

3 copy

RECEIVED BY DTIC JUN 1 1969

**Gulf General Atomic**  
Incorporated

GA-8771

Conf-681059--2

CESIUM SORPTION IN MATERIALS FOR INTEGRAL RESERVOIRS

M. K. Yates and G. O. Fitzpatrick

October 1968

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

# Gulf General Atomic Incorporated

P. O. Box 608, San Diego, California 92112

GA-8771

## CESIUM SORPTION IN MATERIALS FOR INTEGRAL RESERVOIRS\*

M. K. Yates and G. O. Fitzpatrick

This paper was presented at the 1968 IEEE Thermionic  
Conversion Specialist Conference  
Boston, Massachusetts  
October 21 through October 24, 1968

\* This work was sponsored by the U. S. Atomic Energy  
Commission under Contract AT(04-3)-167  
Project Agreement No. 14

### LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights, or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

Project 278

October 1968

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *fly*

ABSTRACT

The cesium vapor pressure/sample temperature/sample loading characteristics were measured for several types of graphite. The isotherms for different types of graphite were similar, but the transition between two cesium-graphite equilibrium states was better defined in some samples than in others. Hysteresis effects were present in most samples but appear to pose no particular problems to the thermionic converter.

In addition, a long term thermal stability test was begun on one sample of graphite, which was operated at  $775^{\circ}\text{C}$  at a cesium vapor pressure of 10 torr. Three thousand three hundred sixty (3360) hours have been accumulated with no changes detected in the sample's pressure temperature characteristics.

Finally, the required temperature control accuracy for some sorption reservoirs is shown to be approximately one-half that required for a liquid cesium reservoir, and tolerable cesium losses in sorption reservoirs are given for a given cesium vapor pressure change.

### INTRODUCTION:

This paper is a continuation of work on cesium sorption in materials for thermionic converters.<sup>(1,2)</sup> The cesium sorption testing of various types of graphite is discussed, where the primary characterization involves the measurement of cesium pressure/cesium loading isotherms. The design of a long term thermal test apparatus is also discussed and results of the first two tests are given. Finally some aspects of the incorporation of sorption reservoirs into thermionic converters are considered, namely tolerable cesium losses and required temperature control for various materials used as sorption reservoirs.

### PRESSURE-TEMPERATURE-LOADING TESTS OF GRAPHITE:

The design of the apparatus used in most of these tests has been described before.<sup>(1,2)</sup> It has been modified slightly since those tests (as shown in Fig. 1) in order to better outgas the sample and to eliminate any possibility that cesium might collect on the reference side of the capacitance manometer. Basically, the apparatus consists of a liquid-cesium reservoir (with approximately 2 grams of cesium having a specific  $\text{Cs}^{134}$  activity of  $250 \mu$  curies/gram), the manometer, and the sample. The sample's cesium loading is determined by counting the radioactive cesium present. The cesium vapor pressure is determined by measuring the temperature of the liquid reservoir and using the P-T curve recommended by Nottingham and Breitwieser as that giving the best fit to experimental vapor pressure data.<sup>(3)</sup> The capacitance manometer is calibrated against the liquid reservoir.

The cesium sorption characteristics of several types of graphite have been determined. The reproducibility of sorption characteristics in nominally identical types was of interest, as well as comparisons between samples of differing types. The graphite samples tested thus far are listed in Table 1.

TABLE 1

<u>Sample No.</u>	<u>Type</u>	<u>Source</u>
1	Annealed Pyrolytic Graphite	Gulf General Atomic
2	Molded Graphite, 3499S	Speer Carbon Products
3 } 4 }	Flat Layered Graphite Cloth Bonded with Graphite, CARB-I-TEX 700	Carborundum Company

The annealed pyrolytic graphite was produced by vapor deposition followed by a high temperature heat treatment ( $3000^{\circ}\text{C}$ ). The result is a dense graphite that is highly oriented with almost all its carbon layers parallel to the substrate surface. As a result its physical properties vary greatly with the axis chosen, i.e., it is very anisotropic.

The molded graphite was made from particles less than .003" in diameter compacted under high pressure. It is less dense, but much more isotropic than the pyrolytic graphite.

The last sample type tested was CARB-I-TEX, a unique structure made up of layered graphite cloth impregnated with a graphite binder. We have found its expansion properties to be anisotropic, expanding much more in a direction perpendicular to the cloth layer planes than in the other two when loaded with cesium. This type of graphite is the least dense of those tested, due to imperfect binder impregnation. Two samples of the same nominal type, but different batches, were tested. The presence in the sample of two forms of graphite, the cloth and the binder, makes it very difficult to get meaningful x-ray data on layer spacing and crystallite size.

The pressure-temperature-loading characteristics of the samples are shown in Figures 2 through 5. Data has been taken over a cesium pressure range of 0.1 - 30 torr and sample temperatures from  $600 - 1100^{\circ}\text{C}$ . Loadings up to 1.2 grams cesium/gram graphite have been obtained.

Evidence of the transitions between the various cesium graphite compounds appeared in all of the samples. In particular, the beginning of the transition between  $\text{CsC}_{24}$  and  $\text{CsC}_{10}$  was well defined in all samples and occurred at nearly identical sample temperatures and cesium vapor pressures. However, the constant pressure regime where the  $\text{CsC}_{24}$  and  $\text{CsC}_{10}$  compounds are in equilibrium was narrow and poorly defined in the CARB-I-TEX samples and very wide and sharply delineated in the annealed pyrolytic sample. The molded graphite samples fell between these two extremes in this respect. Of the other transitions only the one between  $\text{CsC}_{24}$  and  $\text{CsC}_{36}$  was well



defined and that only in the annealed pyrolytic and molded graphite samples. In general, cesium loadings were less than expected if complete formation of a particular compound had taken place.

In an attempt at explaining the difference in the graphite isotherms, various physical characteristics of the samples were measured. These characteristics are listed in Tables 2 and 3 and include density, BET surface area, and purity. Also included are the average layer spacing and crystallite size determined for two perpendicular axis and for a sample average. One measured parameter that seems to correlate with "compound definition" in the samples cesium sorption characteristics is sample density. Higher densities correlate well with more distinctly defined compound states. Also, a larger crystallite size correlated with better plateau definition.

#### HYSTERESIS EFFECTS IN GRAPHITE:

Hysteresis effects were observed in almost all of the graphite isotherms. In order to study these effects, the capacitance manometer was used with one sample (No. 4) to take pressure-temperature data. The data was taken with the valve to the liquid reservoir closed. The results are shown in Fig. 6.

Two curves taken at the same loading are of particular interest; one was taken on an adsorption branch, one on a desorption branch, taken after unloading from 30 torr. Both curves (as well as all of the others) indicated that a transition from one branch to the other would not occur under these conditions. Because of the volume of the measuring system, actual loadings dropped by approximately 1% when going from 0 to 30 torr.

In order to further investigate what effects the hysteresis might have on the pressure temperature curves, small sorption-desorption loops were traversed around one operating point,  $\sim 800^{\circ}\text{C}/10$  torr. The results of the data taken are shown in Figures 7 and 8. When starting from a sorption point and unloading the sample, the initial point could always be reproduced. However, the initial point could not be returned to when starting from a point on the desorption branch and unloading the

TABLE 2

PHYSICAL CHARACTERISTICS

Sample No.	Density gm/cm <sup>3</sup>	N <sub>2</sub> BET Area		X-Ray Data <sup>1</sup> (Å)									
				m <sup>2</sup> /gm		m <sup>2</sup> /cm <sup>3</sup>		Axis 1		Axis 2		Powder	
				L <sub>c</sub>	C <sub>o</sub>	L <sub>c</sub>	C <sub>o</sub>	L <sub>c</sub>	C <sub>o</sub>	L <sub>c</sub>	C <sub>o</sub>		
1	2.08	0.8	1.7	1150	6.734	675	6.729	675	6.719				
2	1.62	2.28	3.69	350	6.750	370	6.713	540	6.724				
3	1.35	0.39	0.56	No meaningful data obtained									
4	1.48	0.75	1.11	No meaningful data obtained									

TABLE 3

SAMPLE IMPURITIES (ppm)

Sample No.	AL	B	Mg	Fe	Ca	Cu	V	Si	Ti
1	< 1	< .5	< .5	< 1	< 20	< 1	< .5	< 10	< 1
2	< 1	1	1	1	< 20	.5	20	40	40
3	2	.5	1	8	40	5	< .5	10	< 1
4	8	2	8	10	< 20	< 1	10	< 10	10

1. Axis 1 and Axis 2 are perpendicular axis, one chosen to correspond approximately to the sample's natural axis determined by anisotropy. The powder tested was obtained from sample scrapings and should represent a sample average.

