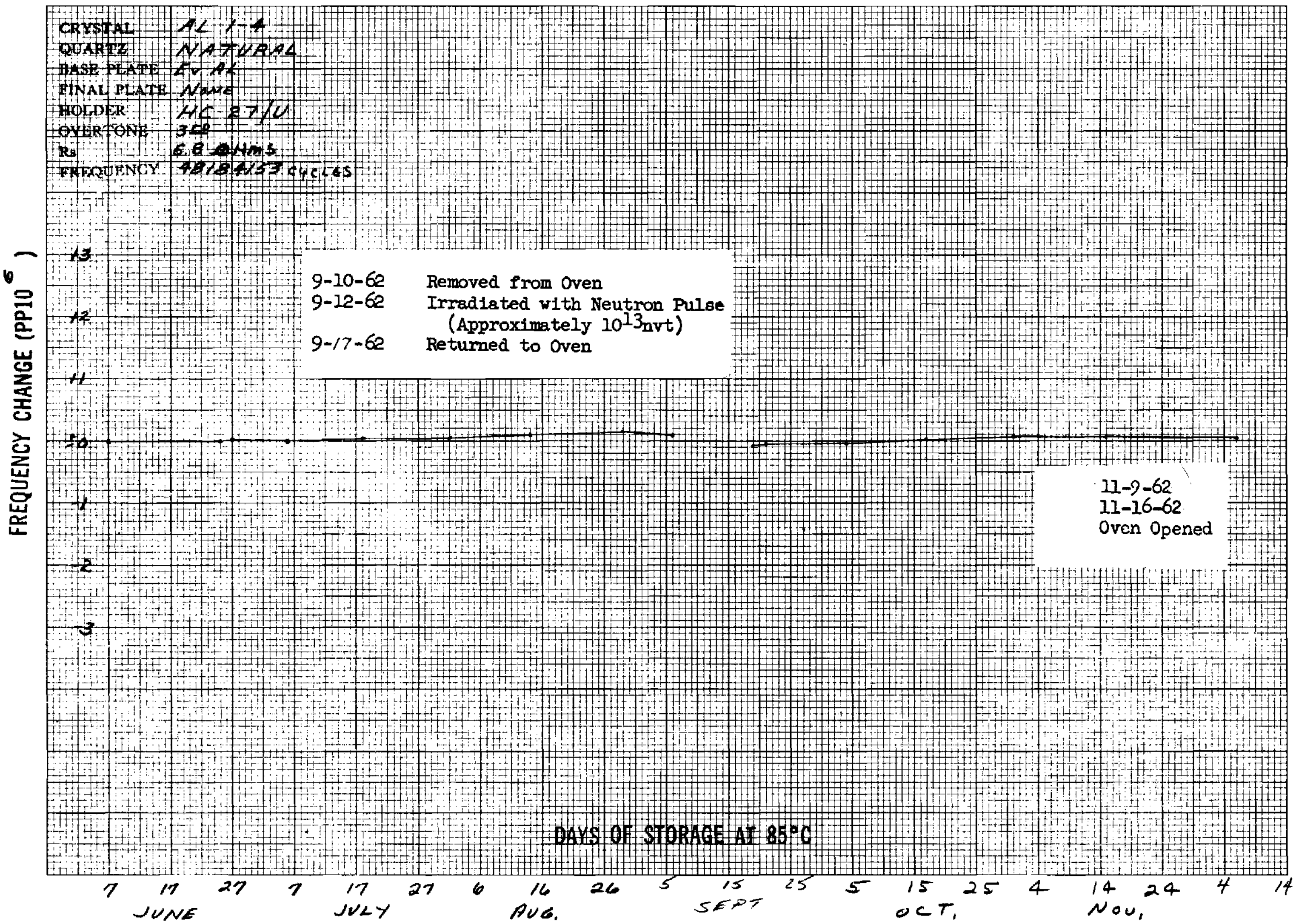

Figure 11. Frequency versus time data for quartz resonator Al 1-4 (natural Quartz), before and after irradiation with a neutron pulse of 10^{13} nvt.

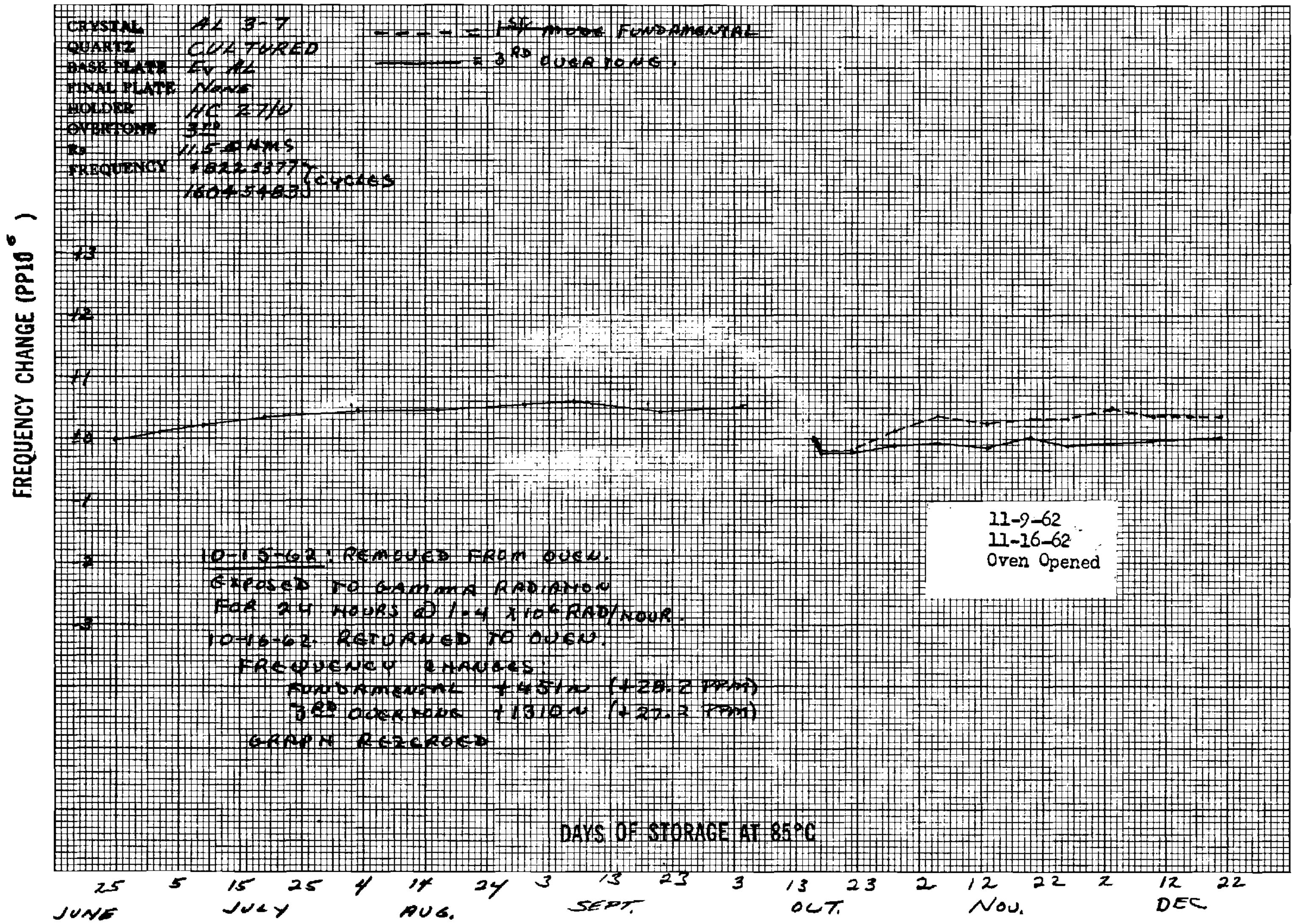

Figure 13. Frequency versus time data for quartz resonator Al 3-7 (cultured) before and after exposure to gamma radiation from Cs-137 source (24 hours).

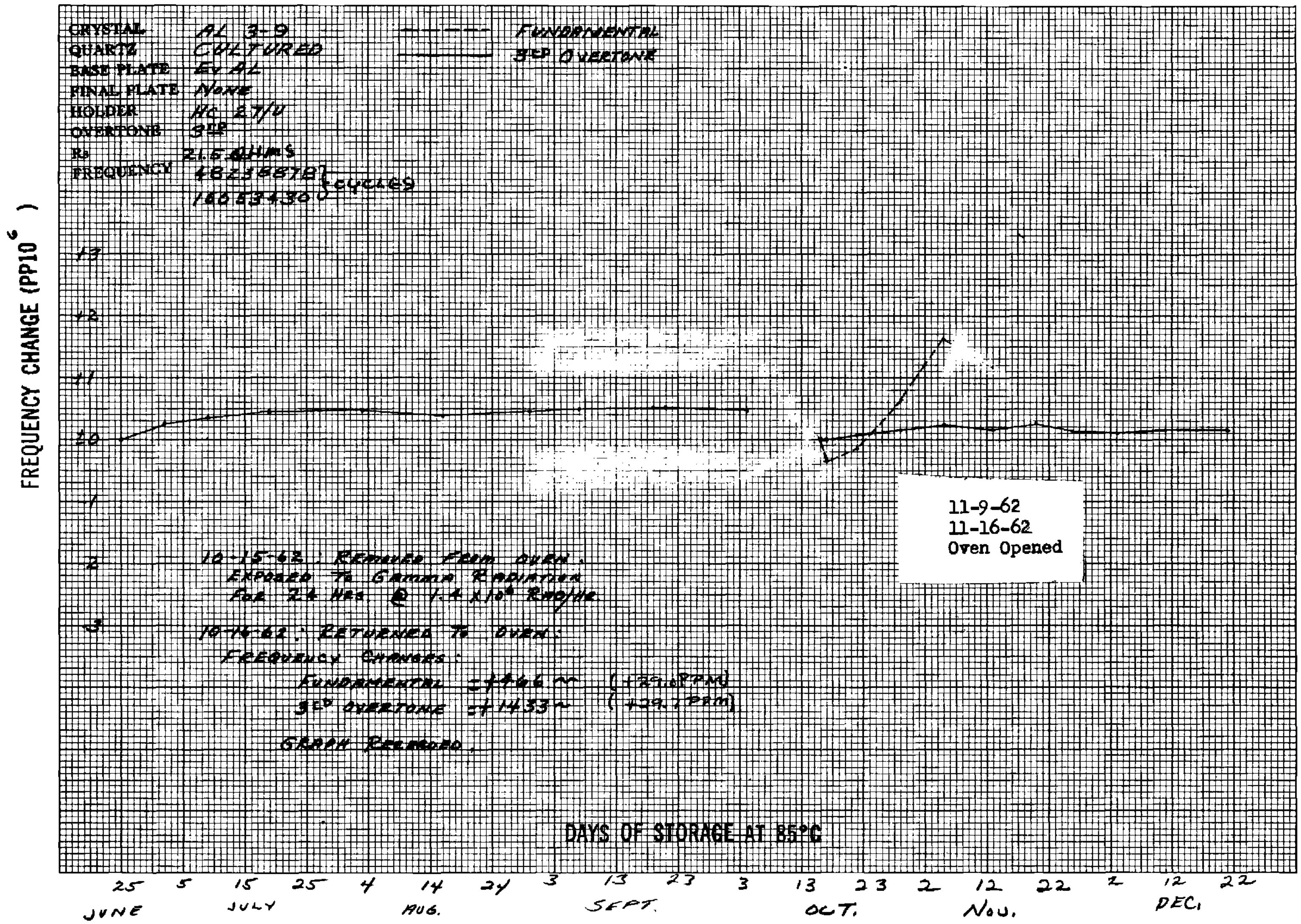

Figure 15. Frequency versus time data for quartz resonator Al 3-9 (cultured), before and after exposure to gamma radiation from Cs-137 source (24 hours).

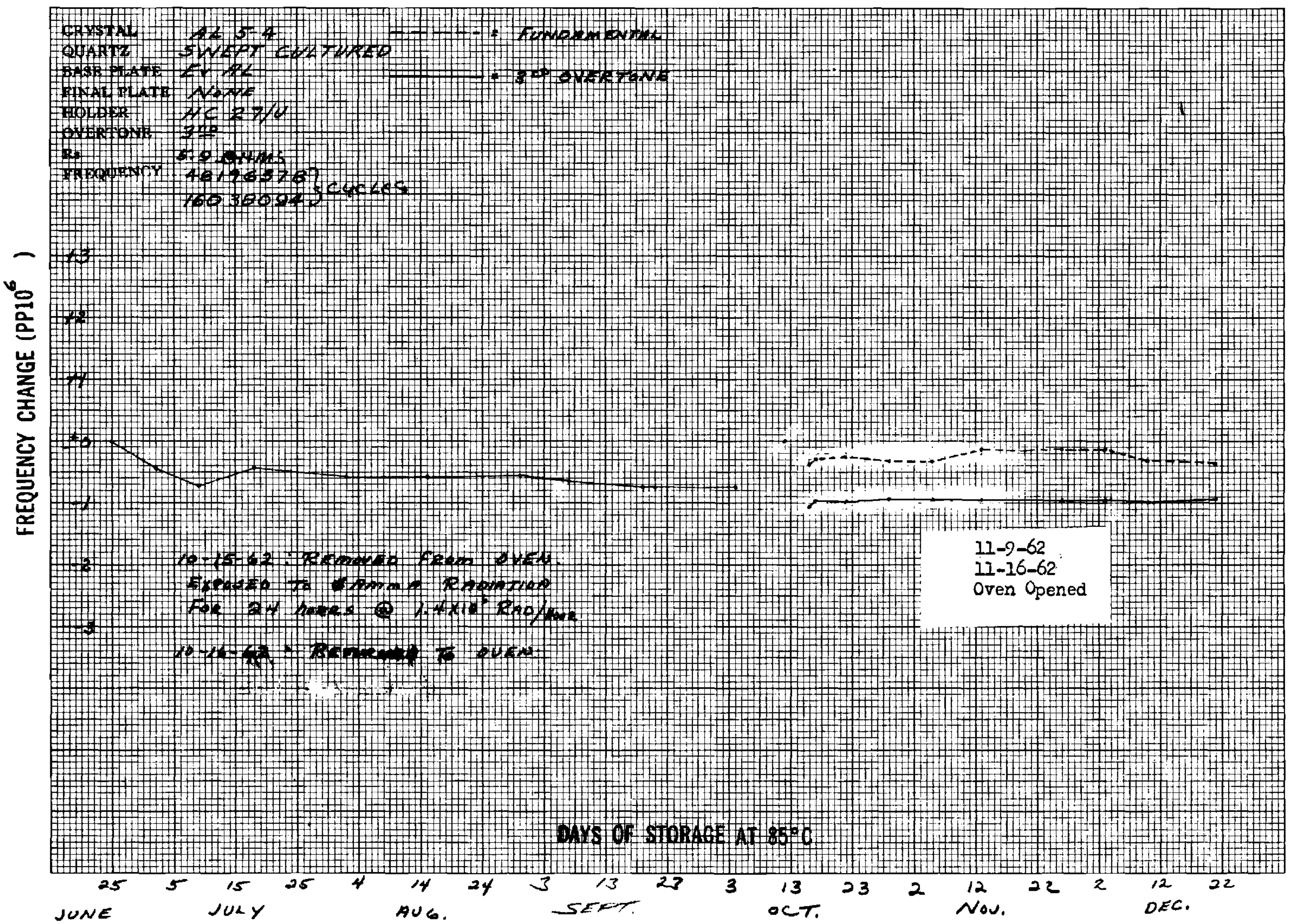

Figure 18. Frequency versus time data for quartz resonator Al 5-4 (swept cultured), before and after exposure to gamma radiation from a Cs-137 source (24 hours).

3. Effects of Continuous Drive

Crystal units being studied for long term aging effects are normally oscillated only during the actual measurement of frequency. The RF voltage applied to the crystal impedance bridge is held at 10 mv for all measurements and the calculated crystal power is about 1 microwatt or less for all modes of operation.

The effects on frequency stability and impedance of resonators subjected to continuous drive at a relatively high drive level (about 2 mw) was studied on units in established positions within the oven using the following procedures.

a. The crystal frequencies at the low drive level were measured using the Rhode and Schwarz Frequency Synthesizer as the RF generator.

b. The drive level on a selected mode was then increased until the voltage across the bridge was of the magnitude* necessary for the crystal to dissipate 2 mw of power with the impedance bridge at balance.

c. During the initial stages of operation, the deviations of the output of the bridge were monitored and the bridge was balanced if the unit tended to drift.

d. The drive was then continued for a period of about 60 hours. The deviations from null were recorded in order to establish that the bridge remained balanced.

e. The drive was returned to the 1 μw level; the frequencies were measured again to determine the magnitude of the changes produced.

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*For most units the RF voltage across the bridge was about 700 mv.

Table 5 gives the data obtained for five continuous drive level experiments. Frequency changes for operation in the fundamental mode were in each case greater than for operation in the third mode. However, considering the experiment in retrospect, the reason for the differences observed may be due to the fact that the frequency of the Rhode and Schwarz synthesizer was doubled before its use at the third overtone; the overtone mode measurement thus had a higher harmonic content than the fundamental measurement.

