IITRI

IITRI Project No. D6096
Second Annual Summary Report

SPACE PROCESSING OF CHALCOGENIDE GLASS

National Aeronautics and Space
Administration
George C. Marshall Space Flight Center
Alabama 35812

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Prepared by:

M. A. Ali
D. C. Larsen

IIT RESEARCH INSTITUTE
10 West 35th Street
Chicago, Illinois 60616

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SPACE PROCESSING OF CHALCOGENIDE GLASSES

1. INTRODUCTION

This project is being conducted for NASA-MSFC to investigate space processing of chalcogenide glasses. Chalcogenide glasses are good infrared transmitters and have good strength, corrosion resistance, and scale-up potential. For these reasons chalcogenide glasses are considered as potential candidate materials for use as laser windows and infrared fiber optics for transmitting a laser beam through a flexible probe. Alkali halides are also considered for window applications, but have the disadvantage of hygroscopicity and availability in only five to six inch diameters, as limited by manufacturing techniques. For fiber optics, Kapany (Reference 1) has demonstrated that chalcogenide fiber optics could not be processed due to limitations related to the presence of the 1-g earth environment.

The disadvantage of (earth-produced) chalcogenide glasses is that their infrared absorption is unacceptably high relative to alkali halides. IITRI believes that this limitation of earth-produced chalcogenide is due to optical nonhomogeneities resulting from environmental and container contamination. Processing the glass in space should improve the infrared-transmission of chalcogenide glasses. The containerless, weightless nature of space processing should eliminate: 1) optical inhomogeneities caused by thermal currents and density fluctuations in the 1-g earth environment, 2) contamination from the earth melting crucible by oxygen and other elements deleterious to ir-transmission, and 3) heterogeneous nucleation of the earth melting crucible-glass interface.

The overall objective of IITRI's program is to determine the manner in which the weightless, containerless nature of in-space processing can be successfully utilized to improve the quality of infrared transmitting chalcogenide glasses. This

program is an effort to: 1) develop the technique of space processing of chalcogenide glass, 2) define the process and equipment necessary to do so, and 3) predict the level of product improvement to be expected through space processing. These goals are being accomplished by a series of earth-bound (1-g) processing experiments with $Ge_{28}Sb_{12}Se_{60}$ glass. Incorporated into these experiments is the use of an acoustic levitation device that will eventually be utilized in the 10^{-4}g space environment to achieve position-controlled containerless processing.

During this second year of the program several significant contributions have been made to meet the requirements of the program. These include 1) the development of $Ge_{28}Sb_{12}Se_{60}$ glass at IITRI which has optical characteristics as good as Texas Instruments $Ge_{28}Sb_{12}Se_{60}$ glass which is designated as TI-1173, 2) experiments on the precursor treatment of the 'as received' material to increase purity and 3) levitation of As_2S_3 glass using the acoustic levitator/position control device that will eventually be used in space.

2.0 EARTH PROCESSING VS. SPACE PROCESSING OF CHALCOGENIDE GLASSES

The standard method of processing chalcogenide glasses on earth entails basically reacting the batch constituents at high temperature in a sealed silica ampoule while simultaneously rocking the furnace/ampoule.

The rocking of the ampoule and the resulting mixing of the liquid is necessary to overcome the micro-inhomogeneities resulting from thermal currents and density fluctuations that are due to the presence of the earth's 1-g gravity field. However, these gravity related phenomena are never completely eliminated by this method. Furthermore, this prolonged contact with the crucible material contaminates the chalcogenide with levels as low as part per million of oxygen and other elements deleterious to ir-transmission at a wavelength of 10.6μ.

By going to space to process chalcogenide glasses both of these problems, thermal currents/density fluctuations and contamination, will be eliminated. The compounding and quenching aspects of the process can be performed in the absence of gravity, eliminating thermal convection. The zero gravity condition provides for the possibility of containerless processing, which will eliminate the contamination effects of the earth melting crucible. Thus, the weightless, containerless aspects of space manufacture has the potential for producing an improved ir-transmitting chalcogenide for use as a large laser window material.

3.0 RESEARCH PROGRAM

During this year of the program processing parameters of $Ge_{28}Sb_{12}Se_{60}$ glass were investigated. Optimum precursor mixing and high temperature processing techniques of high purity $Ge_{28}Sb_{12}Se_{60}$ glass were established. Experiments were also conducted to establish the applicability of processing $Ge_{28}Sb_{12}Se_{60}$ glass in an acoustic levitator/position control device.

3.1 Processing Parameters of $Ge_{28}Sb_{12}Se_{60}$ Glass

Studies were conducted to establish the processing parameters of $Ge_{28}Sb_{12}Se_{60}$ glass. In these experiments the glasses were compounded using reagent grade materials having a purity of 99.5%. The reason for using low purity materials initially was to economically study processing parameters such as reaction temperature and time, ampoule size, and quantity of the reactants. Thus, in the initial experiments high infrared transmission of the glass was not required.

Time and temperature schedules were selected from the published data on TI 1173 glasses (References 2 and 3). The literature information does not specify a particular melting temperature, rather a very broad range of temperature. Hence, our experiments were conducted at selected temperatures within the range of 800-925°C.

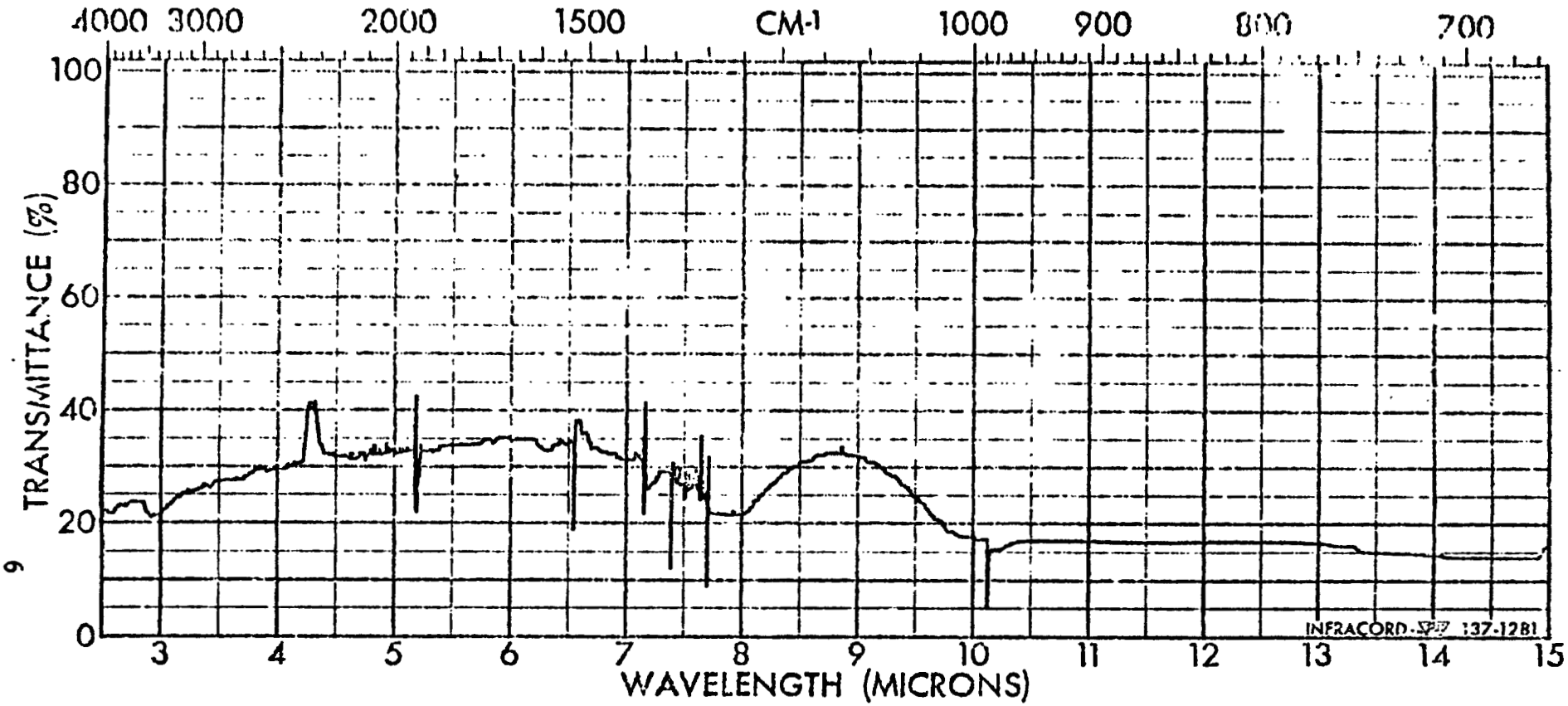
The batch compositions were formulated in a glove box filled with a pure and dry argon gas and the batch materials were transferred to a quartz ampoule. The ampoule was evacuated (4.5×10^{-4} Torr) for 16 hours and then sealed with an oxy-hydrogen torch. The glass inside the sealed ampoule was melted in a rocking furnace. The furnace was rocked for various lengths of time at 800-925°C and the glass was then air quenched. The ampoule containing the glass was then annealed for twelve hours at 300°C.

These experiments indicated that glasses could not be compounded at temperatures below 800°C even when soaked for 16 hours. It was also observed that the compounding of $Ge_{28}Sb_{12}Se_{60}$ glass at higher temperatures (900-925°C) resulted in a surface reaction with the quartz ampoule as evidenced by adherances of the annealed glass to the quartz ampoule wall. It was thus established that the glass should be compounded within a temperature range of 800-900°C, preferably near the lower end of this region.

Following these preliminary processing studies, experiments were also conducted to establish the relationship between the quartz ampoule size and the quantity of the batch material. In earlier experiments with As_2S_3 glasses, it was observed that during glass melting the ampoule would explode due to high pressure buildup from gaseous arsenic and sulfur components, while using a 20 gram batch in a 37 cc ampoule. The initial experiments with $Ge_{28}Sb_{12}Se_{60}$ has established that the ideal batch size for a ≃ 37 cc ampoule is 15 grams.

Following these experiments various additional compositions corresponding to $Ge_{28}Sb_{12}Se_{60}$ glass were formulated. The glasses were made from reagent grade materials using the previously described procedure. Annealed glasses were ground and polished and their infrared transmission was measured to determine the effect of impure batch constituents. Composition No. 28 had a very porous structure probably due to insufficient mixing during the rocking operation. The other two glasses (29 and 30) possessed the lustrous dark appearance of TI 1173. Transmission characteristics of these polished glasses were measured on a Perkin Elmer Infrared spectrophotometer and the transmission curves are presented in Figures 1 and 2.