C<sub>o</sub> represents an average layer spacing determined from the angle of reflection of x-ray peak.

L<sub>c</sub> represents an average crystallite size, determined from the x-ray peaks half-width. A crystallite is a 3 dimensional atomically ordered structure bounded by micropores or highly angled carbon layers.

sample. From this data it appears that it is desirable for a reservoir in a thermionic converter to be operating on the sorption branch of the curve to prevent hysteresis effects.

#### LONG TERM THERMAL STABILITY TESTING OF CESIUM LOADED SAMPLES:

The intention of the long-term testing is to demonstrate the stability of the cesium-substrate system in a realistic temperature environment. The design of the present test vehicle is shown in Fig. 9. The sample is held in a 1/4" diameter 0.030" wall tube by crimps at the top and bottom. On the top is a 10 cm<sup>3</sup> volume. The sample holder is made entirely of niobium with two weld joints and one pinch off (or cold weld).

After placing the sample inside the niobium tube, the assembly is mounted on the pressure-temperature-loading apparatus and the sample outgassed. Then sufficient P-T-L data is taken to insure that the sample's sorption characteristics are stable. Finally the sample is equilibrated at ~ 800°C and 10 torr cesium pressure and separated from the liquid reservoir by closing the valve. After cooling, the sample is pinched off and mounted in a separate vacuum system and instrumented. Pressure-temperature curves are taken by counting the radioactive cesium in the volume at the top of the sample holder. The sample and reservoir temperature are held constant and the pressure-temperature curve is periodically remeasured.

A sample of CARB-I-TEX 700 is presently being tested. In addition, a liquid sample is serving as a control. The liquid control was run at ~ 366°C (10 torr) with a volume temperature of ~ 500°C throughout its life test, and the graphite sample was run at sample and volume temperatures of 775°C and 480°C, respectively. The liquid and graphite tests had run 3270 and 3360 hours, respectively, as of October 8, 1968.

The results of these measurements are shown in Figures 10, 11, and 12. The variation of volume count rate with cesium pressure (determined from reservoir temperature) was used to characterize the liquid sample, and the slopes of the count rate-cesium pressure curves are plotted in Fig. 10. No detectable change ( $\pm 12\%$ ) has been observed thus far.

The graphite pressure-temperature curves are completely characterized by the samples heat of reaction, and the cesium pressure at a given sample temperature. These parameters are plotted in Figures 11 and 12. Again, no detectable changes were noted in either parameter, both of which are considered accurate to  $\pm 20\%$ .

#### APPLICATION TO THERMIONICS:

Two questions which have often come up during discussions of the applications of a sorption reservoir to a thermionic converter have been what accuracy of reservoir temperature control is required for optimum cesium pressure operation and what are the tolerable cesium losses for these reservoir materials.

Table 4 lists the slope of the sample temperature/cesium vapor pressure curves for various materials (taken from References 1, 2) at a typical operating point, 10 torr. The values range from  $\sim 5^\circ\text{C}/\text{torr}$  for a liquid reservoir to  $\sim 11^\circ\text{C}/\text{torr}$  for carbon loaded to 350 mg Cs/g, graphite loaded to 150 mg Cs/g or a porous tungsten reservoir loaded to  $\sim 1$  mg Cs/g. In both carbon and graphite the cesium pressure becomes more sensitive to temperature as the cesium loading increases.

The question of cesium losses to converter components, residual gases, or leakage becomes very important when one contemplates placing material with a cesium reserve of 10's or 100's of milligrams inside the converter envelope. One would prefer a sorption reservoir material which could tolerate the loss of a large fraction of its reserve cesium before the vapor pressure dropped much below the operating value.

Using data reported at the Stresa Conference<sup>(2)</sup>, we compared the tolerable cesium losses in a variety of materials. Choosing an operating point at 10 torr, we calculated the amount of cesium that could be lost before the vapor pressure dropped by 20%. The results are plotted in Fig. 13 as milligrams cesium loss per  $\text{cm}^3$  versus sample temperature during cesium loading.

TABLE 4

Material	Cesium Loading mg Cs/g	Temperature at 10 torr		Slope of P-T curve at 10 torr °C/torr
		°C	°K	
Liquid Cesium (3)		366	639	4.7
Pure Carbon FC-50 <sup>(1)</sup>	350	1031	1304	11.0
	450	866	1139	8.0
	550	758	1031	6.4
	650	686	959	6.0
Graphite <sup>(1)</sup>	150	1053	1326	11.0
	250	960	1233	8.7
	350	942	1215	9.6
	475	795	1068	8.3
Tungsten <sup>(1)</sup>	~ 1	856	1129	11.1

The carbon and graphite samples can tolerate the highest loss, 10-900 mg/cm<sup>3</sup>. On the other hand, the tungsten and alumina samples can lose only 0.02-0.2 mg/cm<sup>3</sup> before the pressure drops 20%. The losses tolerable in the W-10 Ta sample range down from 12 mg/cm<sup>3</sup> depending upon operating conditions.

Tolerable loading losses are not too sensitive to operating temperatures except in the two graphite samples where peaks occur when the transition from one two-phase equilibrium to another occurs. These transitions are sharply defined in the annealed pyrolytic graphite sample and less well defined in the CARB-I-TEX 700 sample. Two conclusions may be drawn from a comparison of the two graphite samples: First, it would be difficult to insure operation in the highest tolerable loss regions of the pyrolytic graphite sample because the allowable sample temperature errors during cesium loading are only  $\sim \pm 10^\circ\text{C}$ ; second, the tolerable loss in this sample drops to the lowest values near the loss peaks, a situation which may favor the selection of a graphite-like CARB-I-TEX 700 which does not show drastic changes in tolerable loss and is therefore more predictable.

REFERENCES

1. Yates, M. K., Fitzpatrick, G. O., "Cesium Sorption in Materials for Thermionic Converters," USAEC Report GA-8574, Gulf General Atomic, Incorporated, 1968.
2. Yates, M. K., Fitzpatrick, G. O., "Cesium Sorption in Materials for Thermionic Converters," Second International Conference on Thermionic Electrical Power Generation Proceedings, Stresa, Italy, May 27-31, 1968.
3. Breitwieser, R. Nottingham, W. B., "Theoretical Background for Thermionic Conversion Including Space-Charge Theory, Schottky Theory and the Isothermal Diode Sheath Theory," National Aeronautics and Space Administration Report NASA TN D-3324, March 1966.
4. Aronson, S., Salzano, F. J., "Thermodynamics Properties of the Cesium-Graphite Lamellar Compounds," J. Chem. Phys., Vol. 43, No. 1, July 1965, P149.