4. Data Analyses

a. General Behavior

The Figures 1-6 exhibit behavior typical of that already outlined in Quarterly Reports No. 5 and 6. Measurements at the fundamental mode have continued to show a greater number of random excursions than have measurements at the 3rd or 5th mode. Further, the fundamental appears to be more susceptible to stress or strain effects which result from mounting or subsequent temperature cycling. This behavior is indicated clearly in Figure 2 (Al + Au 7-8). The tracking of the 3rd and 5th modes is essentially along the same paths on the graphs.

The contrast in behavior between units having the coating Al + Au and Al + Al is also clearly discernible by examination of Figures 2 and 4. The aging rate of unit Al + Au 7-8 (Figure 2) at the 3rd and 5th modes is < 2 parts in 10^7 in approximately 6 months compared with about 6 parts in 10^7 for Al + Al 8-1 (Figure 4) in 5 months and about 4 parts in 10^7 in 6 months for Al + Al 8-4 (Figure 5).

Unit Al 10-7 bonded with pyroceram displays in Figure 6 a typical positive frequency change of the fundamental, apparently due to stress, whereas the 3rd and 5th modes are remarkably stable over a 6 month period.

The latter shows changes < 1 part in 10^7 except for a random excursion in the last 30 days, apparently due to oven opening, a power failure and a part replacement in the bridge which occurred during this period.

b. Resonators with Bimetal Electrodes

The relatively excellent aging behavior of Al + Au units led to the further examination of this plating combination since it was well known that the metal film pair Al and Au alloy at fairly low temperatures.* Hence Group 17, with the plating order Au + Al, and Group 20, with the plating order Al + Au, were fabricated. The latter were put in HC-27/U glass containers.

As noted in Table 2 and in Section IV. C, 1, alloying did occur for the Al + Au group No. 17. Apparently it occurred during bakeout, as suggested by the apparent disappearance of the gold color and the uniformly high R_s values, in the range 11 to 15 ohms, after bakeout. These high values would naturally result in a lower Q value for these units although the values were not measured in time for inclusion in the table.

Similarly in Table 2, for group 20, R_s values for the first three units are high and the films displayed a purple color that is characteristic of the gold-aluminum intermetallic compound Au_4 Al. Reduction of the preheat temperature, during sealing of the HC-27/U container, from 300° to 150° eliminated this apparent alloying action and R_s values dropped from 9-13 ohms to 1 to 3 ohms (except for a value of 60 ohms for one unit).

The frequencies of the units of group No. 17 (Au + Al) were monitored before and after sealing for detection of the shifts in R_s and frequency that

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*See Final Report Contract No. DA-36-039-SC-42453 (1954) and R. B. Belser "Alloying Behavior of Thin Bimetal Films Simultaneously or Successively Deposited," Journal of Applied Physics 31, 562-570 (1960).

might occur as a result of bakeout. The results are at first puzzling, since the R_s values did not exhibit the large changes expected. However, the first values were measured in air at atmospheric pressure whereas the second values were measured in vacuo. Previous experience has shown that an R_s value of approximately 12 ohms will reduce, on baking and sealing of the specimen in vacuo, to a value of 6-8 ohms, i.e., it will be reduced by 1/2 to 1/3 of its original value. As noted in Table 3, however, the R_s values of these units were reduced or increased by $\pm$ 2 ohms. Hence the normal reduction of -4 to -6 ohms did not occur. In fact, five of seven units experienced increases of +0.5 to +3 ohms to show a net R_s increase of about 6 ohms over the values expected had there been no alloying.

An example of the effects of alloying may be seen in the data for the units of Group No. 20 (Al + Au). For the first three specimen, sealed after preheating to 300°C, the R_s value is 11 ohms; for the last seven elements, sealed at 150°C, the R_s is < 3 ohms. The R_s values in the former cases are > 3 times those of the unalloyed specimens.

For the film order Au + Al it is observed from the R_s values that alloying occurred below the resonator bakeout temperature of 175°C (in fact it has been shown to occur at < 100°C in the references cited); but for the order Al + Au, the oxide formed on the Al on exposure to air before plating with gold apparently acts as an effective barrier to alloying at least up to 150°C, as indicated by the results for Group No. 20. It is obvious that the order Al + Au in lieu of Au + Al is the preferred one; moreover, this is the order which has given relatively low aging rates for resonators measured thus far. No information has yet been obtained about the aging associated with the order Au + Al. However the reduction in Q to values 1/3 to 1/2 the possible value as a result of the high R_s values, appears to indicate the undesirableness of this order of deposition. The use of Au as the outer film has other advantages such as larger frequency adjustment ranges for thin films, less gas adsorption, and less corrosion loading. The latter two factors may contribute significant aging vectors to resonator behavior, as was noted for Al + Al films (Figure 4).

The frequency changes indicated for the fundamental and 3rd overtone modes in Table 3 as a result of the alloying are not easily explained. In general, positive changes in frequency were recorded. In a preliminary examination of records of numbers of other resonators fabricated in previous work, it was found that positive frequency changes were often recorded. In some of these previous experiments, frequencies were monitored through each fabrication step of the resonator after it was mounted in the spring clips. Large negative frequency changes were often encountered when the glass stem holding the resonator was joined to the glass container. In turn, a positive change was recorded on evacuating and sealing the resonator. The larger the negative frequency changes observed in the stem sealing step, the larger the positive frequency shift observed in the final sealing phase normally was. The shifts appeared to be related to an adsorption - desorption phenomenon occurring respectively during the stem sealing and final seal phases. Some corrosion of films such as aluminum might occur and sometimes overall negative changes were observed.

It appeared that positive changes occurred consistently when bimetal layers were employed, and it is possible here that changes in the mechanical properties of the film such as hardness and strain as well as the internal friction of the film contribute to the change. Suffice it to say that the data thus far collected have not been analyzed completely, and further, they may not be sufficient to clarify the mechanisms involved. The suggestion

Frequency shifts experienced by the resonators as a result of irradiation were of very similar magnitude at both the fundamental and third modes for the unswept cultured quartz. For the swept resonators the shifts were small but also different, in the two cases depicted in Figures 16 and 17 the change of the fundamental was positive and that of the third mode was negative. Aging at the fundamental continued to exhibit somewhat more erratic behavior than at the third mode.

5. X-ray Topographs of Strain Patterns in Quartz Resonators

By the X-ray topograph system using the Soller slit described in Quarterly Report No. 6 of this Contract (15 August 1962) topographs were made of a quartz resonator after the respective steps of plating with aluminum, mounting, and bonding. Then the bonding material, spring clips and plating were removed and a final topograph of the cleaned crystal was made. The aluminum film was removed with a chromic acid solution and the bonding cement with a mixture composed of 50-50 (by volume) butyl cellosolve and methylene chloride.

The successive topographs are shown in Figures 19-21. It will be noted in the Figures that no observable stress as denoted by the pattern of straight parallel lines in the topograph was developed on the application of the metal plating, but that mounting in the spring clips resulted in distortion of the straight lines into a pattern resembling contour lines on a map or a polarized light pattern in a stressed plastic. This distortion indicates stress. The degree of strain in the crystal is related to the curvature and spacing of the lines. The principal stress occurred upon mounting the crystal blank in spring clips. The subsequent steps of bonding and bond curing appeared to increase the strain in the quartz a relatively small amount more.*

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*A precise method of interpreting the topographs quantitatively has not yet been worked out.

On removal of the bond, mounting clips, and plating, the resonator resumed an unstressed condition similar to that observed in Figure 19A.

It is apparent that the spring clip mounting method alone establishes a significant strain in the quartz and that a mounting method exhibiting less stress could be devised. This in turn would probably allow better long term resonator stabilities for units in the frequency ranges being studied.

V. CONCLUSIONS

Resonators exposed to a 10^{13} nvt burst of fast neutron radiation from the Sandia Pulsed Reactor Facility showed little or no frequency shifts as a result of the exposure. Subsequent stability of the resonators appeared to be unaffected.

Unswept and swept cultured quartz resonators exposed to high intensity gamma radiation (1.4×10^6 Rad/hr.) from a Cs-137 source for about 24 hours differed greatly in frequency shifts observed. Whereas the resonators fabricated from unswept cultured quartz underwent changes of about +30 ppm during exposure, those fabricated from swept cultured blanks changed < 1 ppm. Stability, subsequent to exposure, was slightly better for the swept elements; however, stability in both cases appeared to be good; many units exhibited shifts of < 0.2 ppm in 30 days. Frequency stability at the fundamental was more erratic than at the 3rd mode.

Resonators fabricated by preferred methods using only a base plating of gold, silver or aluminum have continued to exhibit small aging vectors of $< \pm 3$ parts in 10^8 per month. Addition of an Al overcoat to an undercoat of Al has normally increased this vector to about a minus 1 part in 10^7 per month. An Au overcoat added to the Al undercoat, on the other hand, has resulted in an aging vector little different from the resonator coated with the base coat only, provided the resonator was mounted in a GE T-5 1/2 bulb. When the same combination was used in HC-27/U containers the sealing heat alloyed the two films and increased R_s values by a factor > 3; a reduction of vacuum preheat employed during sealing of the HC-27/U from 300°C to 150°C prevented the alloying.

Effects of strain due to mounting and temperature cycling during entry of ovens or power failure have continued to obscure the true aging of some units. Positive aging vectors of large magnitude are associated with relief of such strains and these appear to affect the fundamental mode more than the overtone modes.

Effects on resonators of continuous drive at a 2 milliwatt level for approximately 60 hours were inconclusive since changes observed in frequency and impedance were very small (see Table 5) except in the case of Al 4-8 (Figure 1), a resonator of erratic aging history.

The method of X-ray topography exhibited that the stress applied to a resonator during the steps plating, mounting in spring clips, bonding, and bond curing occurred principally on mounting in the spring clips. Removal of the clips, bonding, and plating resulted in a topograph resembling that of the original unplated blank.

VI. PROGRAM FOR THE NEXT INTERVAL

Frequency and other measurements of resonators prepared for long term aging studies and the effects of neutron and gamma radiation will be continued. The frequencies of approximately 50 resonators, prepared for examination of the variations in aging due to the type of quartz used for the blank, will be followed. The effects of overcoating to adjust to final frequency, of bonding, and of continuous drive on the long term stability of the resonators will be measured. Exploratory studies of mounting stresses will be continued by the method of X-ray topography.

VII. PERSONNEL

The persons employed and the approximate hours worked upon the project by each are listed below.

		Hours
R. B. Belser	Project Director	175
W. H. Hicklin	Assistant Research Engineer	490
N. K. Hearn	Assistant Research Physicist	82
J. O. Darnell	Research Assistant	294
C. M. Shirley	Technician	310
T. L. Spradling	Graduate Research Assistant	248
J. C. Shaw	Graduate Research Assistant	219

Respectfully submitted,

Richard B. Belser
Project Director

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Hewlett-Packard Co. 1501 Page Mill Road Palo Alto, California ATTN: Mr. Donald Hammond	1
Keystone Electronics Co. 922 McCarter Highway Newark 4, New Jersey ATTN: Mr. James M. Ronan	1
Director, Fort Monmouth Office USA Comm. and Elecs. Combat Dev. Agency Fort Monmouth, New Jersey	1
Clevite Corporation 540 East 105th Street Cleveland 8, Ohio ATTN: Dr. D. Hale	1

This contract is supervised by the Solid State and Frequency Control Division, Electronic Components Department, USAELRDL, Fort Monmouth, New Jersey. For further technical information, contact the Project Engineer, Mr. P. E. Mulvihill, Telephone 535-2475 (New Jersey Area Code 201).

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LIST OF TABLES

II. ABSTRACT

Over three hundred AT-cut quartz resonators of 16 Mc fundamental frequency have been meticulously fabricated, stored at 85°C and measured for frequency stability in the fundamental, third and fifth modes over periods of 3 to 15 months. Controlled variables introduced were types of quartz, plating metal, bonding cement, and mounting envelope. Accuracy of measurements was a few parts in 10^9.

Observations made previously with regard to aging being greater and more erratic at the fundamental than at the overtone modes were confirmed. The better units, coated with single layer electrodes of aluminum or gold changed frequency < 2 parts in 10^8 per month and those coated with bimetal layers of Al + Au changed only slightly more. Resonators plated with Al + Al exhibited changes several times greater. Bilayer electrodes of all types, in general, induced greater frequency changes than single layer electrodes and greater susceptibility to frequency shifts due to inadvertent temperature cycling (oven failure and oven opening).

DuPont No. 5504 bonding cement was found satisfactory for use in the T-5 1/2 envelope but Pyroceram 95 plus silver powder cement was found necessary for the HC-27/U container. Stabilities of resonators in the HC-27/U container approached those found in the T-5 1/2.

Variations introduced by the type of quartz, natural or cultured, swept or unswept, did not appear to be significant in the aging of the units examined confirming that surface and fabrication parameters are the predominant factors in the aging of units of fundamental frequencies of 16 Mc when operated at the fundamental or at an overtone mode. On the other hand, resonators of various types of quartz, exposed to massive doses of gamma radiation (34×10^6 Rads) from a Cs-137 source, differed greatly in frequency shifts observed, i.e., < 1 ppm for swept cultured quartz compared to +30 ppm for the unswept type, whereas resonators of natural quartz gave variable results. Resonator Q values varied both with the type of quartz and with the metal of the plating. In general gold plated units exhibited higher Q than aluminum plated units and the Q of swept cultured quartz was as good or better than that of natural quartz but that of the unswept cultured quartz was poorer than either.

Aging, subsequent to exposure, was slightly better for the swept resonators than for the unswept, but both were good and a number exhibited shifts of < 2 parts in 10^7 in 30 days. The observation that swept synthetic quartz is gamma radiation insensitive appears important to current communication problems and is of interest in basic studies of quartz.

Resonators exposed to pulsed neutron radiation from the "Godiva" Pulsed Reactor Facility (10^{13}nvt) exhibited no greater frequency changes ($\pm$ a few parts in 10^7) or subsequent aging than control units transported to the site and returned without irradiation.

Methods of X-ray diffraction topography have been developed for the examination of strains, twinning and other defects in quartz plates. One method based on the distortion of the X-ray source image has exhibited that stress applied to a resonator during the fabrication steps, plating, mounting, mounting in spring clips, bonding, and bond curing, occurred principally on mounting in the spring clips. Removal of the clips, bonding, and plating resulted in a topograph resembling that of the original unplated blank. The source image distortion and Lang X-ray diffraction techniques have provided methods of high discrimination for application to quality control of resonator blanks and to research on the analyses of the effects of strains, twinning or other defects on the stability of quartz resonators.

IV. FACTUAL DATA

A. INTRODUCTION

The objectives of this research as outlined in Section I, Purpose, required the fabrication of approximately 350 quartz resonators, storage of the units at a constant temperature of 85°C, and measurement of the frequency of the units to an accuracy of a few parts in 10^9. Measurements were required at the fundamental frequency and at the third and fifth overtones.

The measurement accuracy envisioned, the relatively large number of measurements to be made, and the high frequencies (up to 100 Mc) required the development of a new measuring technique and considerable modification of equipment. This period of adjustment interrupted the measurements somewhat during the first 10 months of the work but achieved the desired objectives in measurement accuracy and speed. This attainment in turn allowed completion of the other objectives of the project.

At the beginning of the second year, an additional assignment on the measurement of the effects of pulsed radiation on the aging of resonators was undertaken. This was completed; and some additional information was obtained on cumulative effects of exposure to gamma radiation on the aging of quartz resonators.

X-ray diffraction methods employing the techniques of X-ray topography and source image distortion were introduced for the study of strains, twinning and other defects in quartz resonator blanks. These techniques have provided new tools for the study of strains and twinning that result from mounting procedures.

B. APPARATUS

1. Vacuum Equipment

The vacuum equipment consisted principally of two systems including the usual mechanical forepumps and oil-diffusion pumped final stages. With the aid of liquid nitrogen cold-traps and titanium-evaporation gettering, pressures in the range of 10^{-7} were readily obtainable.

a. Base Plating Apparatus

For the base plating of quartz resonators the apparatus in Figure 1 was employed. The horizontal arms of the vacuum chamber include filament and baffle arrangements for pumping by the evaporation of titanium. In the upper arm is a small copper tank of liquid nitrogen for cryogenic pumping, an evaporation filament, and a substrate heater assembly. The lower arm contains a second evaporation filament and heater assembly.

The crystal mask is held horizontally in the center of the chamber between the evaporation filaments and substrate heaters. Pressures of 10^{-7} Torr are attainable by the arrangement exhibited. The substrate temperature is maintained at a desired level by automatic control. The temperature monitor is a thermocouple positioned near the substrate mask. Prolonged degassing at elevated temperatures is thus feasible without continuous surveillance. Viton* O-rings are used for sealing the chamber to the three headers and the base plate. Electrical and thermocouple circuits enter the chamber through sealed packing glands in the headers or the demountable throat of the base plate. The pressure gauge (Figure 1) is attached to the header of one arm of the chamber.

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*Viton is the trade name for a linear copolymer of vinylidene fluoride and hexafluoropropylene and has a lower vapor pressure than neoprene.

(3) After the inlet of argon or air remove the holder, thus sealed at the base, from the chamber.

(4) Remove the container from the chamber and plug the small hole in the envelope with vacuum wax (Apiezon or de Khotinsky).

