CLM-R 23

United Kingdom Atomic Energy Authority

RESEARCH GROUP

Report

A MASS SPECTROMETRIC STUDY OF THE OUTGASSING OF SOME ELASTOMERS AND PLASTICS - Part 2

R. S. BARTON
R. P. GOVIER

Culham Laboratory,

Culham, Abingdon, Berkshire

1963

m H. M. Stationery Office

GS AND SIXPENCE NET

U.D.C.
533.5 : 621.384.8

UNCLASSIFIED
(Approved for Sale)

CLM - R 23

A MASS SPECTROMETRIC STUDY OF THE OUTGASSING OF SOME ELASTOMERS AND PLASTICS
Part 2

by

R.S. BARTON
R.P. GOVIER

A B S T R A C T

This report is an account of the continuation of the work described in CLM - R 16. It shows and interprets mass spectra resulting from the presence of various plastic materials and elastomers in a vacuum system and explains the method by which they were obtained.

U.K.A.E.A. Research Group,
Culham Laboratory,
Nr. Abingdon,
BERKS.

April, 1963

(C/18) /IMG

C O N T E N T S

	Page
INTRODUCTION	1
APPARATUS	1
TECHNIQUE	2
EXPERIMENTAL RESULTS	4
DISCUSSION	7
ACKNOWLEDGEMENT	9
REFERENCES	9

T A B L E

TABLE I	10

INTRODUCTION

1. The composition of the residual gas within a clean leak-free vessel after prolonged pumping is (directly or indirectly) a result of the materials of construction. It is therefore extremely important that the engineer and experimentalist should possess the maximum knowledge of the outgassing properties of the materials which, for one reason or another, they feel a need to introduce.

2. The purpose of this paper is to report information obtained by means of mass-spectrometry on the outgassing characteristics of a number of materials about which frequent enquiries have been made and is followed by a discussion on the results described in both sections of the report.

APPARATUS

3. Fig.1 shows diagramatically the apparatus used to obtain the results described later in the report. It consists of a mass spectrometer with a 60^{o} tube, T, of 15 cms radius of curvature, attached at the ion source end to a sample chamber S_3 via a one inch all-metal valve V_7. The sample chamber was connected to the inner section S_2 of a vacuum lock, by the all-metal valves V_4 and V_5. S_2 communicated with the outer section S_1 of the vacuum lock via the 'butterfly' valves V_2 and V_3. The mass spectrometer tube T, S_3 and S_2 were each attached to separate liquid nitrogen trapped oil diffusion pumps to facilitate independent pumping when necessary. S_1 was pumped by a two stage rotary pump fitted with a liquid nitrogen trap which was filled whenever V_1 was opened to reduce the hydrocarbon background due to the rotary pump oil.

Materials of Construction

4. The mass spectrometer tube, ion source electrodes and the seating cones of V_4 and V_5 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 kovar-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 S_2 and S_1 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 V_4 after baking in the muffle M. This can be better understood by reference to Fig. 2.

Seals

5. To allow baking of the mass spectrometer and sample chamber system at 250°C, aluminium wire, gold wire or diamond cross section copper ring seals were used throughout. Those in the S_2 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 S_1, were made of perbunan-base 'O' rings.

Pressure Obtained

6. 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 S_2 (which was unbaked) was 2×10^{-7}.

Diffusion Pump Boiler Medium

7. D.C.705 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

8. A rectangular sample, 3.8 × 0.3 × 0.3 cms, of the material for test was introduced into the lock S_1 (Fig.1) through an entrance port E_1, where it was allowed to remain resting on the valve V_2 (see also Figure 2) 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 for two days, this having been found experimentally to be an adequate time for most materials to reach an outgassing rate which for

practical purposes could be regarded as constant.

9. It was then 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 fifteen 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.

10. A series of scans of the gas composition resulting from the sample was made, extending over the period necessary to reach a state of pressure equilibrium within the system. (Three hours was usually sufficient with a few exceptions.) 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 hours. 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 gas in the empty mass spectrometer and sample chamber was made, so that the natural outgassing of the chamber could be subtracted from the total outgassing in the presence of the sample to obtain a figure for the gas evolution from the material under test.