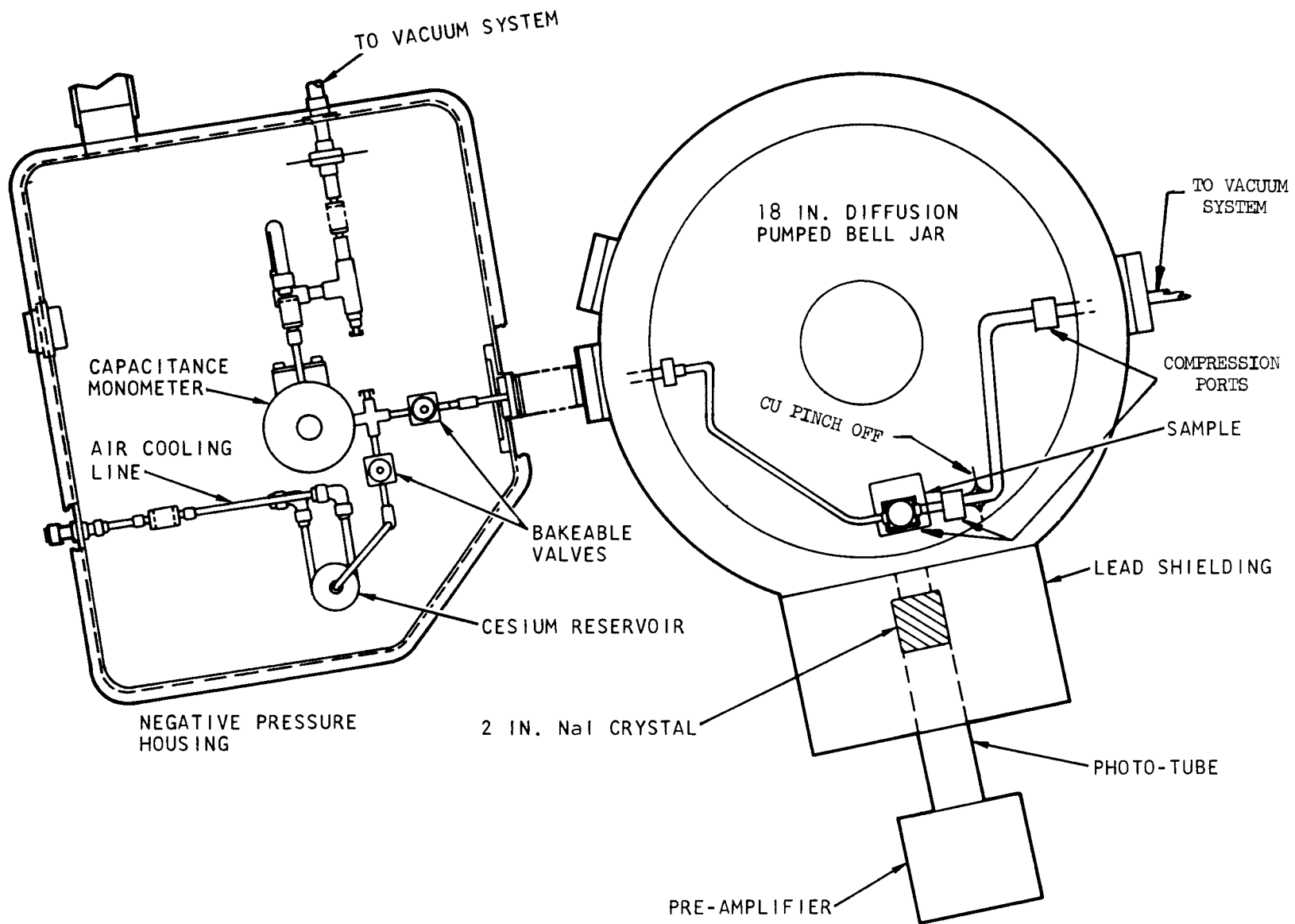


Fig. 1--Plan view of pressure-temperature-loading apparatus



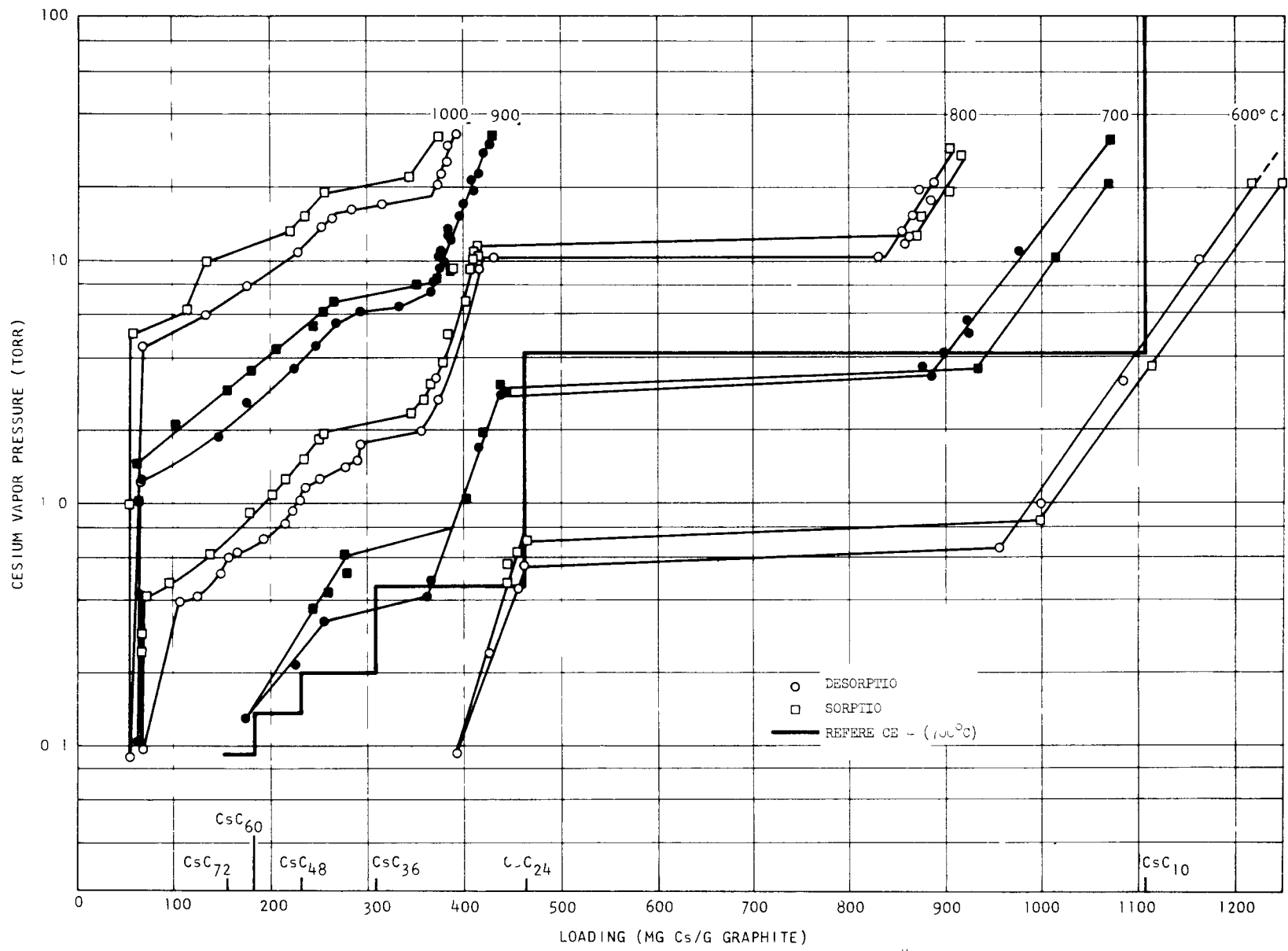


Fig. 2--Pressure-loading isotherm--sample #1  
Gulf General Atomic

