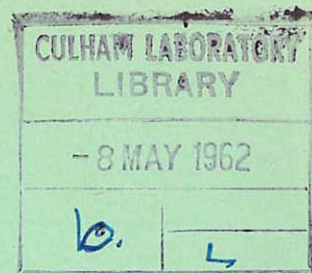


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United Kingdom Atomic Energy Authority
RESEARCH GROUP
Report

A MASS SPECTROMETRIC STUDY
OF THE OUTGASSING OF SOME ELASTOMERS
AND PLASTICS

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Culham, Abingdon, Berks.

1962

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A MASS SPECTROMETRIC STUDY OF THE OUTGASSING OF SOME
ELASTOMERS AND PLASTICS

By

R. S. BARTON AND R. P. GOVIER

ABSTRACT

The report gives an account of the composition of the residual gas in a vacuum system resulting from the presence of Viton A, a polyurethane rubber, an epoxy resin, polythene and polytetrafluorethylene and presents the mass spectra from which the conclusions were drawn.

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March, 1962

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INTRODUCTION

1. Since the composition of the residual gas in a clean empty vacuum system is largely dependent upon the materials of construction and many vacuum processes can be influenced by the gases present, it is important for both designer and experimentalist to possess a knowledge of the residual gas composition likely to result from the use of various materials with favourable electrical or mechanical properties. For the purposes of obtaining this information concerning the five materials described, a sample of each was introduced, under carefully controlled conditions, into a very high vacuum system of known residual gas composition and the resultant mass spectrum observed. In each case the sample was first examined after being pumped for a sufficiently long period for a steady outgassing state to prevail. It was then baked under high vacuum conditions at the maximum permissible temperature without re-entering the atmosphere and again studied after cooling to room temperature. Upon completion of the analysis, the sample was re-introduced to the atmosphere of the laboratory for a period, and after a further pumping for the same time as originally adopted, another mass spectrometric examination was made. By this method it was possible to determine:-

- (1) The composition of the gas emanating from the material under test, in the unbaked state.
- (2) The advantage, if any, derived from bakeout of the material.
- (3) The effect on the outgassing properties due to re-introduction to the air, such as would happen by letting a system up to atmosphere without special precautions being taken.

APPARATUS

2. Fig. 1 shows diagrammatically the apparatus used to obtain the results described later in the report. It consists of a mass spectrometer with a 60° tube, T, of 15 cms radius of curvature, attached at the ion source end to a sample chamber S₃ via a one inch all-metal valve V₇. The sample chamber was connected to the inner section S₂ of a vacuum lock, by the all-metal valves V₄ and V₅. S₂ communicated with the outer section S₁ of the vacuum lock via the "butterfly" valves V₂ and V₃. The mass spectrometer tube T, S₃ and S₂ were each attached to separate liquid nitrogen trapped oil diffusion pumps to facilitate independent pumping when necessary. S₁ was pumped by a two stage rotary pump fitted with a liquid nitrogen trap which was filled whenever

V₁ was opened to reduce the hydrocarbon background due to the rotary pump oil.

Materials of construction

3. The mass spectrometer tube, ion source electrodes and the seating cones of V₄ and V₅ were of copper and the electron multiplier dynodes (see method of operating mass spectrometer) of beryllium copper. Source and electron multiplier insulators were constructed from pyrex glass or quartz and all electrical leads were introduced into the vacuum system through kover-to-glass seals. The remainder of the mass spectrometer and sample chamber including the mass spectrometer pumping system was of stainless steel. Both sections of the vacuum lock S₂ and S₁ were of pyrex glass to facilitate transfer of a sample from the lower to the upper part of the lock by a magnet drawn along the outer surface of the tube wall; each sample being equipped with a small tag of vacuum-baked mild steel. The need to lift a sample arose when it had to be re-admitted to the sample chamber through V₄ after baking in the muffle M. This can be better understood by reference to Photograph 1.

Seals

4. To allow baking of the mass spectrometer and sample chamber system, aluminium wire, gold wire or diamond cross section copper ring seals were used, throughout. Those in the S₂ region were of indium wire with the exception of the butterfly valve seating rings which were of perbunan-base elastomer. All seals in the outer rough vacuum lock S₁, were made of perbunan-base 'O' rings.

Pressure obtained

5. The base pressure in the ion source region, where the conductance was about 4.7 litres per second, was approximately 1×10^{-9} Torr*. A similar pressure existed in the sample chamber, but that measured in the inner lock S₂ (which was unbaked) was 2×10^{-7} Torr.

Diffusion pump boiler medium

6. D.C.704 silicone oil was used in all the diffusion pumps. Automatic trap filling was used and the traps remained cold throughout the entire interval between bakeout periods.

TECHNIQUE

7. A rectangular sample, 3.8 x 0.3 x 0.3 cms, of the material for test was introduced into the outer lock S₁ (Fig. 1) through an entrance port E1 where it

was allowed to remain resting on the valve V_2 (see also Photograph 1) until the pressure in S_1 had been reduced to its ultimate value by the liquid nitrogen trapped rotary pump P_1 . It was then dropped into S_2 by rotation of the butterfly valve on which it was resting. Isolated in S_2 , it continued to be pumped until a steady outgassing state was reached (2 to 3 days), when it was introduced into S_3 through V_4 for examination. Before doing so, however, the valve V_7 was closed and the sample chamber exposed to its own pump by opening V_6 . The sample having been introduced into S_3 and V_4 closed, the sample chamber S_3 was allowed to pump for 15 minutes before isolating S_3 from the pump P_3 and re-opening the valve V_7 . This was done as an extra precaution to avoid unnecessary contamination of the mass spectrometer source by exposure to the inner lock, which was unbaked.

8. A series of scans of the gas composition resulting from the sample was made, extending over the period required to reach a state of pressure equilibrium within the system (several hours). Following completion of this stage of the examination, S_3 was again isolated from the ion source and exposed to the pump P_3 . The sample was then dropped into S_2 by opening the valve V_5 . S_3 having been again isolated from the lock and normal pumping conditions resumed, the sample was introduced into the muffle M, and baked near its highest recommended working temperature for 24 hrs. Upon cooling and when the base pressure composition of the mass spectrometer and sample chamber had reached equilibrium, the sample was again placed in the sample chamber S_3 , where a further examination was made, following the procedure previously described. It was then withdrawn through the vacuum lock and re-admitted to the undried atmosphere through the exit port E_2 . After 24 hours exposure it was admitted to S_2 again via E_1 , S_1 and V_2 , and further examination carried out after remaining in S_2 for the same period of time as previously adopted. Before each stage of the examination, analysis of the empty mass spectrometer and sample chamber was made for purposes of comparison.

Method of operating mass spectrometer

9. Mass scanning was carried out by variation of the magnetic field at a fixed accelerating voltage of 2KV. Ionization of the gas was produced by electrons at 70 eV. energy produced by a hot tungsten filament using 100 microamps emission; the positive ion current was measured by a D.C. amplifier and electron multiplier.

EXPERIMENTAL RESULTS

Viton a Elastomer (F.P. 101/70) Supplied by James Walker.

10. Viton A is a co-polymer of vinylidene fluoride and hexafluoropropylene.

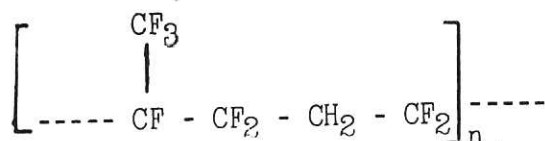


Fig. 2 shows the mass spectrum from a sample of the material after 52 hours pumping. The total pressure due to the sample was about 1×10^{-7} Torr of which approximately 90% was due to water, 5% to nitrogen and the remainder to hydrogen, oxygen and light hydrocarbon fragments.

11. After 24 hours in vacuo at 200°C the outgassing rate was reduced to about 2% of its original value and resulted almost entirely from water (Fig. 3). Following exposure to air of 53% humidity at 24°C and a further pumping of 48 hours, the outgassing rate had risen to approximately 30% of the original value and this also appeared to result almost entirely from water (Fig. 4).

Poly-urethane elastomer

12. A sample of poly-urethane rubber, based on poly-ethylene adipate and naphthalene di-isocyanate, was examined after 48 hours pumping; the resultant mass spectrum is presented in Fig. 5. The total pressure due to the sample was about 2.3×10^{-7} Torr of which 93% was apparently due to water while the remaining 7% was attributed to carbon monoxide, hydrogen and oxygen. Following bakeout in vacuo at 100°C for 41 hours the outgassing rate had fallen to 1.5% of that observed after 48 hours pumping and of this 3% resulted from water, 60% from carbon dioxide about 30% from carbon monoxide and the remainder oxygen. (Fig. 6). Exposure to air of 50% humidity at 22°C followed by 48 hours pumping (Fig. 7) resulted in an outgassing rate which was 70% of the original value. 93% of the emanating products was due to water and the remaining 7% apparently consisted of carbon monoxide, hydrogen and oxygen.

Epoxide Resin Cured at 150°C for two hours.

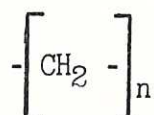
13. This consists of:- 100 parts MY 740[/] (Diglycidyl ether of Bis phenol A, low molecular fraction, epoxide equivalent 190).
80 parts methyl nadic anhydride^{//}. (Diels Alder adduct of methyl cyclopentadiene and maleic anhydride).
0.6 parts accelerator 1266[/] (Amine salt).

[/] Supplied by CIBA, ARL, Duxford, Cambridge.

^{//} Supplied by National Aniline Div., Allied Chemical Corp., New York.

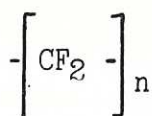
14. A mass spectrum of the material taken after 51 hours pumping (Fig. 8) showed a pressure due to the sample of 1.5×10^{-8} Torr of which 96% was due to water 2.5% to carbon dioxide with the remainder most probably resulting from nitrogen and argon. After bakeout at 85°C for 24 hours the material was not emanating sufficient gas to be observed (Fig. 9). Following exposure to atmosphere of 42% humidity at 23°C and a further 51 hours pumping, the outgassing rate was 93% of the original value obtained after 51 hours pumping and was entirely due to water (Fig. 10).

Polythene (Poly-ethylene)



15. A sample of the high density form of polythene^{†††} examined after 262 hours pumping produced a mass spectrum consisting mainly of hydrocarbon groups extending from mass 12 to 150. (Fig. 11) resulting in a partial pressure of 3×10^{-8} Torr. Following pumping at 80°C for 24 hours, the rate of gas evolution had fallen to 17% of that observed initially after 262 hours pumping at room temperature. (Fig. 12). Exposure to atmosphere of 51% humidity at 29°C and a further 94 hours pumping resulted in an outgassing rate of 6% of that originally observed and about 40% of the figure following bakeout at 80°C . (Fig. 13). This suggests only slight gas take-up during exposure to atmosphere and also a continuous steady improvement under vacuum.