Method of Operating Mass Spectrometer

11. Mass scanning was carried out by variation of the magnetic field at a fixed accelerating voltage of 2 kV. 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

12. In common with all the other pressure measuring devices whose function depends upon the ionization of a gas, the sensitivity of a mass spectrometer is dependent upon the ionization probability of the gas being studied. This in itself does not necessarily present a serious problem if a single, known, gas is being studied because the sensitivity of the mass spectrometer can be determined by introducing a sample of the gas in question and making a direct calibration. The problem does, however, become serious when several unknown gases of complex molecular structure, such as the hydrocarbons, are present in unknown quantities. These break down under electron bombardment in the ionization chamber to a complex system of lighter masses. Although the pattern for most of the common hydrocarbons is known, it becomes a formidable task to determine the parent materials when several are present, since many of the secondary products may be common and if the parent materials cannot be identified, it follows that the sensitivity of the machine to the gases in question cannot be determined. In some cases it might be possible to overcome the problem by using a machine of very high resolving power, but this would be extremely costly and for the purpose of the work being described unjustified, since the main object of the experiments was to find materials which do not contaminate the vacuum. For this reason 'nitrogen equivalent pressures' are used throughout the text of this report (i.e. based on the assumption that the mass spectrometer has the same sensitivity to all gases as that for N_2).

13. The outgassing rates for the materials examined are presented in Table I together with the conditions under which the figures were obtained and, here, in cases where water vapour was the predominant component of the mass spectrum, outgassing rates based on the true pressure are quoted in addition to the nitrogen equivalent rates.

14. The results tabulated in Table I are supported by the following notes outlining the special points of interest and the mass-spectra observed at each stage of the experiment. These are presented (1) logarithmically, for the purpose of convenience in the presentation of the entire observed

mass-spectrum; (2) linearly in the 'A' series of diagrams presenting each peak as a percentage of the mass 18 (H_2O) peak observed in the initial examination of the material, to emphasize the relative importance of each mass present. In this series, components smaller than 1% of the original mass 18 peak are neglected.

Araldite AT1

Cured at 140 - 150°C for 15 hours.

Consisting of:- Diglycidyl ether of Bisphenol A, high molecular weight cured with anhydrides.

Araldite CT200 with Hardener HT901

Cured at 140 - 150°C for 15 hours.

Consisting of:- 100 grms CT200 (Diglycidyl ether of Bisphenol A, high molecular weight, epoxide equivalent 900); 25 - 30 grms phthalic anhydride.

Araldite CT200 with HY906 and X33/1266

Cured at 140 - 150°C for 15 hours.

Consisting of:- 100 grms CT200 (Diglycidyl ether of Bisphenol A, high molecular weight, epoxide equivalent 900); 30 grms HY906 methyl nadic anhydride (Diels Alder adduct of methyl/cyclopentadiene and maleic anhydride); 0.5 cc X33/1266 accelerator (Amine Salt).

These resins were short-listed as possible adhesives for cementing together sections of a ceramic toroidal vacuum vessel for which purpose the following characteristics were necessary.

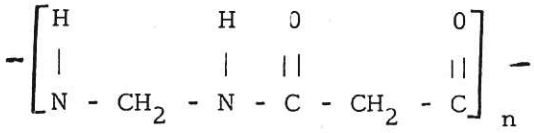
1. Good vacuum properties such as:- Low vapour pressure
   Low outgassing rate
   Low permeability.
2. High dielectric strength and electrical resistance.
3. Mechanical strength equal at least to that of the ceramic.
4. Ease of application (Ref. 1).

From the vacuum aspect, the worst of the three materials initially was AT1, but was the best after bake. CT200 + HT901 showed about the same improvement after bake as CT200 + HY906 + X33/1266 but was not so good initially. It had the advantage, however, of taking up less water than either of the others upon exposure to air. This suggests that if bakeout is not possible, CT200 + HY906 + X33/1266 is the best of the three materials, but where bakeout is possible, AT1 is probably the best choice. In all three cases the gas evolution was almost entirely water vapour.

Mycalex

This sample showed a much lower rate of gas evolution than any of the three preceding materials but, again the gas evolved was almost entirely water. A very marked improvement was achieved by the bake at 300°C and even after exposure to air for 24 hours, the outgassing was approximately only one third of that observed at the outset.