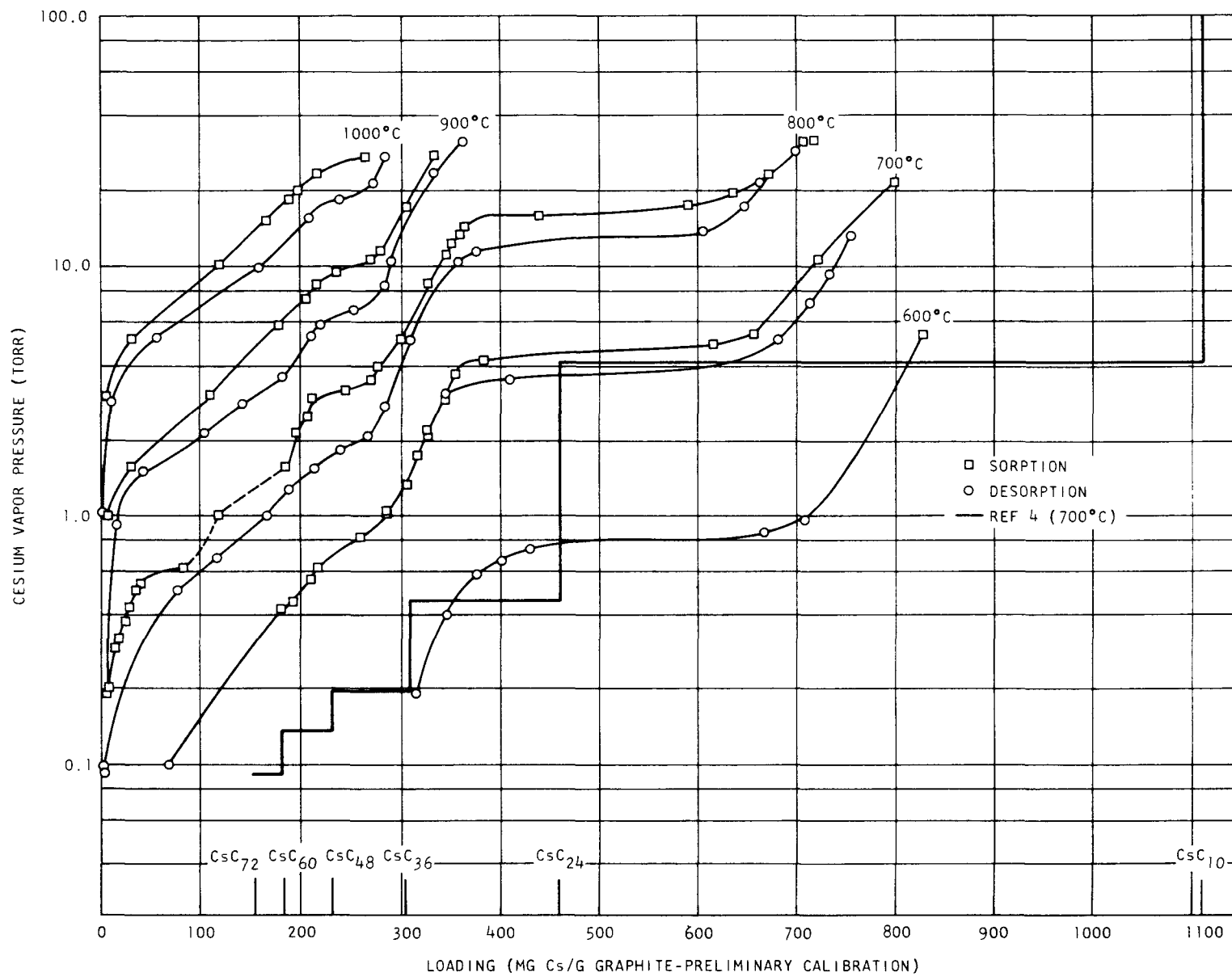


Fig. 3--Pressure-loading isotherm--sample #2  
Speer 3499S

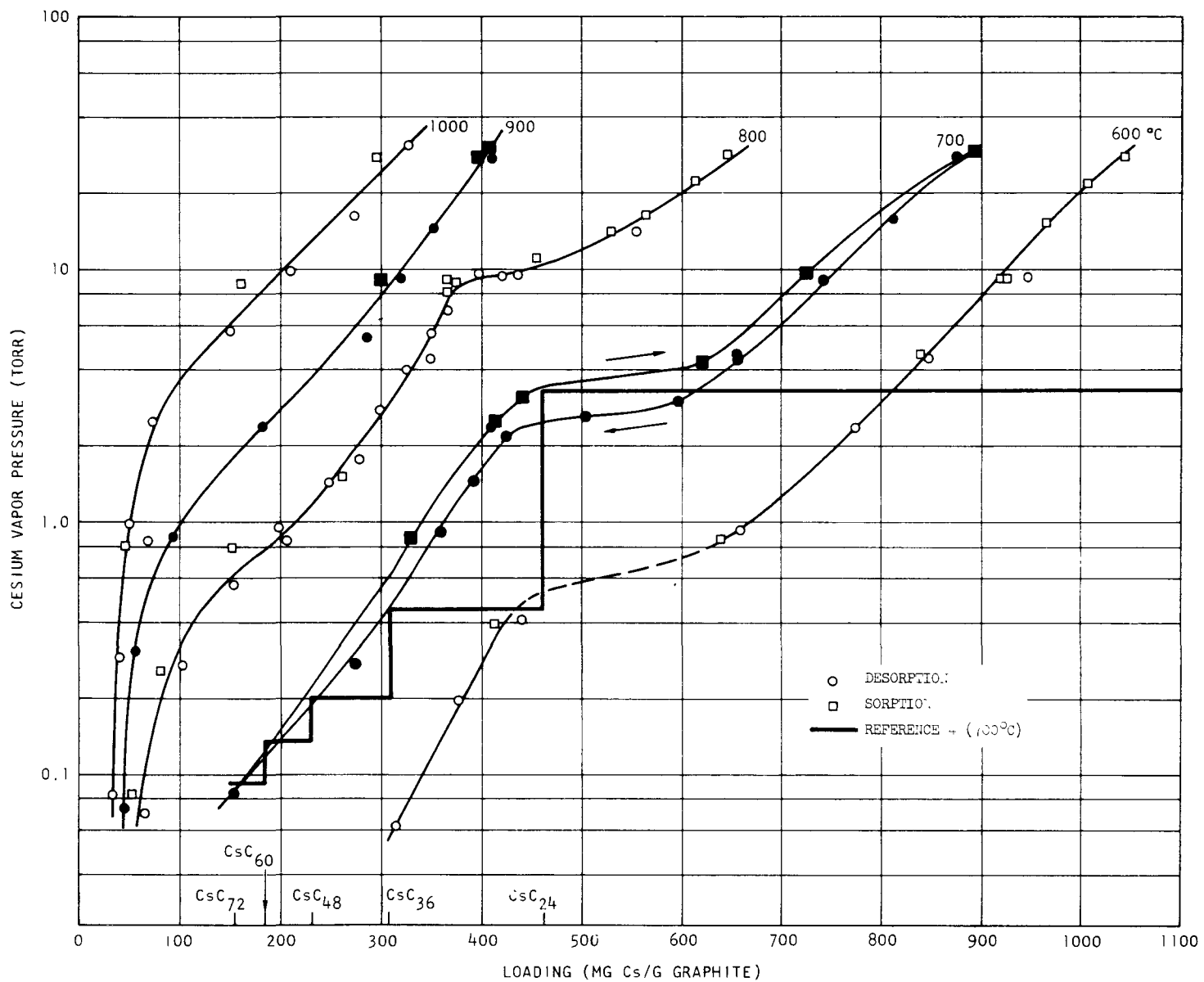


Fig. 4--Pressure-loading isotherm--sample #3  
 Carborundum CARB-I-TEX 700