Polytetrafluorethylene (P.T.F.E.)^{††††}



16. After 48 hours pumping this material produced a partial pressure of 3.5×10^{-10} Torr. 16% of the evolving gas was water, 80% appeared to be carbon-monoxide and the remainder carbon dioxide. (Fig. 14).

17. After a further 21 hours, the rate of outgassing had fallen too low to influence the composition of the base pressure, a mass spectrum of which is shown in (Fig. 15). For this reason the sample was not baked. In view of the clean nature of the material, an additional mass-spectrum was obtained after 24 hours pumping following exposure to air. This showed 11 times the outgassing rate noted originally after 48 hours and analysis indicated 3% water, 54% nitrogen, 40% carbon monoxide and a further 3% consisting of argon, oxygen and

^{†††} Supplied by I.C.I. Chemicals.

^{††††} Supplied by James Walker.

carbon dioxide, (Fig. 16). A further 24 hours pumping gave 70% of the originally observed rate of gas evolution and appeared to contain 17% water, 77% carbon monoxide and 6% carbon dioxide. Twenty one more hours pumping reduced the out-gassing to a level too low to be observed.

*All quoted pressures are approximate, assuming a sensitivity equivalent to that for nitrogen.

CONCLUSION

18. The following conclusions were drawn from the fore-going studies on the behaviour of the materials at room-temperature.

Viton A. Elastomer

19. It is seen from the experimental results (Table I) that a baked-out sample of area 4.7 cm^2 produced a "nitrogen-equivalent" partial pressure of 2×10^{-9} Torr at the ion source region, where the conductance was about 4.7 litres per second.

TABLE I

Pressure in ion source region resulting from outgassing of the materials studied

Pressure resulting from outgassing in Torr			
Material	Before bake	After bake	After exposure
Viton A	1×10^{-7}	2×10^{-9}	3×10^{-8}
Polyurethane Elastomer	2.3×10^{-7}	3.5×10^{-9}	1.6×10^{-7}
Epoxide Resin	1.5×10^{-8}	Too low to observe	1.4×10^{-8}
Polythene	3×10^{-8}	5.1×10^{-9}	1.8×10^{-9}
P.T.F.E.	3.5×10^{-10}	-	2.5×10^{-10}
	down to too low to observe		down to too low to observe

Taking speed to be:-

$$S = C \left(1 - \frac{P_2}{P_1}\right)$$

where P_2 = Base pressure in Torrs.

P_1 = Total pressure in Torrs.

C = Conductance in litres per second.

then the quantity Q of gas evolved per cm^2 per second is given by:-

$$Q = S \frac{(P_1 - P_2)}{A} = \frac{C \left(1 - \frac{P_2}{P_1}\right) (P_1 - P_2)}{A}$$
$$= \frac{4.7 \left(1 - \frac{1}{3}\right) (3 \times 10^{-9} - 1 \times 10^{-9})}{4.7} = 1.3 \times 10^{-9} \text{ Torr}$$

litres per cm^2 per sec. (approx.)

20. From this it follows that with a pumping speed of 13 litres per second, a pressure of 10^{-8} Torr could be expected with 100 cm^2 of the baked material in the system, assuming that the water vapour being evolved is roughly obeying Boyles Law in this pressure region and that there is no other source of outgassing. This elastomer would therefore seem useful as a gasket and valve seating material for use down to pressures of the order of 10^{-8} Torr in systems of moderate pumping speed (see also ref. 1).

Polyurethane Elastomer

21. Considering outgassing only, this material offers no advantage over Viton 'A' and is very difficult to manufacture. Its main attribute lies in its greater resistance to some types of radiation.

Epoxide Resin

22. After bake-out at 85°C , the specimen showed an outgassing rate which was too low to be observed by the equipment used. Copious water take-up on exposure to atmosphere however, makes very extensive use of the material for construction purposes in vacuum engineering a matter for considerable caution. The reason for the apparent preferential sorbtion of water is not thoroughly understood, but, it is hoped that experiments now in hand may lead to a better understanding of the process, and hence its possible elimination.

Polythene

23. During the 24 days over which the examination extended, the sample showed a steady reduction in outgassing rate, resulting in a final figure of 1.2×10^{-9} Torr litres per second per cm^2 . It is possible after prolonged pumping that a lower rate of outgassing could be obtained, but in view of the fact that almost all of the gas emanating is hydrocarbon, it is not a very desirable material for very high vacuum service.

P.T.F.E.

24. The very low outgassing rate which this material exhibits coupled with the fact that it can tolerate baking up to 250°C make it, considered from the present aspect, a material which should have a wide range of use in systems which are subjected to only medium baking temperature.

ACKNOWLEDGEMENTS

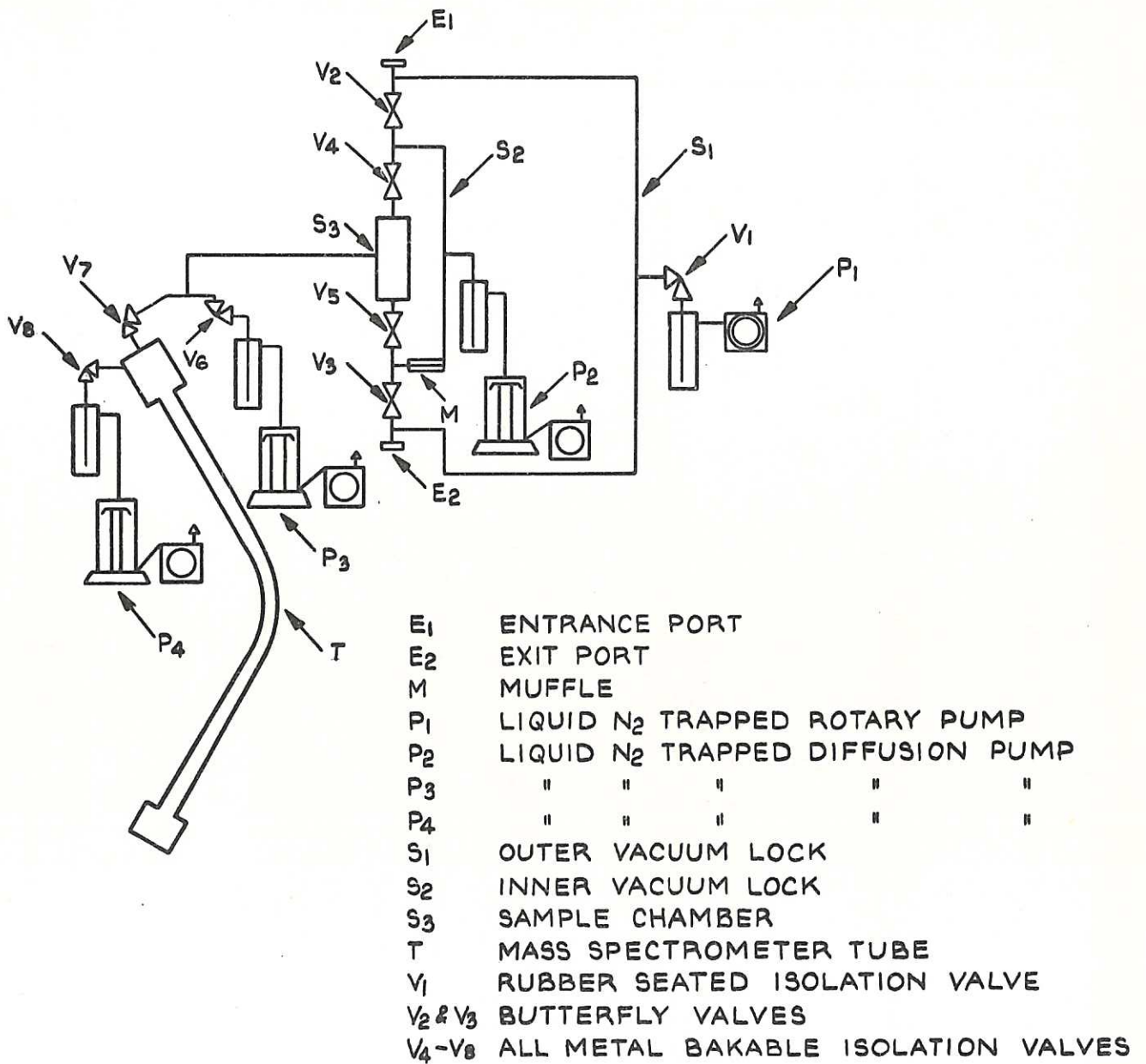
Thanks are due to Mr. A. H. Turnbull of the Mass Spectrometry Group of Chemistry Division, A.E.R.E., Harwell and to Mr. R. Sheldon of N.I.R.N.S. for advice on matters of mass spectrometry and polymer chemistry respectively.