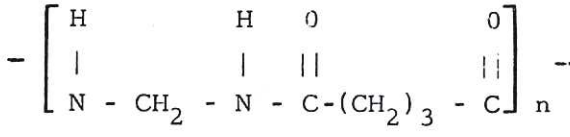
Nylon 31



Examination after 51 hours pumping showed more than 90% of the gas evolution to be water (Figure 14). Following the bakeout period, the outgassing was reduced by about 2 orders of magnitude (Figure 15) and the partial pressure of many of the hydrocarbon fragments had fallen beyond the limit of sensitivity of the machine. After exposure to air, however, it was noted that although the peaks resulting from water had grown by an order of magnitude, many of the carbon compound peaks were absent (Figure 16). It was assumed therefore that these arose from incompletely polymerised material which was removed or greatly reduced by the bake. Among the most important were:-

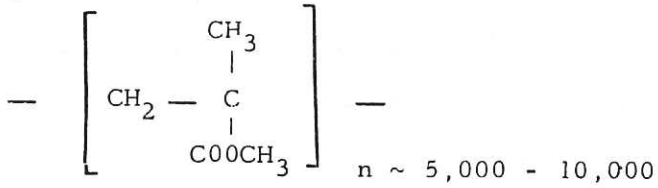
Mass	(43 CHNO)	Suggested composition of ions
	(45 CH_3NO)	
	(58 CH_2N_2O)	

Nylon 51



The behaviour of this polymer follows the same pattern as Nylon 31 but the sample was a very slightly cleaner material (Figure 17) and was approaching a factor of 10 better after bake (Figure 18). Following exposure to air there was a similar absence of many of the carbon compounds (Figure 19), notably those already mentioned in the previous case.

Perspex (Unplasticized)



Water was by far the most predominant component (Figure 20) and was reduced by the bake to about 5% of the original quantity (Figure 21). Examination following exposure to air showed this to have returned to approximately 50% of the original quantity.

Perbunan base elastomer

This was a typical example of perbunan base elastomer of the type used for sealing rings and couplings in vacuum systems. It will be seen from Figure 23 that this gave rise to carbon compounds of nearly all possible masses ranging from over 200 down to 12 and is clearly not a suitable material for use in very clean systems. Samples from three different sources were examined and varied in total outgassing rate from 1 to 4 $\times 10^{-7}$ torr litre $\times$ $sec^{-1} \times cms^{-2}$.

Silastomer '80'

Upon exposure to atmosphere the sample took up almost as much water as it originally contained, nevertheless the total outgassing remained at approximately 50% of that observed initially before bake at 200°C. This represents a substantial reduction in the background of carbonaceous material and it will be noted that the outgassing rate is comparable with that of Viton 'A'. Attention is drawn, however, to the fact that the permeability of Silastomer '80' to H_2, He, N_2, O_2 and Ar is several thousand times greater than Viton 'A' (Refs, 2, 3 and 4).

DISCUSSION

15. It will be noted that the most predominant component in all cases except polythene (Part 1, CLM - R 16) was water. This becomes apparent by reference to the 'A' series of Figures in which the components of the mass spectra are plotted on linear paper as a percentage of the mass 18 (H_2O) peak observed at the time of the initial examination of each material, neglecting any which are less than 1%. This however, unless used with discrimination, can be somewhat misleading, a particularly good example arising in the case of perbunan base elastomer where the total hydrocarbon background unseen in Figure 23A amounts to 10% of the quantity of all the components present (Figure 23). In some cases, (e.g. Araldite), hydrocarbon peaks were present in the mass spectrum but were so similar in quantity and mass number to those

seen in a spectrum resulting from the introduction of water into the system that the probability of their arising due to the emanation of water from the material appeared high. A typical mass spectrum obtained by introducing the vapour of distilled water into the mass spectrometer is seen in Figure 24 together with a mass spectrum of the residual gas in the empty system before the introduction of the water (Figure 25).

16. In other cases (e.g. Nylon) several peaks completely disappeared or were greatly reduced by the bake and did not appear again after exposure of the material to atmosphere. Such components were regarded as having resulted from the material under test, probably due to incomplete polymerisation. The perbunan base elastomer showed carbon compounds extending over a very wide mass range and these undoubtedly resulted from substances evolved from the elastomer, possibly mainly from the plasticisers and fillers.

17. The choice of a material for a particular purpose will depend among other things upon the degree of cleanliness and ultimate pressure required. Attention is therefore drawn to the fact that the absence of evolution of carbonaceous components from a material is not necessarily synonymous with absence of hydrocarbons from the vacuum system. A material can be the indirect cause of hydrocarbon production by evolving water which can react with the hot surface of another material bearing carbon as an impurity (e.g. tungsten filaments). These hydrocarbons together with carbon monoxide result from reaction with the atomic hydrogen and oxygen produced by the dissociation of the water at the surface.