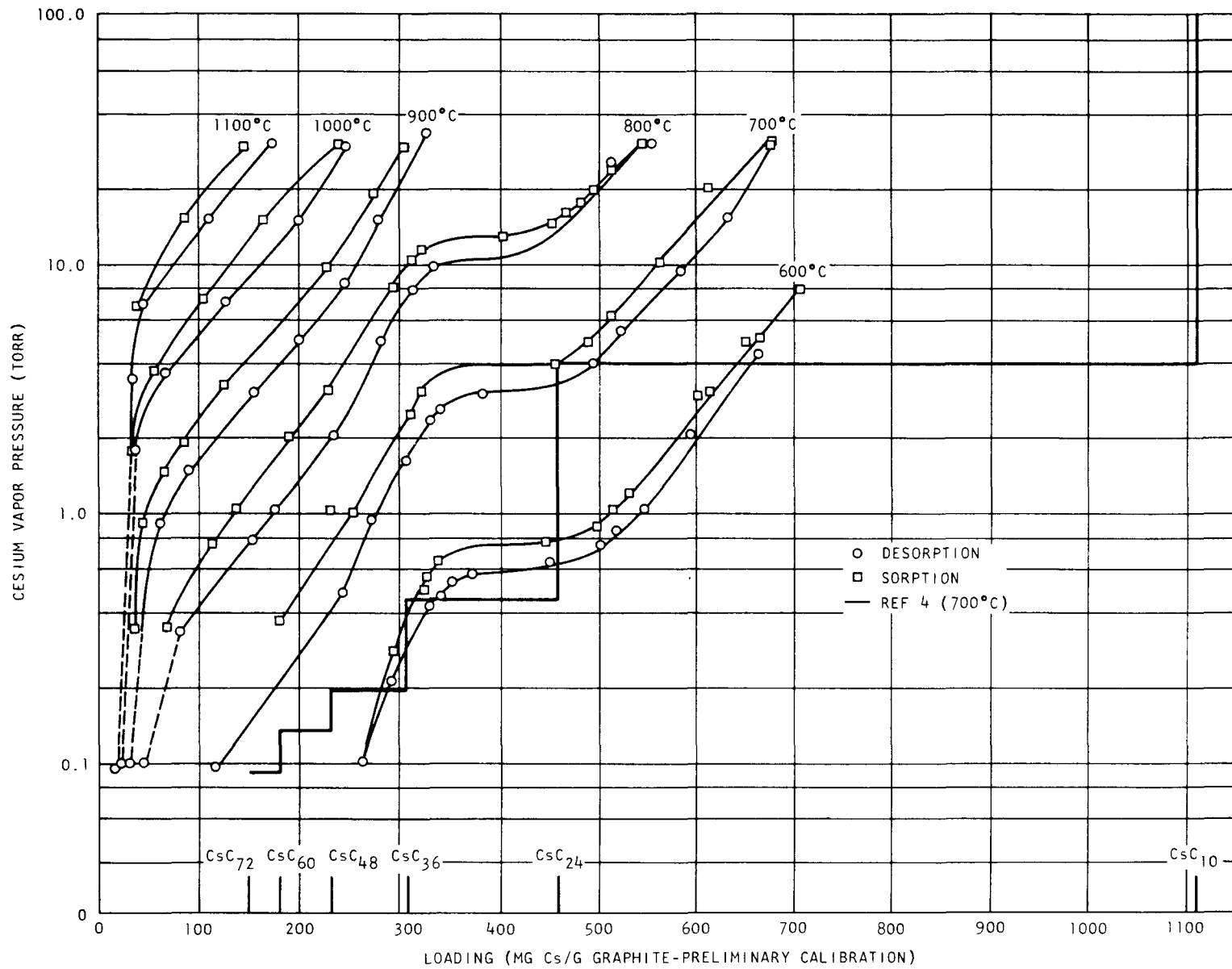


Fig. 5--Pressure-loading isotherm--sample #4  
Carborundum CARB-I-TEX 700

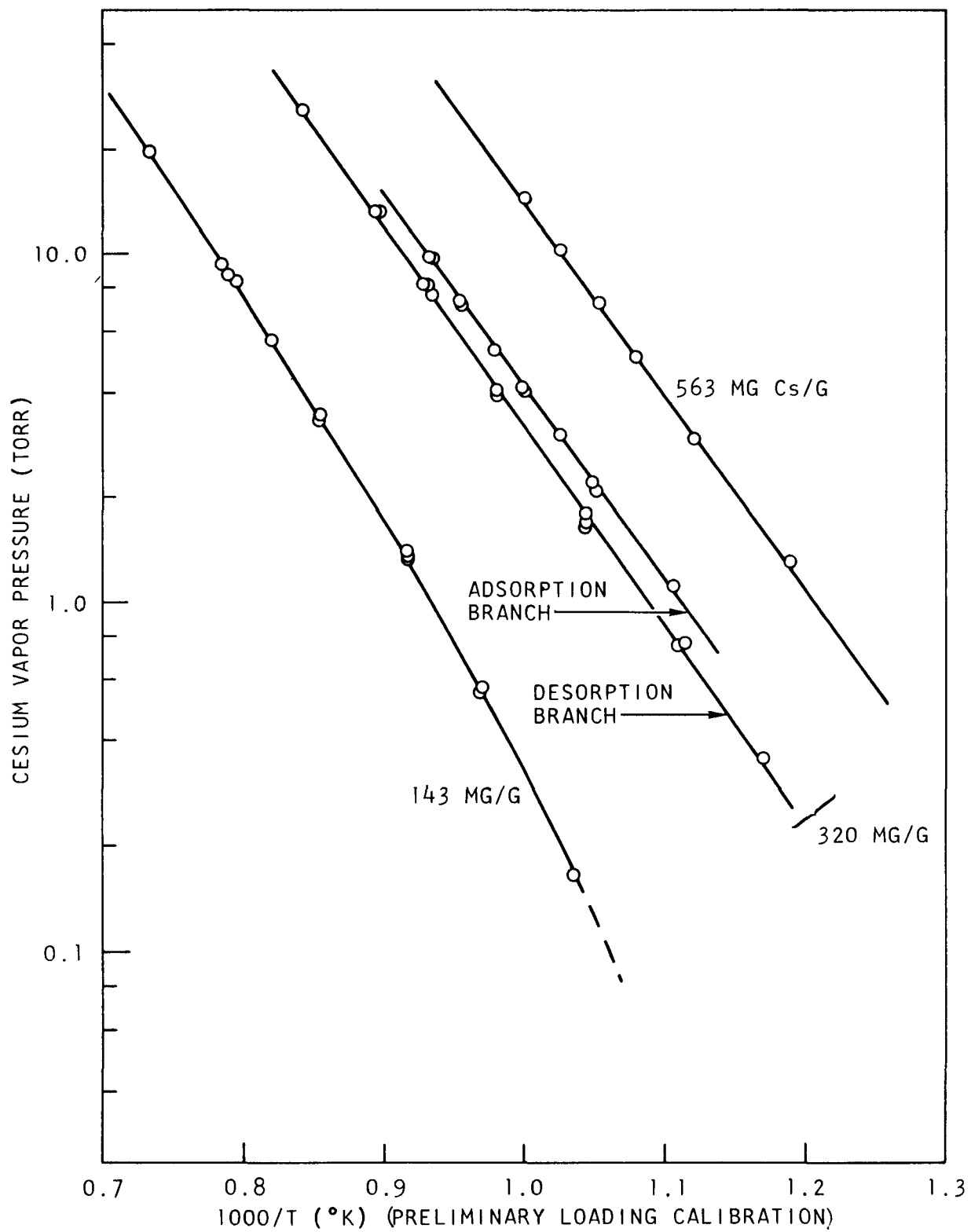


Fig. 6--Pressure-temperature isostere--sample #4

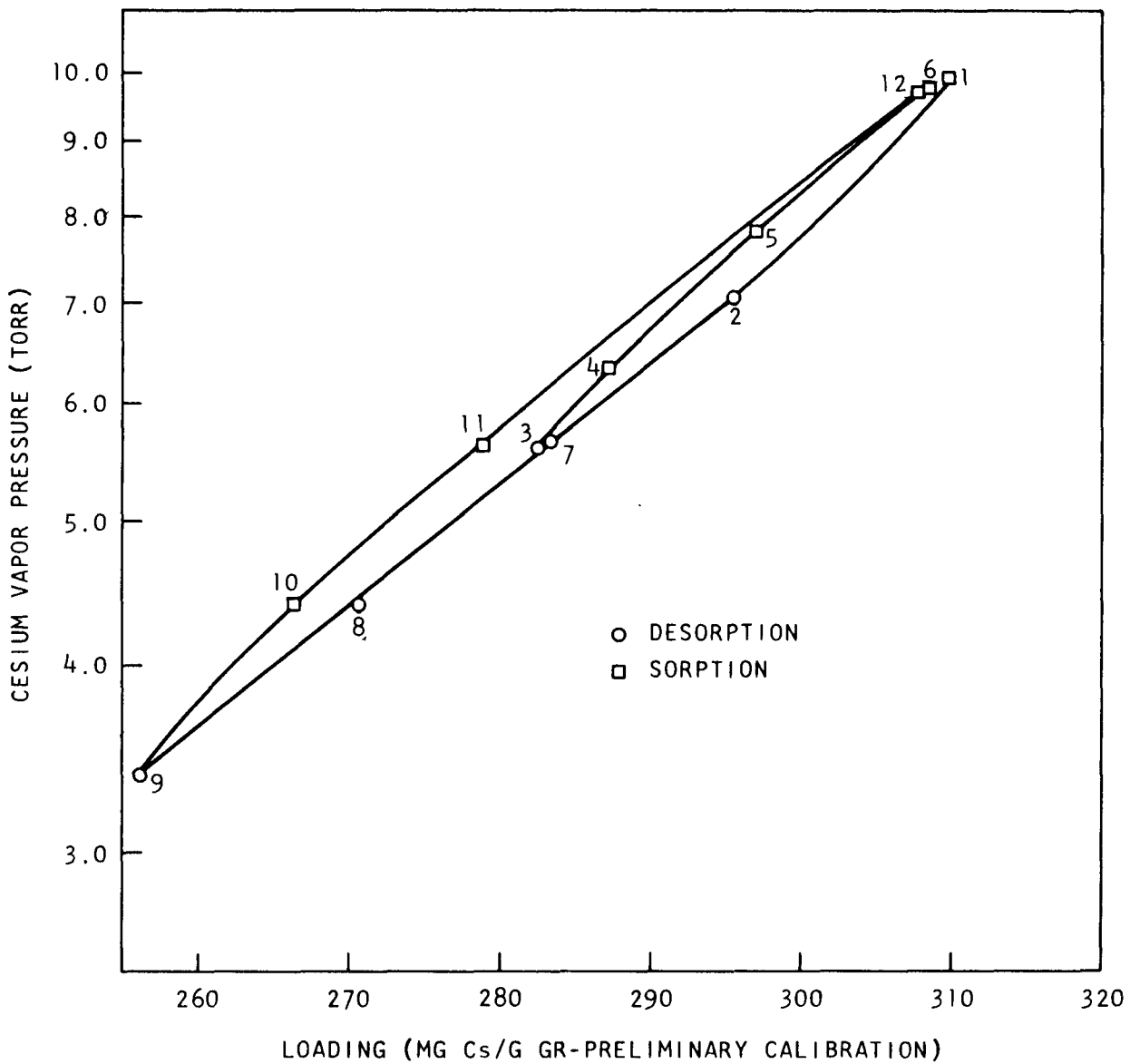