REFERENCES

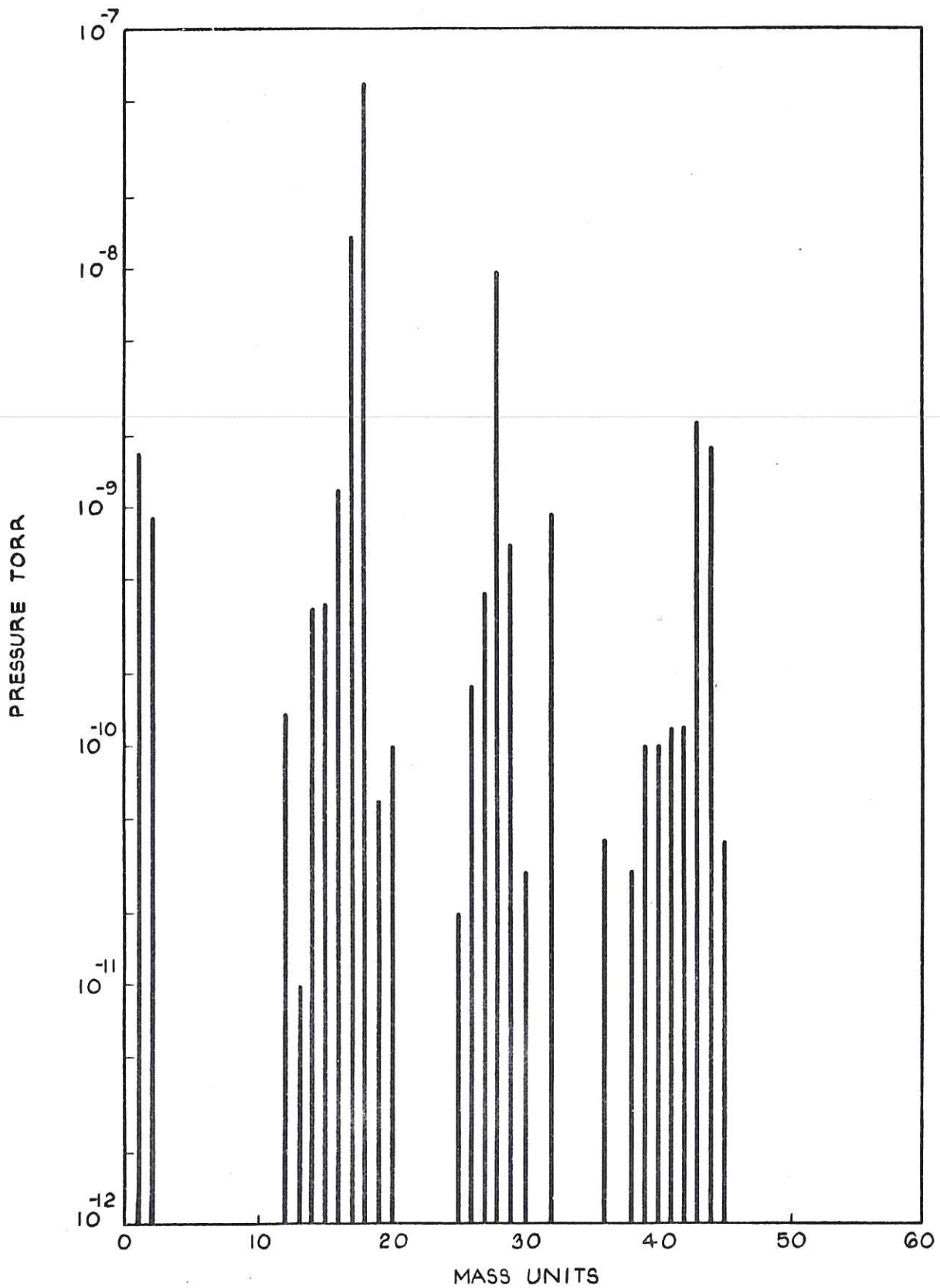
1. Evaluation of a New Fluoroelastomer as a Gasketing Material for High Vacuum Systems.

R. R. Addiss, Jr., L. Pensak and N. J. Scott.

Proceedings of the Seventh National Symposium of American Vacuum Society, 1960.

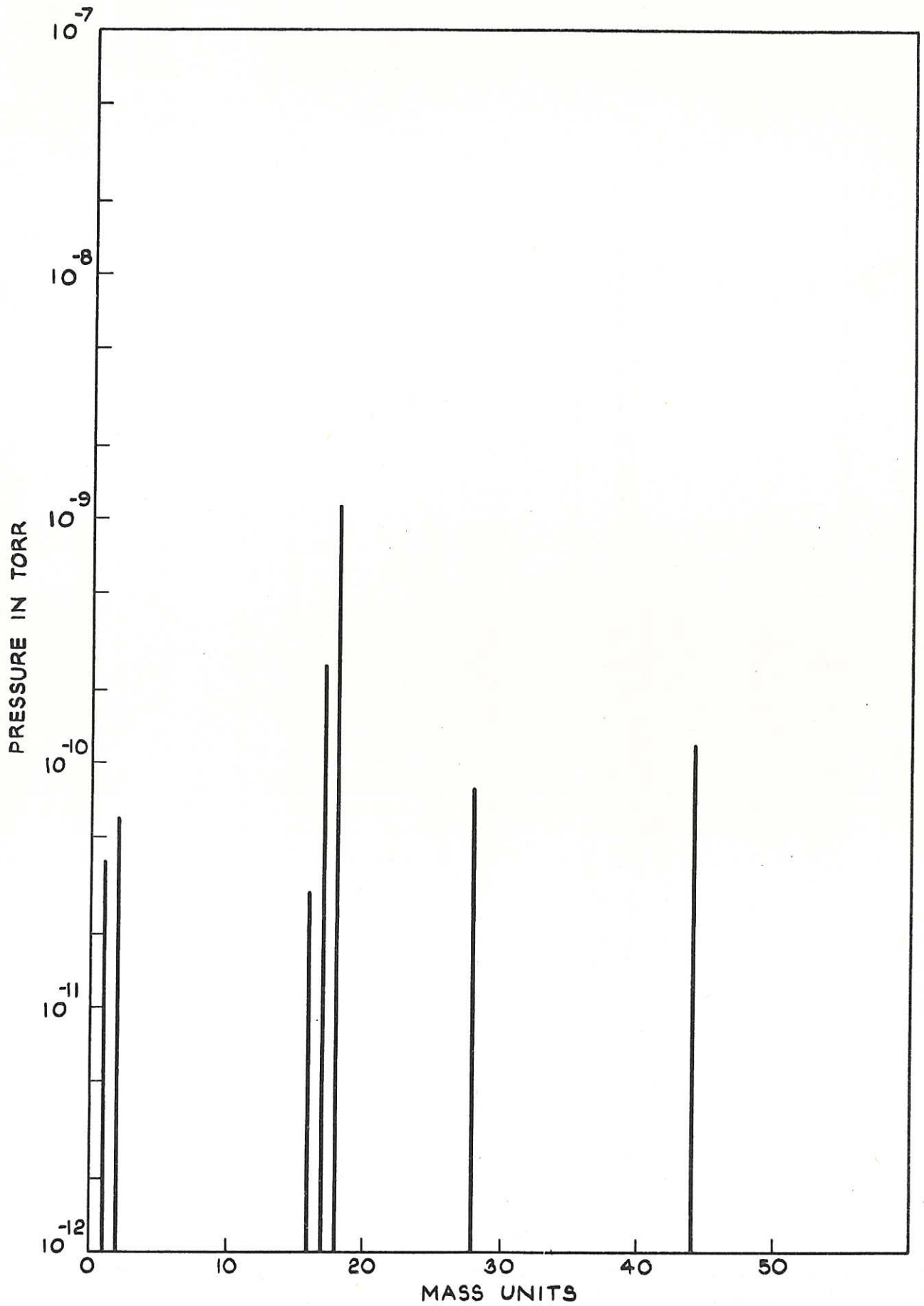


CLM-R16 FIG. I. SCHEMATIC DIAGRAM OF APPARATUS.



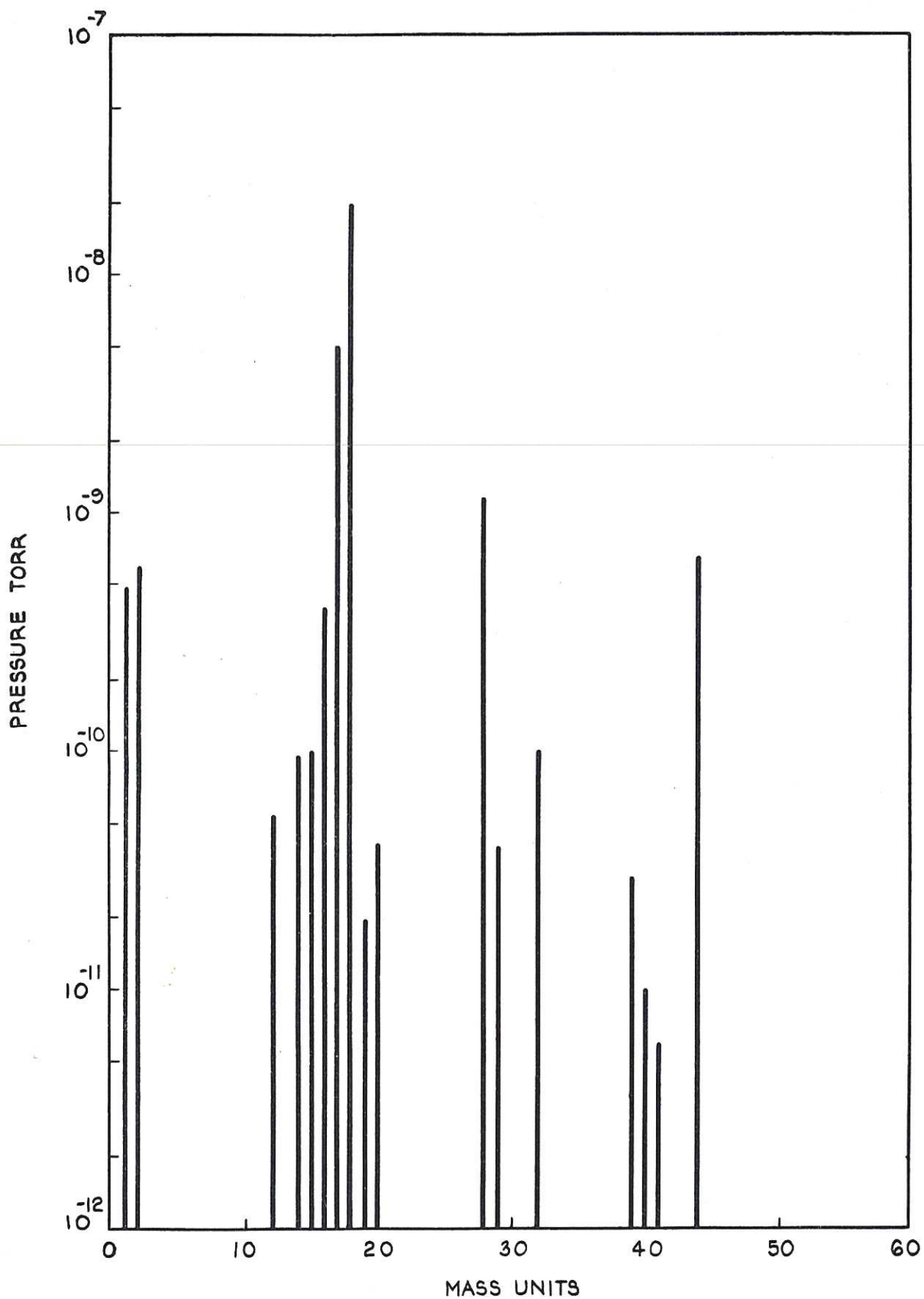
CLM-R16. FIG. 2. VITON A (E.P.101/70) AFTER BEING PUMPED FOR 52 HOURS.