18. Similar products are probably produced by ion or electron bombardment; for example some of the traces of hydrocarbon seen in the Araldite mass spectra may result from one or other of these processes or a combined action within the ion source of the mass spectrometer, though the possibility of their arising in the material itself must not be overlooked. Further, attention is drawn to the fact that the mass spectra frequently represent a picture of the secondary products resulting from dissociation of molecules of the primary gas by electron bombardment in the ionization chamber of the mass spectrometer, which in this case have an energy of 70 eV. In a vacuum system containing an ionization gauge an even more complex pattern of by-products would be expected since ionization gauges operate with electron energies between 100 and 200 electron volts.

ACKNOWLEDGEMENT

19. Thanks are due to Mr. R. Sheldon of N.I.R.N.S. for advice on matters of polymer chemistry.

REFERENCES

1. Development of ceramic bonding techniques I.C.S.E. 'B' Torus. LAB 2/6562. D. Napier & Son, Ltd., Luton Airport, Luton, Beds.

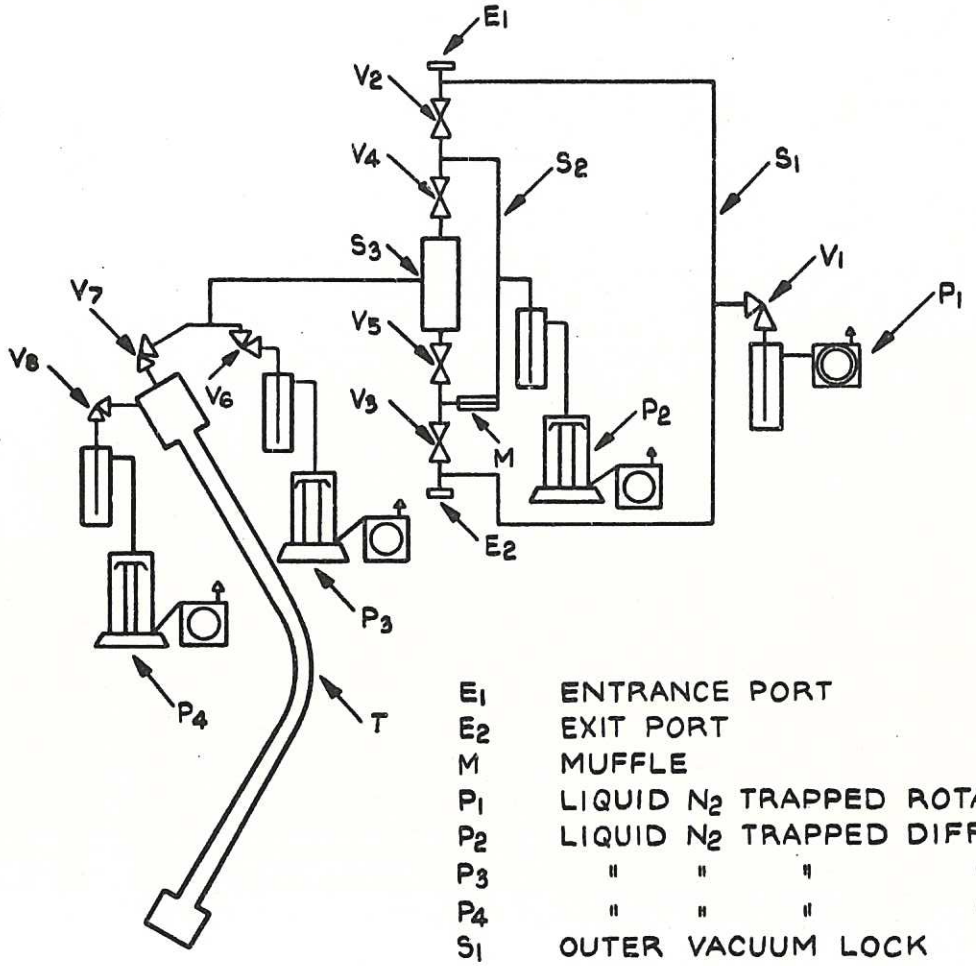
2. TURNBULL, A.H., BARTON, R.S. and RIVIERE, J.C. An introduction to Vacuum Techniques. Newnes. 1962.

3. BARTON, R.S. The permeability of a natural rubber and some rubber-like materials to H_2,He,N_2,0_2 and Ar. A.E.R.E. Z/M 210. 1958.