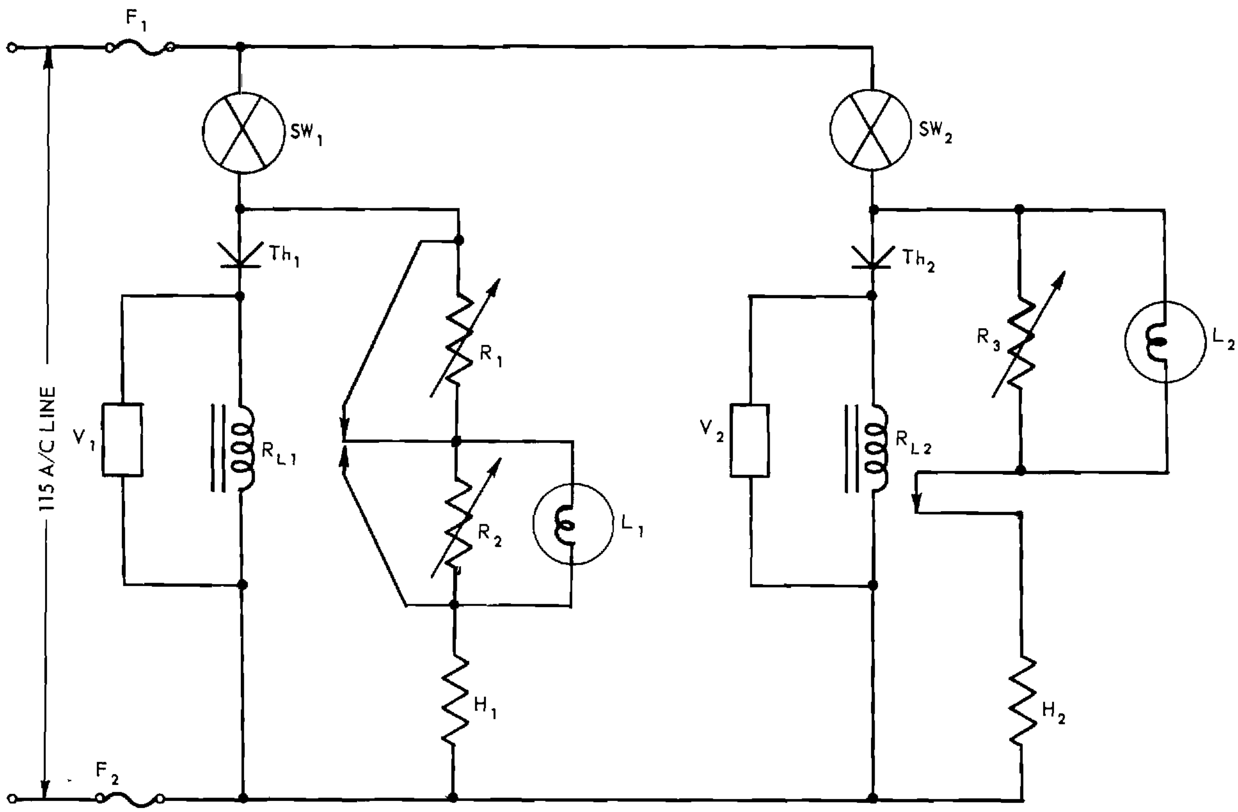
(5) Make a vacuum oil leak test of the sealed container in the manner described in the Final Reports of Contracts Nos. DA-36-039-SC-74946, p. 10, July 31, 1958, and DA-36-039-SC-78910, pp. 77-85, February 28, 1957.

3. Ovens

Three 85°C ovens were in operation during the project. Two of the ovens had 36 positions each and one had a capacity of 200 positions. The capacity of the latter after a short trial period was reduced to 100 positions in order to improve its temperature stability.

Nested construction was employed for all ovens. A top view of the interior of one of the small ovens, typical of all, is shown in Figure 5. Sections 2 and 4 (numbered from the outer section) were fitted with heating elements on the outer, vertical walls. The wall temperatures were controlled by means of a fixed-contact mercury thermostats. Section 2 was maintained at 75°C and Section 4 at 85°C. The control circuit associated with the thermostats is shown in Figure 6. The outer oven had an on-off control. The inner oven was driven with a modified proportional control system.

Temperature stability of ±0.005°C was obtained when the ambient room temperature remained in the range 24 to 26°C. However, on excessively cold or hot days when the building air conditioning system failed to take care of extreme conditions, temperature excursions of about ±0.01°C were experienced. (See Figures 13-15).



LEGEND

F_1, F_2 FUSES
H_1 HEATER COIL 85°C OVEN
H_2 HEATER COIL 75°C OVEN
L_1 NEON INDICATOR LAMP 85°C OVEN
L_2 NEON INDICATOR LAMP 75°C OVEN
R_1 VARIABLE RESISTOR 85°C OVEN
R_2 VARIABLE RESISTOR 85°C OVEN
R_3 VARIABLE RESISTOR 75°C OVEN

LEGEND

R_{L1} RELAY FOR CONTROL 85°C OVEN
R_{L2} RELAY FOR CONTROL 75°C OVEN
SW_1 SWITCH FOR 85°C OVEN
SW_2 SWITCH FOR 75°C OVEN
Th_1 MERCURY THERMOSTAT 85°C OVEN
Th_2 MERCURY THERMOSTAT 75°C OVEN
V_1 VARISTOR 85°C OVEN
V_2 VARISTOR 75°C OVEN

NOTE: Reloy Contocts Show Ovens Heoting

Figure 6. Heater control circuit for the 85°C crystal ovens.

4. Measuring Equipment

a. Introduction

A requirement to measure hundreds of quartz crystal units of 16, 48 and 80 Mc in frequency in a short period of time with an accuracy of a few parts in 10^9 was a stringent specification which had not been met by anyone at the time this research program was undertaken. Two measurement methods were attempted. The second proved successful.

b. AGC-AFC frequency measurement system

Efforts were first made to develop an AGC-AFC frequency measurement system in which automatic controls would diminish the time normally consumed in measuring the frequencies of resonators (5 minutes each) by the bridge method previously used. Work on this technique was continued for about nine months and resulted in the systems exhibited by block diagram in Figures 7 and 8. Details of the progress and development are contained in Quarterly Reports Nos. 1-3 of this project dated respectively (15 May, 15 August and 15 November, 1961). Although it appeared that difficulties arising in the circuits, due principally to uncontrolled phase shifts in the signals, could be eliminated with time and effort, no further time could be expended without undue loss of required data. An alternate measurement system was therefore sought.

c. Passive bridge frequency measuring system

The development of a passive bridge frequency measuring system was next undertaken.

The circuit displayed in Figure 9 is that of the active bridge system used previously with the frequency measurement equipment. This was used successfully for 100 Mc and 80 Mc frequency measurements to parts in 10^7. The transformer T_1 must be a theoretically perfect transformer if the

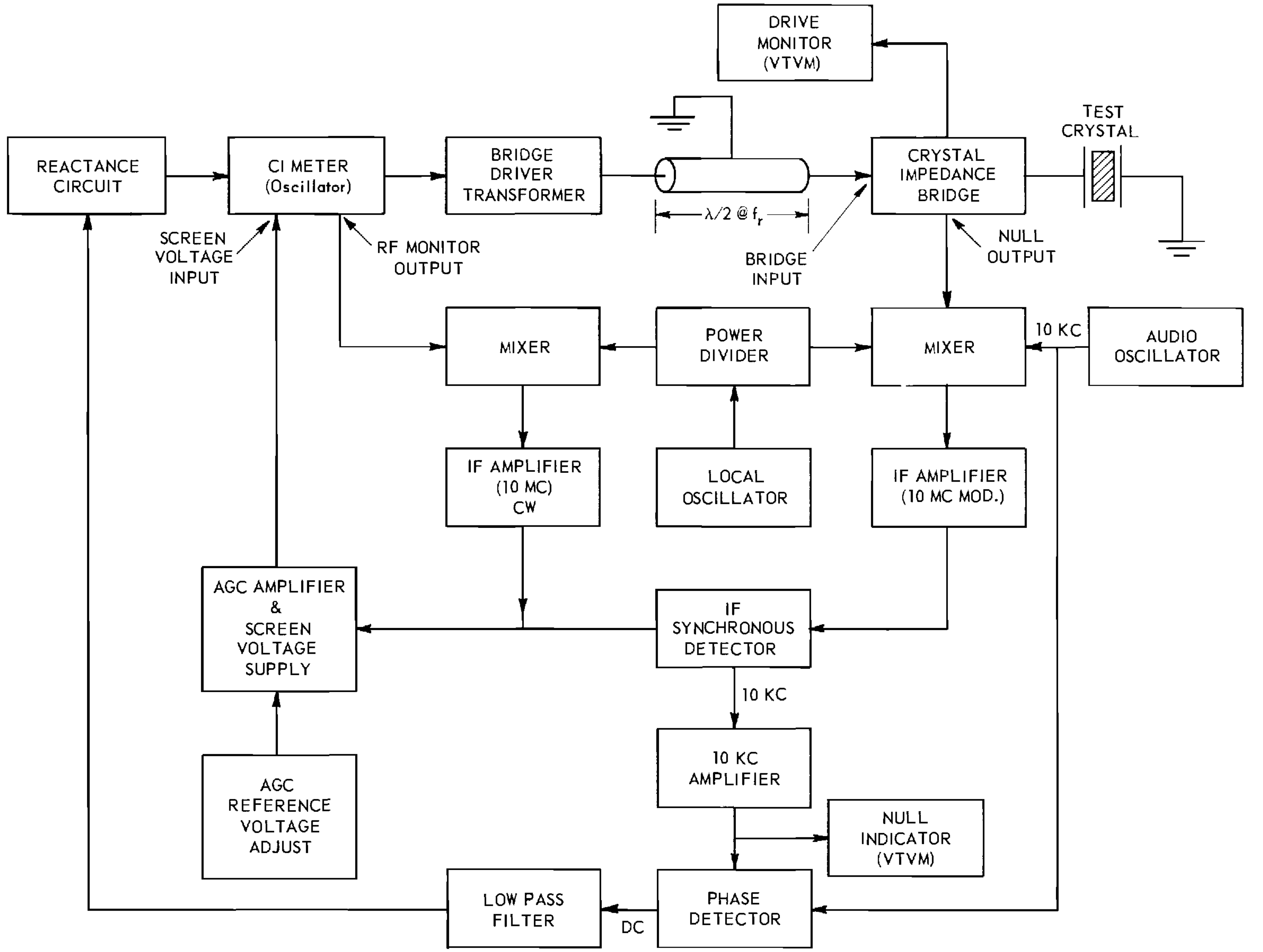


Figure 7. Block diagram of early design of AGC-AFC frequency measuring system.

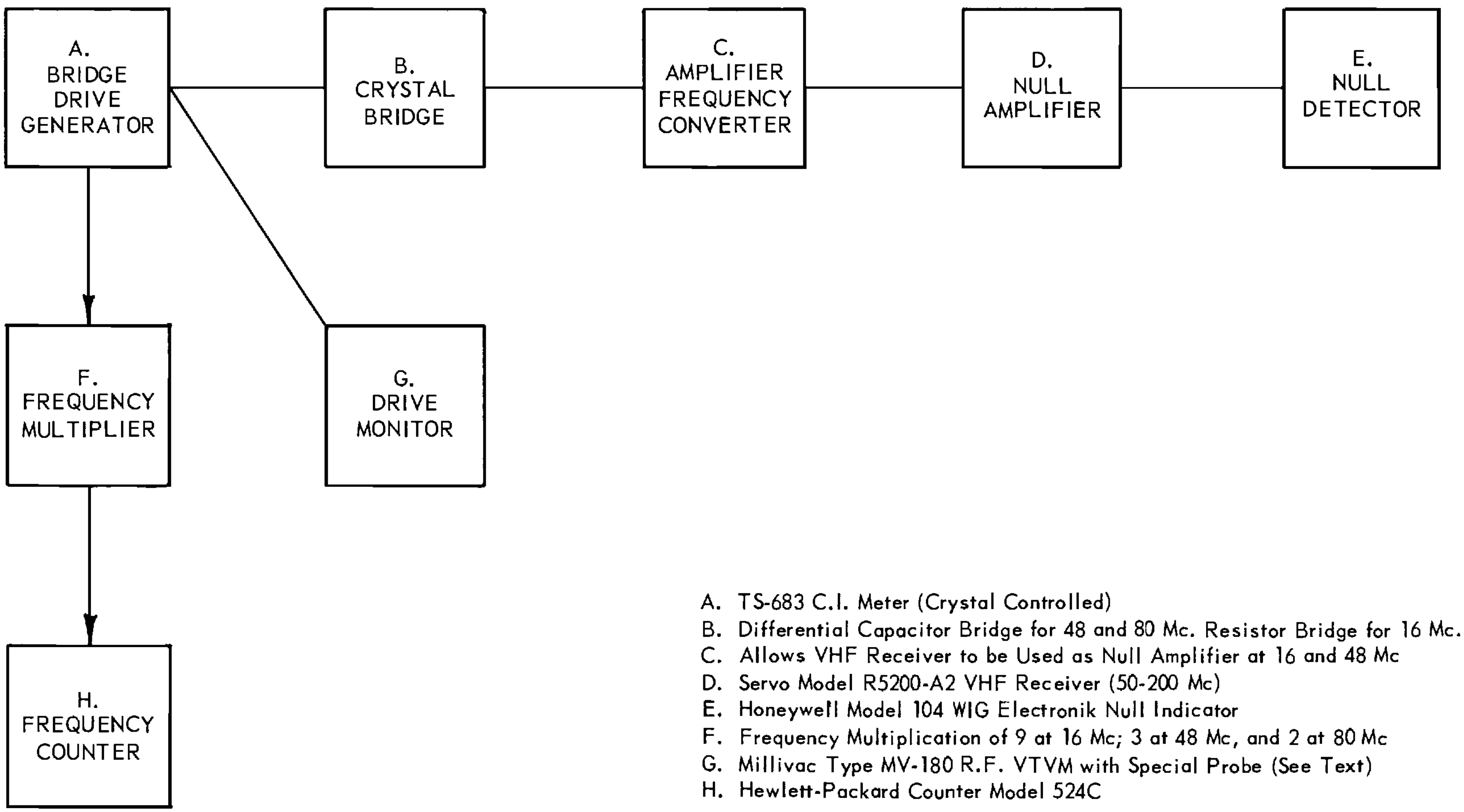


Figure 10. Passive bridge frequency measuring system.

Table 1
Details of Fabrication of Resonators for Regular Aging Studies

Group No.	No. of Units	Fabrication Date	Type Quartz	Base Plate	Final Plate	Mount	Bond	Holder	Final Seal: Bake	Final Seal: Pressure ATM(MMHg)	Remarks
1	10	5-25-61	Natural Unswept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
2	10	5-30-61	Natural Unswept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	Cement cured 1 hour at av of 300°C
3	10	6-5-61	Cultured Unswept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
4	10	6-19-61	Cultured Swept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$3x10^{-7}$	
5	10	6-27-61	Natural Unswept	Al	Au	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
6	6	7-10-61	Natural Unswept	Al	Al	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
7	6	7-14-61	Natural Unswept	Al	Au	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
8	10	8-7-61	Natural Unswept	Al	Al	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
9	9	12-11-61	Natural Unswept	Al	None	HC-27/U	Pyroceram	Tab Clips	10 min-250°C	$2x10^{-4}$	Sealed w/induction heater 5/1 Pyr.
10	10	1-2-62	Natural Unswept	Al	None	GE Glass	Pyroceram	Tab Clips	3 hrs-225°C	$2x10^{-7}$	5/1 Pyr.
11	10	1-15-62	Cultured Swept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-225°C	$2x10^{-7}$	
12a	9	2-27-62	Natural Swept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$3x10^{-7}$	
12b		2-27-62	Cultured Swept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$3x10^{-7}$	
13a	9	3-5-62	Natural Unswept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
13b		3-5-62	Cultured Unswept	Al	None	GE Glass	5504A	.006 Springs	3 hrs-175°C	$2x10^{-7}$	
S-1	9*	9-17-62	Natural Unswept	Al	None	GE Glass	5504A Pyroceram	.006 Springs	3 hrs-175°C	$4x10^{-7}$	Strain studies (misaligned and annealed clips)

*Units of Group S-1 were never placed in ovens for aging studies.