AUG. 1961



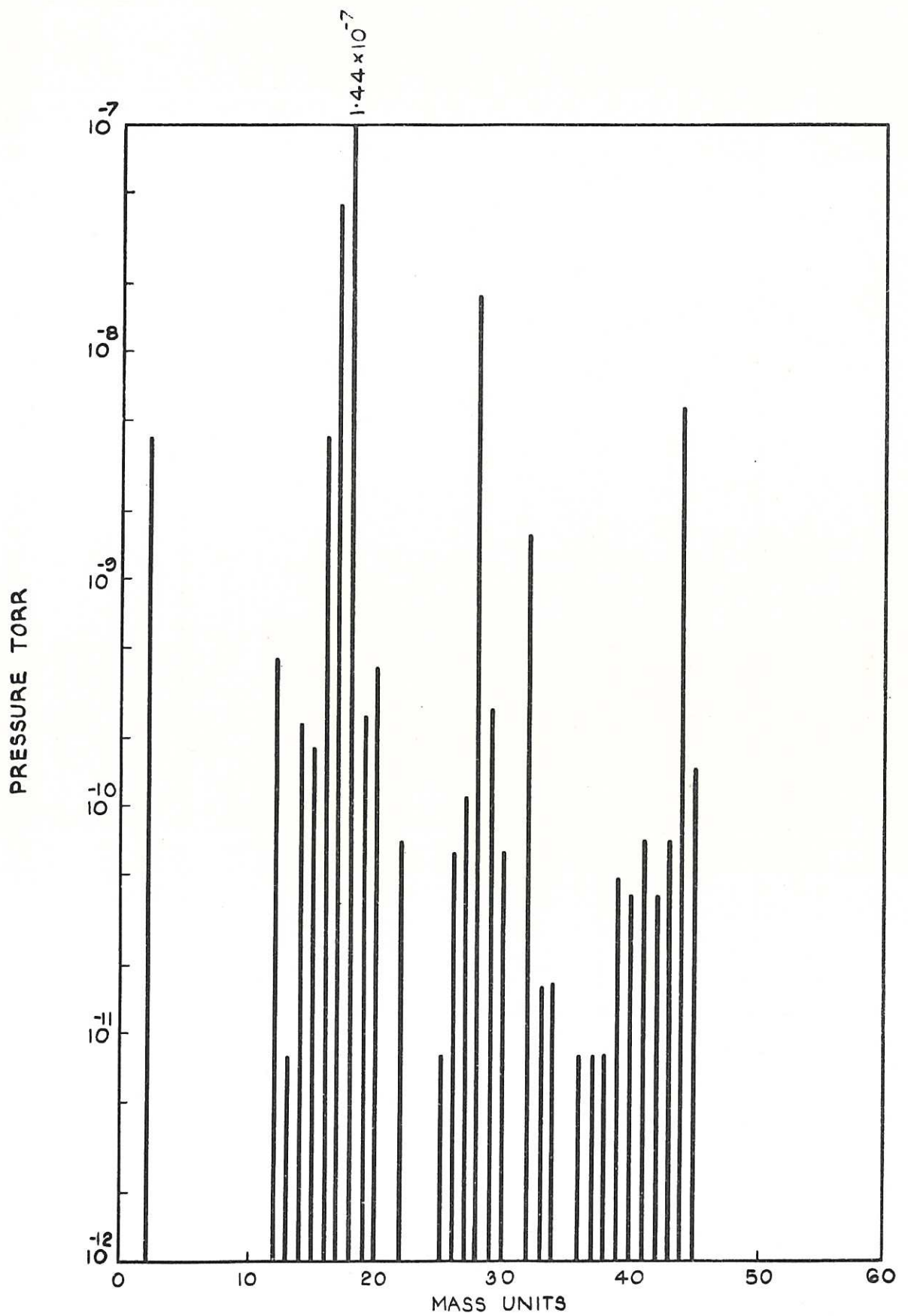
CLM-R16. FIG. 3. VITON A (E.P. 101/70) AFTER 122 HOURS PUMPING
INCLUDING 24 HOURS AT 200°C.

AUG. 1961



CLM-RI6. FIG. 4. VITON A (E.P.101/70) AFTER EXPOSURE TO ATMOSPHERE FOR 24 HOURS. HUMIDITY 53% . TEMP. 24 °C. (APPROX.) FOLLOWED BY 48 HOURS PUMPING.

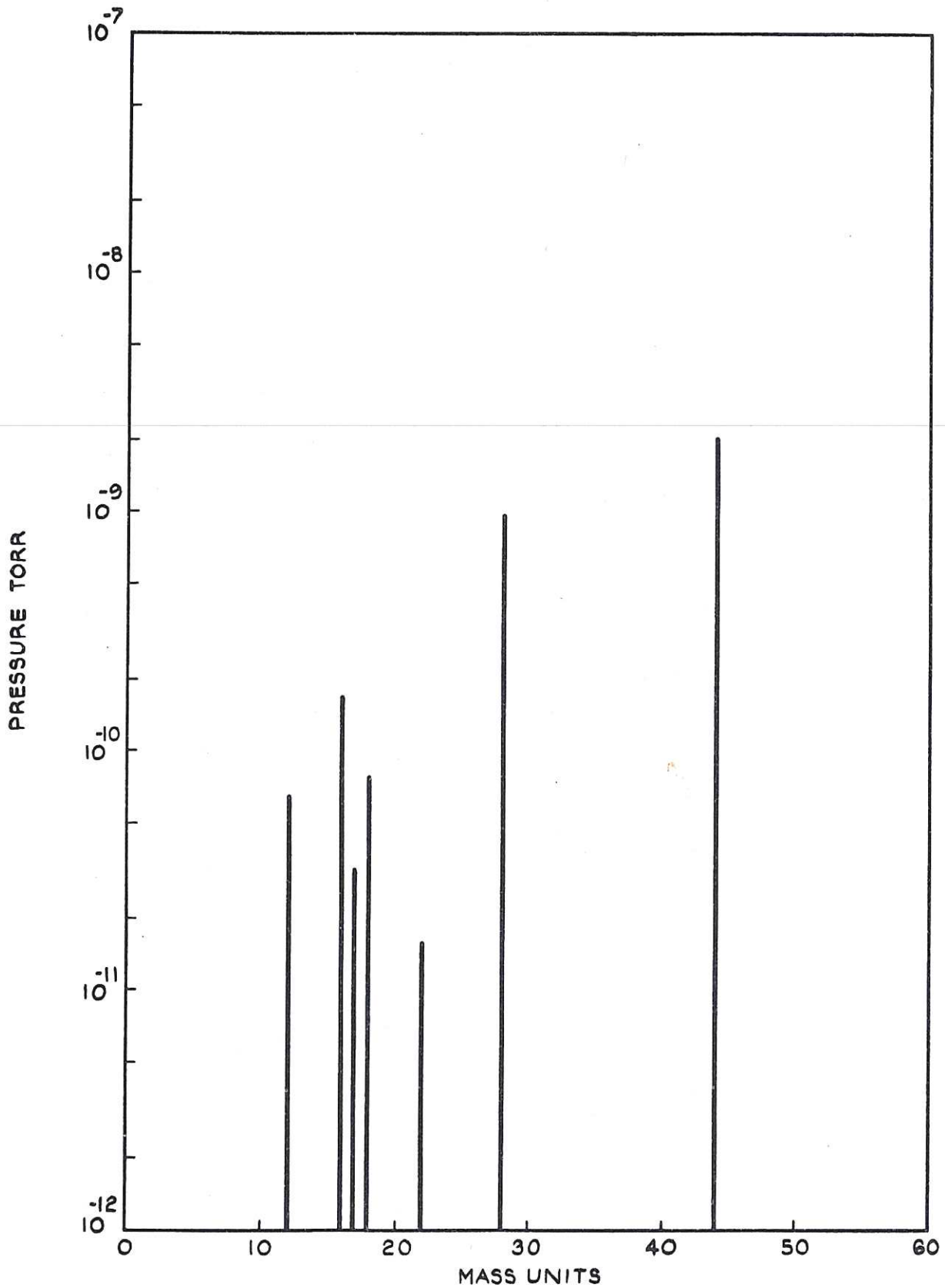
AUG. 1961



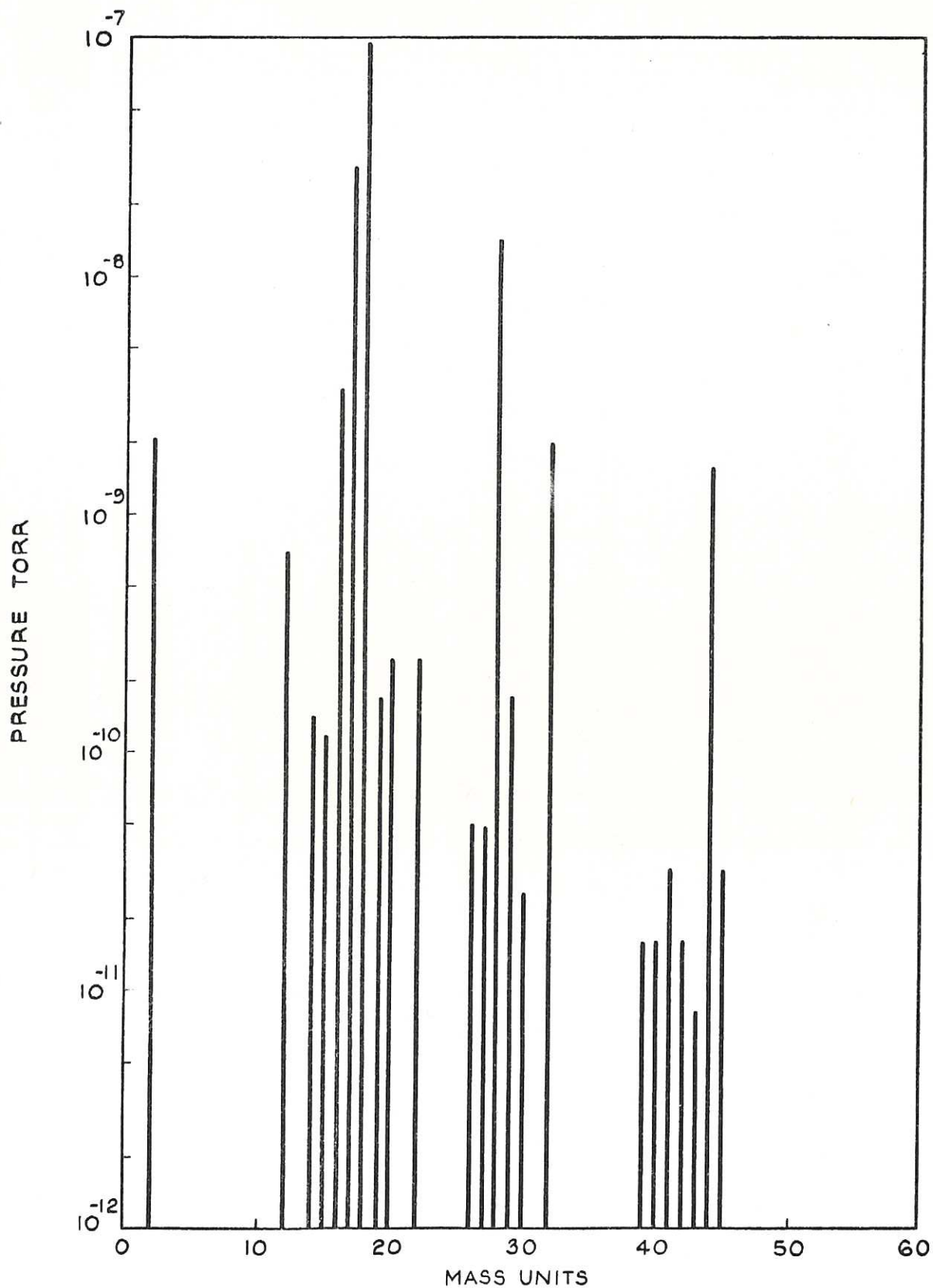
CLM - RI6, FIG. 5. POLY-URETHANE RUBBER. AFTER BEING PUMPED FOR 48 HOURS.