Fig. 7--Isotherm hysteresis on sorption branch  
Carborundum CARB-I-TEX sample #4

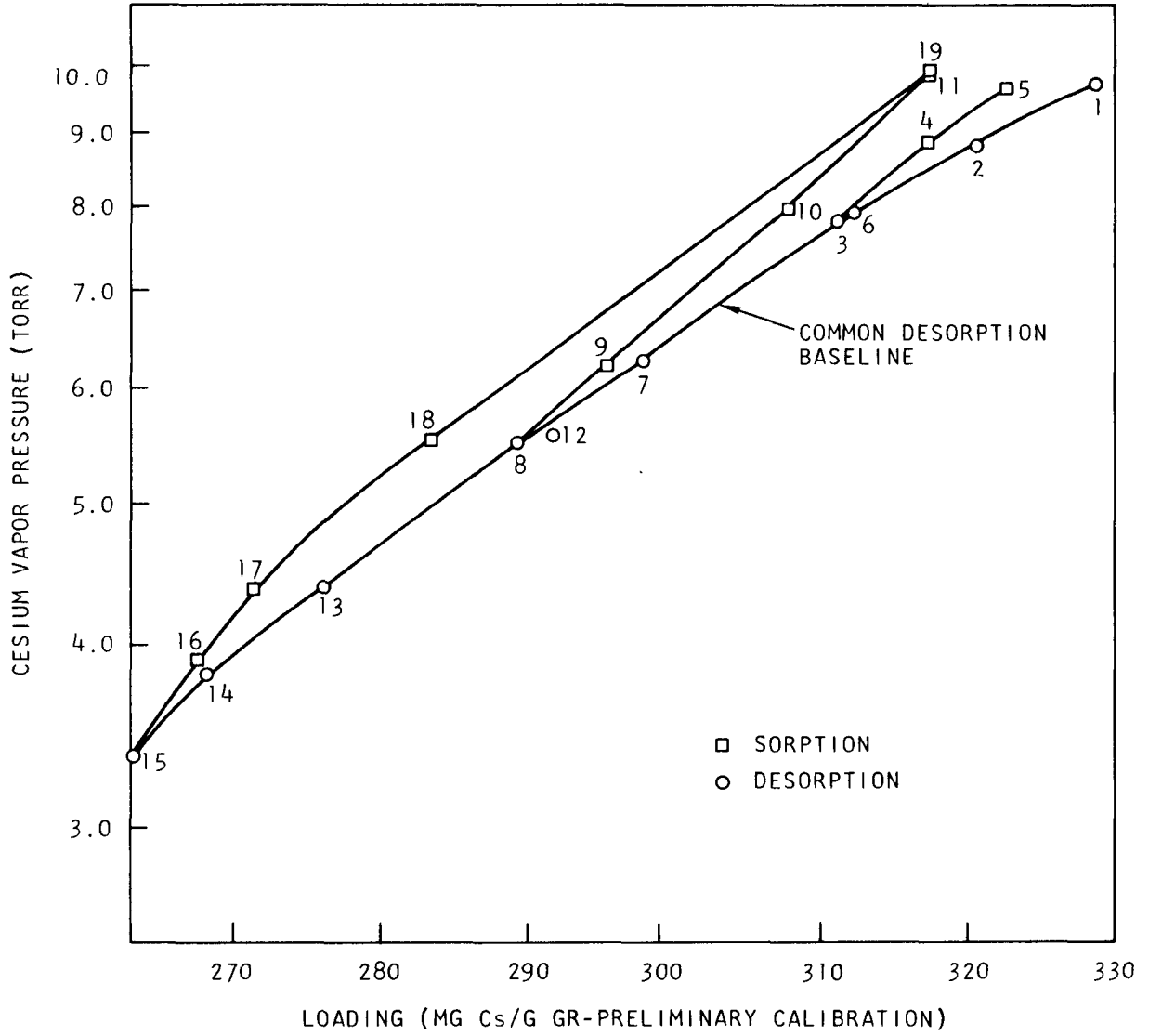


Fig. 8--Isotherm hysteresis on desorption branch  
 Carborundum CARB-I-TEX sample #4