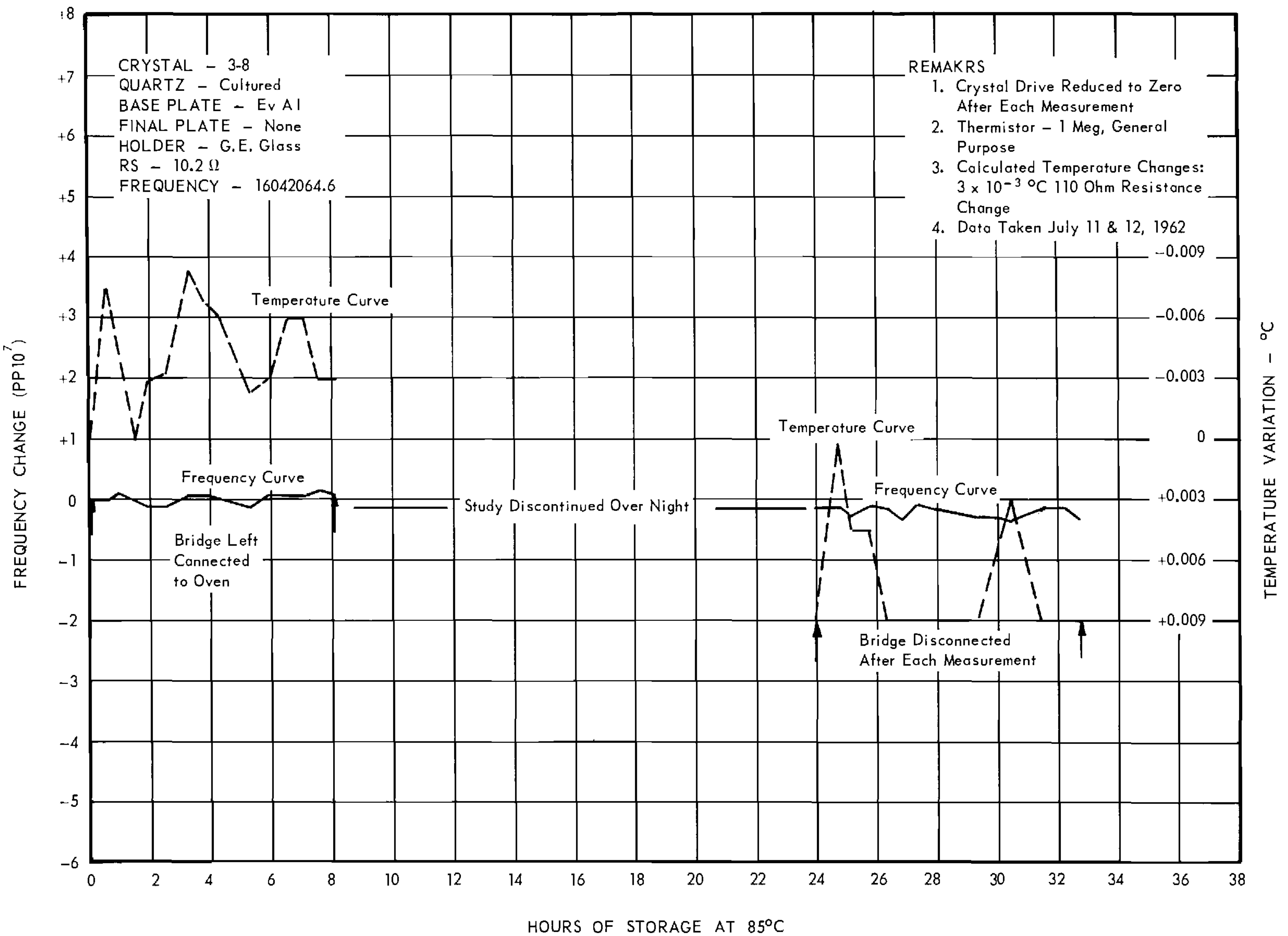


Figure 13. Short-term aging of an aluminum-plated, cultured quartz resonator (Al 3-8) operated at the fundamental frequency.

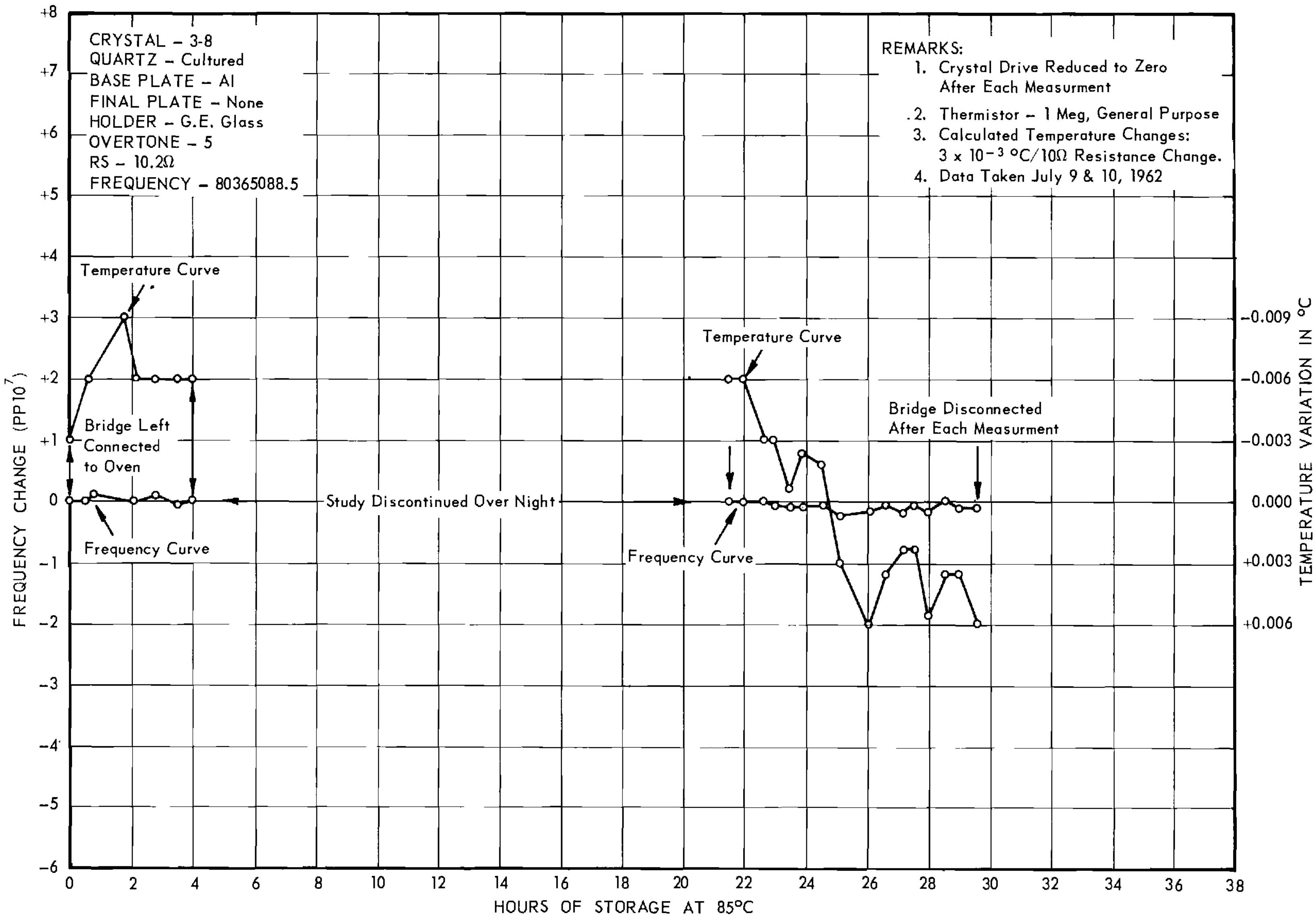


Figure 15. Short-term aging of an aluminum-plated, cultured quartz resonator (Al 3-8) operated at the fifth overtone.

The emphasis on aluminum coated resonators as noted in the table above was the result of operation in overtone modes since gold plated units may be excessively damped at the fifth overtone mode.

Although it had been previously shown that overcoating may degrade stability* somewhat, the amount to be expected, when utilizing refined fabrication and measurement procedures, and methods of minimizing it remained to be explored. Moreover, although employment of metal overcoats different from the base plating is common in industry, the exact behavior of such electrodes has not been well defined. The effects of the types of plating listed above have been examined with frequency measurement discrimination of ±1 part in 10^8, at least an order of magnitude better than previously used here.

A second principal objective of this study was a comparison of the respective aging of a resonator at its fundamental, 3rd and 5th modes and measurements of the resonators were made at each mode where feasible.

(1) Resonators plated with aluminum base plate only

A series of typical frequency measurement versus time data for resonators coated with aluminum base plating only are shown in Figures 16-18. It should be noted here that the principal plotting scale is parts in 10^7 and that a few parts in 10^9 are discernible.

Figure 16 exhibits a moderate difference in the stability of resonator 2-10 (Al only) at the fundamental and third mode. The larger fluctuations which occur appear to be the result of temperature changes and stresses developed when ovens were opened or power failed (six occurrences). In spite of these, stability at the fundamental was maintained within a variation

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* See Final Report of Contract No. DA-36-039-SC-78905 or Paper by the authors in the Proceedings of the 14th Annual Frequency Control Symposium.

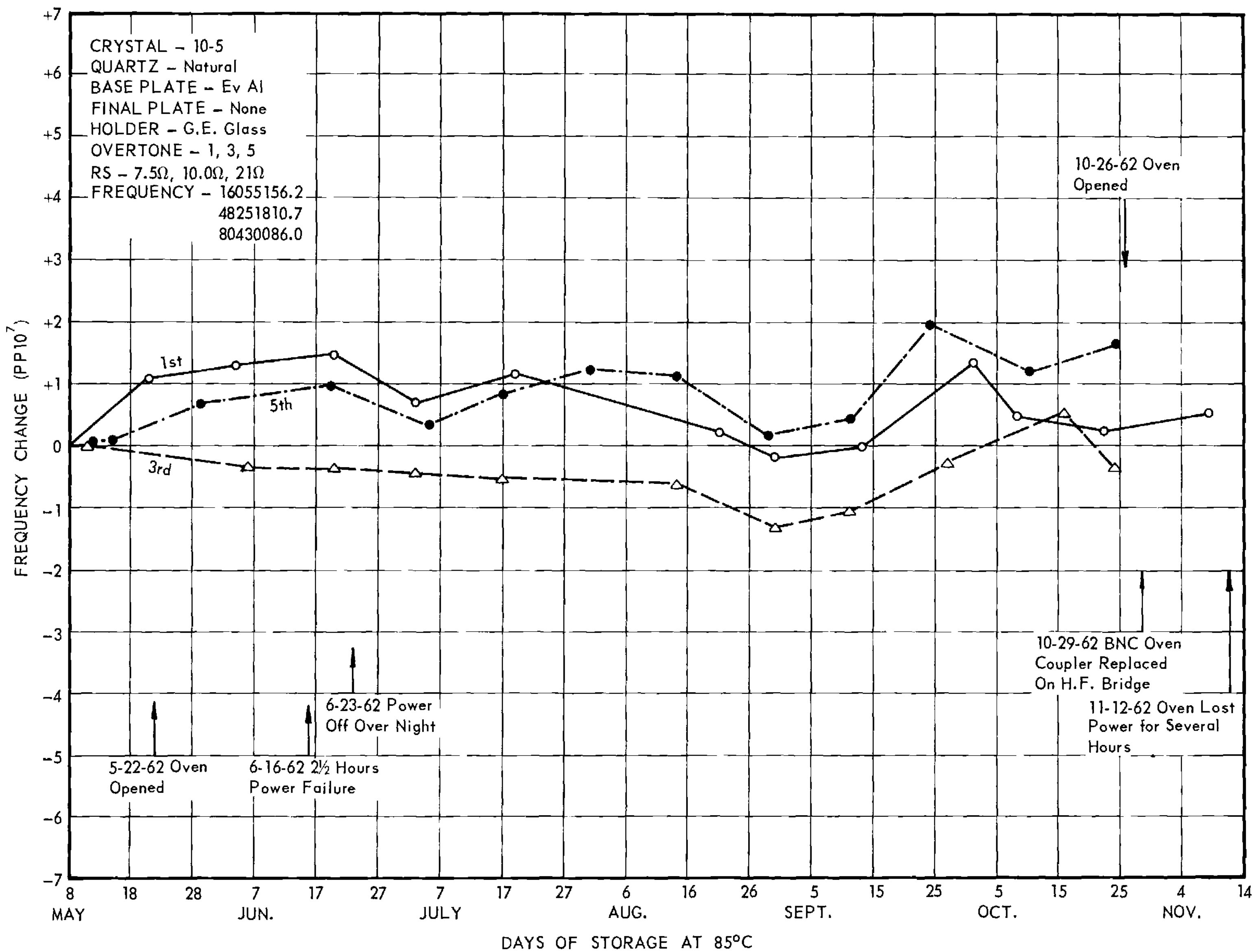

Figure 18. Aging data for natural quartz resonator Al 10-5, bonded with Pyroceram-Ag cement.

$< \pm 1$ part in 10^7 for 9 months. Aging at the 3rd overtone was somewhat less and showed lesser fluctuations with temperature change or thermal shock.

Figure 17 (Al 10-1) exhibits a remarkable case of stability for seven months where data for both of the overtone modes tracked relatively well with that of the fundamental. Aging was inappreciable and stability was maintained to variations of less than ± 5 parts in 10^8 for the fundamental, ± 7 parts in 10^8 for the third overtone mode, and ± 3 parts in 10^8 for the fifth overtone mode.

Figure 18 exhibits the aging pattern of a unit which appears to be moderately sensitive to thermal stress.

(2) Resonators plated with Al + Al

Quartz resonator blanks coated with Al + Al and mounted in the T-5 1/2 envelope exhibited with rare exception downward drifts of a few parts in 10^7 over a six month period. A typical pattern of behavior is that in Figure 19 (Al + Al 8-9). The departure of the data of the fundamental from that of the overtone modes is striking. An effort to reduce this typical drift by applying the overcoating aluminum at a temperature of 300°C did not give greatly improved results except in the one case exhibited in Figure 20 (Al + Al 18-4). The large increase in frequency observed on 22 January for the fundamental mode as a result of oven failure for 72 hours was characteristic of most of these units. This large frequency increase implied the presence of strain as a result of thermal shock. The radiant heating to 300°C after plating may have induced strain in the blanks beyond that encountered by the usual Al + Al resonator. Additional studies of this technique of plating are necessary for its proper evaluation.

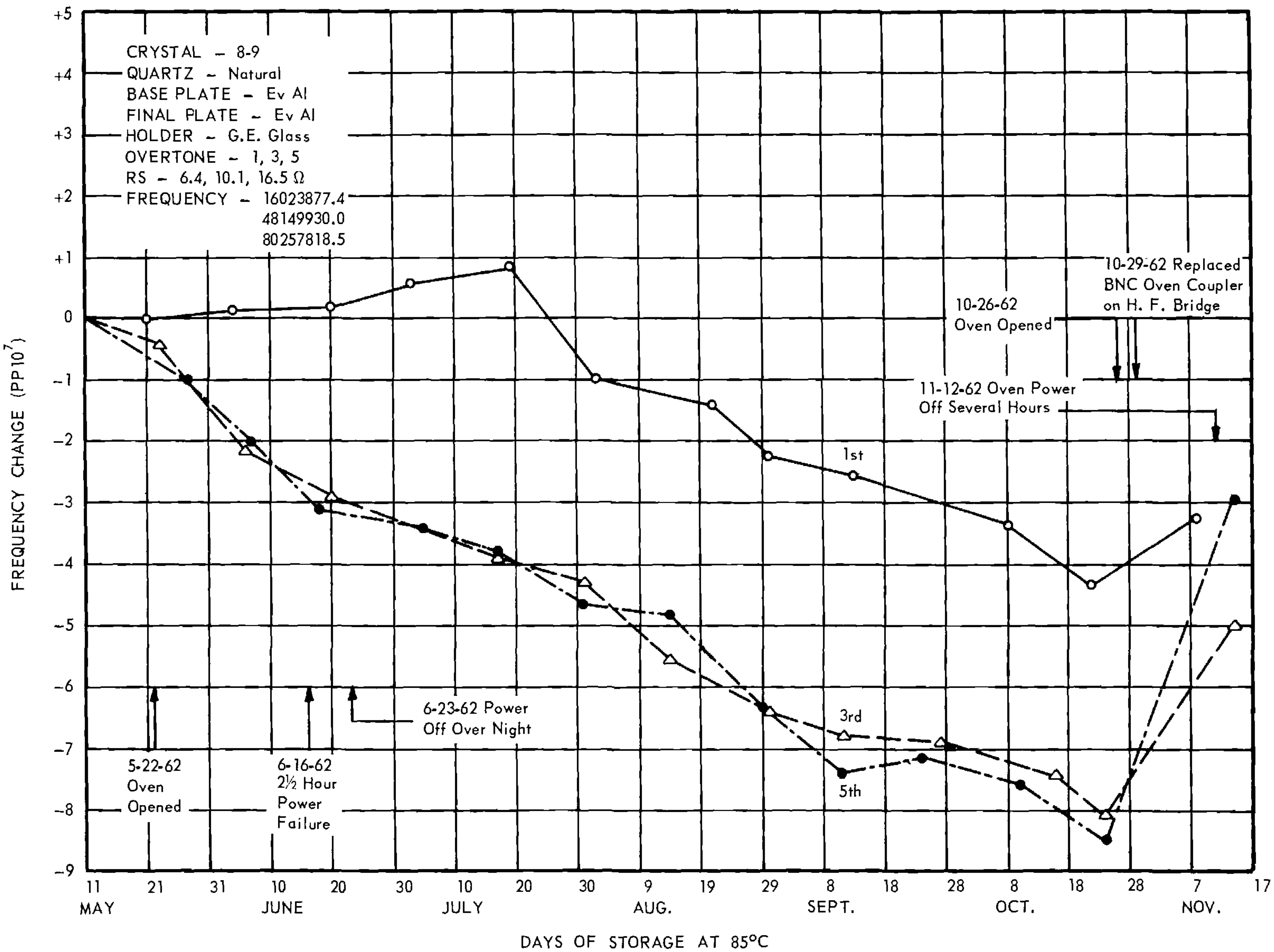

Figure 19. Aging data for natural quartz resonator Al + Al 8-9.