JANUARY 1961

SCAN COMMENCED AT MASS 2.

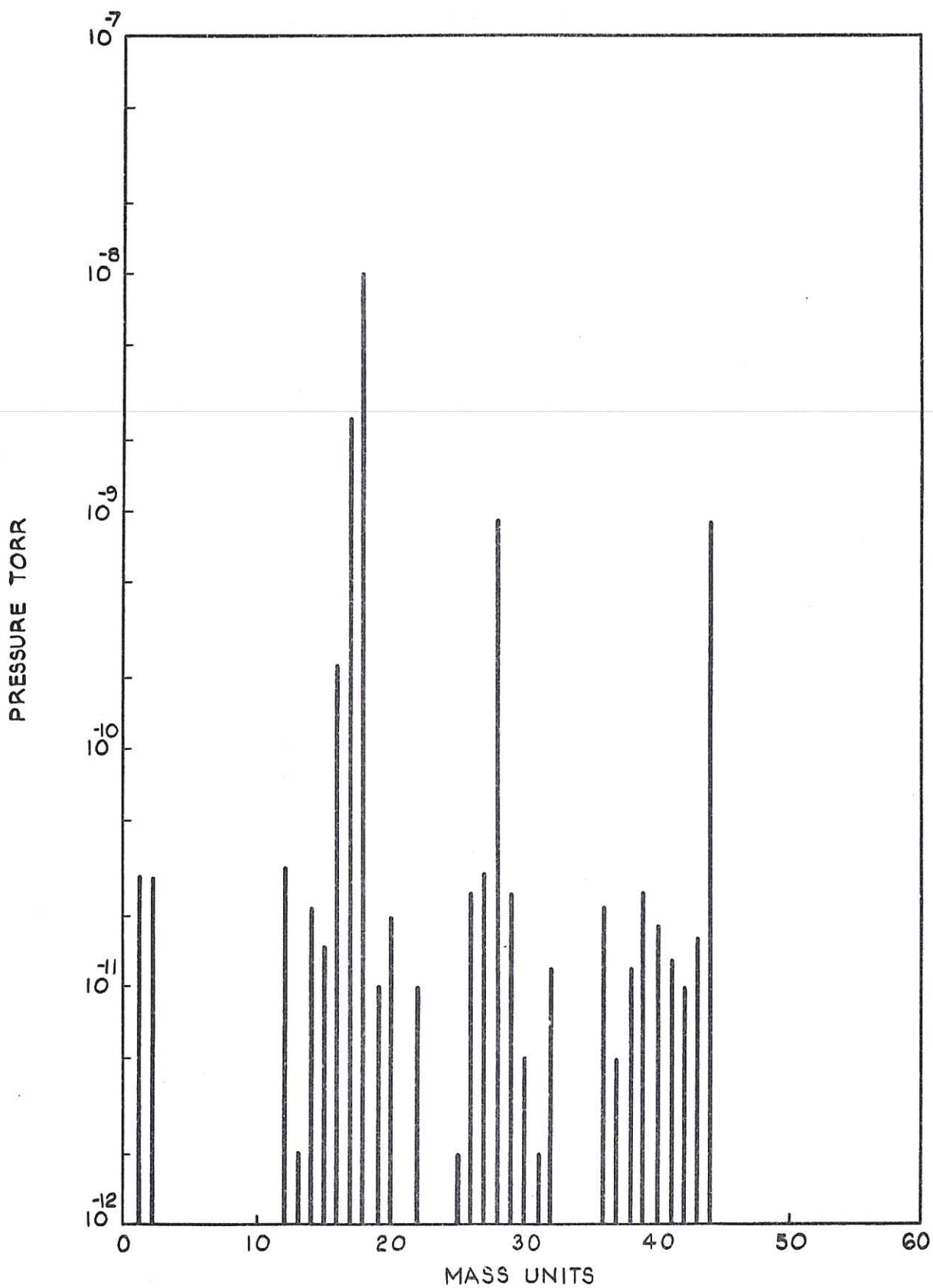


CLM-R16, FIG. 6. POLY-URETHANE RUBBER. AFTER 98 HOURS
PUMPING INCLUDING 41 HOURS AT 100°C. SCAN COMMENCED
AT MASS 2.
JANUARY 1961

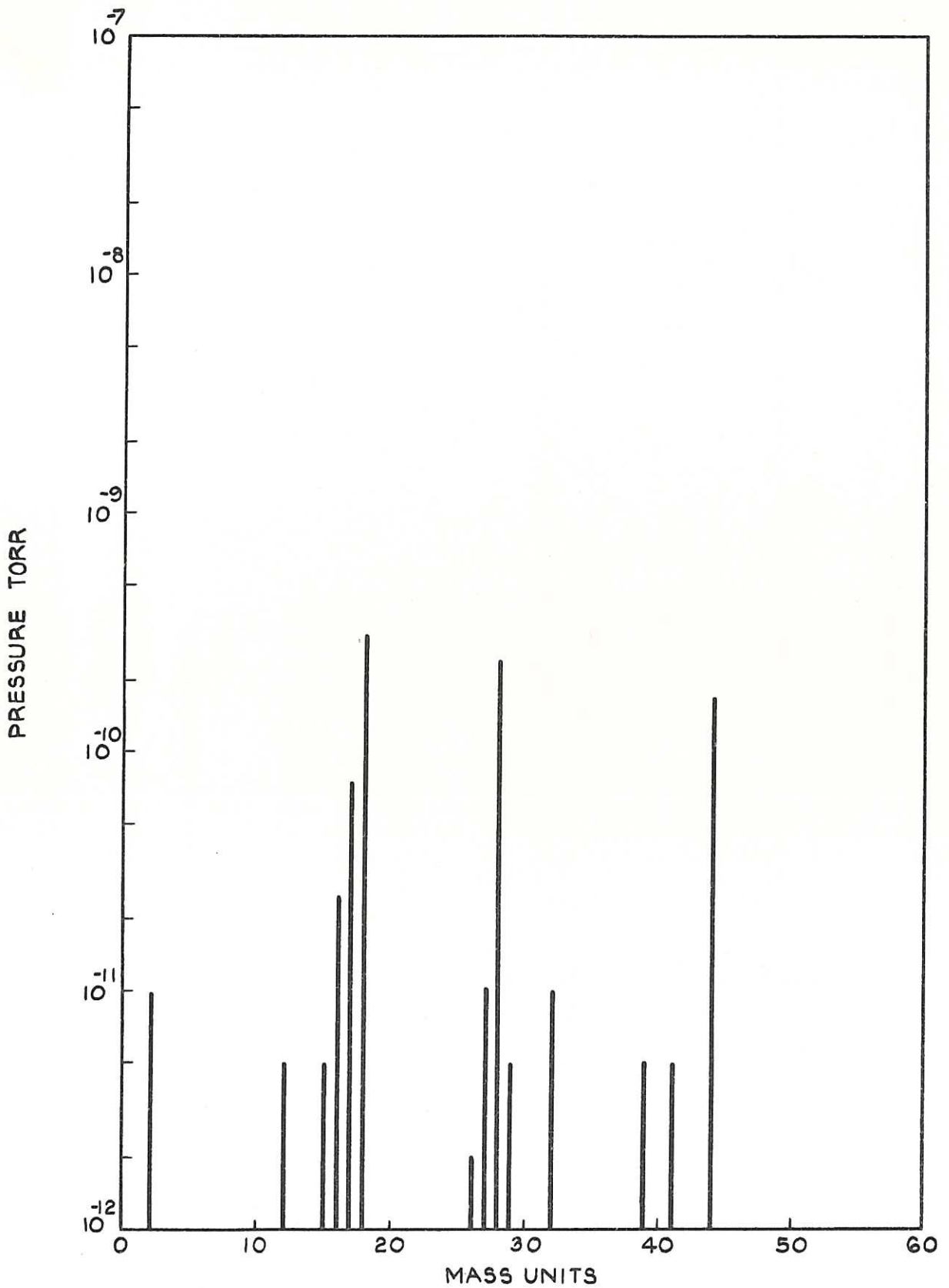


CLM-R16. FIG. 7. POLY-URETHANE RUBBER. AFTER EXPOSURE TO AIR OF 50% HUMIDITY AT 22°C. FOLLOWED BY 48 HOURS PUMPING. SCAN COMMENCED AT MASS 2.