When studying these transmission curves, it should be remembered that these glasses were prepared using reagent grade materials. The erratic pattern in Figure 1 is due to noise background from the instrument. The noise was dampened while running



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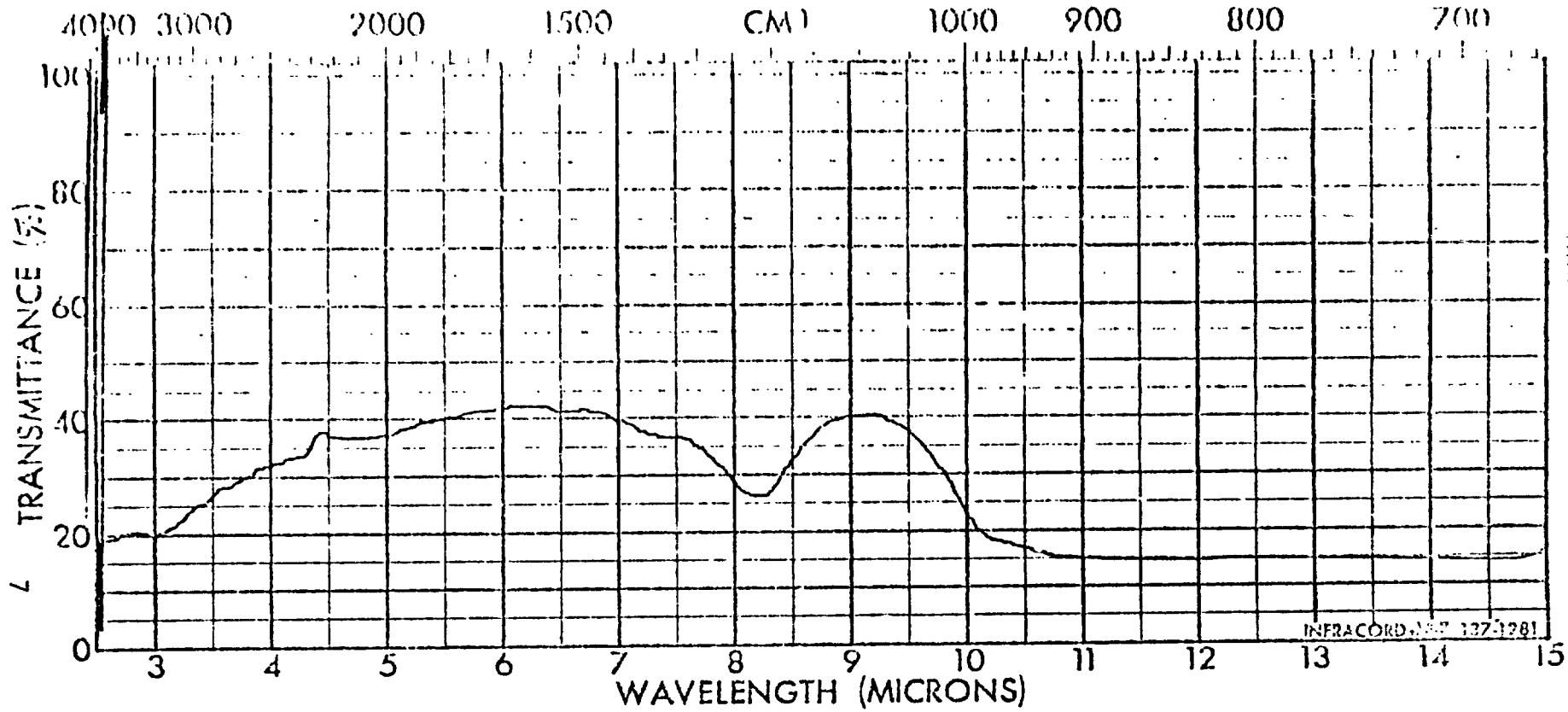
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE 29, 10 gram		1.	Erratic lines on the
$Ge_{28}Sb_{12}Se_{60}$	PURITY Low Reagent Grade, 99.5%	2.	pattern are due to
	PHASE	DATE 3/19	instrument noise.
	THICKNESS 2 mm	OPERATOR	

SPECTRUM NO. ___ SAMPLE ___

Figure 1 Infrared Transmission



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE 30		1.	
$Ge_{28}Sb_{12}Se_{60}$	PURITY Reagent Grade, 99.5%	2.	
	PHASE	DATE 3/19/75	
	THICKNESS 2 mm	OPERATOR	

SPECTRUM NO. SAMPLE

Figure 2 Infrared Transmission

the pattern for glass No. 30 and Figure 2 presents a clear pattern. The transmission hump around 8-10 microns is not observed in TI-1173, and is probably characteristic of the impurities in the reagent grade materials.

The experiments described above served to establish the basic processing parameters of $Ge_{28}Sb_{12}Se_{60}$ glass using precursor materials of reagent grade purity. The work described in the following sections deals with the use of high purity precursors.

3.2 Precursor Treatment Experiments

In this phase of the program the experimental techniques developed at Texas Instruments, Inc. to increase the purity level of the as-received precursor powders were adapted for the processing of IITRI chalcogenide glass.

Ultra high purity powdered materials (Ge, Se and Sb all of purity 99.999%) were procured. Table 1 presents suppliers' analyses of the high purity materials. The surface impurities primarily surface absorbed oxygen, was removed by vacuum distillation. In this technique, the materials were sealed separately in an evacuated ampoule. The ampoule was then transferred into a vertical tube furnace. The lower (metal containing) end of the tube was heated. The absorbed oxygen was driven off, and collected at the cold upper end of the ampoule. The ampoule was held overnight at the treatment temperature, which was much lower than the melting point of the particular material being treated. For germanium the treatment temperature is 450°C, for antimony 400°C, and for selenium it is 150°C.

The vacuum distilled materials were transferred into a dry argon-filled glove box, and a stoichiometric batch composition corresponding to $Ge_{28}Sb_{12}Se_{60}$ was formulated. The weighed batch composition was then put into a clean and dry quartz ampoule. The ampoule was evacuated to remove possible

Table I Suppliers' Analyses of the High Purity Materials

Material	Percent Purity	Form	Supplier
Germanium	99.999	Powder	Atomergic
Germanium	99.999	Bar	Eagle-Picher Industries, Inc. Quapaw, Oklahoma
Selenium	99.999	Powder	Atomergic
Selenium	99.99	Pellet	Kawechi-Berylco Industries New York, New York
Antimony	99.999	Powder	Atomergic
Antimony	99.999	Bar	Cominco American, Inc. Spokane, Washington

oxygen contamination by placing it under vacuum (4.5×10^{-4} Torr) for 16 hours, after which it was sealed with a torch.

The batch inside the sealed ampoule was compounded by melting in a rocking furnace for 15 hours at 820°C, followed by air quenching. The quenched glass was again remelted in an inert atmosphere of argon, and the glass was annealed from 275°C to room temperature in 10 hours.

Ten glasses compounded using the above procedure all exhibited the characteristic metallic lustre of the TI-1173 glass. They were ground and optically polished, and their optical transmission in the infrared region were measured.

None of these glasses showed any transmission in the infrared region of interest. Samples of the 'as received' and vacuum distilled powder precursor materials were analyzed by the Center for Trace Characterization, Texas A & M University, College Station, Texas. Their analyses indicated that the concentration of oxygen in the 'as received' high purity selenium powder was 275 ± 15 ppm, and that this was only reduced to 250 ppm after vacuum distillation.

Discussions with the Texas Instrument, Inc. technical group (Reference 4) indicated that although the high purity (99.999%) germanium, antimony, and selenium powders are free from metallic impurities, the purity level drops considerably when all the elements including oxygen are taken into account. The purity of the fabricated form of material such as powder, is considerably lowered due to the high surface area available for adsorption of O_2. The oxygen contamination would also be present in non-powdered forms such as bar or pellet; however, it would be several orders of magnitude lower due to smaller surface area of the bar or pellet. Therefore, it was recommended that the starting materials should be of high purity (99.999%) and in the form of bars or pellets.

Based on these analyses, it was decided to fabricate the $Ge_{28}Sb_{12}Se_{60}$ glass using commercially available high purity bars or pellets. Further experiments on the precursor treatment of the as-received materials (in the form of bars and pellets) were set aside until the evaluation of glasses compounded without the treatment was performed. The rationale for this is if high ir-transmitting glasses could be compounded without the treatment, then this would be a cost-effective approach in the eventual space processing of the glass.

3.3 Processing and Evaluation of High Purity $Ge_{28}Sb_{12}S_{60}$ Glasses

Infrared transmitting $Ge_{28}Sb_{12}Se_{60}$ glasses were processed and evaluated. The glasses were processed using the high purity (99.999%) germanium, selenium and antimony in the form of bars and pellets. Table 1 presents the pertinent details on these materials. Stoichiometric batch compositions corresponding to $Ge_{28}Sb_{12}Se_{60}$ were formulated. Table II (Page 15) presents the composition and processing parameters investigated. An optimum stepwise procedure for processing the glass by conventional earth methods was also established. During the processing of the glass several improvements were made in the vacuum system. The processed glasses were evaluated for their infrared transmitting characteristics.

3.3.1 Glass Processing Procedure

Based on our own experiences and consultations with Texas Instruments, Inc. (Reference 4), a glass processing procedure for high purity bars and pellets was adapted. The following sequential procedure outlines the steps:

1. All glass batch preparation was performed in a glove box having a continuous flow of pure and dry argon gas.

2. Individual constituents (chunks or pellets or germanium, selenium and antimony) were accurately weighed and transferred to a clean and dry quartz ampoule purged with the argon gas.

3. The ampoule was heated to 105°C and simultaneously placed under vacuum for 16 - 24 hours; then sealed.

4. The sealed ampoule was transferred into a rocking furnace. The temperature was gradually raised to about 600°C in four hours and held constant for 1-1/2 hours.

5. The temperature was raised to 700°C in one hour and held constant for another half an hour.

6. The temperature of the rocking furnace was raised to the final reaction temperature (800-900°C) in one hour and held constant for 16 to 24 hours.

7. The temperature of the rocking furnace was lowered to 600-700°C and held at that temperature for 1/2 to one hour.

8. The glass was quenched (inside the sealed ampoule) to room temperature.

9. The ampoule containing the glass was annealed at 275°C for 16 hours.

10. The annealed glass was removed and ground and polished using the standard optical glass polishing technique and care.

In the course of establishing this procedure it was determined that the use of double cold-trapped oil diffusion vacuum system was superior to the use of a turbo-molecular system. Figure 3 presents the details of the oil diffusion system which provided vacuum as low as 10^{-6} Torr.

3.3.2 Measurement of IR Characteristics of the High Purity Processed Glasses

All the processed high purity glasses were evaluated in terms of their infrared transmission characteristics. The infrared transmission of the ground and optically polished samples (5 mm thick) were measured in the 2-15 micron region. All measurements were made using a Perkin Elmer Model 21 spectrophotometer.