Other resonators (10) plated with Al + Al and mounted in the HC-27/U container exhibited aging rates not greatly different from those in the T-5 1/2 tube. Data for the best unit, Al + Al (19-10) is exhibited in Figure 21. These units were only operated about 10 weeks.

(3) Resonators plated with Al + Au

For plating aluminum base plated resonators to final frequency a metal of greater density than aluminum would be advantageous, provided there were no deleterious effects on the future stabilities of the resonators. Gold and silver have been used at various times for the overcoating material. Although it has been shown in the past* that bi-metal layers as electrode materials may be unstable, they have been used successfully by the resonator industry in limited combinations for some purposes (Au + Ni and Ag + Ni). As a result a restudy of this problem with greater measurement precision has been undertaken.

Three groups of resonators comprising a total of 25 units were fabricated. Two groups Al + Au-5 and Al + Au-7 were mounted in the T-5 1/2 container and one group (Al + Au-20) in the HC-27/U holder. Group Al + Au-5 proved to possess very poor activity, apparently, because the gold overcoat was too thick. No aging data were obtained for specimens of this group. Units of group Al + Au-7 exhibited total frequency shifts of only a few parts in 10^7 over a period of nine months. An example of data for a typical unit is shown in Figure 22.

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* Final Report Contract No. DA-36-039-SC-64613, pp. 46-51, July 1957.

Pyroceram, exhibited relatively poor stability compared with those of Group Au-15. Aging for these units was in the range 3 to 25 parts in 10^7 in 100 days. The resonators exhibiting the greatest frequency changes appeared to have leaks or gas sources in the respective containers.

(5) Resonators coated with Au + Al

It has been shown by one of the authors* that the oxide coating usually formed on aluminum film electrodes on exposure to air and before overcoating to frequency with gold, as discussed in the preceding section, acts as an effective barrier to alloying between the aluminum and gold so long as certain temperature limits are not exceeded. In order to examine the effect of alloying where no oxide barrier existed a series of seven resonators were fabricated with bimetal films in the order Au + Al. Even though these units were mounted in the T-5 1/2 glass container alloying occurred during fabrication and bakeout as evidenced by the high R_s values of the units. Since, as noted in the reference in the footnote below, the Au + Al film pair has been shown to begin alloying at $< 100°C$, it was impossible to fabricate resonators using the standard resonator fabrication techniques developed for this work without the occurrence of alloying. To deviate from the standard procedures sufficiently to prevent alloying would have introduced too many unknown variables to interpret the resultant data.

The resonators had a somewhat higher R_s than normal for this type of resonator but were relatively stable as shown in Figure 26 (Au + Al 17-6).

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* R. B. Belser, "Alloying Behavior of Thin Bimetal Films Simultaneously or Successively Deposited," Journal of Applied Physics 31, 562-570 (1960).

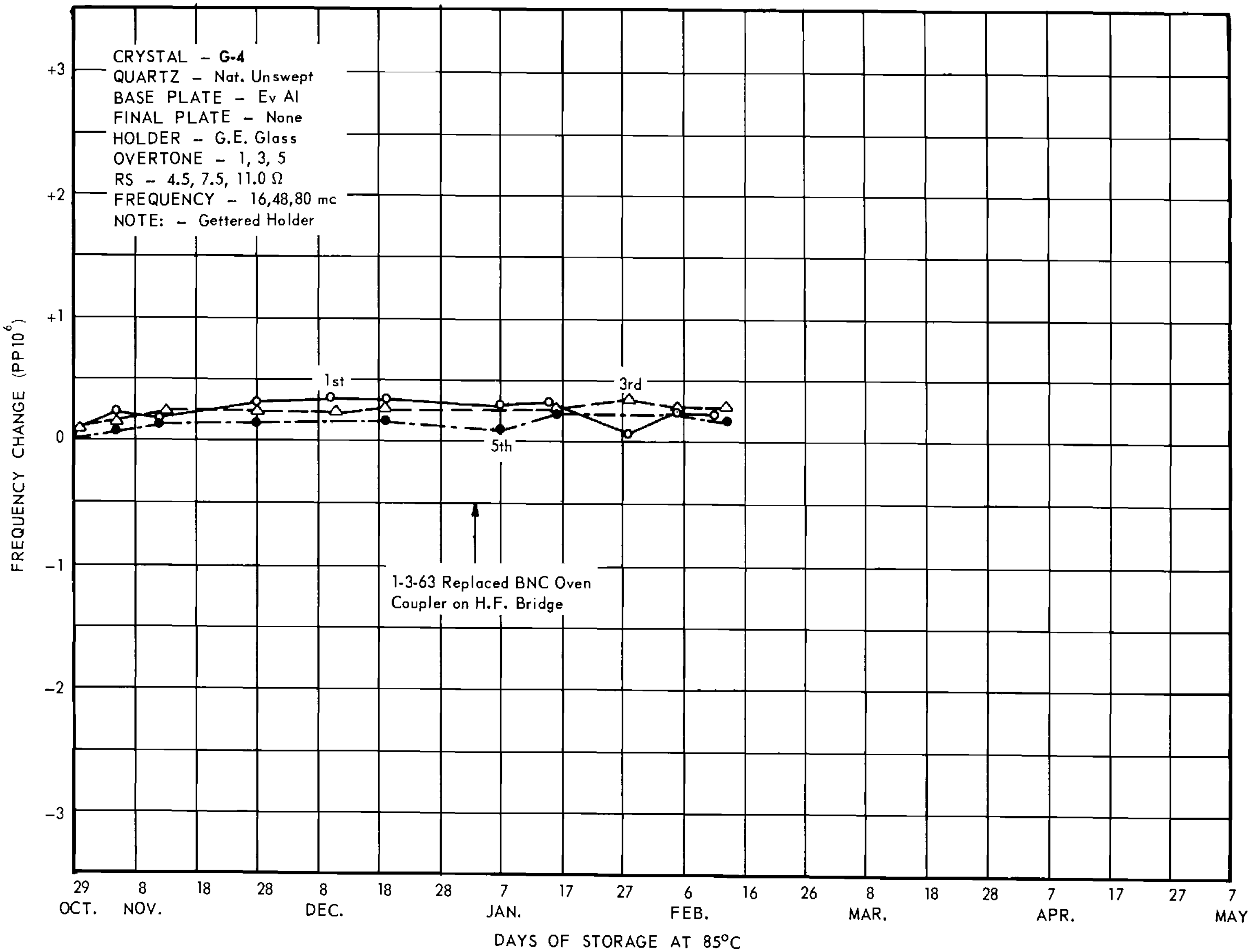

Figure 27. Aging data for natural quartz resonator Al G-4, gettered.

resonators were fabricated and examined. These were made up in the quantities and types of quartz listed below:

natural	107*
swept natural quartz	53
cultured	29
swept cultured	18

Measurements of the electrical parameters, R_s, C_o and Q, and the aging of the units stored at 85°C were made. A close examination of Tables 1 and 2, which list the types of quartz and other parameters of each unit, provides data for comparison and analyses. Specifically, Groups Al-12, Al-13, Au-14 and Au-15, were split between two types of quartz as follows:

Group No.	Type of Quartz
12a(1-5)	Swept Natural
12b(6-10)	Swept Cultured
13a(1-5)	Natural
13b(6-10)	Cultured
14a(1-5)	Natural
14b(6-10)	Swept Natural
15a(1-5)	Cultured
15b(6-10)	Swept Cultured

Examination of the Q values (omitting deviations lower than 65 percent of the normal) for these units, yields the following average data.

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* (Group S-1 consisting of 9 units was never measured)

	Aluminum Plated	Gold Plated
Natural	40,425(13a)	79,975(14a)
Cultured	37,033(13b)	79,720(15a)
Natural Swept	52,725(12a)	83,480(14b)
Cultured Swept	53,500(12b)	134,950(15b)

It is observed that natural and cultured quartz resonators exhibit almost the same dependence of Q on the metal plating, aluminum or gold. On the other hand, the swept natural and swept cultured are of higher Q than the unswept quartz. The difference between aluminum plated and gold plated resonators is quite marked. The gold plated swept cultured quartz gave by far the highest values of Q obtained.

A further analysis of Q values may be made by averaging the values in Table 2 for the units by groups and by subdividing these measurements as to types of quartz and metal plating. This sorting is done in Table 3.

Although variation in a group is considerable, and this variation may be further emphasized by the fact that no values were measurable for some units at the fifth overtone mode, it is quite apparent that the 3rd overtone generally exhibits the higher Q whereas the Q of the 1st and 5th modes are lower and of approximately the same value for about 30 percent of the measurements. There is, however, a tendency for the 5th mode value to be higher than the fundamental value. A part of this latter effect is undoubtedly due to lack of Q values at the 5th mode for units of low Q since these particular units are almost always characterized by high R_s values at the 5th mode. Inclusion of estimated Q values for these units would reduce the quoted Q values at the 5th mode by 10 to 20 percent in a number of cases.

TABLE 3

Summary of Q Measurements of AT-Cut Quartz Resonators
Operated at the Fundamental, Third and Fifth Modes.*

Group Designation	Q_1	Q_2	Q_3	Remarks
		Plating Metal - Al Only		
1-N	63,150	84,290	61,370	
2-N	45,044	75,811	59,825	
9-N	30,193	80,633	83,850	{ HC-27/U, tab clips Pyroceram
10-N	57,912	112,433	88,755	Pyroceram, tab clips
13a-N	40,425	73,800	68,325	
G-N	64,600	96,475	71,612	
12a-NS	49,960	80,280	55,100	
3C	56,500	74,930	55,543	
13bC	37,033	62,570	58,333	
4CS	50,611	74,950	63,550	
11CS	43,991	90,740	72,720	
12bCS	53,300	79,370	76,470	
		Plating Metal - Al + Al		
6N	55,810	96,280	66,600	
8N	29,500	68,800	54,544	
18NS	—	—	—	
19NS	—	—	—	
		Plating Metal - Al + Au		
5N	73,733	113,264	70,833	
7N	37,655	75,683	63,150	
20 NS	—	—	—	
		Plating Metal - Au Only		
14aN	79,975	104,400	59,073	
S-2N	—	—	—	

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*The letters N, NS, C and CS designate the type of quartz from which the resonator was made; namely, natural, natural swept, cultured or cultured swept.

TABLE 3 (Continued)

Summary of a Q Measurements of AT-Cut Quartz Resonators
Operated at the Fundamental, Third and Fifth Modes

Group Designation	Q_1	Q_2	Q_3
Plating Metal - Au Only			
14bNS	83,480	106,340	86,150
16NS	—	—	—
15aC	81,980	79,720	108,900
15bCS	100,900	130,750	130,425
Plating Metal - Au + Al			
17NS	—	—	—

The Q of the natural quartz crystals plated with each metal is quite variable, ranging from 30,000 to 80,000 at the fundamental.

A comparison of Q values found for the gold plated units has already been made; a comparison of the values for aluminum plated resonator follows:

Aluminum Plated Resonators	Q Value Range at Fundamental Mode
Natural Quartz	30,000 to 65,000
Cultured Quartz	37,000 to 57,000
Natural Swept (one group only)	50,000
Cultured Swept	44,000 to 53,300

It appeared on the basis of completed data for a relatively few resonators plated with gold only that the latter exhibited significantly higher Q values than those plated with Al only. Likewise those plated with Al + Au, without subsequent alloying, gave high Q values (Table 3).

With respect to the aging of quartz resonators made of the various types of quartz, in the numbers listed on page 60, it appears that aging as now being measured is dependent more on the actual fabrication parameters of each group than on the material of the quartz. Examples of aging of natural quartz specimens may be observed in Figures 16, 17, 18, 27 and 28. These resonators were all plated with aluminum only.

Examples of the aging of units made of natural swept quartz are shown in Figures 20 (Al + Al), 21 (Al + Al), 23 (Al + Au), 24 (Au + Al) and 26 (Au + Al). Figure 25 (Au 15-2) depicts the aging of a unit of cultured unswept quartz.

Additional comparisons of units plated with gold only are shown in Figures 29, 30 and 31 for natural swept, cultured, and cultured swept

Although one would expect the intrinsic differences among the types of quartz to affect aging rates, it is evident that these effects may only be detectable by measurements of resonators in which the aging is principally a characteristic of the quartz alone and not principally of the fabrication materials and techniques employed; or else the difference is so small as to be undetectable when frequency measurement is accurate to less than a part in 10^9.

5. Effects of cements

One of the variables in quartz crystal fabrication and aging is the type of cement used to bond the spring clip or tab to the plated metal electrode and the quartz. In the past very stable resonators have been successfully fabricated using duPont No. 5504A epoxy silver cement and Hanovia No. 2.

The duPont No. 5504A cement, principally employed, was the one component type. After application it was cured for 3 hours at 150°C in air. After the resonator units were assembled the cement underwent a further baking for 3 hours in vacuo at 175°C before the resonator was sealed. Of the 23 groups (about 10 each) of resonators fabricated duPont 5504A was used for 17 groups. Aging curves of resonators employing this cement are shown in previous Figures 16, 19, 20, 22, 25, 28, 29, 30 and 31.

Some variations in the curing and baking schedule for the cement and resonators have been attempted, usually but not always with resultant degradation of the expected resonator stability. For instance, units of Group No. A1-2 received a curing treatment at 300°C for one hour instead of 3 hours at 150°C. Figure 16 demonstrates a typical aging curve for a resonator of this group. It cannot be stated from the behavior of this

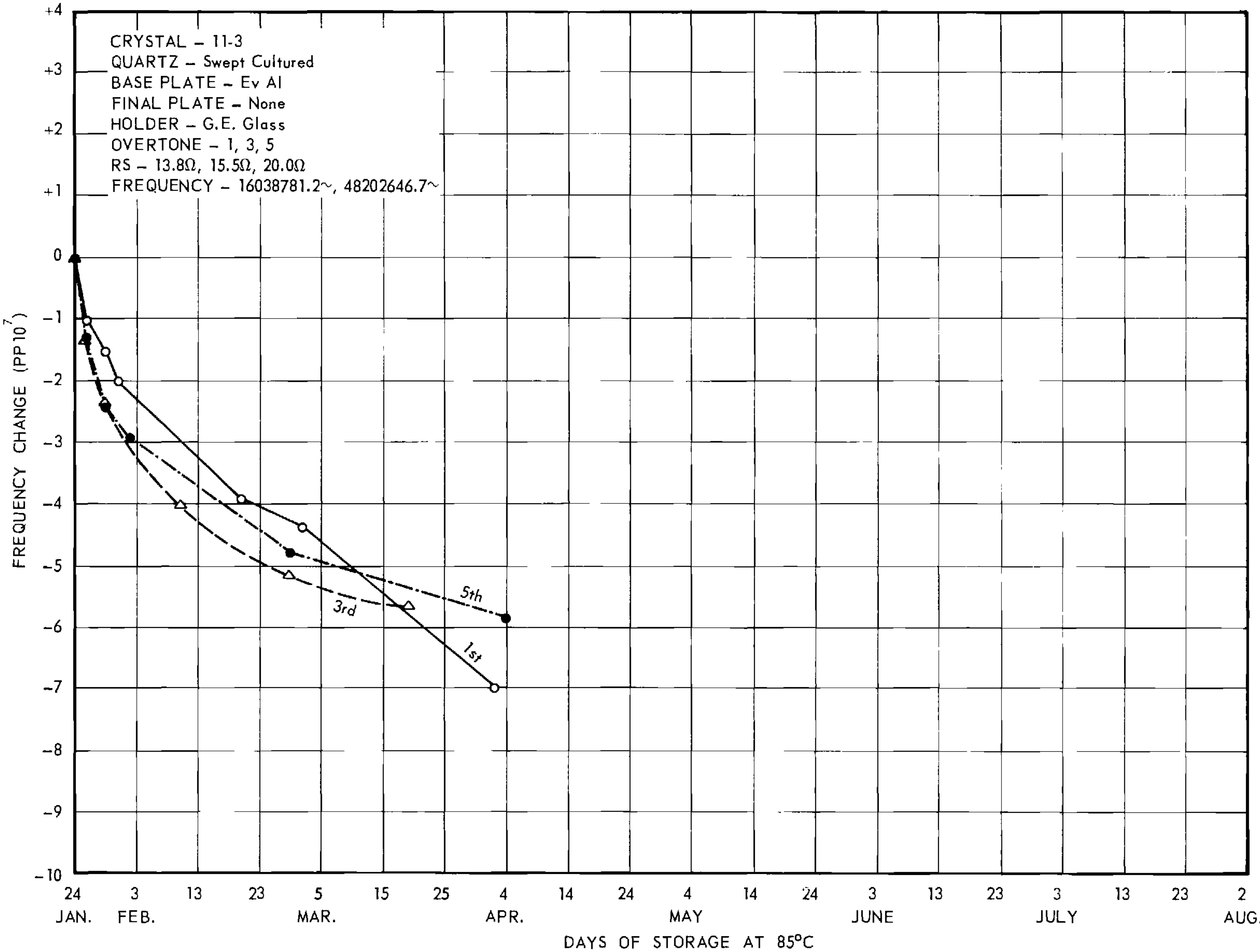

Figure 32. Aging data for swept cultured quartz resonator Al 11-3 bonded with 5504 cement and vacuum baked three hours at 225°C.

Those for the fundamental mode of operation were in each case greater than for operation in the third mode.