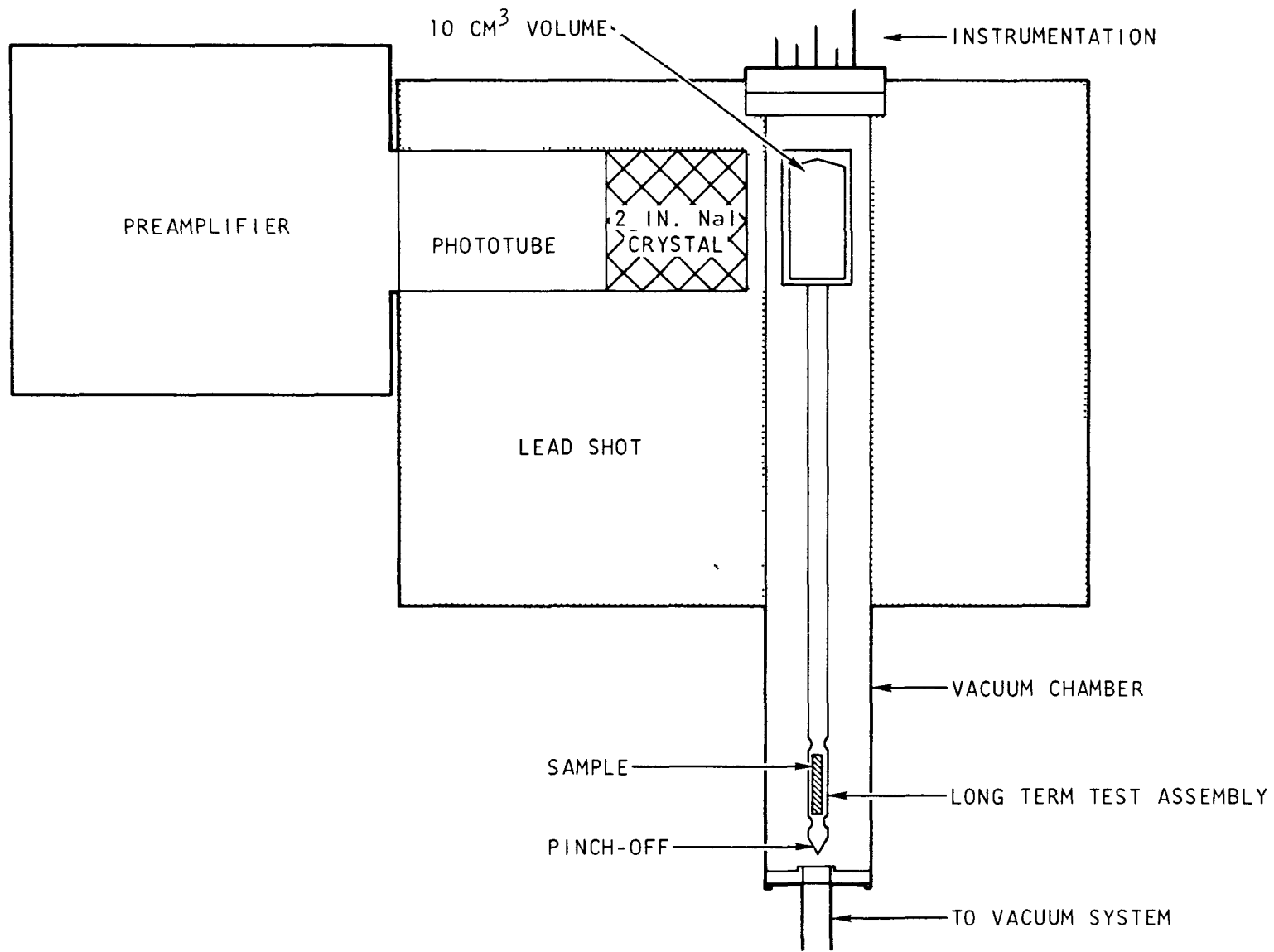


Fig. 9--Long term stability test station



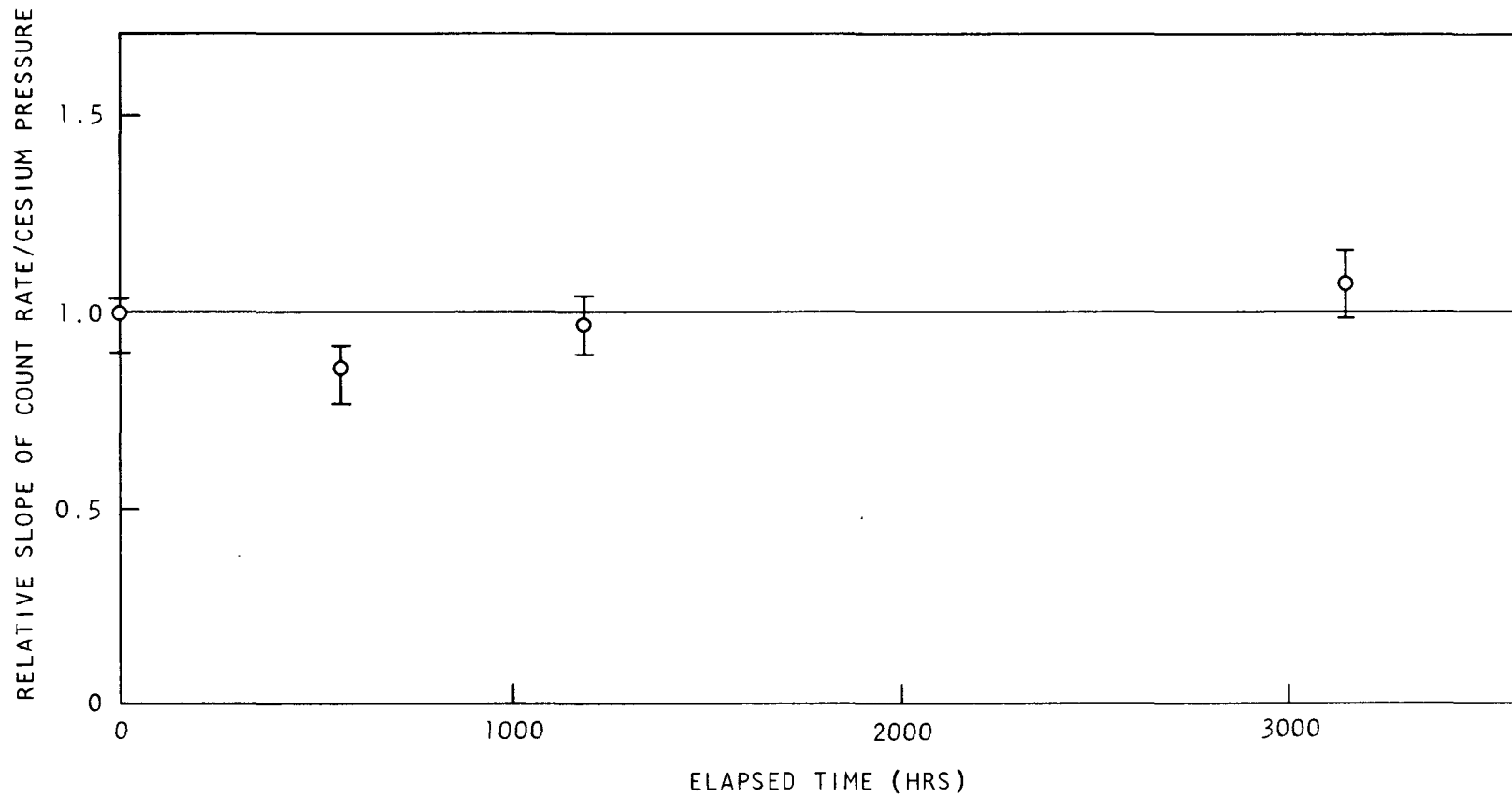


Fig. 10--Long term stability test--liquid sample

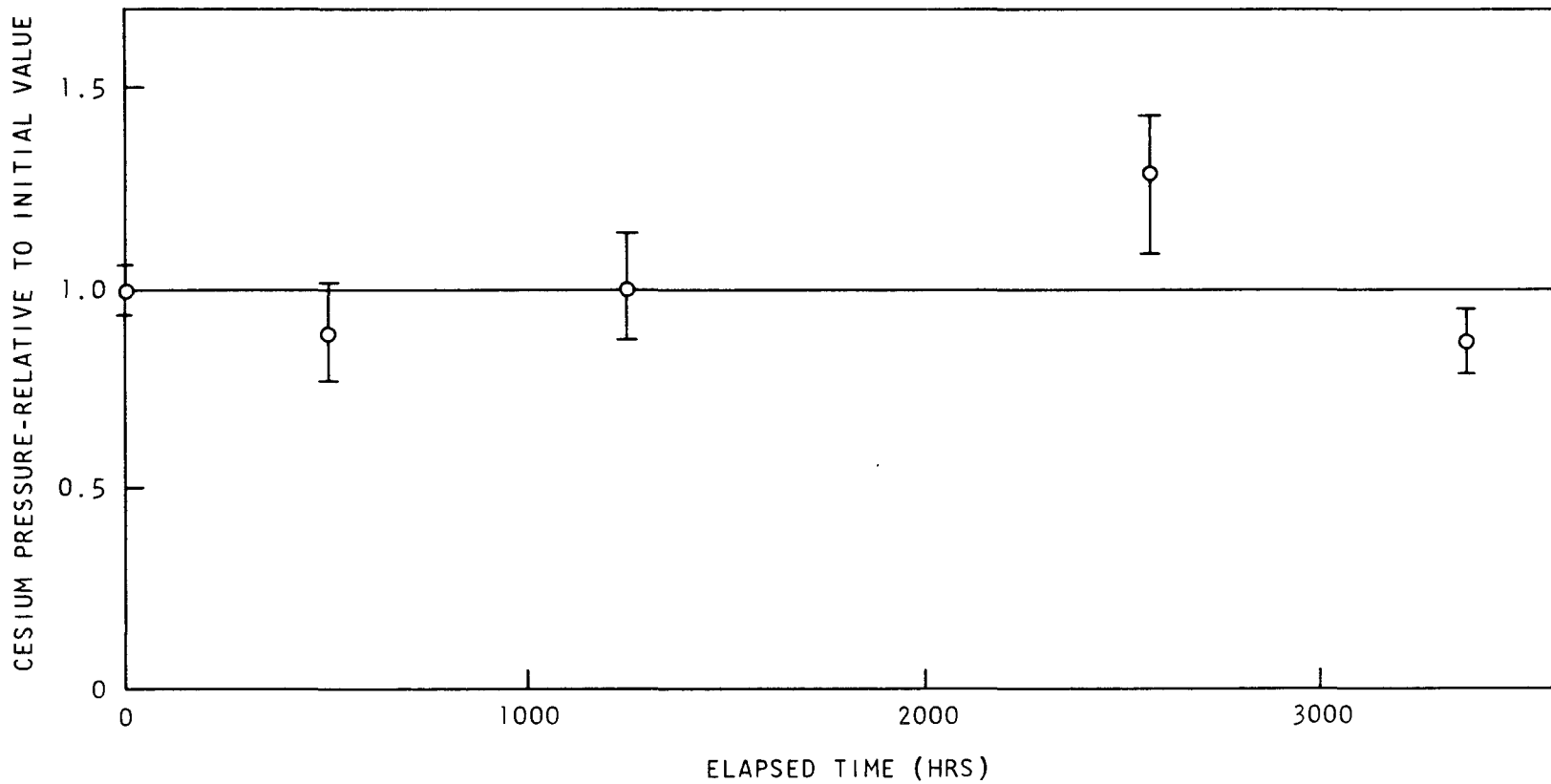