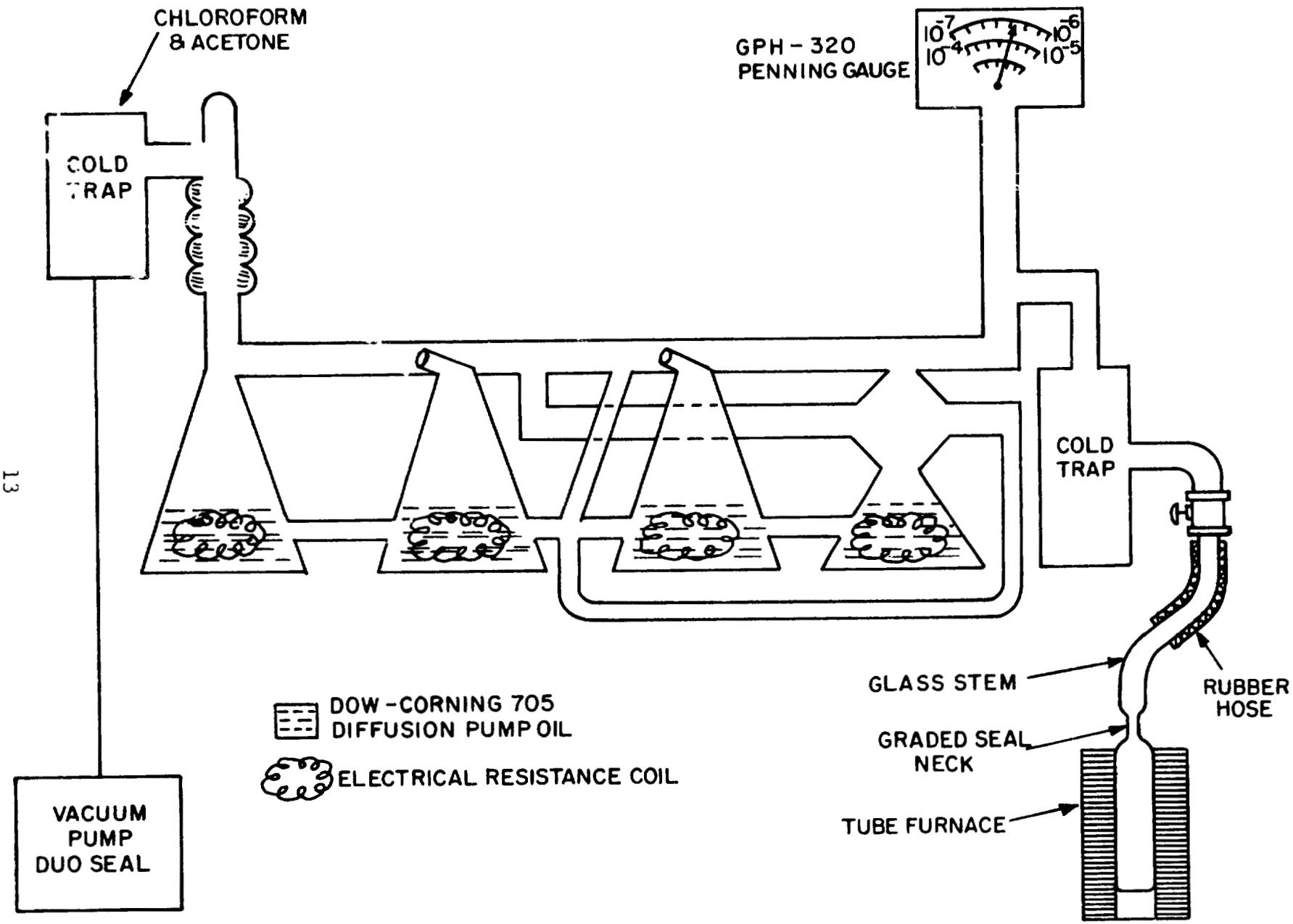


Figure 3 Diffusion Vacuum Pump System

It has been observed that this model spectrophotometer quite often develops background noise and other instrument related bands which interfere with the actual transmission characteristics of the sample. For this reason, before measuring the transmission of the glass sample, the spectrophotometer was run blank (without the sample) so as to locate the background noise and other instrument related absorption or inverse absorption bands. It is a normal practice not to run the blank at 100% full-scale so that the magnitude of the inverse absorption bands can be established. Blank runs were made at 90% full-scale and the instrument related bands were observed at 4.25, 9.75, 12.5 and 15 micron regions. Before measuring the transmission characteristic of the glass sample, the scale was returned to 100% full-scale so as to measure the true transmission.

The internal inhomogeneities, possible impurities and optical defects in the glass were viewed using an infrared microscope (Model D manufactured by Research Devices, Inc.). The microscope is attached with a Polaroid camera. This added facility has greatly improved our capability by permitting us to qualitatively identify the causes of poor ir-transmission. The microscope was successfully used to analyze the internal homogeneities and improve the processing techniques so as to maximize the optical transmission of $Ge_{28}Sb_{12}Se_{60}$ glass.

3.3.3 Evaluation of High Purity Glasses

Up to the time of writing this report, a total of 12 high purity glasses have been processed and evaluated. Table 2 presents the details which include the composition and the processing parameters. The processing parameters include 1) the surface-oxygen removal temperature 2) the vacuum pressure 3) the molten glass reaction temperature, 4) the molten glass reaction time, 5) the density of the processed glass, and 6) the optical transmission characteristics of the processed

FOLDOUT FRAME 1

Table II Composition, Pr
Characteristics

Run No.	Composition (Grams)				Surface O_2 Removal Temp. °C	Pressure Torr.	Reaction Temp. °C	Time at Reaction Temp. Hours	Density of Glass Grms/cc
	Ge	Sb	Se.	% Dopant Al.					
TI-1173	$Ge_{28}Sb_{12}Se_{60}$			--	--	--	--	--	4.71
41	3.75	2.7	8.55	--	200	18.0×10^{-3}	845	16	--
42	3.75	2.7	8.55	--	101	12.5×10^{-3}	845	16	5 06
43	3.75	2.7	8.55	--	175	8.3×10^{-4}	884	16	4.92
44	3.75	2.7	8.55	--	105	5.0×10^{-5}	884	16	4.94
45	3.75	2.7	8.55	0.33	105	3.5×10^{-5}	867	16	4.79
46	3.75	2.7	8.55	0.10	105	2.6×10^{-5}	884	16	4.69
47	3.75	2.7	8.55	0.05	105	1.6×10^{-5}	884	16	4.69
48	3.75	2.7	8.55	0.10	105	1.2×10^{-5}	884	41	4 62
49	3.75	2.7	8.55	0.10	105	1.0×10^{-5}	884	21	4.71
50	3.75	2.7	8.55	0.05	105	1.5×10^{-5}	834	21	4.61
51	3.75	2.7	8.55	0.10	105	8.3×10^{-6}	825	21	4.68
52	3.75	2.7	8.55	0.10	105	8.3×10^{-6}	800	66	4.70

FOLDOUT FRAME 2

ocessing Parameters and
of $Ge_{28}Sb_{12}Se_{60}$ Glasses.

Transmission 2-8μ %	Transmission 8-14μ %	REMARKS
60-63	63-58	Small Absorption Band Around .3μ.
60-60	--	Absorption Bands at 2.9, 6.3, 8-0 and a Bell Shaped Band 11-14μ.
51-52	52-50	Absoroption Band Between 12-14μ.
41-42	42-	Strong Bands @ 2.9,3,8 and a Bell Shaped Band 11-14μ.
44-45	45-42	Bell Shaped Band Between 11.5-14μ.
28-34	34-18	
60-63	63-52	No Absorption Bands.
42-44	44-40	No Absorption Bands.
41-41	41-40	No Absorption Bands.
50-54	54-48	No Absorption Bands.
46-48	48-42	No Absorption Bands.
51-53	53-48	No Absorption Bands.
60-63	63-52	No Absorption Bands.

chalcogenide ($Ge_{28}Sb_{12}Se_{60}$) glass in the 2-8 micron and 8-14 micron regions. Complete optical transmission pattern of these 12 glasses are presented in Appendix A, (A1-A12). Density and optical characteristics of TI-1173 glass determined at IITRI has also been included (Figure A13).

Glass composition No. 41 and 42 were fabricated using a vacuum of 12 -18 x 10^{-3} Torr which was not sufficient to drive out all the oxygen and oxygen-related impurities from the system. This resulted in absorption bands at 2.9, 6.3, 8.0 microns and a strong bell-shaped band between 11-14 micron regions, (see Figure A1 and A2). Figure 4 presents a picture of glass taken by an infrared microscope. Dark spot in the picture shows the areas of inhomogeneities and directly related to the processing defects of the glass.

Glass composition Numbers 43 and 44 were fabricated using the diffusion pump vacuum system as described in Figure 3. This improved vacuum system was intended to eliminate the oxygen-related absorption bands. However, the transmission characteristics of these glasses in Figures A3 and A4 again exhibited strong absorption bands. This phenomenon was discussed in detail with Texas Instrument, Inc. staff (Reference 4). It was emphasized that the vacuum system alone would not be sufficient to eliminate all the oxygen and related impurities. In their experiences, it was necessary to add pure aluminum which acts as a getter for oxygen. The quantity of aluminum should be determined by actual experimentation.

Based on these extremely helpful discussions and suggestions, several glasses were formulated in which selected quantities of aluminum were added.

Composition No. 45 included 0.05 grams of aluminum which corresponds to 0.33% of the total batch contituents (15 grams). The glass was reacted for 16 hours at 867°C.

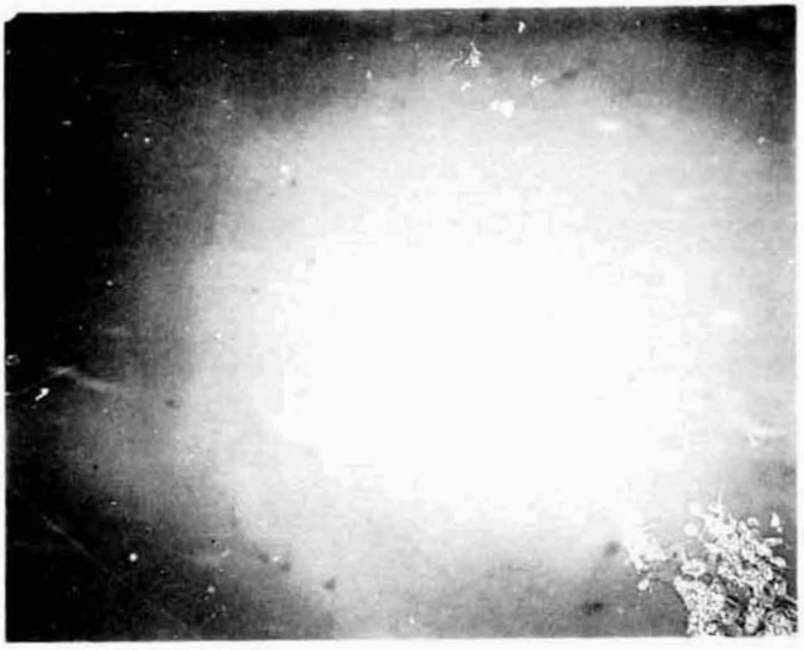


Figure 4 Infrared Microscope Picture of IITRI-4 $Ge_{28}Sb_{12}Se_{60}$ Glass

The resulting poor transmission indicated the possibility that the quantity of aluminum added (0.05 grams) as a dopant was too high (Figure A5).

In composition No. 46 and 47 reduced quantities of aluminum were added. These (reduced quantities) were 0.015 grams and 0.008 grams corresponding to 0.1% and 0.05% respectively. These glasses were reacted for 16 hours at 884°C. Figure A6 and A7 presents the infrared transmission of these glasses. Composition 46 had an excellent transmission of 60% whereas composition 47 had a relatively low transmission of 42%. These experiments showed that there exists an optimum quantity of aluminum that should be added to achieve a maximum optical transmission in the glass. Based on the purity of raw materials used in this study (99.999%) and the quantity of the batch size, the results indicated that 0.0158 grams (0.1%) of aluminum should be incorporated to eliminate the -OH and oxygen related absorption bands.

In space processing, time is a critical factor. Hence, it was felt necessary to establish the effect of longer reaction time on the optical transmission characteristics of the glass. Run No. 48 was processed by keeping the aluminum content (0.0158 grams) and reaction temperature (884°C) constant and increasing the reaction time to 41 hours. The result presented in Figure A8 showed that under these controlled conditions the increased reaction time did not improve the transmission characteristic of the glass. Further, it was also observed that higher reaction temperatures would initiate a reaction between the container (quartz ampoule) and the processed glass. This effect was quite pronounced in presence of large quantities of aluminum.

At this stage a series of experiments were conducted to establish the relationship between the glass reaction time and

temperature. The purpose of these experiments was to correlate the time/temperature factors with 1) power availability in the in-space processing chamber, 2) time constraints of a given space processing mission, and 3) the operational characteristics of the acoustic levitator.

Four glasses (Nos. 49 to 52), were processed at progressively lower temperatures (884, 834, 825, and 800°C) while keeping the reaction time at a constant 21 hours, except in run No. 52 where visual observation indicated a need for a longer reaction time of 66 hours. The infrared transmission characteristics of these glasses (A9 to A12) indicated a definite relationship. At lower reaction temperatures, the molten glass requires a longer reaction time to obtain a maximum transmission of the glass. Composition No. 52 provides a good example of this phenomenon. The glass was processed at 800°C for 66 hours, and the compounded glass had a transmission around 63%. Work is now in progress to varify and establish the limitations of these parameters.

These experiments have indicated that IITRI produced $Ge_{28}Sb_{12}Se_{60}$ glasses (conventional 1-g processing) are comparable in quality to Texas Instruments, Inc. TI-1173. Our efforts are now directed to those aspects of processing that will eventually be used in space to improve ir-transmission.