Resonator G-8, the unit showing the largest frequency change (+277 cycles), was a gettered unit that was not vacuum baked (not degassed thoroughly in vacuo before sealing). The continuous high drive level may have caused a net loss of adsorbed gas from the resonator surfaces. These were captured by the getter thus preventing their return under the conditions of the test.

Frequency changes occurring appeared to be particular to the resonator rather than the group. It does appear, however, that a continuous drive at the level employed (2 mw) is sufficient to cause significant frequency shifts for most of the resonators of the types examined.

8. Effects of Exposure to Neutron and Gamma Radiation on Aging of Quartz Resonators

a. Pulsed Neutron Radiation

Eleven groups (10 ea) of resonators were fabricated for studies of the effects of pulsed neutron radiation on crystal aging. The fabrication details of each group are given in Table 6. The electrical parameters of the individual units (except those of Groups Al-3, Al-4, and Al-5 for which no data were taken) are given in Table 7 (Appendix).

The units were placed in 85°C ovens when completed and held at that temperature for thirty days before starting aging measurements. The measurements were then continued for ninety days.

On 10 September 1962 selected units were removed from the 100 unit oven for exposure to pulsed irradiation; 17 specimens were reserved as

control specimens and kept in the laboratory at room temperature and 29 units were left in the oven. The 49 units to be irradiated were taken to the Sandia Pulsed Reactor Facility on 11 September and irradiated on 12 September.

These were arranged about the perimeter and immediately adjacent to the core of the reactor with the plated faces of the quartz crystals perpendicular to radii of the reactor core. The units were supported in this position in a foamed plastic as suggested by operators of the reactor. After irradiation with a neutron pulse of 10^{13} nvt* and after a short cool-off period the units were retrieved and repacked for return to Georgia Tech.

A measurement of the residual radioactivity of the resonators on return revealed that the red paint used to mark the containers of each unit for identification was the only part of the resonator giving off radiation at any appreciable level.

The irradiated units arrived at the laboratory on 14 September 1962, and nine of them were immediately replaced in the oven. On 17 September the parameters of the nine units were measured; immediately afterwards the oven was opened again to return the balance of the units to their original test positions.

A summary of frequency changes observed are presented in Table 8. Graphs of typical frequency stabilities are shown in Figures 33, 34 and 35. It will be noted that eight of the eleven groups of resonators examined were fabricated of natural quartz; three groups were fabricated of cultured quartz, one unswept and two swept. Although 6 aluminum plated

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* This dose is small compared to ones causing known structural damage. The latter are in the 10^{19} nvt range.

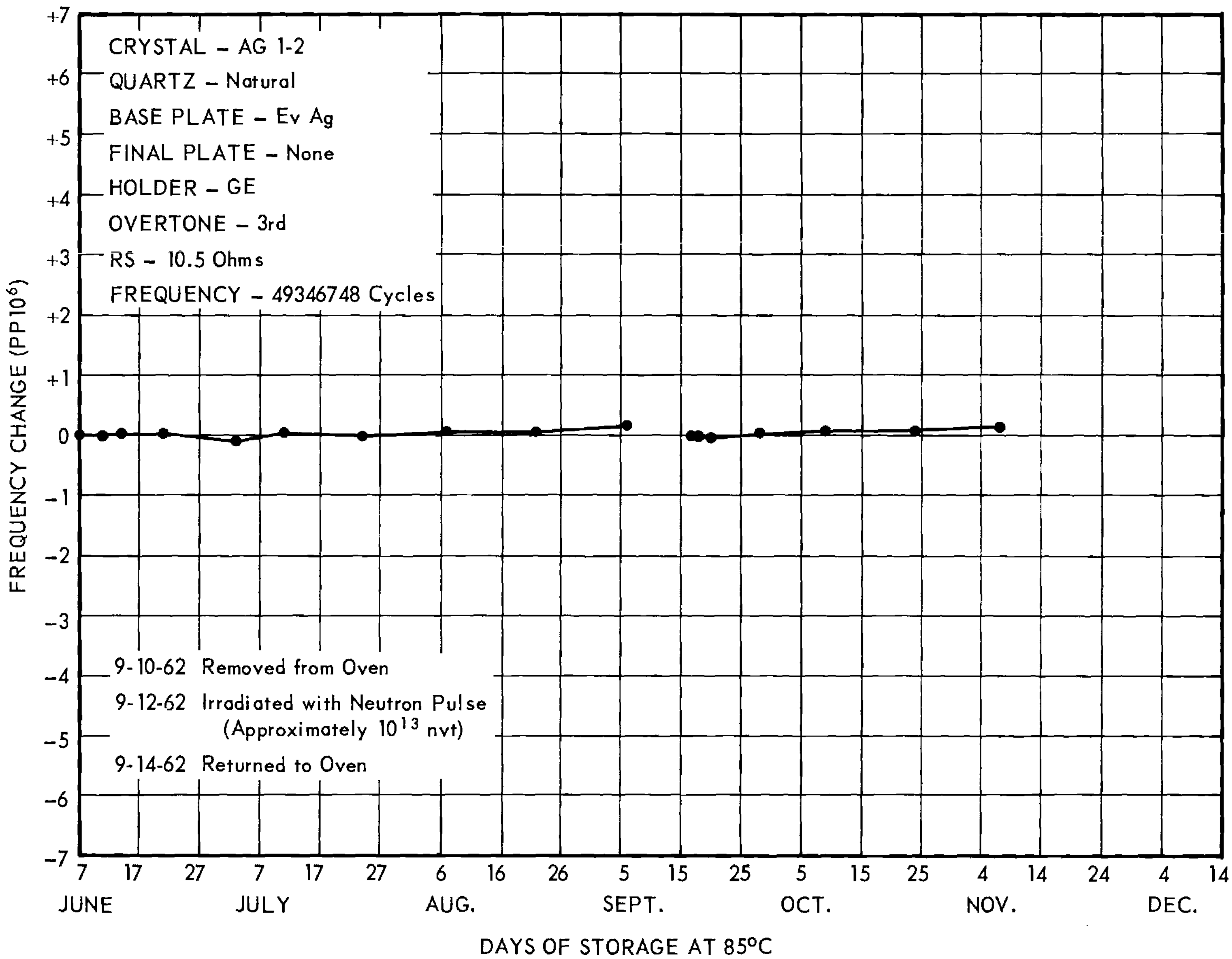

Figure 33. Effect of pulsed neutron radiation on natural quartz resonator Ag 1-2.

resonators of swept cultured quartz exhibited the largest changes in frequency observed, -5 parts in 10^7, this change can not be clearly ascribed to the quartz. Some of it appears to be related to the aluminum plating.

From Table 8 and Figures 33, 34 and 35 it is readily observed that the effects of exposure to a single fast neutron burst of 10^{13} nvt is insufficient to seriously disturb either the original frequency or the subsequent aging of the resonators. Frequency changes recorded as a result of the exposure were at most only a few parts in 10^7 and specimens removed from the oven, stored and returned to it along with the exposed specimens suffered changes of the same order of magnitude.

b. Effects of Gamma Radiation

(1) Summary of earlier experimental work

It has been shown previously by Frondel[7] that exposure of a natural quartz resonator to X-rays of high intensity or for a long period of time resulted in a shift in the frequency of the resonator; and at the time the irradiation of the quartz was suggested as a possible method of adjusting resonators to frequency.

Subsequently, under Contract No. DA-36-039-SC-85363, the authors showed that natural quartz resonators exposed to intense gamma radiation from a 12000 Curie Cs-137 source (1.4×10^6 Rad/Hr) underwent significant negative frequency shifts in periods of five to thirty minutes.[8] Changes as large as -10 ppm were registered. Afterwards these resonators underwent changes of frequency with time of as much as +1 ppm in 30 days. This relatively rapid upward drift decreased with time and stabilized after about 90 days at a value about 1.3 ppm above the original minimum. Figure 36 exhibits an example of this behavior.

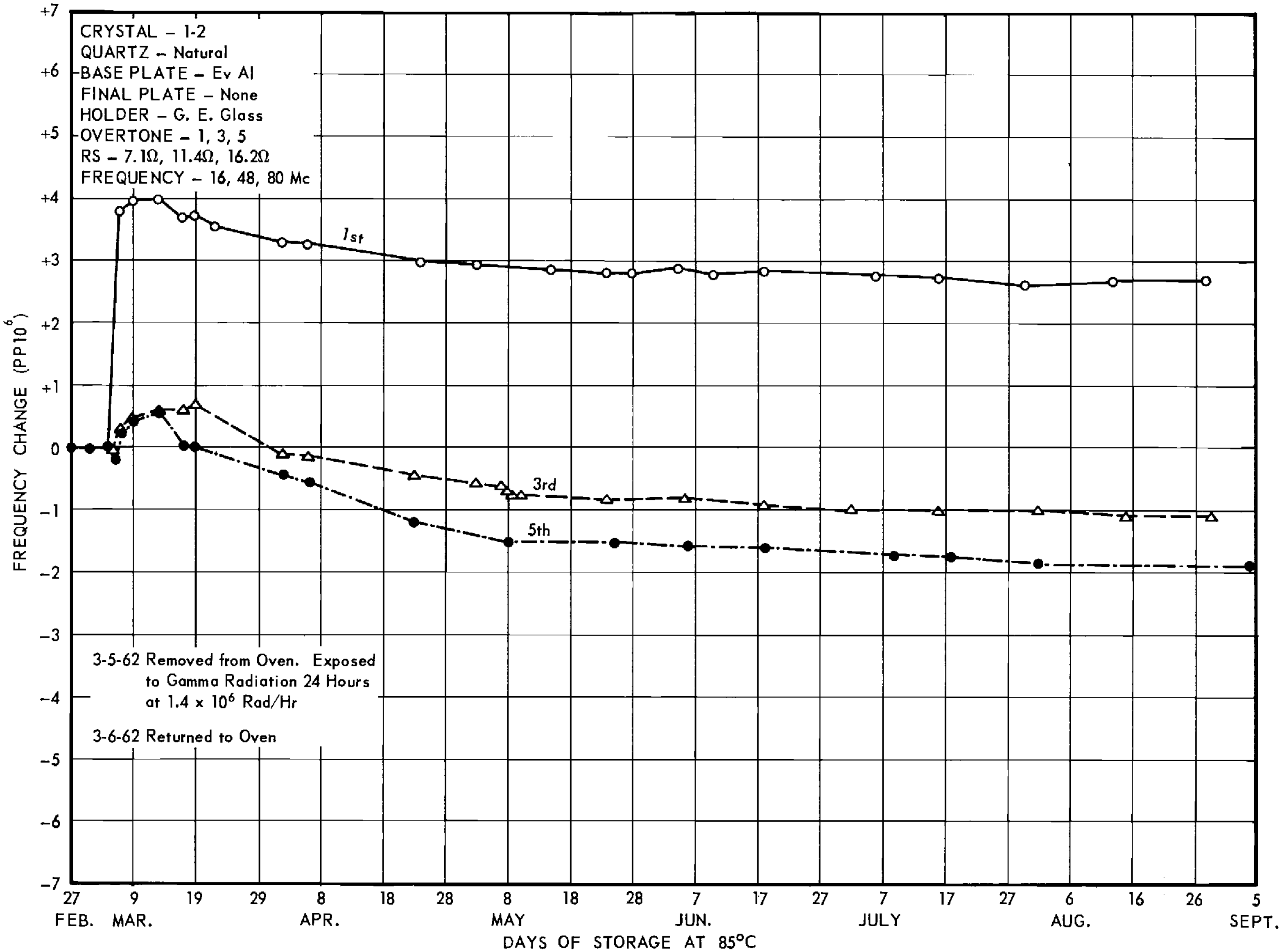

Figure 38. Aging data for natural quartz resonator Al 1-2 after exposure to gamma radiation (1.4×10^6 Rad/Hr) for 24 hours.

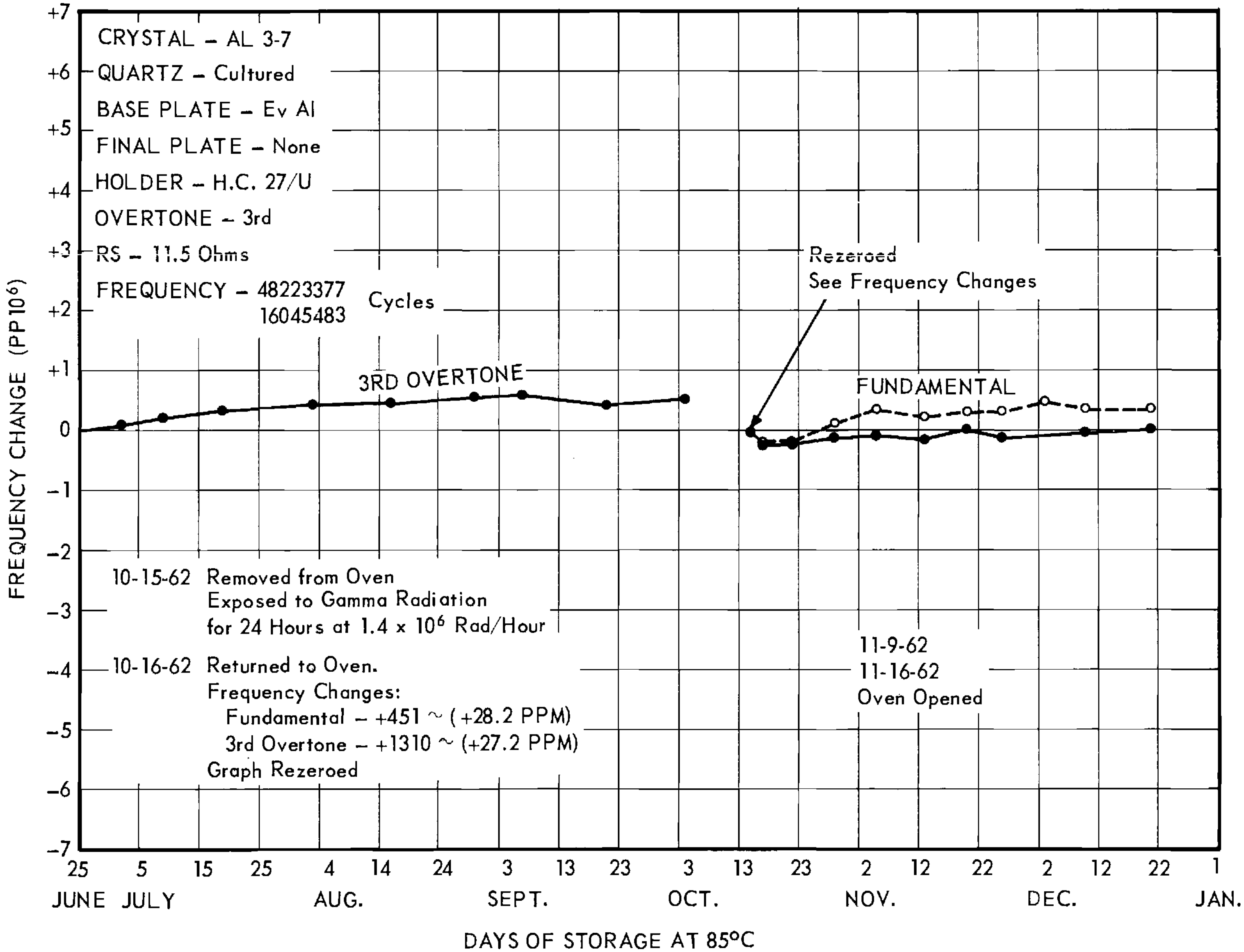

Figure 40. Frequency versus time data for quartz resonator Al 3-7 (cultured) before and after exposure to gamma radiation (1.4×10^6 Rad/Hr) for 24 hours.