4. BARTON, R.S. The permeability of some plastic materials to H_2,He,N_2, 0_2 and Ar. A.E.R.E. M-599. 1960.

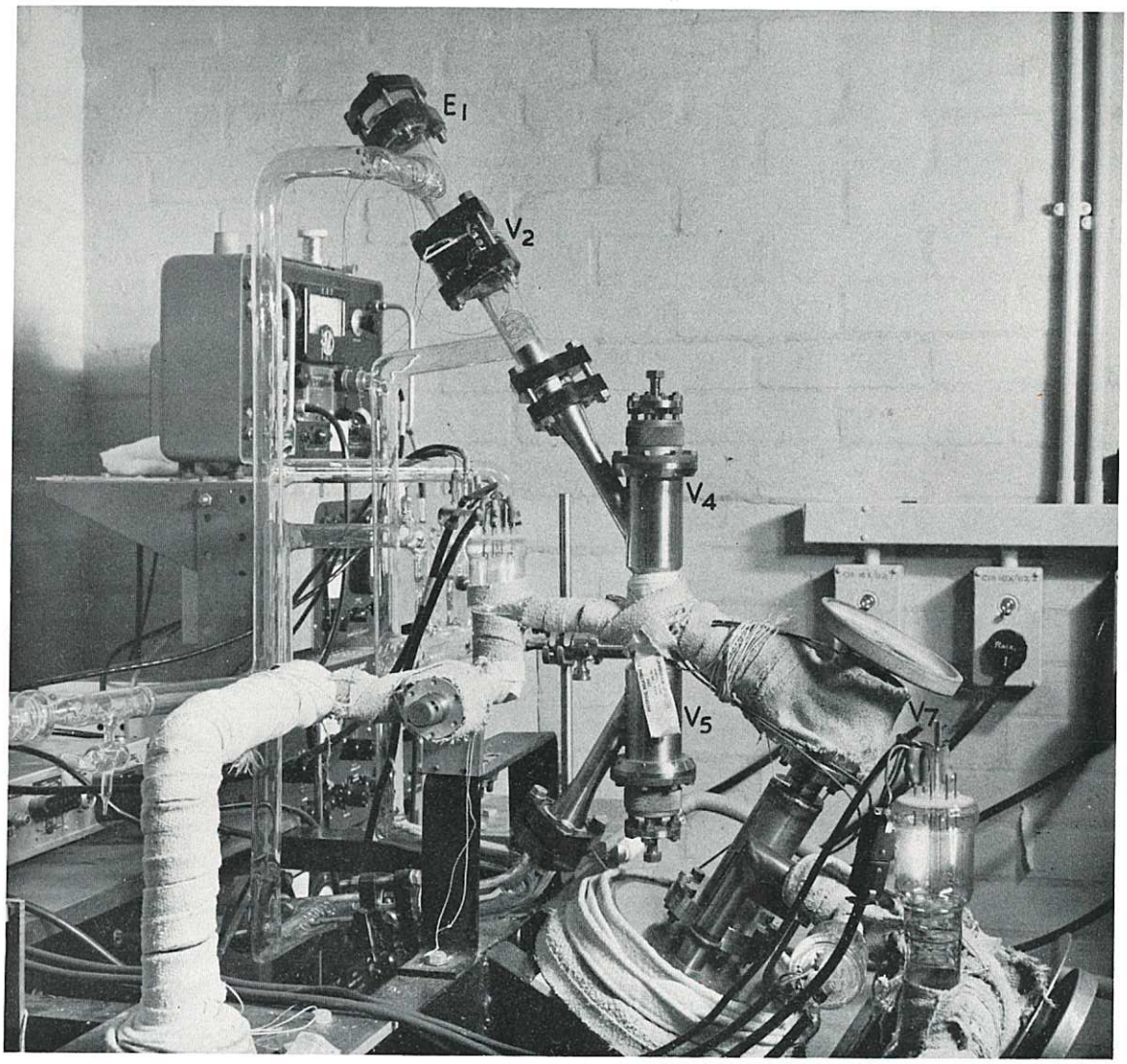
TABLE I

Material	Hours of pumping: Before bake	Hours of pumping: Including 24 hrs bake	Hours of pumping: After exposure to air for 24 hrs.	Baking Temperature °C	Outgassing rate N_2 equivalent in torr litres per second/cm^2	Outgassing: True outgassing in torr litres per second/cm^2	Figure Number
Araldite ATI	51				2600×10^{-10}	1300×10^{-10}	3, 3A
Araldite ATI		83		100	Not detectable	Not detectable	4
Araldite ATI			51		450×10^{-10}	225×10^{-10}	5, 5A
Araldite CT 200 + HT901	51				1100×10^{-10}	550×10^{-10}	6, 6A
"		98		100	2×10^{-10}	1×10^{-10}	7,
"			51		190×10^{-10}	95×10^{-10}	8, 8A
Araldite CT200 + HY906 + X33/1266	51				400×10^{-10}	200×10^{-10}	9, 9A
"		95		100	1.3×10^{-10}	0.6×10^{-10}	10
"			51		350×10^{-10}	175×10^{-10}	11,11A
Mycalex	52				20×10^{-10}	10×10^{-10}	12,12A
Mycalex		83		300	Not detectable	Not detectable	-
Mycalex			51		7.5×10^{-10}	3.7×10^{-10}	13,13A
Nylon 31	51				830×10^{-10}	415×10^{-10}	14,14A
Nylon 31		80		120	6×10^{-10}	3×10^{-10}	15
Nylon 31			51		67×10^{-10}	33×10^{-10}	16,16A
Nylon 51	51				400×10^{-10}	200×10^{-10}	17,17A
Nylon 51		82		120	0.8×10^{-10}	0.4×10^{-10}	18
Nylon 51			51		60×10^{-10}	30×10^{-10}	19,19A
Perspex	51				1000×10^{-10}	500×10^{-10}	20,20A
Perspex		102		85	60×10^{-10}	30×10^{-10}	21,21A
Perspex			51		500×10^{-10}	250×10^{-10}	22,22A
Perbunan base elastomer (PB60)	51				2000×10^{-10} approx.	-	23,23A
Silastomer 80	51				220×10^{-10}	-	26,26A
Silastomer 80		101		200	11×10^{-10}	-	27,27A
Silastomer 80			51		100×10^{-10}	-	28,28A



E_1	ENTRANCE PORT
E_2	EXIT PORT
M	MUFFLE
P_1	LIQUID N_2 TRAPPED ROTARY PUMP
P_2	LIQUID N_2 TRAPPED DIFFUSION PUMP
P_3	" " " " "
P_4	" " " " "
S_1	OUTER VACUUM LOCK
S_2	INNER VACUUM LOCK
S_3	SAMPLE CHAMBER
T	MASS SPECTROMETER TUBE
V_1	RUBBER SEATED ISOLATION VALVE
V_2 & V_3	BUTTERFLY VALVES
V_4-V_8	ALL METAL BAKABLE ISOLATION VALVES

CLM-R 23 Fig. 1 Schematic diagram of apparatus.



CLM-R 23 Fig. 2 Sample system and part of the vacuum lock system.