Fig. 11--Long term stability test--Carborundum CARB-I-TEX 700

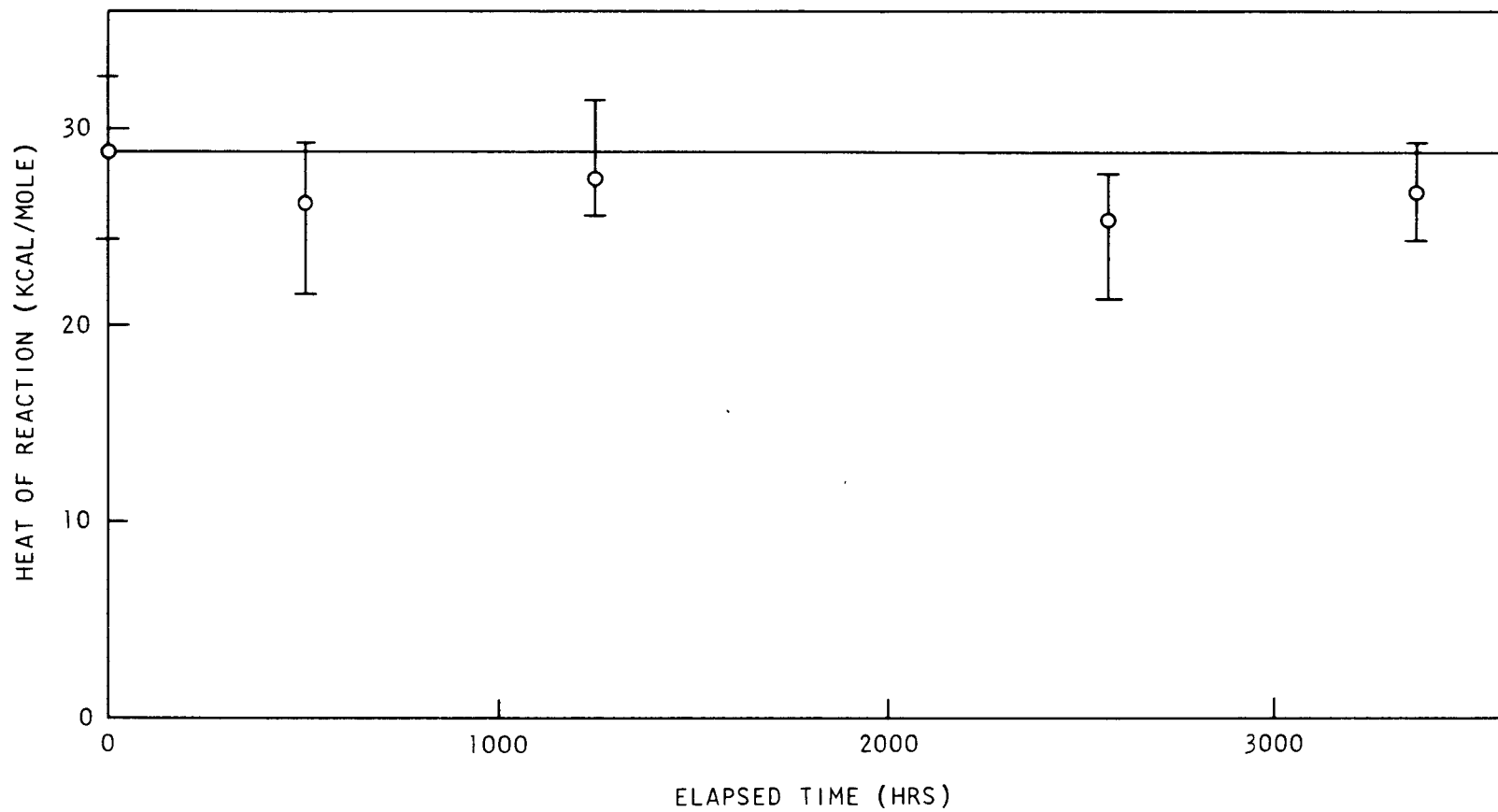


Fig. 12--Long term stability test--Carborundum CARB-I-TEX 700

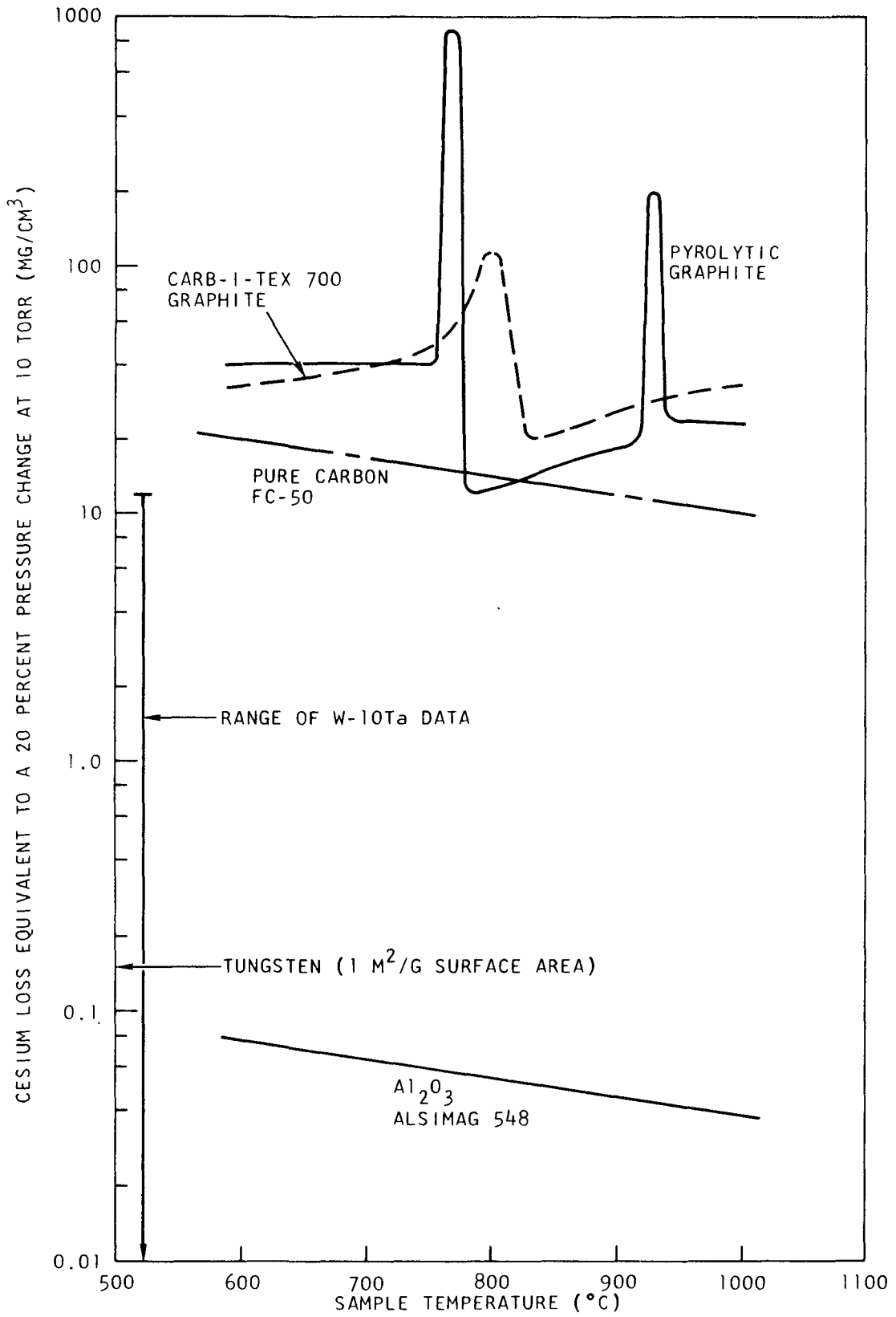


Fig. 13--Tolerable cesium losses versus sample temperature