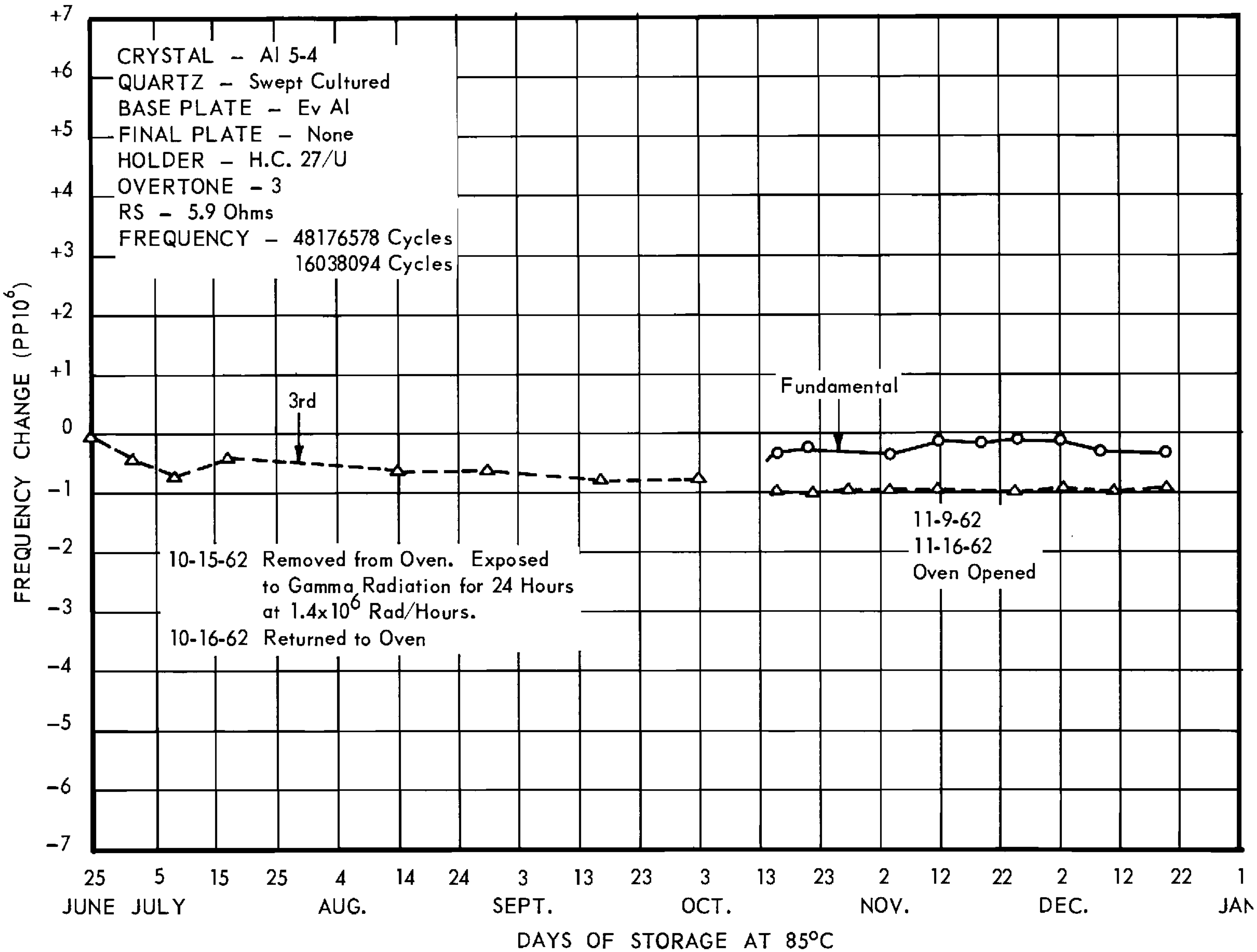

Figure 41. Frequency versus time data for quartz resonator Al 5-4 (swept cultured) before and after exposure to gamma radiation (1.4×10^6 Rad/Hr) for 24 hours.

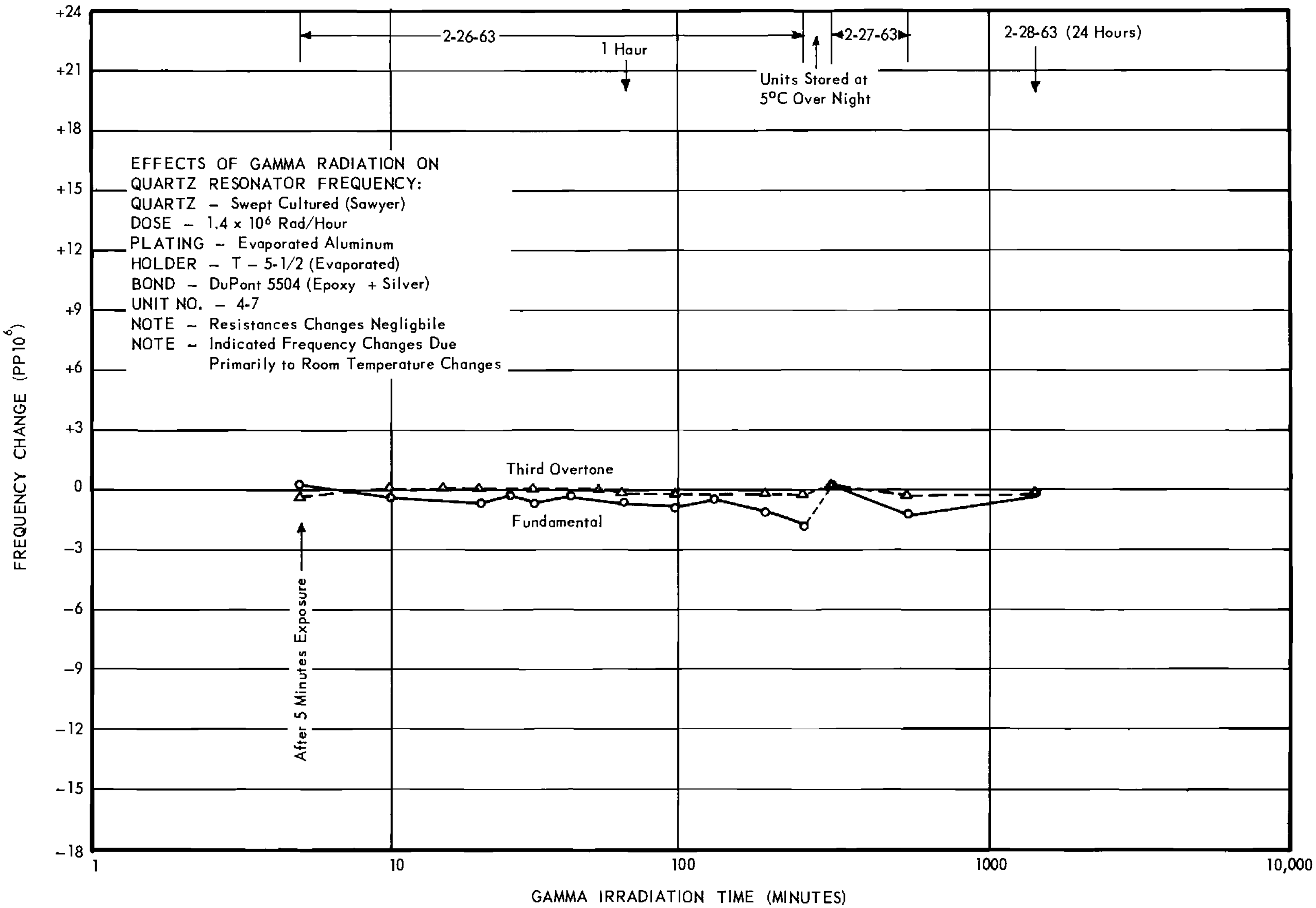

Figure 43. Effects of gamma radiation on swept cultured quartz resonator Al 4-7.

Observations were made after exposures of as short a time as 30 seconds in the well of the Cs-137 source up to periods covering a duration of 24 hours.*

Natural and swept natural quartz resonators displayed a greater scatter in reaction to irradiation than did the cultured and swept cultured resonators. This scatter appears to be related to the probably greater diversity of impurity atoms in natural quartz.

The findings of Verhoogen,[6] Bond and Andrus,[12] Keith and Tuttle,[13] King,[1] Sawyer,[3] and Young[14] all indicate that the impurities in quartz are quite variable depending on source, although in quantities approaching the limits of ready chemical or spectrochemical analysis. The variation in Q (Sawyer), acoustic absorption (King), and effects of radiation on the frequencies of quartz resonators reported herein and, by Stanley, and data obtained in X-ray topographic examination of quartz as recently reported by us, by Smith and Spencer[15] of Bell Telephone Laboratories, and by Hale, Carlson and Krueger of Clevite Corporation[16] point to significant variations in the impurity and structure differences in the quartz that may be controlled, by growing techniques in the case of cultured quartz, and benefitted by the act of sweeping for both natural and cultured quartz.

Verhoogen reported diffusion rates at 500°C of monovalent ions through the quartz lattice parallel to the C axis as follows:

$$D_{Li} = 1.1 \times 10^{-8} \text{ cm}^2 \text{ sec}^{-1}$$

$$D_{Na} = 5.8 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$$

$$D_{K} = 2.0 \times 10^{-10} \text{ cm}^2 \text{ sec}^{-1}$$

Numerical error was estimated as a factor of 2 or 3. These values for

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* The data incorporated in this paragraph will be given in greater detail in the Quarterly Report No. 1 of the succeeding research contract.

natural quartz were actually calculated from data obtained by a method of sweeping, apparently first devised by Verhoogen, in which a potential was applied across the quartz plate while heated. The potential was in the range 1000 to 1500 volts per cm. Spectroscopically detectable quantities of these ions could be found at the cathode. Very small amounts of Mg^{++} were detectable on the cathode after a period of several days and the diffusion rate was estimated as 10^{-12} cm^2 sec^{-1}. On the other hand, the diffusion of Ca^{++}, Fe^{++} and Al^{+++} were undetectable. It thus appears that the alkali metals are the ones most likely to be removed by sweeping. This observation has also been confirmed by Sawyer[3]; and King[2] and Rowen (and Foster)[4] stated that the presence of oxygen atoms in the atmosphere was essential to sweeping since short circuiting occurred in the quartz during sweeping in vacuo, apparently due to partial reduction of the quartz.

It would thus appear from the Q studies cited and the radiation effect studies completed by us that the alkali metal atoms in the quartz are a source of one of the principal degradatory factors both in the Q differences observed between natural, cultured and swept cultured quartz and the frequency changes experienced by resonators exposed to high gamma ray intensities.

The fact that natural quartz may respond less well to sweeping or in a more erratic manner under irradiation than synthetic quartz is ascribed to its growth from aqueous solutions of unknown and variable mineral content and to deposit at temperatures, pressures and rates, particular to a specific geologic situation. These undoubtedly varied over a wide range of possible conditions. Structural differences other than those provided by impurity content may also make a contribution to the differences observed,

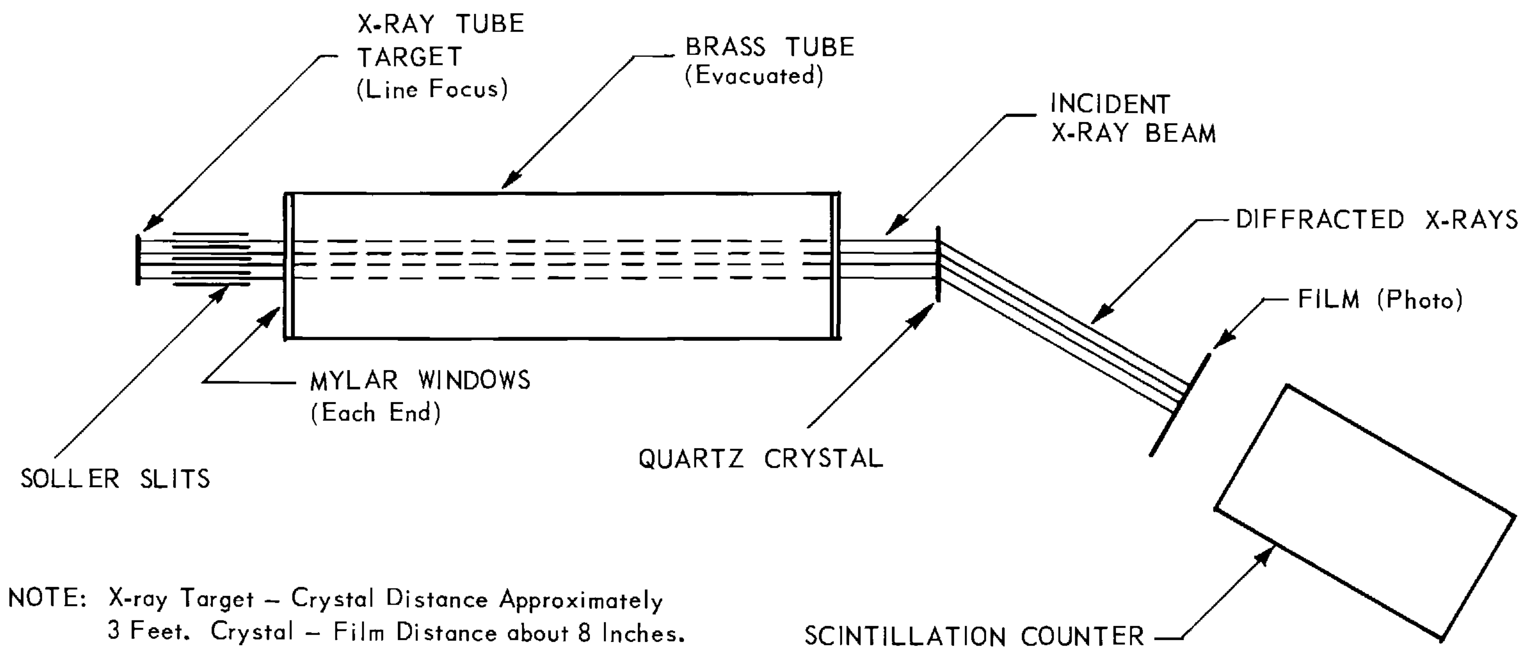
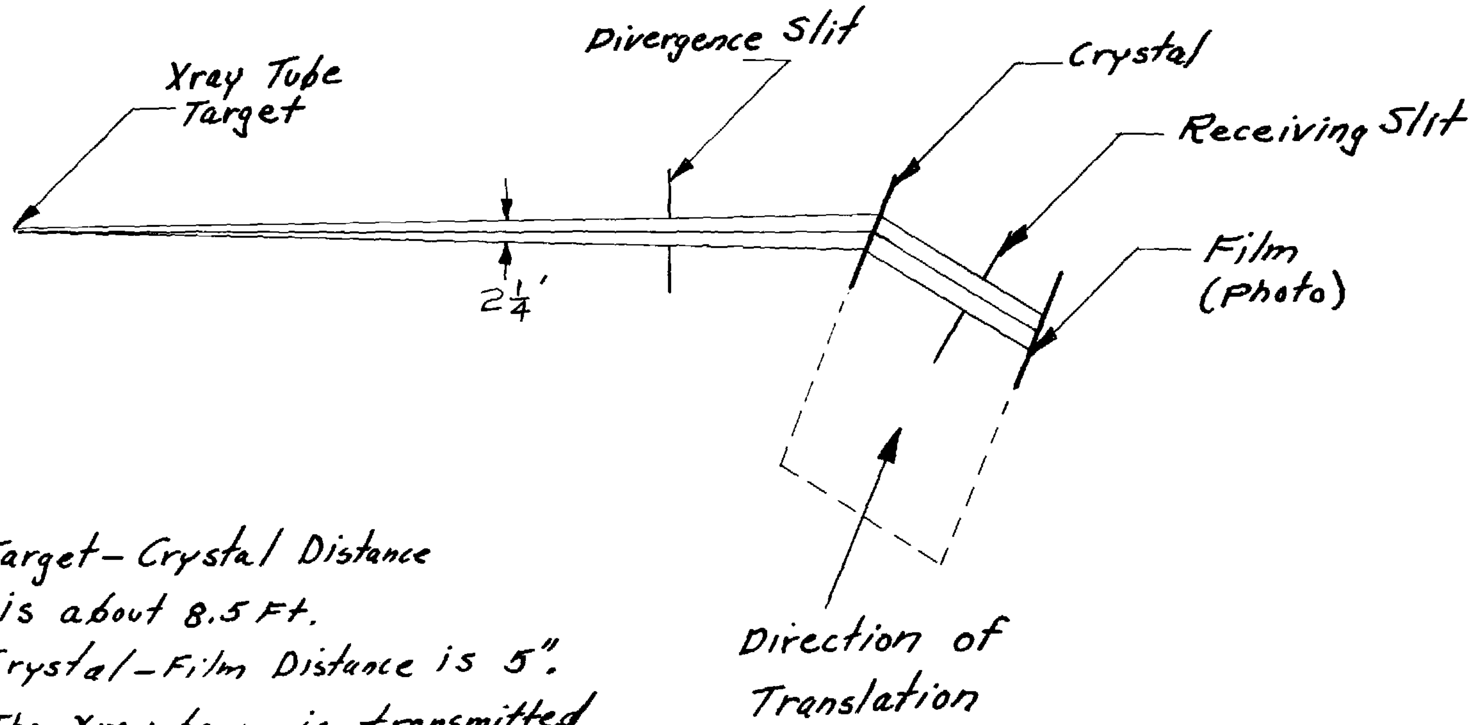


Figure 44. Sketch of x-ray-topographic apparatus used to observe strain patterns in quartz plates.



Note: Target–Crystal Distance is about 8.5 Ft.
Crystal–Film Distance is 5".
The Xray beam is transmitted through an evacuated brass tube between the target and crystal.
The tube is about 8 ft in length.

Figure 46. Sketch of x-ray topographic apparatus using Lang's technique.

Dauphiné (or electrically) twinned areas. A $(30.\bar{1})$ Bragg reflection was used in this diffraction topograph because of its sensitivity to Dauphiné twinning. There is a very large difference in the X-ray intensity in the $(30\text{-}\bar{1})$ and $(\bar{3}0.\bar{1})$ reflections, yet the $(30.\bar{1})$ of one region of the crystal occurs at the same angle as the $(\bar{3}0.1)$ of the adjacent Dauphiné twinned region. Consequently, the exposure in the areas "A" is small enough so that they appear to be complete voids in the crystal's diffraction image. As seen in the photograph a large portion of the plate (the more opaque section) is twinned with respect to the remainder. The large amount of twinning occurring is undoubtedly responsible for the changes in frequency and temperature-frequency behavior of quartz resonator Al 4-1 and others in which large frequency shifts were observed. Dr. Young,[14] has discussed the occurrence of Dauphiné twinning at temperatures well below the α-β phase transition temperature of quartz. Twinning of this type must have occurred in this specimen during the sealing phase. One of the peculiarities of this twinning is that some quartz specimens are more susceptible to it than others. This susceptibility is probably related, in turn, to the entire history of the quartz of the particular plate from its time of original growth. This variation is susceptibility may account for the variation in twinning of resonators fabricated in a similar manner.*

The experiments outlined have revealed a tool of considerable value in the further study of quartz as a frequency control element and the pursuit of more intensive work along the lines noted is planned.