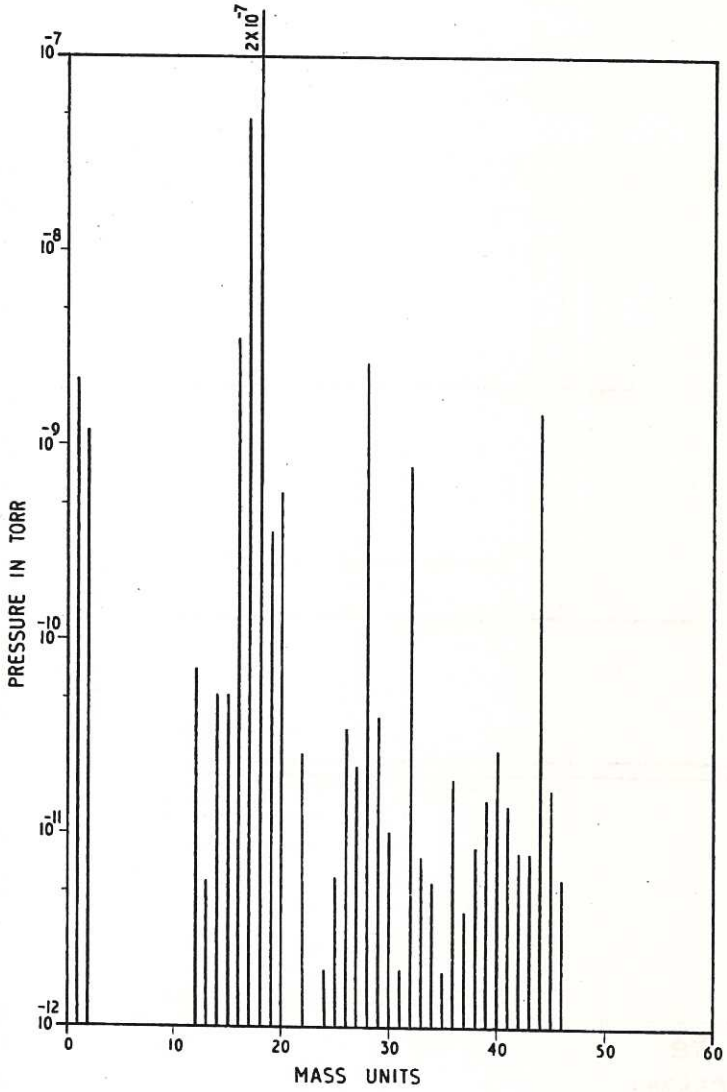


Fig. 3