JANUARY 1961

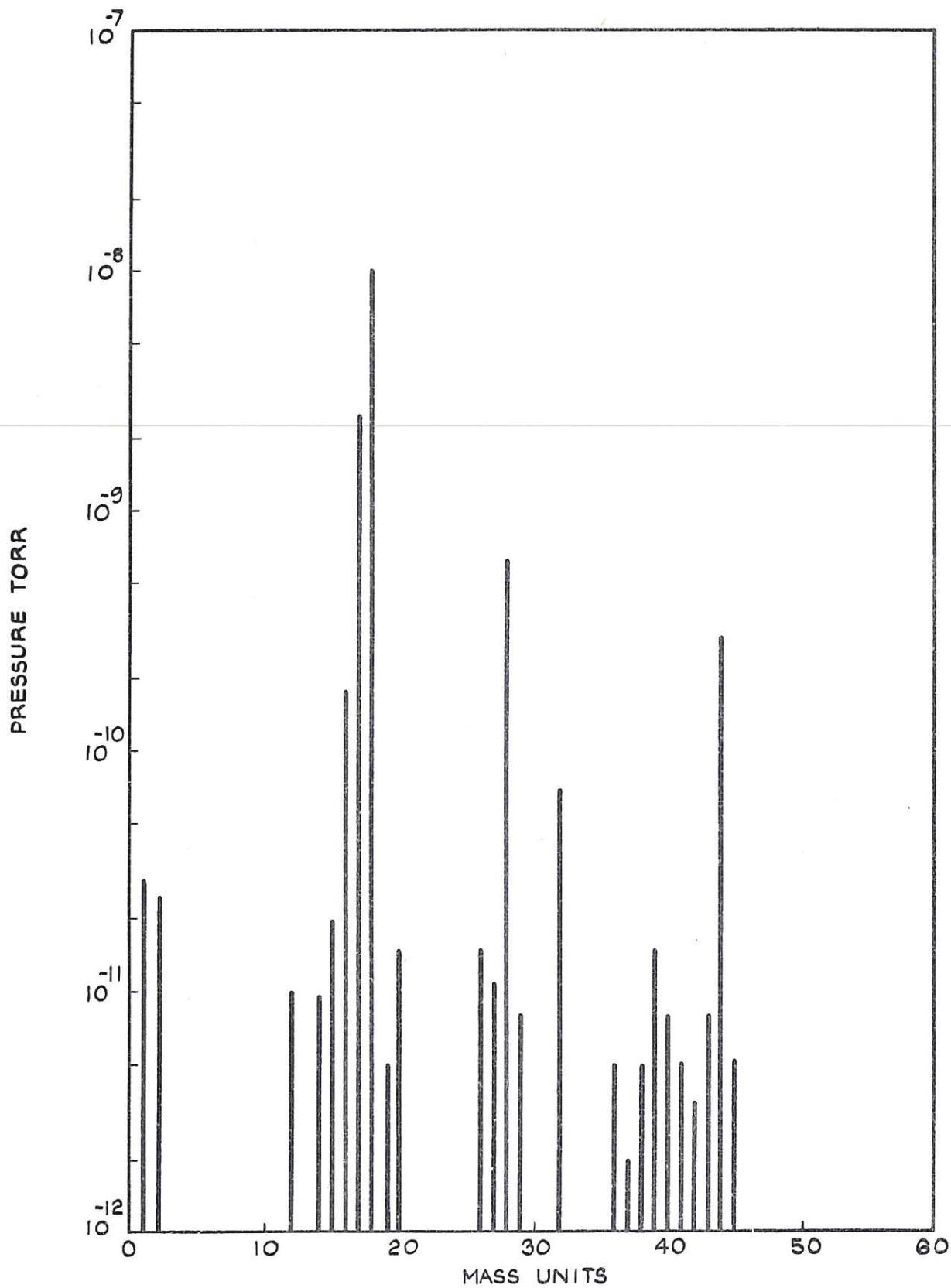


CLM - R16. FIG. 8. ARALDITE MY 740, MNA AND 1266. AFTER
51 HOURS PUMPING.
NOVEMBER 1961



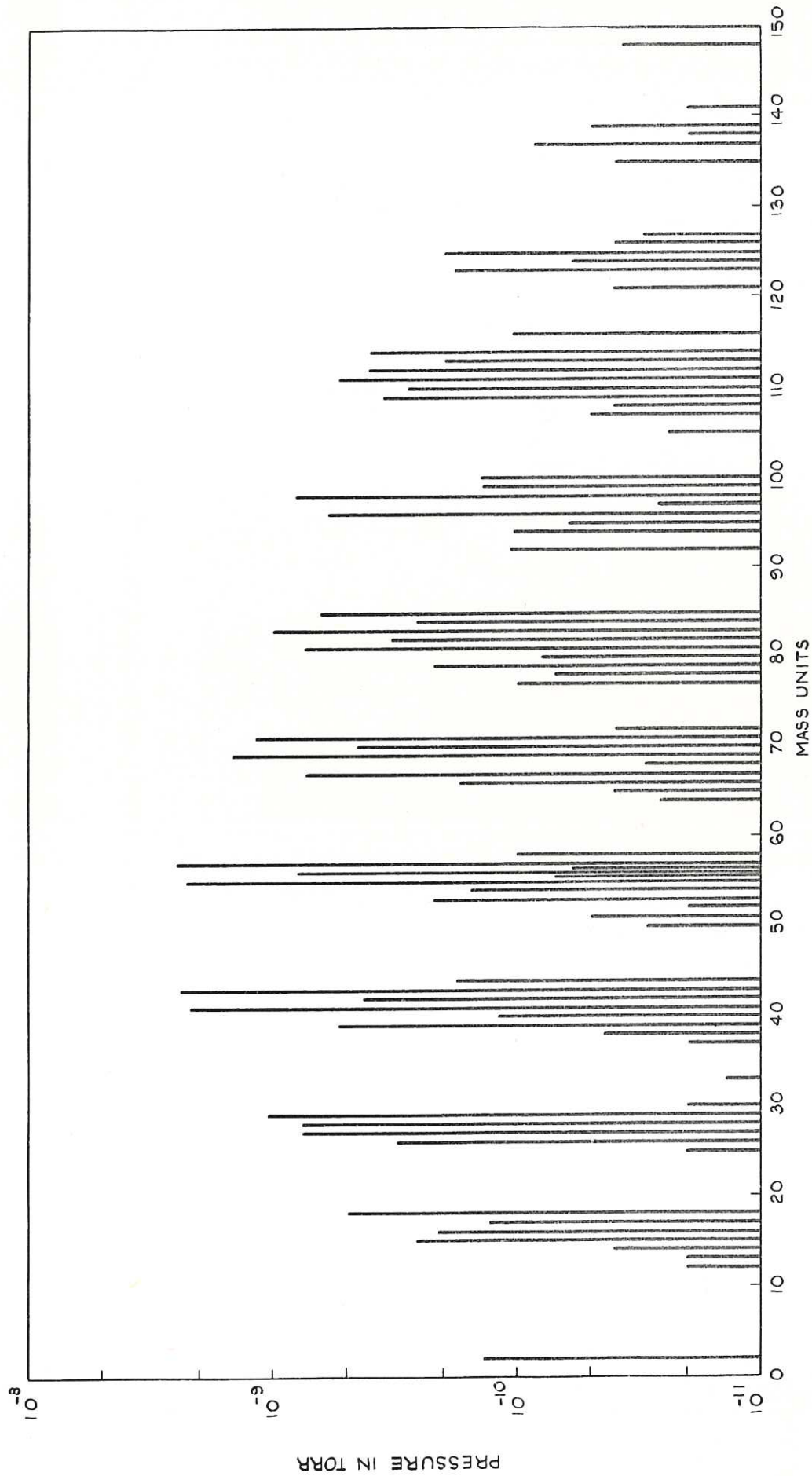
CLM-R16. FIG. 9. ARAIDITE MY 740, MNA AND 1266. AFTER 115 HOURS PUMPING INCLUDING 24 HOURS BAKE AT 85°C. THE GROUPS SHOWN ARE IDENTICAL WITH BASE PRESSURE.

NOVEMBER 1961

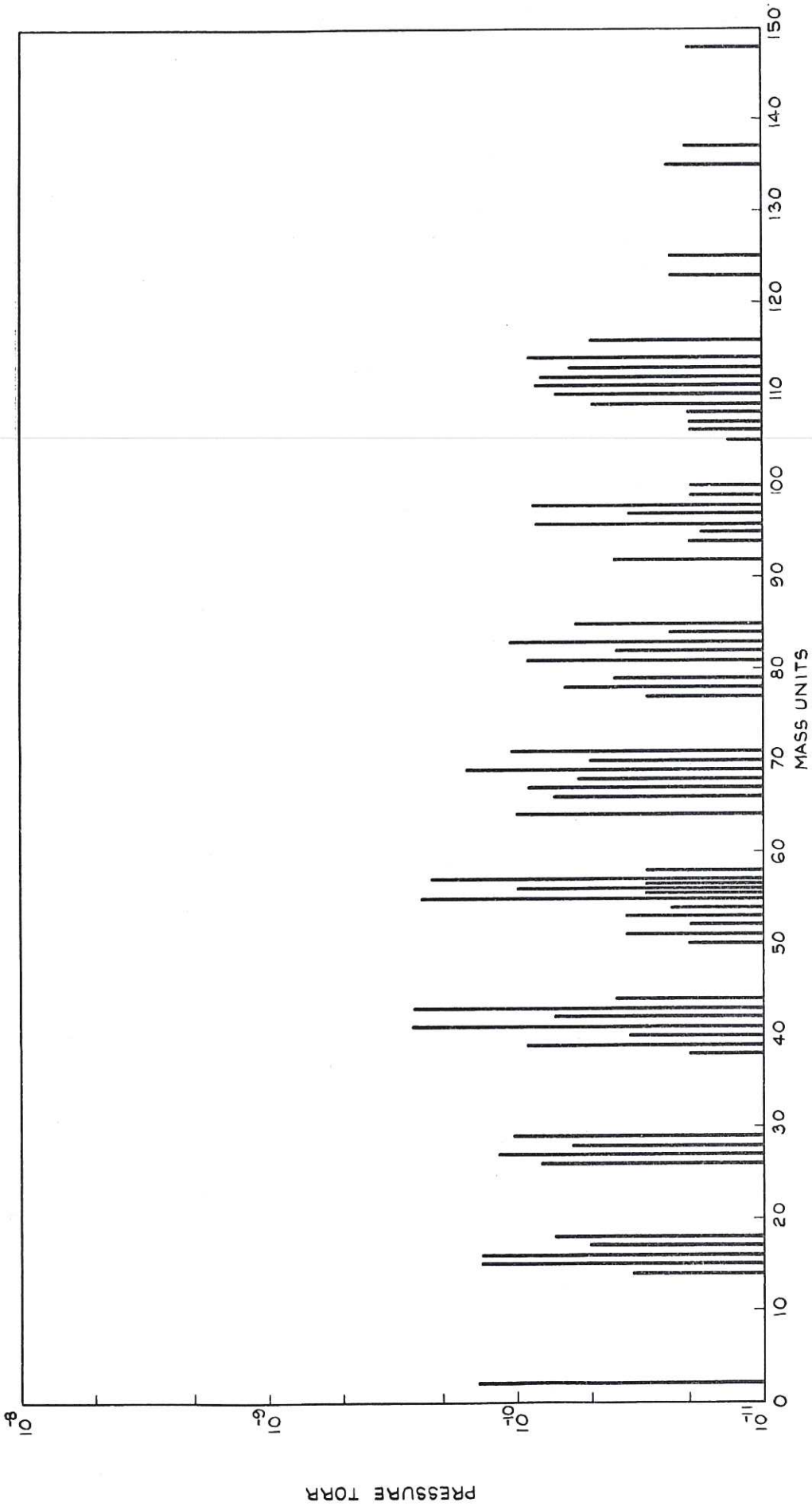


CLM - R16. FIG. 10. ARA LDITE MY 740, MNA AND 1266. AFTER EXPOSURE TO AIR OF 42 % HUMIDITY AT 23 °C. PUMPING TIME FOLLOWING EXPOSURE WAS 51 HOURS.