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* Very recently some indications have been obtained from fabrication results that swept cultured quartz is more susceptible to twinning than natural quartz during its exposure to the temperatures required to seal the HC-27/U glass container.

VI. IDENTIFICATION OF KEY TECHNICAL PERSONNEL

The persons listed below have been employed on the work of this Project. The number of hours devoted to it by each is noted.

Individual	Position	Hours
R. B. Belser	Project Director	1600
W. H. Hicklin	Asst. Res. Engr.	4000
D. S. Harmer	Res. Assoc. Prof. of Physics	80
W. B. Warren	Research Engineer	219
R. A. Young	Res. Assoc. Prof. of Physics	4
N. K. Hearn, Jr.	Asst. Res. Physicist	82
J. O. Darnell	Research Assistant	3000
C. M. Shirley	Research Technician	3000
J. C. Shaw	Graduate Research Assistant	237
T. L. Spradling	Graduate Research Assistant	439

Mr. Belser, M.S., Physics, has worked in the field of quartz crystal fabrication and measurement for 13 years. Mr. Hicklin, graduate of Valpairaiso Technical Institute, has been associated with Mr. Belser for eleven years. Radiation tests were conducted under the supervision of Dr. D. S. Harmer, who received his graduate degree in Nuclear Chemistry from the University of California. The work on X-ray diffraction topography was conducted under the supervision of Dr. R. A. Young, Head of the Solid State Branch and the X-ray Diffraction Laboratories of the Engineering Experiment Station, by Mr. N. K. Hearn, a Physics graduate of Kansas State College (Emporia). Mr. Warren, M.S. degree in Electrical Engineering, has been working in the fields of electronic circuitry and precision measurements for 12 years and is a project director of related work. Messrs Darnell and Shirley are skilled assistants, familiar with electronic, mechanical and vacuum technology. Messers Shaw and Spradling have B.S. degrees in Electrical Engineering from Georgia Tech and are working on graduate degrees.

Table 2
Measurements of Electrical Parameters of Quartz Resonators for Regular Aging Studies

	Fundamental			Third Overtone			Fifth Overtone			Q Meter Measurements						
Unit	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	ΔQ1	ΔQ3	ΔQ5	Coi (uuf)	Cos (uuf)	Cos (uuf)	
1-1	16036728	3.8	71,300	48193900	9.4	83,700	80353358	19.2	52,400				8.3	8.6	8.5	NAT. AL ONLY
2	16043935	7.1	38,700	48215583	11.4	66,100	80370136	16.2	57,200				8.3	8.6	8.5	
3	16046237	4.0	67,500	48223720	9.1	90,200	80383254	13.2	63,900				8.5	8.5	8.5	
4	16053803	3.9	71,000	48244416	8.6	100,600	80416685	16.0	66,500				8.5	8.6	8.5	
5	16039456	3.7	75,100	48203003	8.2	93,000	80349115	13.1	69,900				8.4	8.6	8.6	
6	16043486	5.0	65,900	48214480	7.2	81,900	80368320	13.2	69,100				8.1	8.5	8.3	
7	16048102	4.3	64,800	48227490	9.4	81,000	80389606	14.2	62,300				8.3	8.6	8.7	
8	16043151	4.2	65,000	48213400	8.8	84,000	80366542	14.2	62,200				8.5	8.6	8.7	
9	16037698	4.8	58,500	48196100	9.8	80,900	80337212	16.2	60,400				8.3	8.3	8.4	
10	16039725	5.2	53,700	48202189	9.4	81,500	80347560	19.0	49,800				8.3	8.5	8.3	
			63,150			84,290			61,370							
2-1	16057440	5.0	54,300	48257105	9.8	75,900	80439134	13.2	66,500				8.4	8.5	8.8	NAT AL ONLY
2	16050290	4.8	57,500	48235540	8.6	86,000	80403524	12.9	67,600				8.4	8.6	8.5	
3	16036637	6.0	46,100	48193707	9.7	80,500	80333123	15.0	64,500				8.4	8.5	8.5	
4	16046551	6.2	45,100	48223301	9.6	81,100	80382536	19.0	50,300				8.2	8.3	8.3	
6	16065045	6.4	43,300	48280000	9.8	73,200	80477821	14.8	55,100				8.4	8.4	8.2	
7	16043861	7.4	37,700	48217031	11.7	63,500	80372615	15.0	56,900				8.2	8.3	8.2	
8	16081678	6.6	42,700	48328802	11.5	66,700	80556289	38.0					8.3	8.4	8.2	
9	16057275	7.7	35,500	48256929	9.8	75,400	80439247	16.0	54200				8.4	8.4	8.5	
10	16054592	6.4	43,200	48247938	9.5	80,000	80423870	14.7	63,500				8.4	8.5	8.6	
			45,044			75,811			59,825							
3-1	16057152	9.8	28,200	48255062	14.7	57,300	80449842	31.0					8.3	8.4	8.4	CUL. AL ONLY
2	16043999	19.0	14,600	48216021	16.3	49,900	80369762	18.0	59,400				8.3	8.3	8.2	
3	16045568	5.4	51,700	48221503	12.6	61,500	80377246	35.0	—				8.4	8.4	8.3	
5	16043812	4.5	60,200	48216316	8.4	88,600	80371135	14.1	64,000				8.4	8.5	8.3	
6	16051585	6.1	45,500	48239954	10.8	66,600	80410901	16.5	50,200				8.3	8.4	8.2	
7	16040743	4.0	69,900	48203921	9.5	90,300	80349242	17.0	69,500				8.5	8.5	8.2	
8	16043163	5.4	51,000	48214263	10.2	72,200	80368119	17.3	47,600				8.3	8.5	8.5	
9	16050785	5.0	64,500	48237888	9.5	74,900	80407439	17.5	46,400				8.4	8.4	8.4	
10	16045331	5.2	52,700	48219867	11.2	70,400	80376441	19.2	51,700				8.4	8.5	8.5	
			56,500			74,930			55,543							

Table 2 (Sheet 3)
Measurements of Electrical Parameters of Quartz Resonators for Regular Aging Studies

	FUNDAMENTAL			THIRD OVERTONE			FIFTH OVERTONE			Q METER MEASUREMENTS						
UNIT	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	ΔQ1	ΔQ3	ΔQ5	Co1(uuf)	Co3(uuf)	Co5(uuf)	
8-1	16034655	9.0	27,850	48184718	12.0	73,100	80316571	20.0	56,400				9.7	10.0	10.2	NAT. AL + AL
2	16044931	10.5	26,700	48213458	13.0	66,600	80365347	16.5	68,900				8.6	8.7	8.6	
3	16041937	9.4	29,650	48203804	17.7	47,000	80350360	45.5	23,150				8.6	8.7	8.7	
4	16040189	6.0	45,100	48202214	9.6	84,500	80347035	14.0	70,700				8.6	8.7	8.9	
5	16034227	16.2	16,200	48183943	17.7	48,100	80315893	21.5	51,700				9.0	9.2	9.0	
6	16028521	38.0	°6,940	48163644	41.5	°12,400	80281602	58.0					9.4	8.5	9.2	
7	16063616	56.0	°4,650	48270324	66.0	°16,500	80457938	64.0	°37,420				9.6	8.5	9.5	
8	16026880	15.5	17,800	48161119	20.0	43,400	80277435	26.0	43,500				8.0	8.2	9.0	
9	16025171	6.4	42,500	48151768	10.1	117,900	80260946	16.5	53,600				9.1	9.3	9.3	
10	16022864	8.2	30,200	48148374	13.5	69,800	80254721	22.5	68,400				9.9	10.3	9.9	
			29,500			68,800			54,544							
9-1	16055559	8.6	32,000	48251828	15.3	51,800	80431352	36.0					7.3	7.1	5.5	NAT. AL ONLY
2	16067031	11.2	23,900	48285876	11.5	72,500	80487759	20.7	58,300				7.5	7.3	5.8	
3	16039745	16.0	17,050	48283782	12.5	65,100	80350530	16.0	74,000				7.4	7.2	5.7	
4	16058919	6.5	50,500	48255988	8.3	111,900	80436620	17.0	80,000				7.0	6.9	5.2	
5	16045754	10.1	28,200	48221686	9.8	83,700	80380430	13.5	88,000				7.3	7.2	5.7	
6	16066371	14.0	19,990	48283523	13.0	64,500	80483210	16.6	75,600				7.3	7.1	5.4	
7	16053234	11.9		48242272	11.5	75,100	80414133	13.2	100,000				7.3	7.1	5.3	
8	16051733	16.4		48238959	8.6	101,000	80408563	12.6	103,000				7.3	7.2	5.6	
9	16037220	7.1	39,800	48194044	9.4	93,000	80333702	14.6	92,000				7.2	7.1	5.5	
			30,193			80,633			83,850							
10-1	16033782	10.0	28,600	48182129	4.4	195,100	80313649	9.4	124,800				8.0	7.3	6.9	NAT. AL ONLY
2	16052844	3.3	89,700	48240610	6.5	130,500	80411234	11.3	104,000				8.1	7.4	6.9	PYROCERAM + AG BOND.
3	16037335	7.5	36,000	48196176	8.9	93,400	80337539	12.0	88,900				8.2	7.6	7.0	
4	16046645	2.7	102,000	48223336	5.1	160,000	80382756	9.4	116,000				8.0	7.3	6.9	
5	16057017	7.5	92,500	48252621	10.0	81,400	80431311	21.0	49,600				7.9	7.3	7.0	
6	16047530	2.2	128,800	48224799	6.6	126,200	80385482	16.5	69,400				8.0	7.3	6.9	
7	16044904	24.0	11,620	48218260	13.7	63,900	80374113	15.5	75,000				7.7	7.4	6.8	
9	16042024	25.0	12,290	48202732	10.0	94,900	80347449	12.6	107,500				7.7	7.0	6.5	
10	16047356	10.8	24,700	48227098	13.0	66,500	80389229	16.5	64,600				8.2	7.6	7.1	
			57,912			112,433			88,755							

Table 2 (Sheet 7)
Measurements of Electrical Parameters of Quartz Resonators for Regular Aging Studies

	FUNDAMENTAL			THIRD OVERTONE			FIFTH OVERTONE			Q METER MEASUREMENTS						
UNIT	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	Fs(~)	Rs(Ω)	Q	ΔQ1	ΔQ3	ΔQ5	Co1(uuf)	Co3(uuf)	Co5(uuf)	
18-1	16046570	5.8		48220993	10.2											AL + AL
2	16016113	6.8		48131513	10.0											
3	16013089	6.2		48119161	10.5											
4	16024253	6.7		48152643	9.0											
5	16027357	10.1		48159370	14.0											
6	16060139	31.0		48259439	17.0											
7	16025043	9.0		48151232	12.5											
8	16045007	8.0		48213309	11.9											
9	16033284	8.5		48178288	14.5											
10	16021784	6.4		48141903	9.8											
19-1	16026342	10.0		48149633	15.2											AL + AL
2	16014348	2.8			6.7											
3	16039856	3.8		48198041	7.5											
4	16016181	4.0		48128858	7.1											
5	16075676	5.3		48306452	10.7											
6	16009929	2.7		48111807	6.2											
7	16031554	11.8		48176040	12.0											
8	16026656	7.5		48154681	8.8											
9	16032707	6.4		48180341	11.0											
10	16034971	7.3		48142223	13.0											
20-1	15935209	9.2		47877237	18.5											FILM ALLOYED DURING SEALING
2	15925759	10.0		47835502	15.5											"
3	15930472	13.1		47860426	18.0											"
4	15936032	2.6		47880709	6.6											NO VISIBLE ALLOYING
5	15948653	1.2		47916890	8.5											"
6	15962190	1.7		47955931	7.2											"
7	15932106	1.5		47868123	7.0											"
8	15942228	6.0		47897878	24.0											"
9	15943766	2.7		47904003	7.5											"
10	15951713	2.8		47926793	8.0											"

Table 7

Electrical Parameters of Resonators for Pulsed Radiation Studies

Unit	$R_s(\Omega)$	$F_s(\sim)$	$R_a(\Omega)$	$F_a(\sim)$*	ΔF (F_a-F_s)	$\frac{C_o}{\mu\mu f}$	Q
			Gold Plated Resonators[1]				
Au-1-2	6.8	47328832	9.8	47330332	1500	6.1	202200
Au-1-4	7.4	47294893	10.0	47296366	1473	6.1	192000
Au-1-5	10.0	47341642	14.0	47343243	1601	6.1	130000
Au-1-7	10.5	47379920	15.5	47381450	1530	6.1	130000
Au-1-8	10.3	47415630	14.0	47417150	1520	6.1	133500
Au-1-9	9.7	47342936	16.0	47344387	1451	6.1	148500
Au-2-1	8.8	47580880	13.5	47581190	390?	6.1	
Au-2-4	6.8	47537450	11.5	47538730	1280	6.1	240000
Au-2-7	8.2	47540156	12.7	47541393	1237	6.1	206200
Au-2-8	8.2	47491025	12.0	47492268	1243	6.1	205500
Au-2-10	6.6	47533480	10.5	47534840	1360	6.1	233000
Au-2-12	10.5	47565198	15.5	47566350	1152	6.1	172800
Au-2-13	7.2	47682186	11.0	47683603	1417	6.1	205000
Au-2-15	11.3	47491114	18.0	47492204	1090	6.1	169000
Au-2-17	7.0	47407040	11.3	47408450	1410	6.1	211000
Au-2-20	11.2	47290070	15.5	47291476	1406	6.1	132800
Au-2-21	8.2	47417185	10.0	47418590	1405	6.1	181400
Au-2-22	7.1	47598425	11.5	47599585	1160	6.1	253800
Au-3-1	6.8	47235520	9.4	47237014	1494	6.1	205500
Au-3-2	6.3	47395230	10.5	47396750	1520	6.1	218400
Au-3-16	7.0	47338431	11.0	47339870	1439	6.1	205500
Au-3-19	9.0	47604772	11.0	47605850	1078	6.1	215500

[1] Quartz: Natural; Holder: HC-27/U; Bond: 1 part pyroceram + 2 parts silver (by volume) fired 5 minutes at 450°C.

*R_a + F_a obtained using a series load condenser of 32 μμf.

Table 7 (Continued)

Unit	$R_s(\Omega)$	$F_a(\sim)$	$R_a(\Omega)$	$F_a(\sim)^*$	ΔF (F_a-F_s)	$\frac{C_o}{\mu\mu f}$	Q
Au-4-1	7.2	47279475	8.5	47280722	1247	6.1	233000
Au-4-2	5.8	47289371	9.0	47290605	1234	6.1	292000
Au-4-5	7.0	47210612	10.5	47211771	1159	6.1	257500
Au-4-6	6.0	47263608	11.3	47264839	1231	6.1	282500
Au-4-7	8.4	47273495	12.2	47274683	1188	6.1	209000
Au-4-8	6.7	47173198	8.9	47174586	1388	6.1	225000
Au-4-9	6.6	47207566	10.0	47208733	1167	6.1	272000
Au-4-10	6.8	47231838	10.7	47232940	1102	6.1	281000
		Silver Plated Resonators[2]					
Ag-1-1	9.5	49209678	13.8	49211025	1347	8.0	153800
Ag-1-2	10.5	49348614	16.0	49349860	1246	8.0	152400
Ag-1-3	12.5	48985592	17.5	48986995	1403	8.0	113200
Ag-1-4	16.0	48998740	26.0	49000077	1337	8.0	93000
Ag-1-5	10.5	48986986	13.0	48988459	1474	8.0	128800
Ag-1-6	10.5	49190650	15.5	49191852	1202	8.0	157800
Ag-1-7	9.2	49505251	15.0	49506630	1379	8.0	157000
Ag-1-8	9.2	49111317	13.5	49112570	1255	8.0	172200
Ag-1-9	17.5	49193350	28.0	49193930	580?	8.0	- - - -
Ag-1-10	10.0	49052491	13.0	49053990	1509	8.0	132000
Ag-1-11	9.0	49127018	13.0	49128260	1242	8.0	177500
Ag-1-12	9.5	49341631	15.5	49342834	1203	8.0	173000
Ag-1-13	8.0	49147207	13.5	49148387	1180	8.0	212000
Ag-1-14	10.5	49145985	14.5	49147238	1253	8.0	151200
Ag-1-15	20.0	49186157	28.0	49187500	1343	8.0	74200
Ag-1-16	9.7	49072261	15.0	49073723	1462	8.0	140000
Ag-1-17	11.2	49345871	16.5	49347000	1129	8.0	157700
Ag-1-18	10.5	49357900	15.5	49359018	1118	8.0	164000
Ag-1-19	9.3	49424508	16.0	49425773	1265	8.0	169000
Ag-1-20	32.0	49264307	38.0	49264903	596?	8.0	- - - -
Ag-2-1	10.5	49276940	- - -	- - - -	Unable to measure R_a and F_a		

[2]Quartz: Natural; Holder: GE Glass; Bond: DuPont 5504A cement cured 3 minutes at 150°C

*R_a and F_a obtained using a series load condenser of 32 $\mu\mu f$.