3.4 Acoustic Levitation Experiments

The first annual report on this program described the initial acoustic levitation experiments (Reference 5). These experiments entailed the room temperature levitation of various density materials to gain experience with the device. Figure 5 exhibits the complete acoustic levitator unit. Figure 6 presents the room temperature levitation of a polystyrene sphere. During the early part of the current reporting period various components of the system were returned to Intersonics, Inc. for subsequent

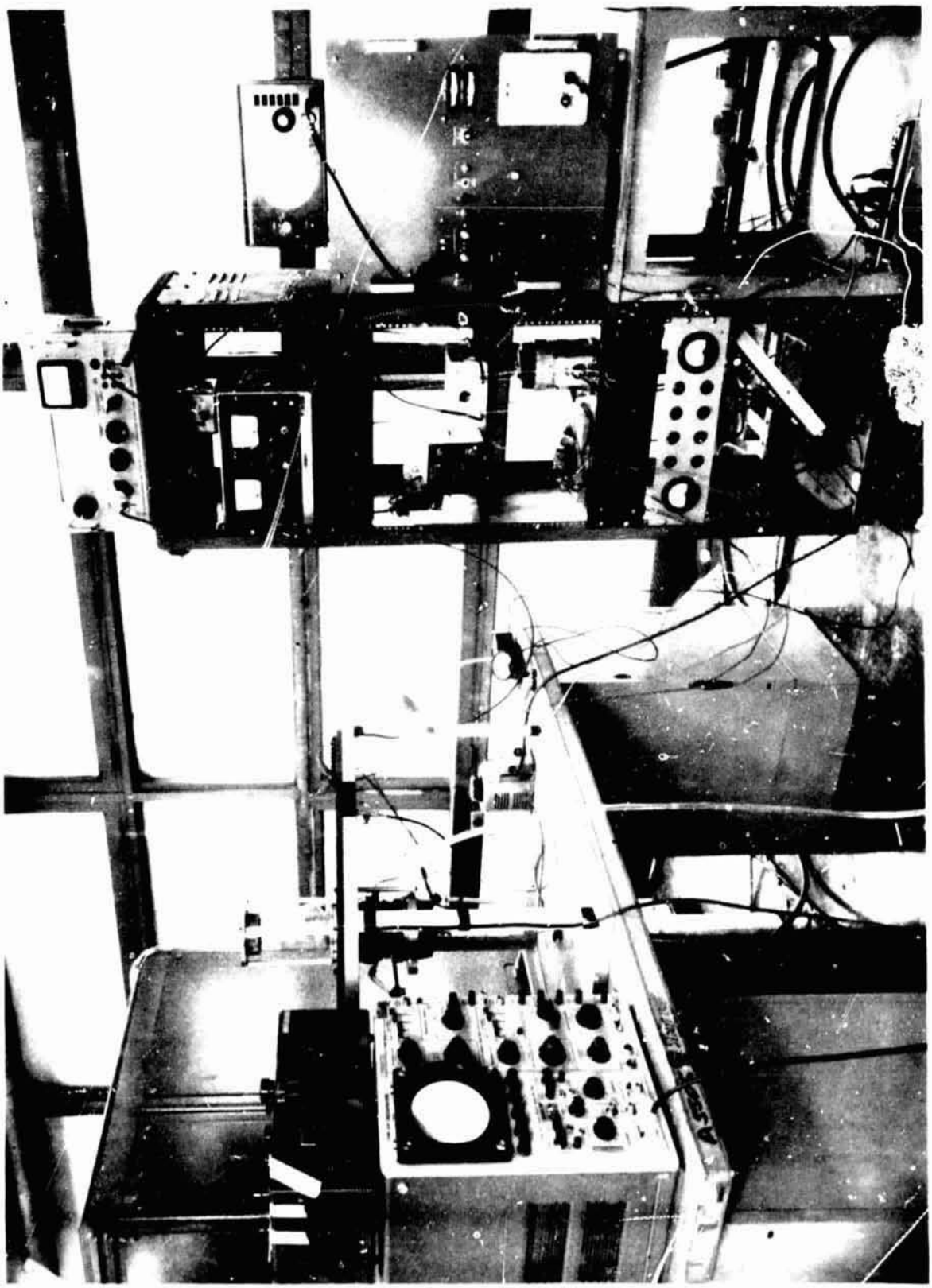


Figure 5 Acoustic Levitator Unit

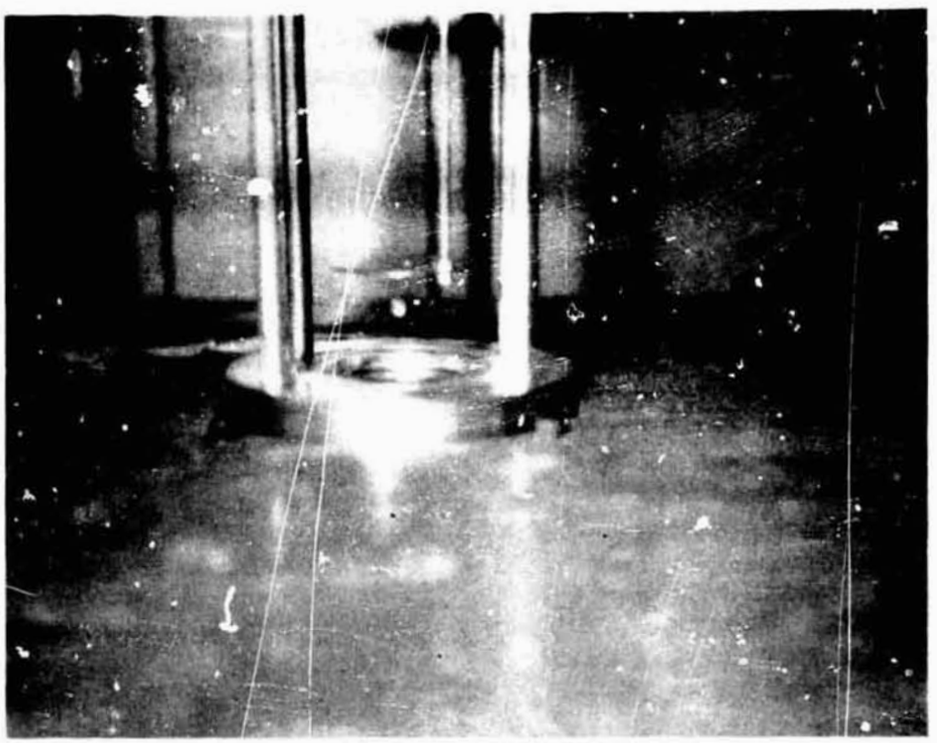


Figure 6 Room Temperature Levitation of Polystyrene Sphere

Drop Tower testing at MSFC. R. R. Whymark reports (Reference 6) that these experiments were very successful. Suitable sample injection and stable levitation were obtained for 1/4 and 3/8-inch diameter aluminum spheres at ≃ 800°C under the short duration of near-weightlessness attained during the tests. It is significant that the power required for this levitation was very small as compared to the power necessary for 1-g earth levitation. This indicates that the problems of stability and control that have been experienced in the earth experiments (Reference 5) will be greatly diminished in space.

When the levitator system components were returned to IITRI, a series of experiments were initiated. These experiments included high temperature levitation of molten polystyrene, and room temeprature levitation of commercial As_2S_3 glass. These experiments lead to several modofications of the device, and are described as follows.

3.4.1 High Temperature Experiments

Experiments were conducted to study the high temperature control and stability of the intersonics, Inc. acoustic levitator. Figure 7 shows the furnace/chamber system. Polystyrene discs about 1/4" in diameter and 1/16" thick were levitated at room temperature. When the temperature was raised to ~ 400°F (~200°C), stable levitation was maintained. However, when enough time has elapsed to melt the polystyrene disc, the molten disc would splatter out of the minimum energy well and splash on the silica tube. Reducing the size of the specimen did not improve this situation. Apparently, when the molten material flattens and spreads out, it exceeds the boundaries of the minimum energy nodal point. Therefore larger minimum energy nodal points are required.

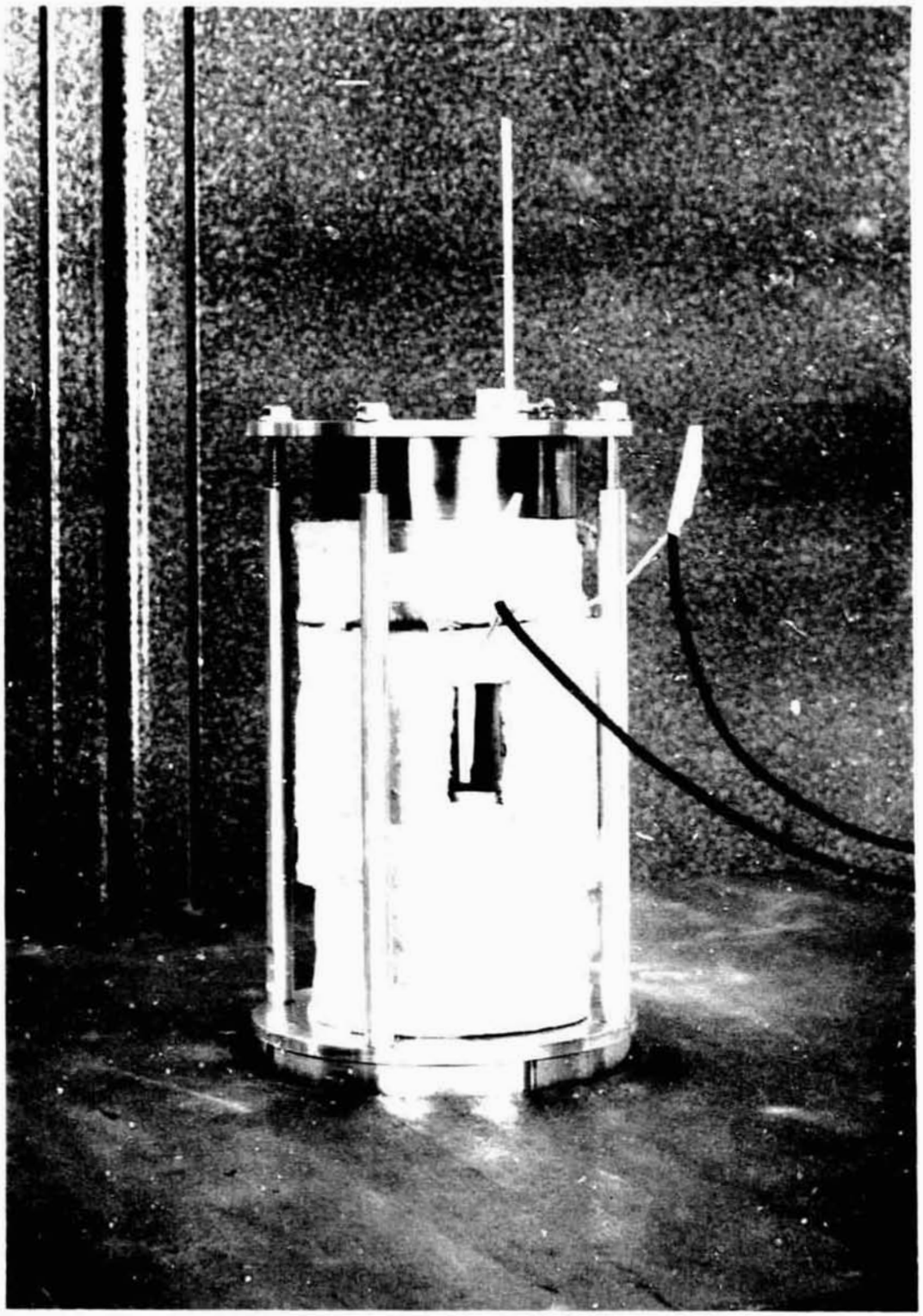


Figure 7 Accustic Levitator - Furnace/Chamber System

3.4.2 As_2S_3 Glass Experiments

Room temperature levitation experiments were also conducted using As_2S_3 (arsenic trisulphide) glass developed during the course of this program.