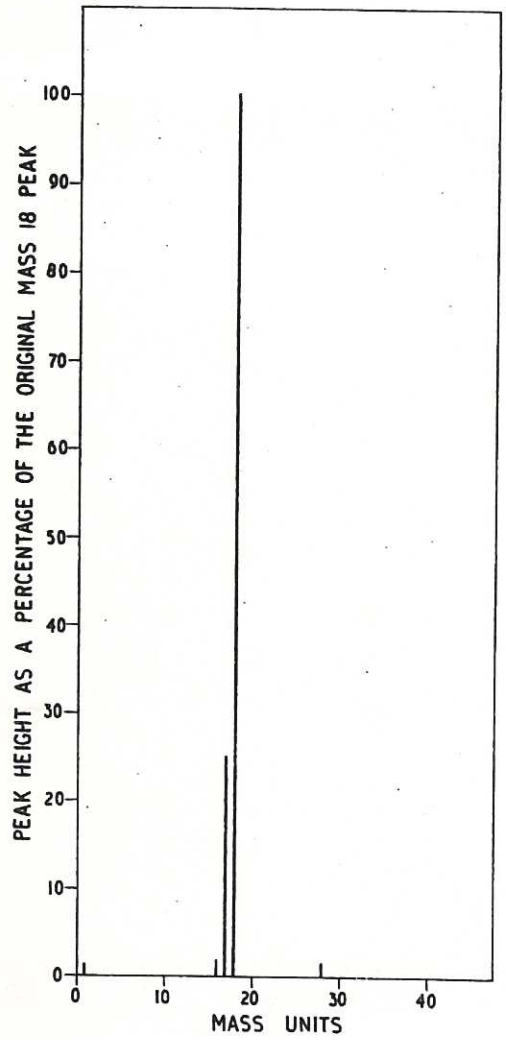
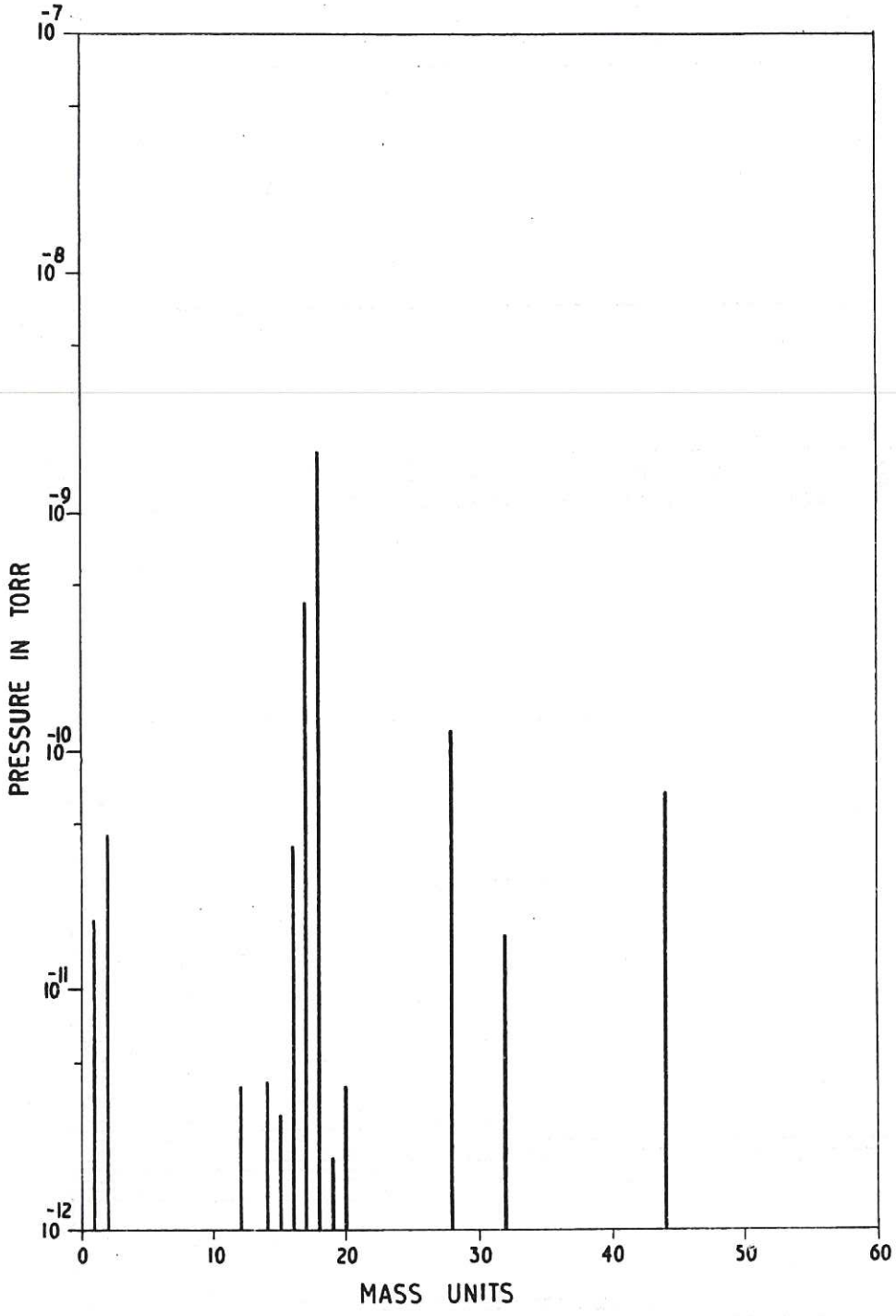