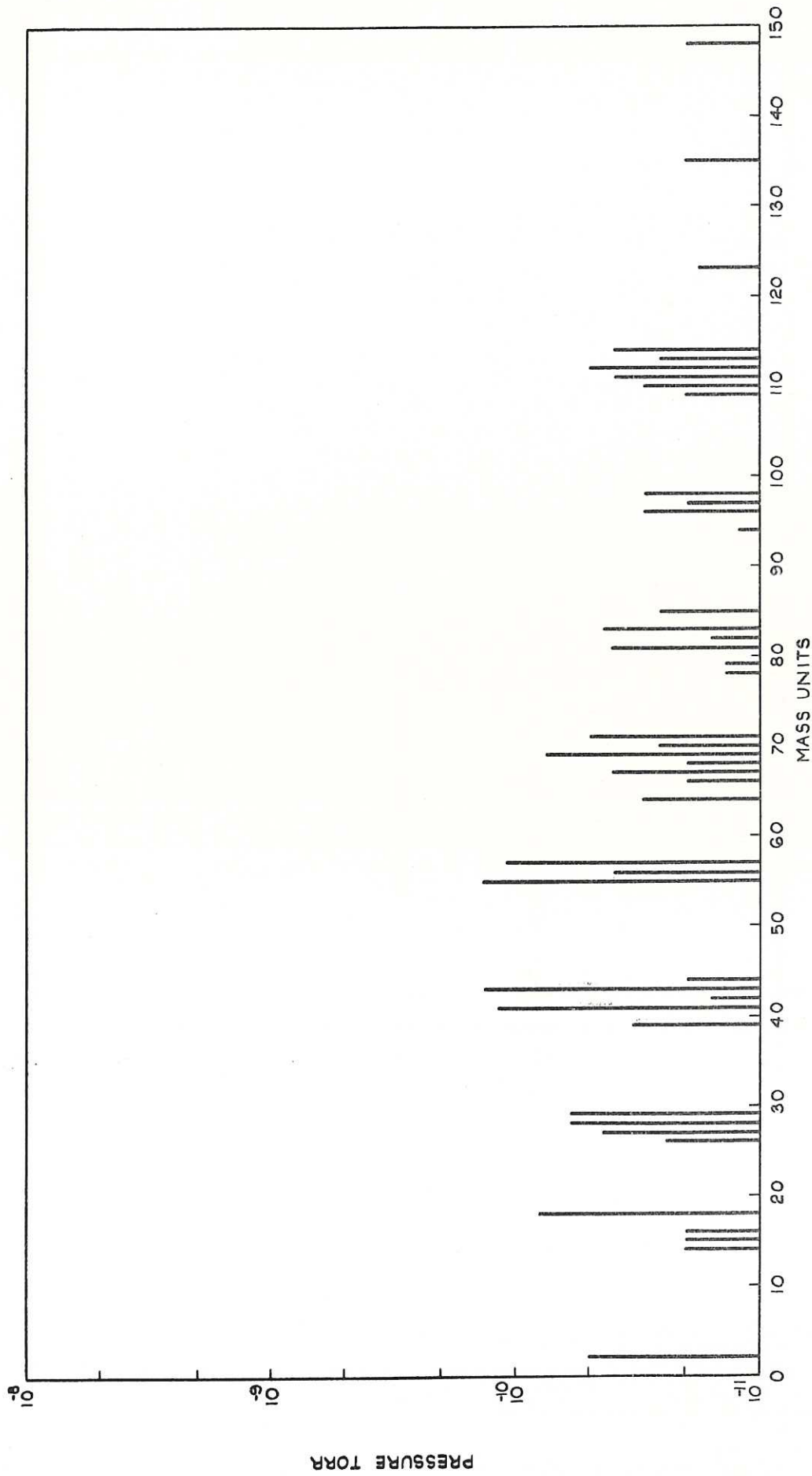
NOVEMBER 1961.



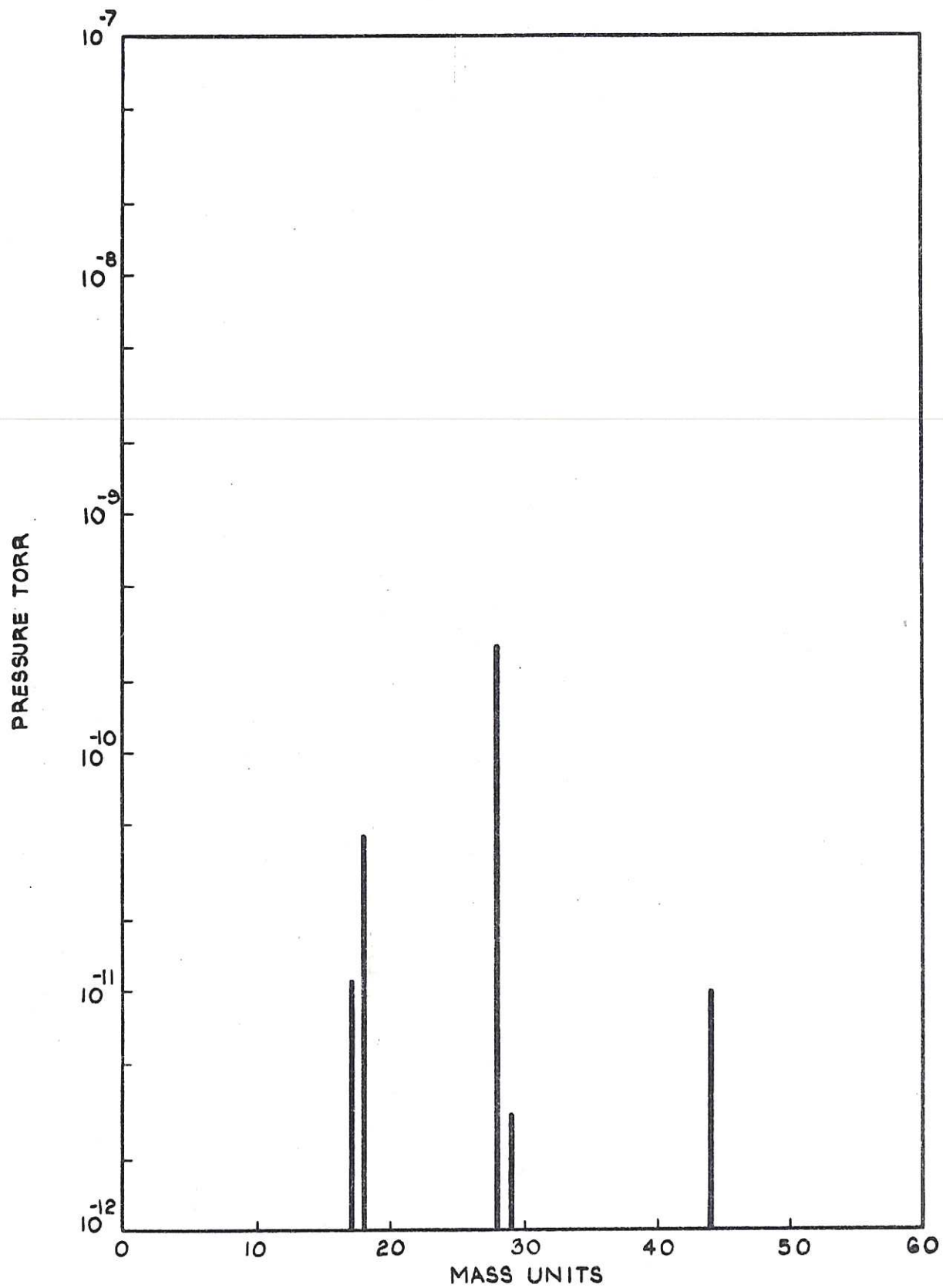
CLM - R16. FIG. II. POLYTHENE AFTER 190 HOURS IN OUTER SYSTEM. + 72 HOURS IN MASS SPECTROMETER TUBE.



CLM-R16. FIG. 12. POLYTHENE AFTER 406 HOURS PUMPING. + 24 HOURS AT 80°C. 66 HOURS IN MASS SPECTROMETER.