Our room temperature As_2S_3 experiments resulted in only short periods of successful levitation and frequent burn-out of the levitator drive coil due to the high power level required during operation. These experiments led to several modifications of the device and general observations regarding its operation which are as follows:

1. Water-cooled levitator head: In earlier experiments with low density materials (0.9 gm/cc) it was determined that the addition of convective cooling permitted operation at higher power levels. For the higher density As_2S_3 glass (3.4 gm/cc), this cooling method was insufficient. Water cooling was then added (figure 8). This resulted in successful operation at higher power levels, but not high enough to be adequate for long term As_2S_3 melting experiments.

2. Bottom Screen: The purpose of the wire mesh screen located near the bottom of the levitation chamber (Figure 9) was to assist in the acoustic 'lift-off' of the sample. It has been determined that use of a stinger type wire device instead of the screen permits more suitable introduction of the sample into the acoustic field. Additionally, we have found that elimination of the wire screen results in more stable levitation.

3. Chamber diameter/vibrator diameter: The levitator was provided with a chamber consisting of a 2-1/4 inch diameter silica tube. R. R. Whymark had suggested (Reference 7) that a portion of the stability problems we had encountered were perhaps due to the small size of this chamber relative to the vibrator head diameter causing sound wave interference patterns. To check this, we tried to levitate 5 mm glass beads using a

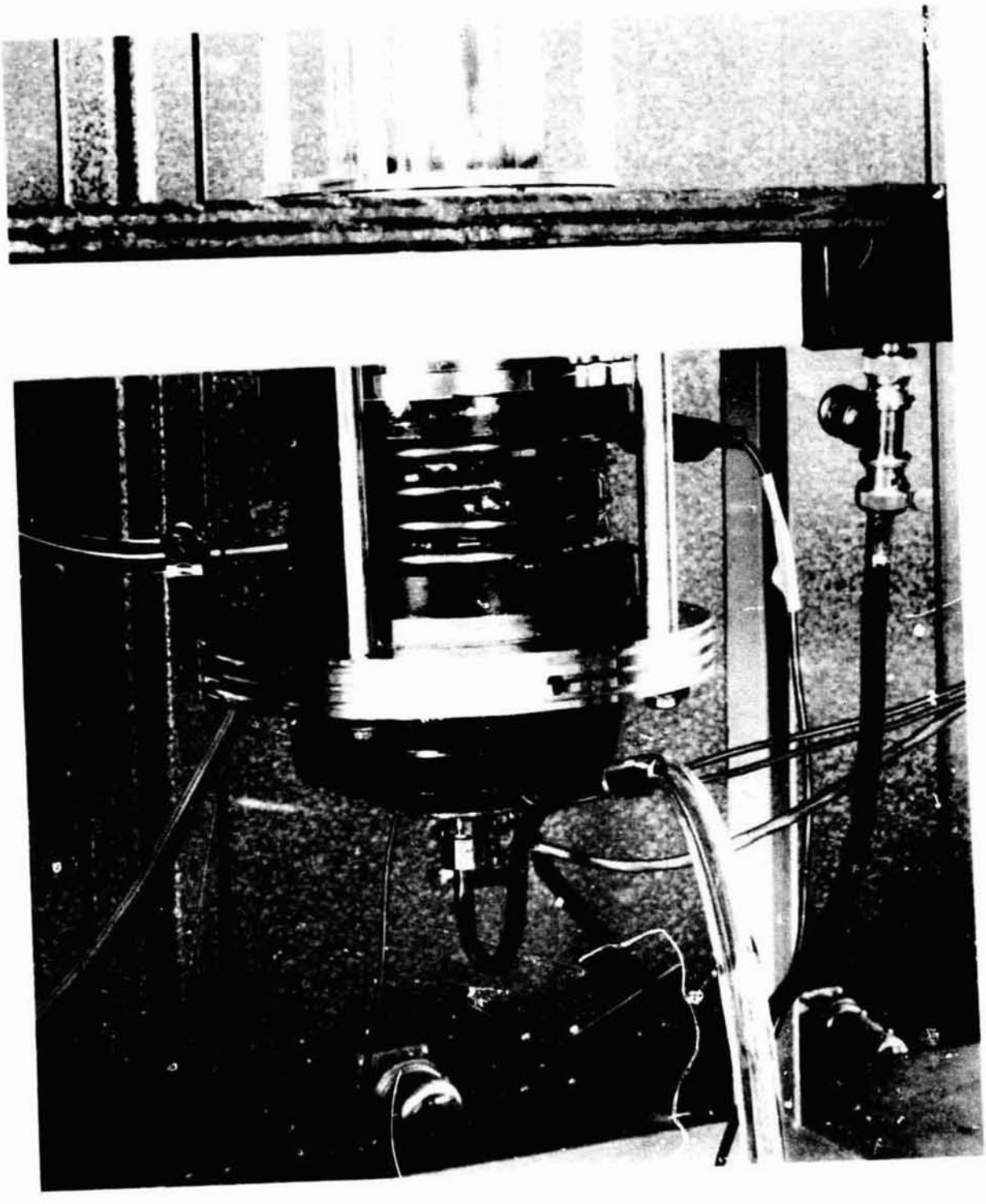


Figure 8 Acoustic Levitator Head with Water-Cooled Coils

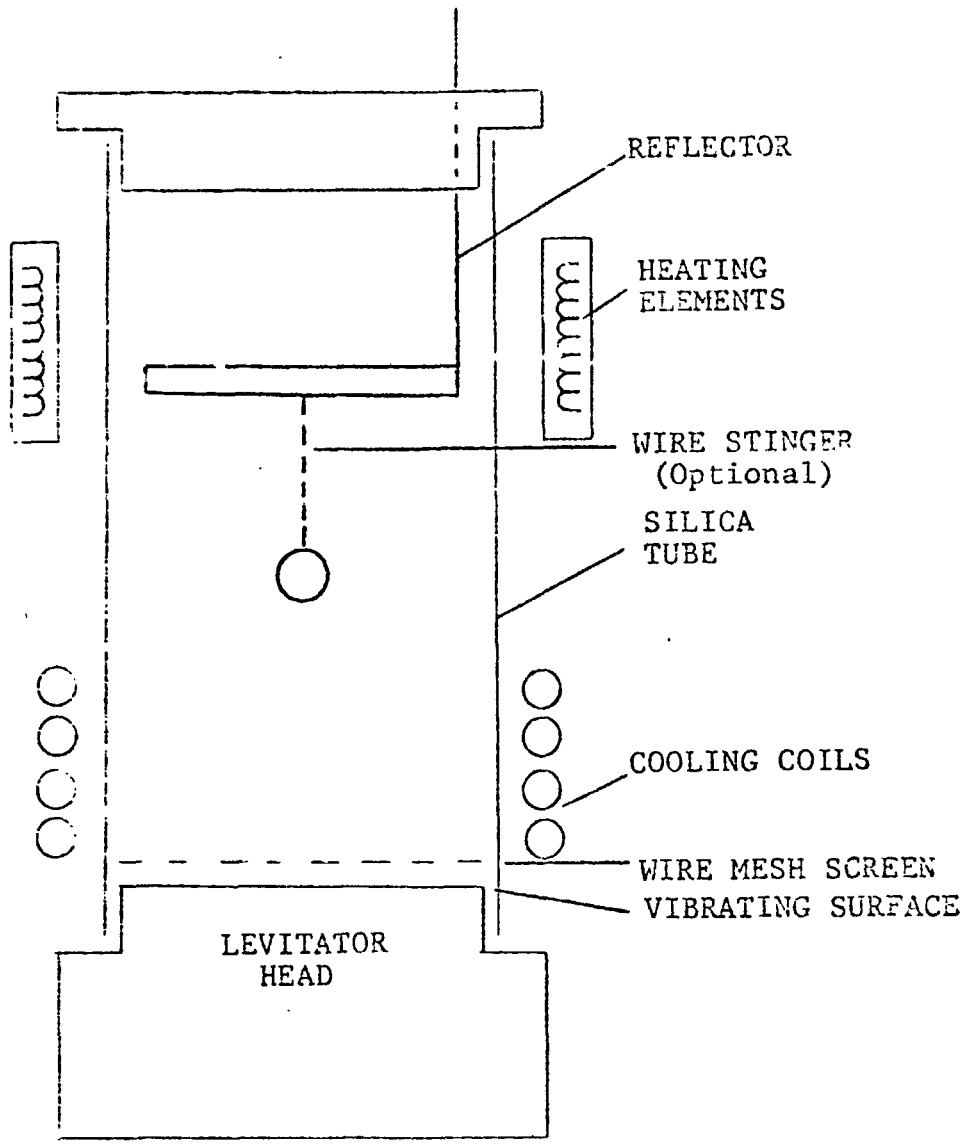


Figure 9. Levitation Melting

4-inch diameter chamber. This resulted in increased stability and successful levitation for periods of time up to 15 minutes.

4. Plunger Frequency: Another operational problem that was observed with the acoustic levitator was an unstable plunger oscillation frequency. Operating properly, the plunger had a free air resonance of 20 KHz as established at Intersonics, Inc. However, during our testing it was observed that this frequency varied unpredictably between 15-20 KHz, necessitating continual retuning of the feedback circuit. This situation was probably a major cause of our inability to levitate in a stable manner for long periods of time. It is believed that more stable electronics are required to solve this problem.

5. Reflector Position: Referring to Figure 9, we have observed that levitation would improve with decreasing distance between the reflector and the vibrating head. For our application, a sufficiently large reflector to vibrator distance will be necessary to accommodate suitable heating and cooling sections within the chamber.

All these factors were discussed in detail with the Intersonic, Inc. and MSFC personnel at a July 10, 1975, meeting held at IITRI. Both had recognized the limited capability of the existing unit. The existing MSFC/Intersonic device was not designed for long term levitation in a 1-g field. It was determined that to meet the requirements of IITRI's present ground-based program, modification of the device was necessary. IITRI's general requirements for the levitation/position control device that were discussed with Intersonics and MSFC personnel are listed as follows:

1. Stability and control during long term (8-10 hour) experiments.
2. Operation under 1-g conditions.
3. High temperature operation (up to 900°C).

4. Use with typical high density chalcogenide glasses and precursor constituents.

5. Use with solid spherical or disc-shaped samples up to 8 mm diameter; and liquid disc samples up to 4 mm diameter.

6. Use with a purging gas atmosphere.

7. Ability to change the shape of liquid samples in a controlled manner as described by Whymark (Reference 6).

Negotiations are currently in progress between MSFC and intersonics, Inc., for the design and construction of an approved device that will meet IITRI's requirements. It is anticipated that such an improved device will be supplied GFE to IITRI during our next year's work with $Ge_{28}Sb_{12}Se_{60}$ glasses.

4.0 CONCLUSIONS

Several conclusions have been reached during this phase of the program. They are outlined as follows:

1. Laboratory experiments conducted at IITRI have established the techniques, processes and equipment necessary for the production of high purity chalcogenide glasses. This gives IITRI a baseline from which to work -- in developing the techniques that will eventually be used in space.

2. The processing techniques developed at Texas Instruments, Inc. have been successfully adopted for IITRI -- $Ge_{28}Sb_{12}Se_{60}$ glass. These processing techniques have been adopted within the constraints of 1-g environment (by conventional earth manufacturing methods).

3. The $Ge_{28}Sb_{12}Se_{60}$ glasses that have been processed at IITRI have optical transmission around 63% (5 mm thick) which is comparable to Texas Instrument's $Ge_{28}Sb_{12}Se_{60}$ glasses (TI-1173).

4. Laboratory experiments have established that the use of precursor materials in powdered form increases the oxygen contamination of the processed glass. This indicates that high purity precursor materials in bar or pellet form should be used.

5. Modofications were made at IITRI on the MSFC acoustic levitator in an attempt to improve levitation stability during long-time experiments. Room temperature experiments on As_2S_3 glasses and high temperature experiments on polystyrene were conducted. These experiments have established the need for additional modifications. MSFC personnel are currently pursuing the procurement of such an improved device.

5.0 PLANS FOR FUTURE WORK

In the coming months it is planned to conduct the major portion of the work in the area of acoustic levitation. A few preliminary experiments will also be conducted in the area of chalcogenide fiber optics. This will be a feasibility type of study constituting 1-2% of the total effort. The levitation work will involve various experiments with the $Ge_{28}Sb_{12}Se_{60}$ type chalcogenide glasses to achieve stable, long time (16 hours) acoustic levitation in a 1-g field at temperatures ranging from 25-900°C. These levitation experiments will combine all the aspects of chalcogenide glass production processes developed at IITRI which are applicable for in-space processing.

The first series of experiments will entail the melting of compounded $Ge_{28}Sb_{12}Se_{60}$ glass in the levitation chamber with the sound field on. A stinger support will be utilized. The parameters to be investigated include stability and control of levitation, heating and cooling methods, gas purging methods, and the method of introducing the sample into the sound field.

The next series of experiments conducted involves compounding the $Ge_{28}Sb_{12}Se_{60}$ glass. The purity precursors will be held on a stinger (such as wire) while in the acoustic field. Variables to be studied during compounding will include:

i) Reaction kinetics

ii) Stoichiometry of the glass product relative to the precursor composition

iii) Effect of evolved volatile gasses on the levitation.

iv) Optimum gas pressure necessary for the processing of the glass.

v) Acoustic field strength to sample volume ratio.

vi) Effect of minimal container contact,

vii) Feasibility of non-contact homogenization through the use of cyclic variations in the levitator sound field intensity.

The item regarding non-contact homogenization refers to our "massaging the melt" concept. This entails deforming the molten sample in a cyclic manner while being levitated (a phenomenon that has been observed by Whymark (Reference 6)). This should promote non-contact homogenization of the melt and will replace the contaminating rocking SiO_2 ampoule method used in conventional earth-bound chalcogenide processing. These earth experiments will also be conducted with the aid of a stinger, and will entail determining how the sound field intensity can be varied to change the shape of a low viscosity material being supported by a stinger.

During the course of our work on this program we have become aware that in-space processing would have applications to the fabrication of chalcogenide fiberoptics. A need for such fiberoptics exists in diagnostic medical devices. To date, earth processing of such fibers has resulted in poor quality of fibers due to processing difficulties (Reference 1).

It is IITRI's belief that space processing of chalgonide fibers would lead to high quality of fibers exhibiting improved drawability and dimensional control. During our next year's work on our present program we intend to add on a limited set of experiments that will indicate the feasibility of this hypothesis. A small probe will be used to fiberize molten $Ge_{28}Sb_{12}Se_{60}$ glass positioned in the acoustic levitator. This will be accomplished by the use of a properly located sound attenuation screen in the vicinity of the pulling probe.

6.0 ACKNOWLEDGEMENT

We like to acknowledge the very many helpful suggestions made by Dr. A. R. Hilton, Texas Instruments, Inc., during the course of this work. These have been extremely valuable and is greatly appreciated.

7.0 CLOSURE

Based on the results and conclusions arrived in this year's work, it is our firm belief that substantial progress has been made, in particular, in the area of processing of chalcogenide glasses and adapting the processing parameters for future space processing.

Respectfully submitted,
IIT RESEARCH INSTITUTE

Mir Akbar Ali
Research Engineer
Mechanics of Materials Division

D. C. Larsen
Research Engineer
Mechanics of Materials Division

APPROVED

S. A. Bortz
Assistant Director
Mechanics of Materials Division

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APPENDIX A

(INFRARED TRANSMISSION CHARACTERISTICS OF IITRI $Ge_{28}Sb_{12}Se_{60}$ GLASSES)

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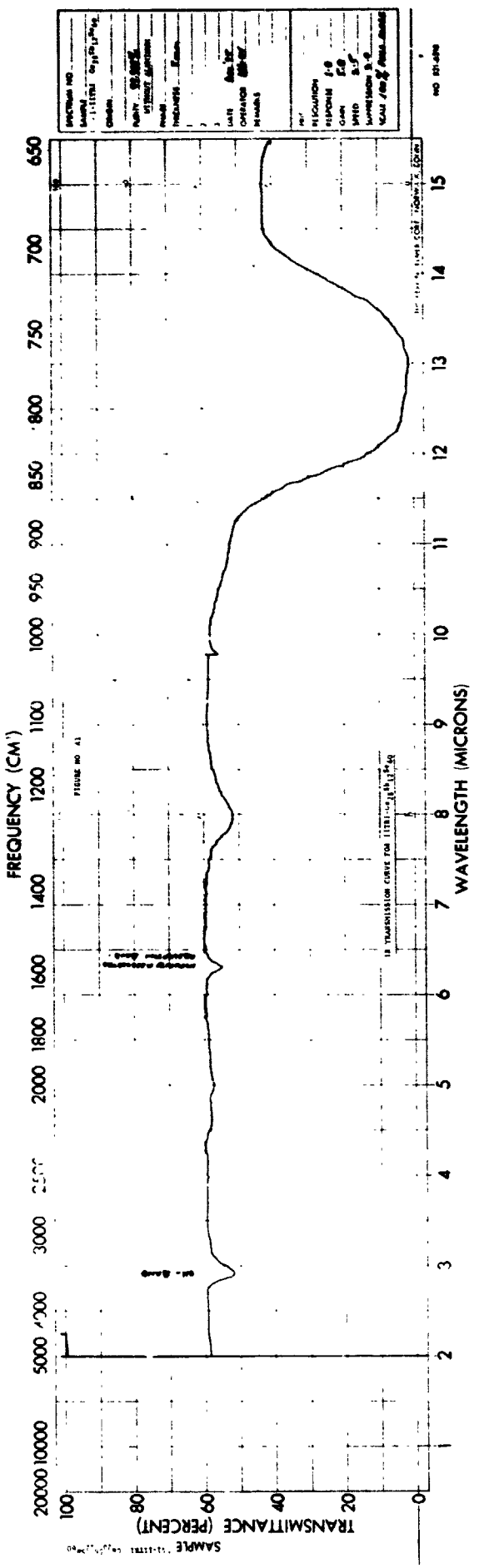

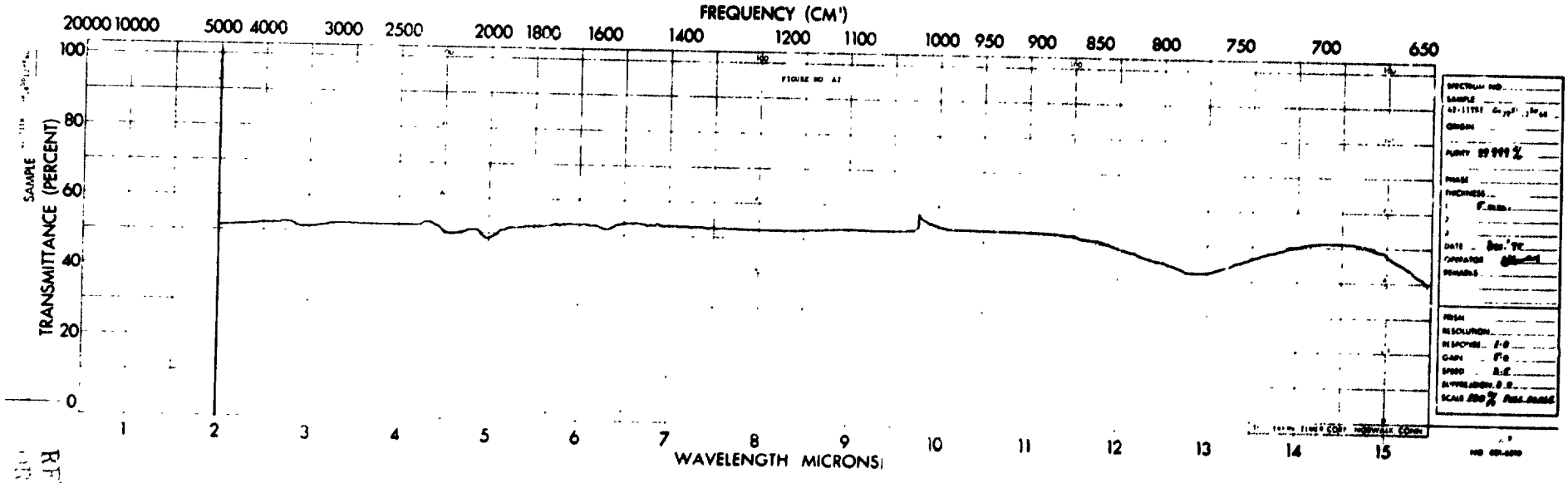
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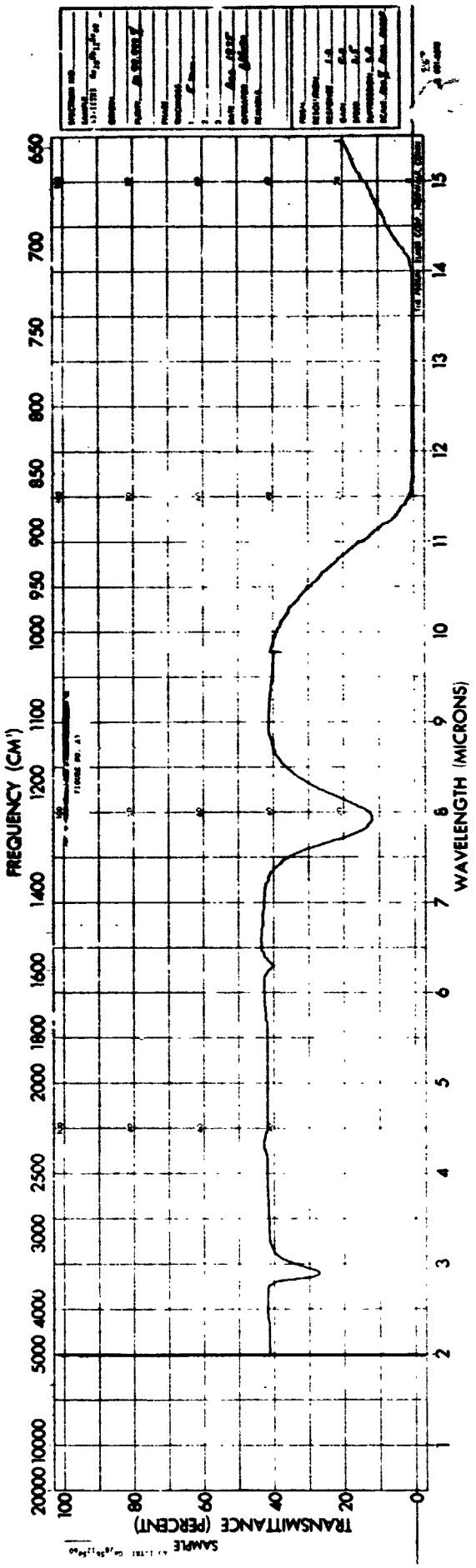