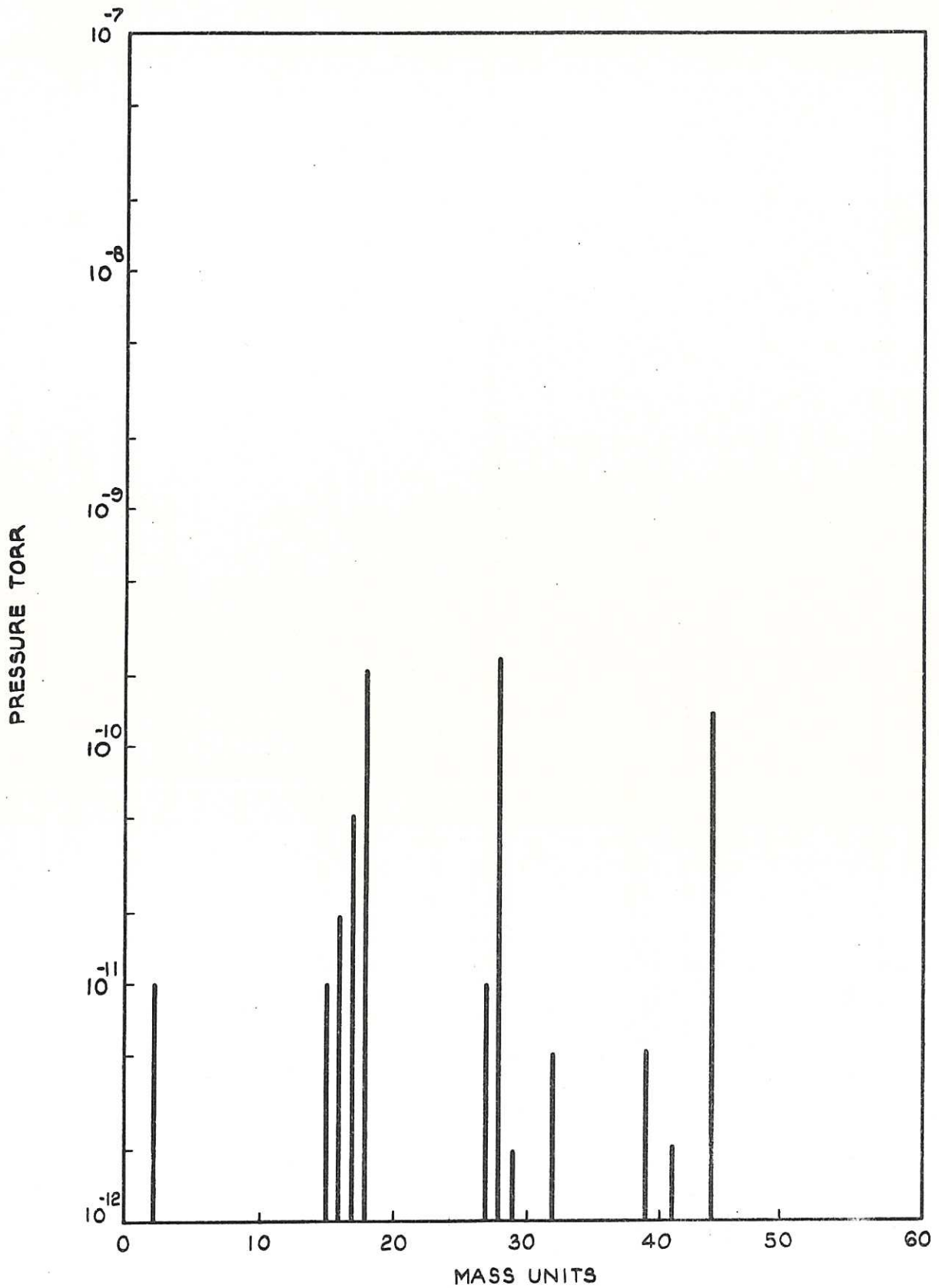


CLM - R16. FIG. 13. POLYTHENE AFTER EXPOSURE TO AIR FOR 24 HOURS AT 51% HUMIDITY AT 29°C. + 72 HOURS PUMPING IN LOCK. + 22 HOURS PUMPING IN MASS SPECTROMETER.

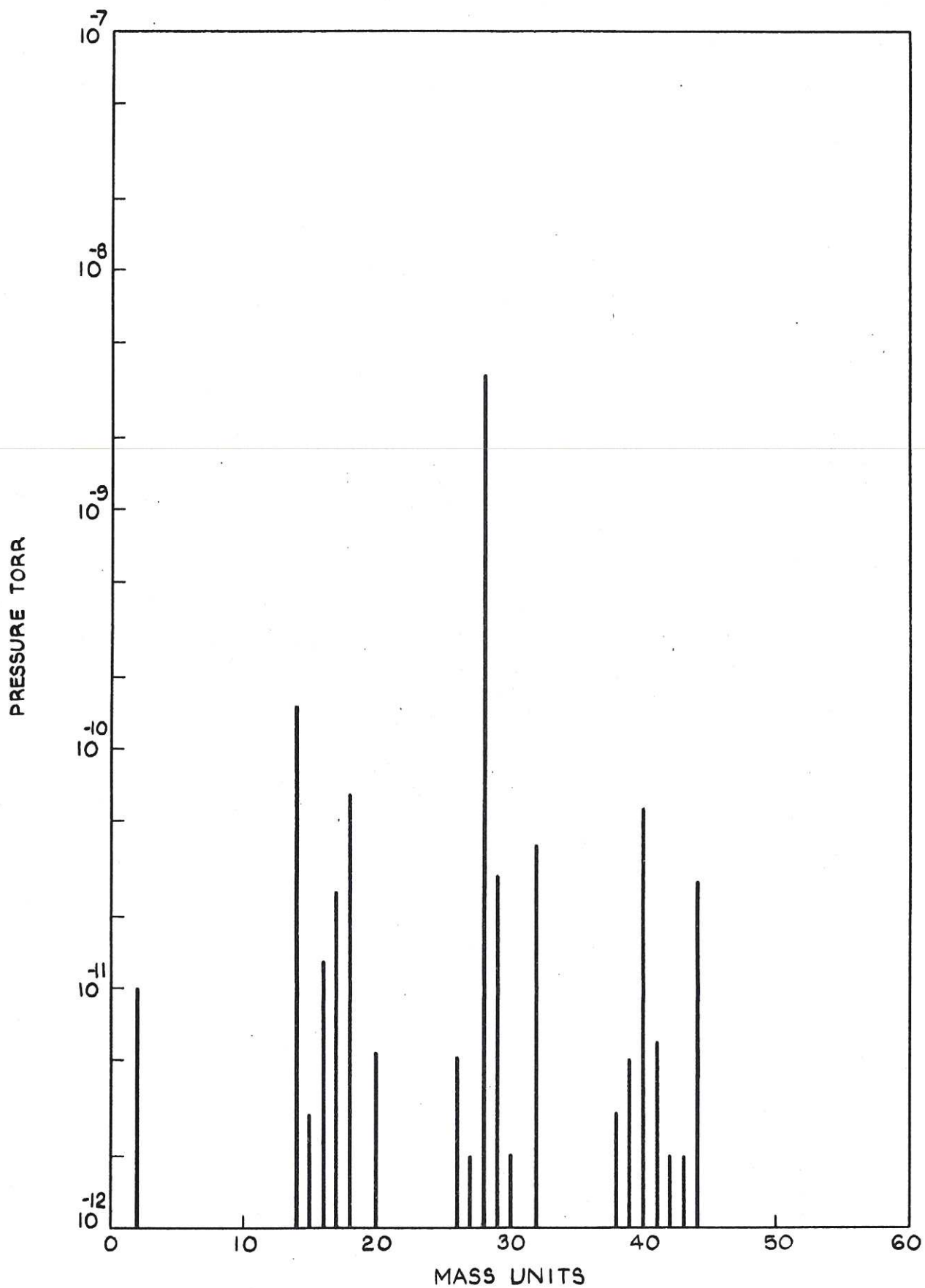


CLM-R16. FIG.14. P.T.F.E. AFTER 48 HOURS PUMPING.

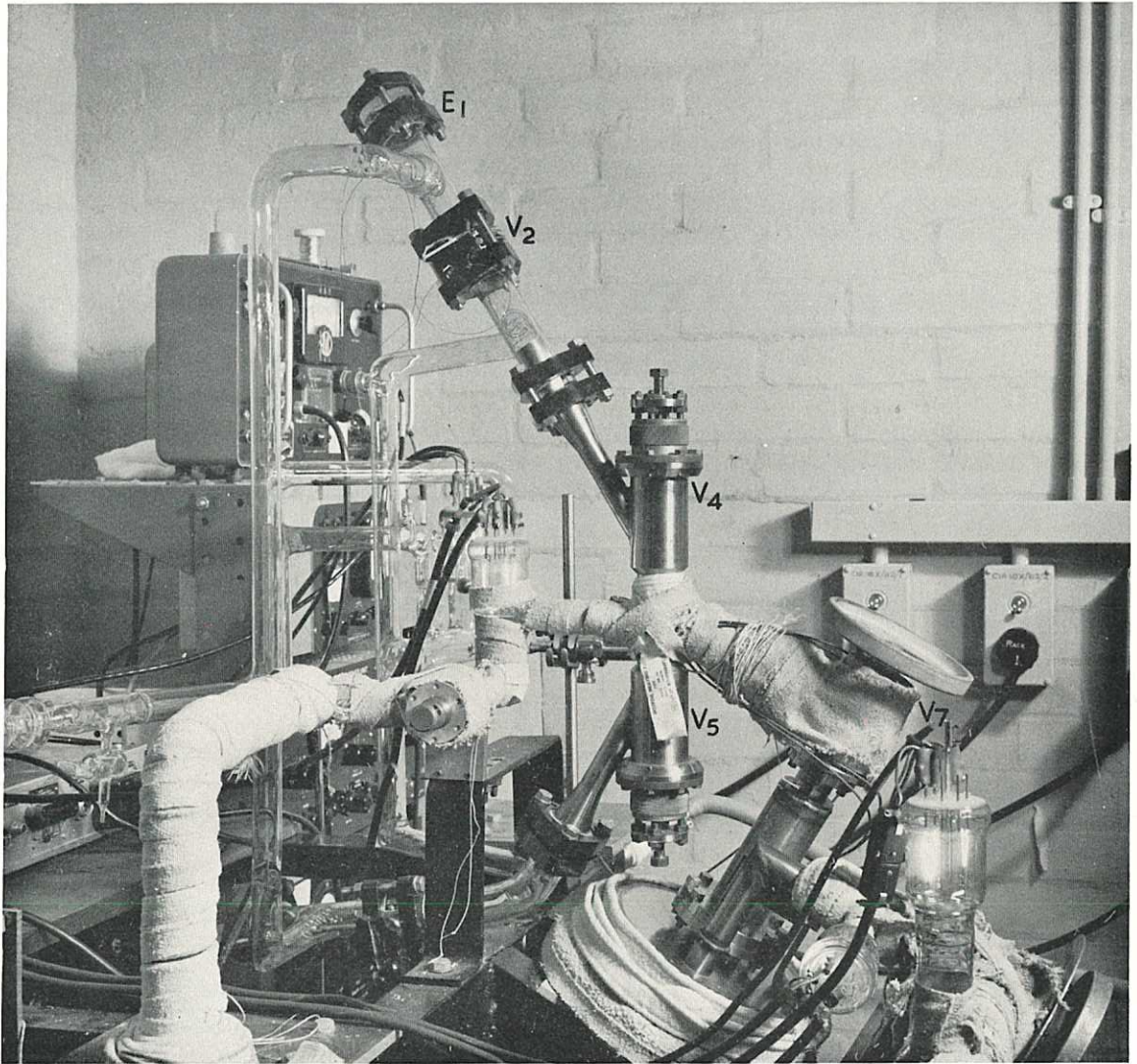
DECEMBER 1961



CLM-R16. FIG.15. P.T.F.E. BASE PRESSURE , UNEFFECTED BY THE MATERIAL AFTER 69 HOURS PUMPING .
DECEMBER 1961



CLM-R16. FIG. 16. R T. F. E. AFTER EXPOSURE TO AIR FOR 24 HOURS WITH HUMIDITY 34% & TEMP. 23°C FOLLOWED BY 24 HOURS PUMPING
DECEMBER 1961



CLM - R.16 Photograph 1.
Sample system and part of the vacuum lock system.