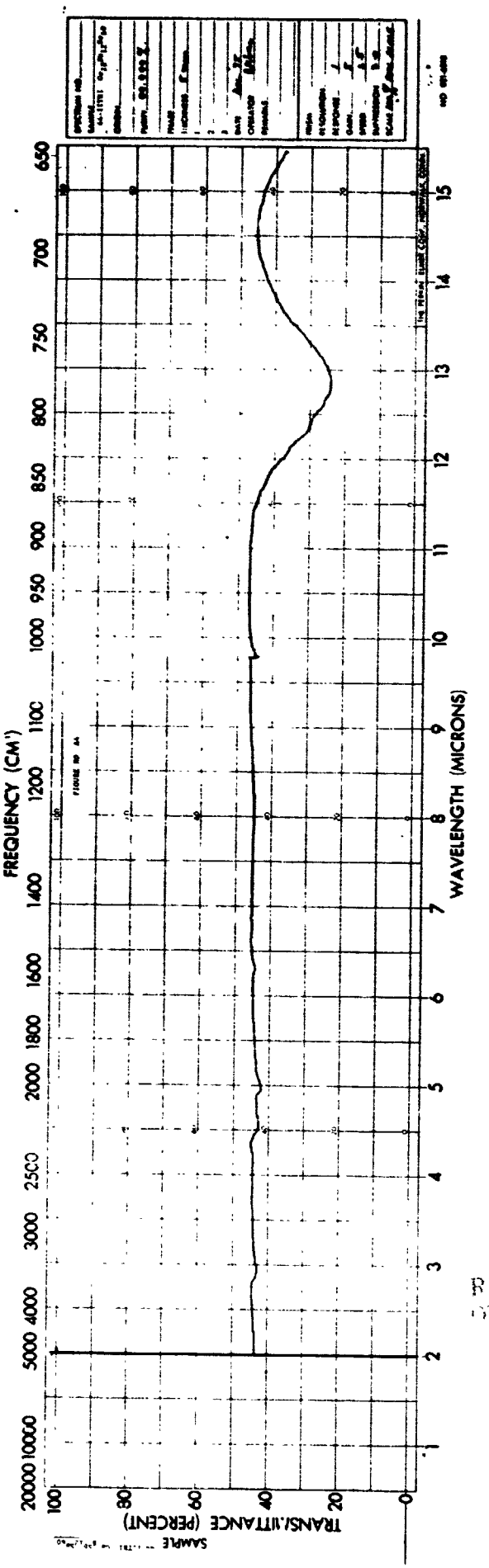
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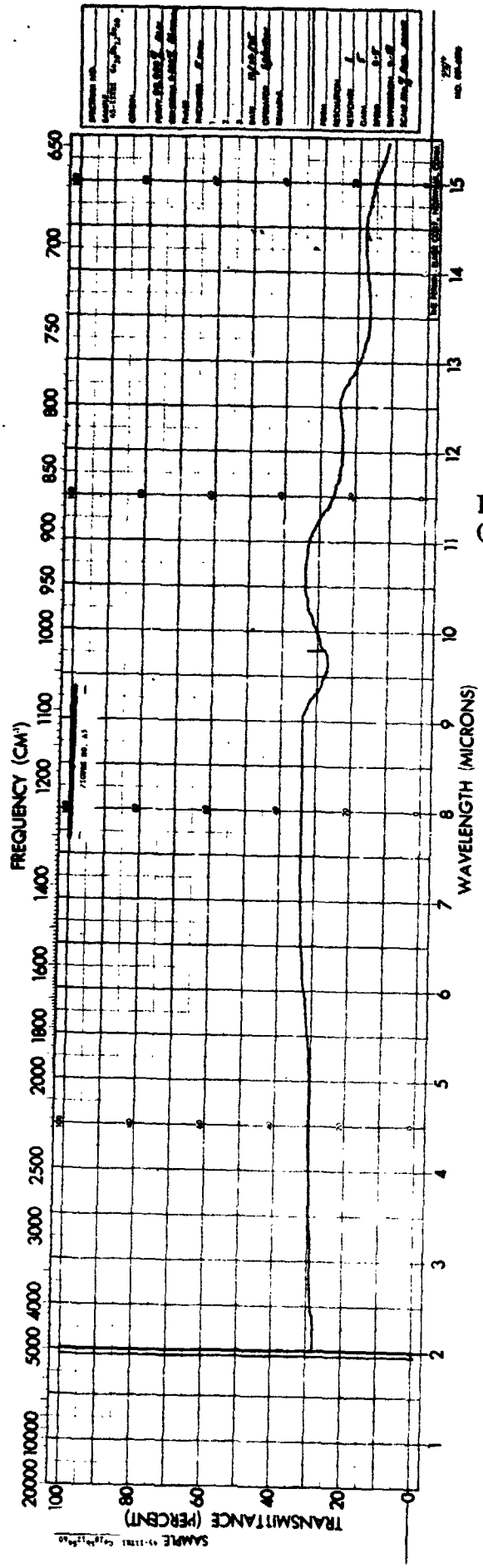

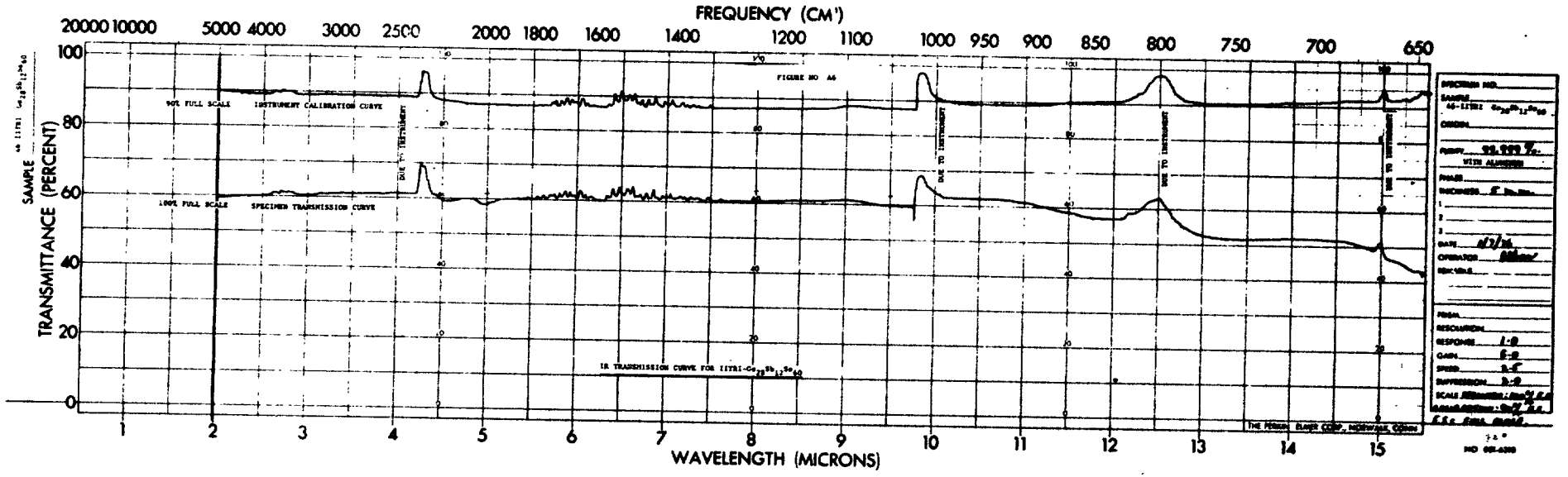
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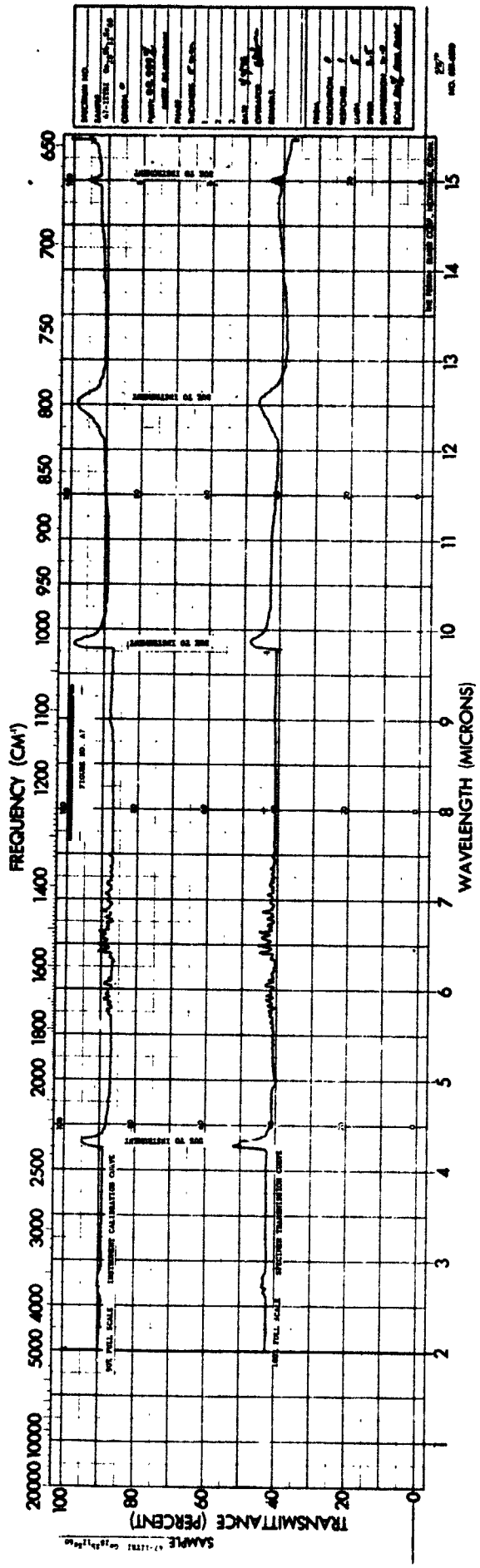

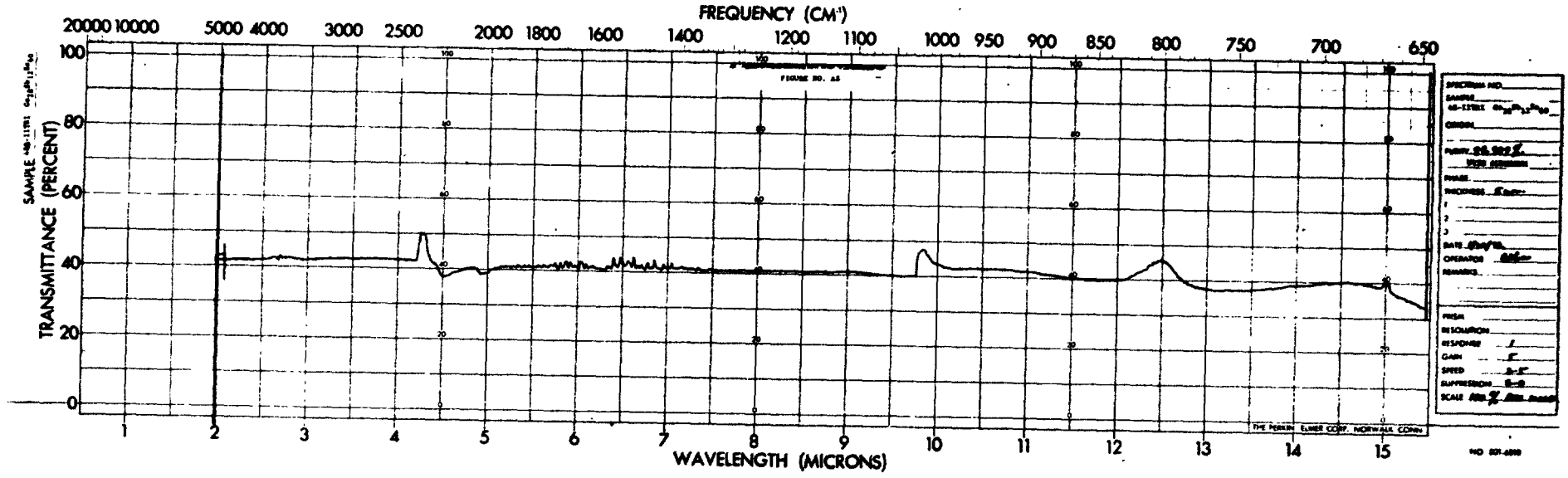
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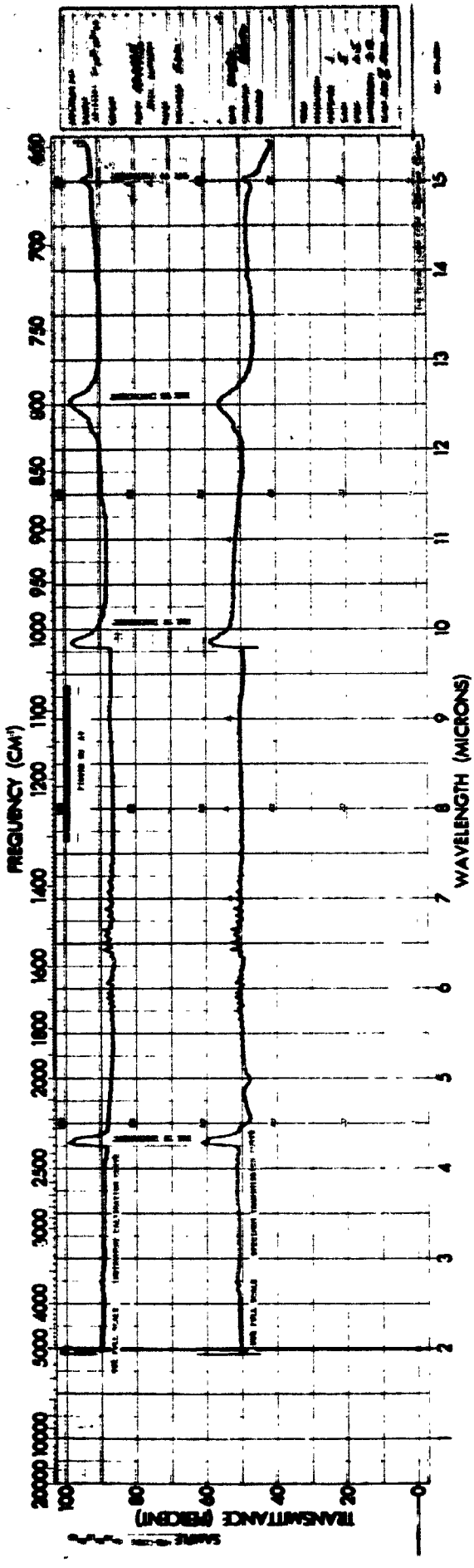
THE PERKIN ELMER CORP. NORWALK CONN.



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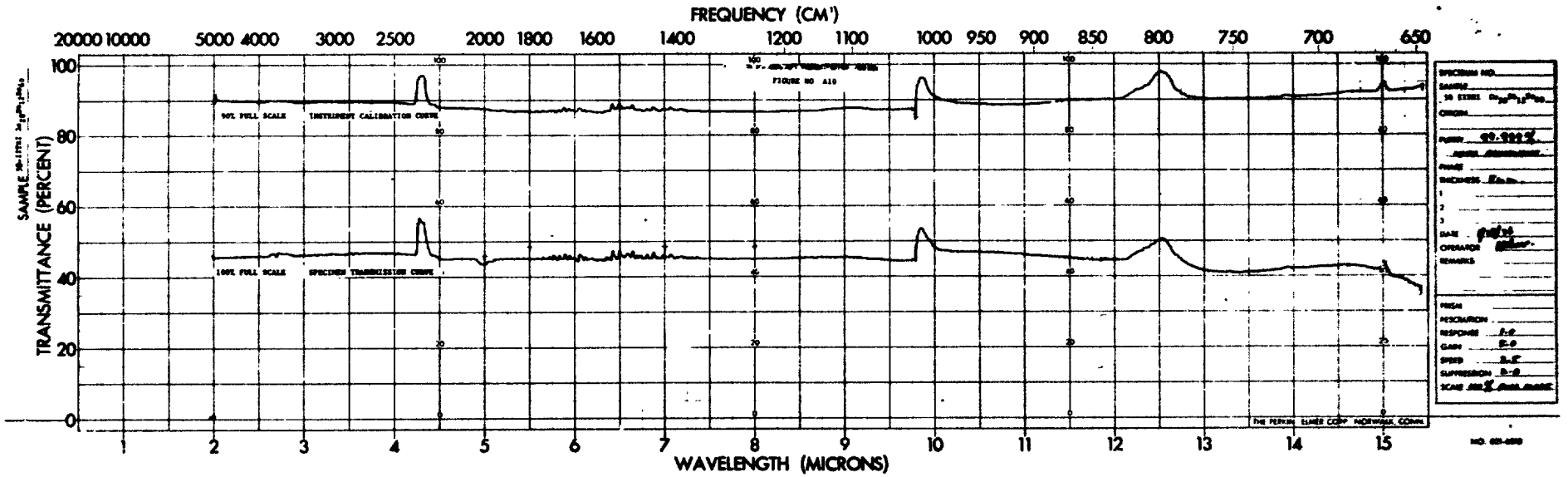
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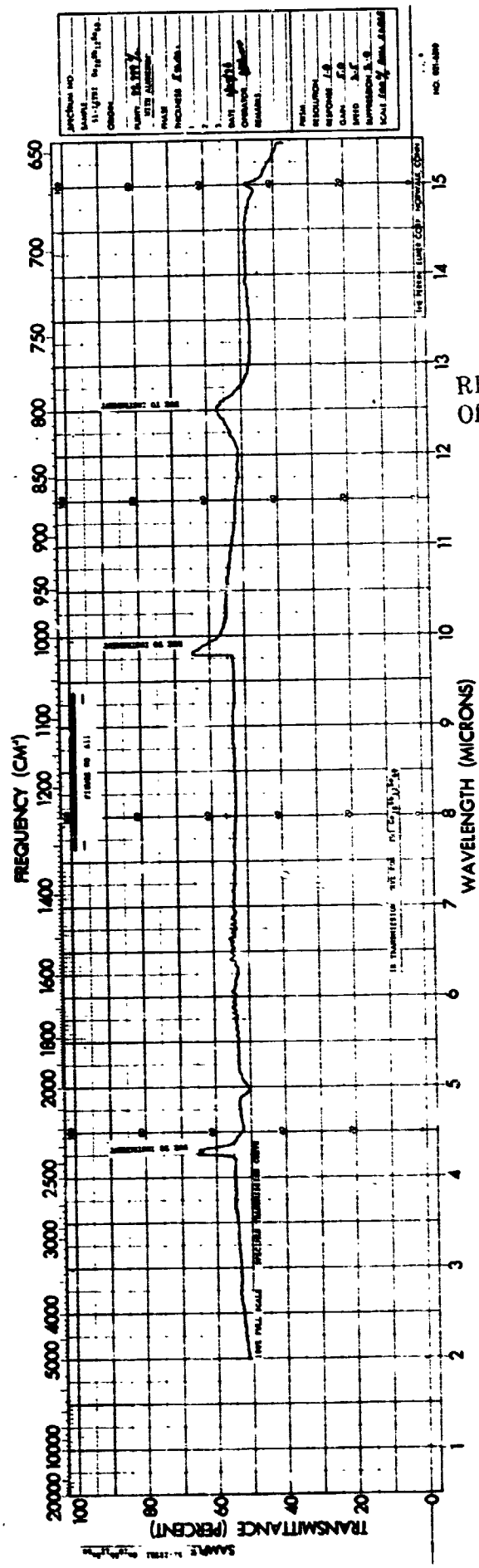

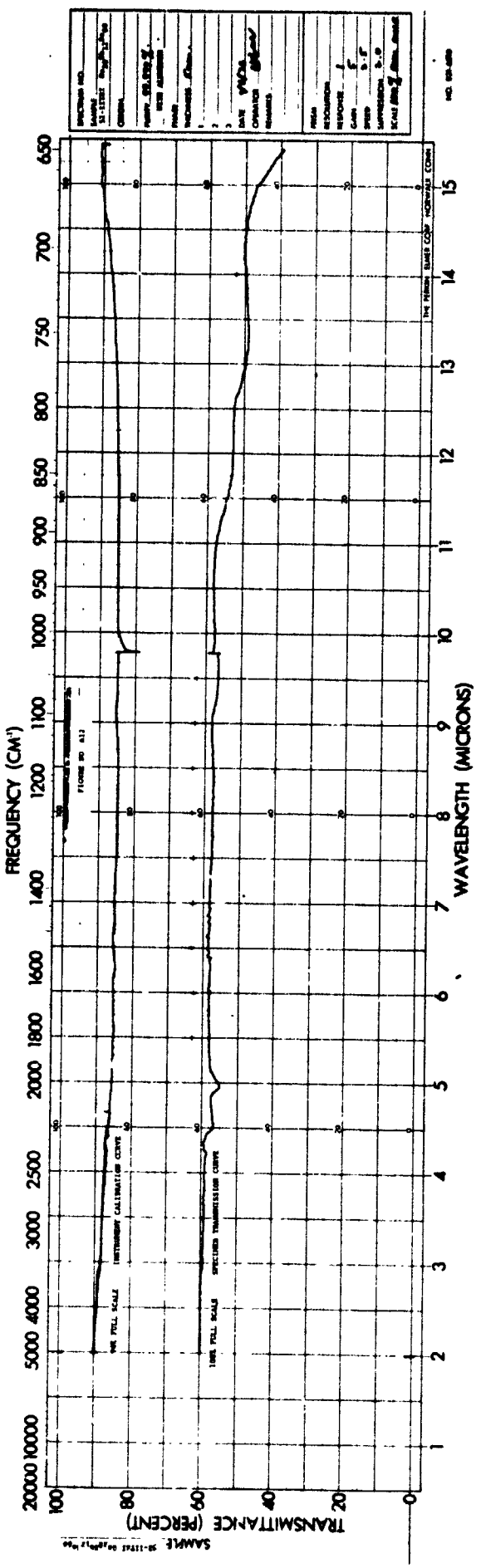
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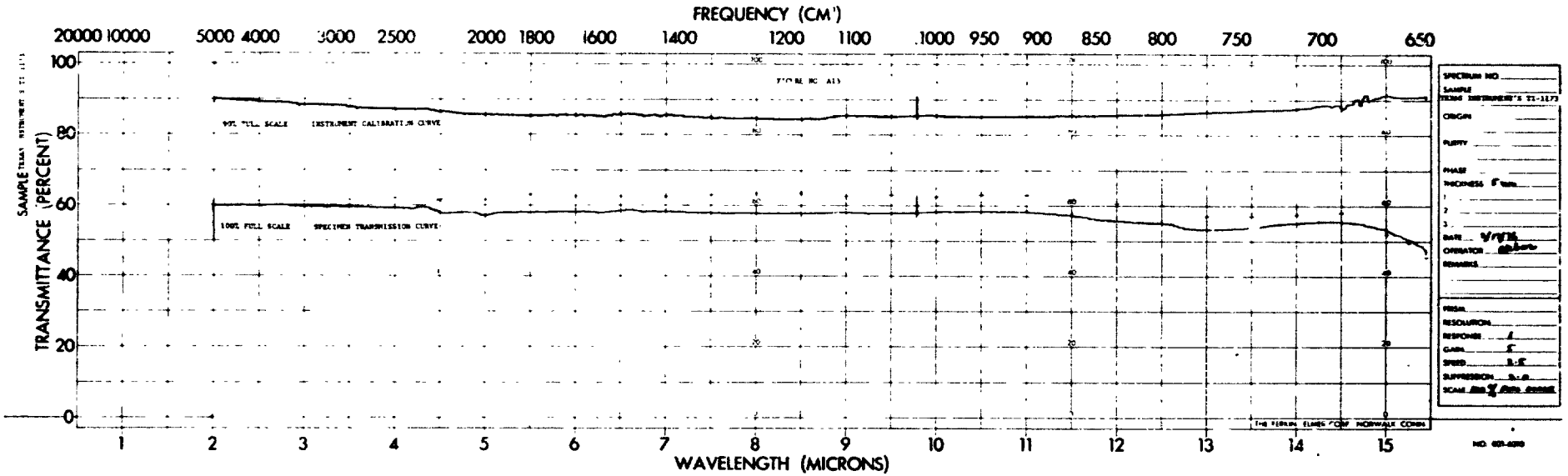
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