Fig. 3 A

CLM-R 23

Araldite A.T.1. After 51 hrs. pumping. September, 1962.



CLM-R 23 Fig. 4 Araldite A.T.1. After 83 hrs. pumping including 24 hrs. at 100°. September, 1962

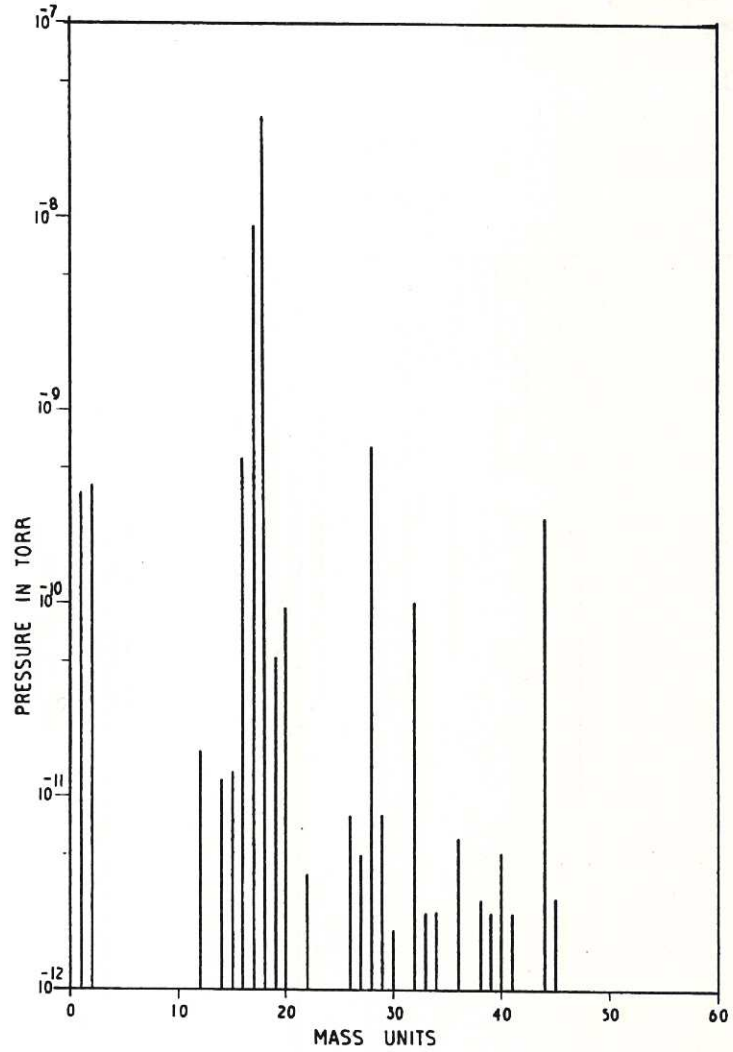


Fig. 5

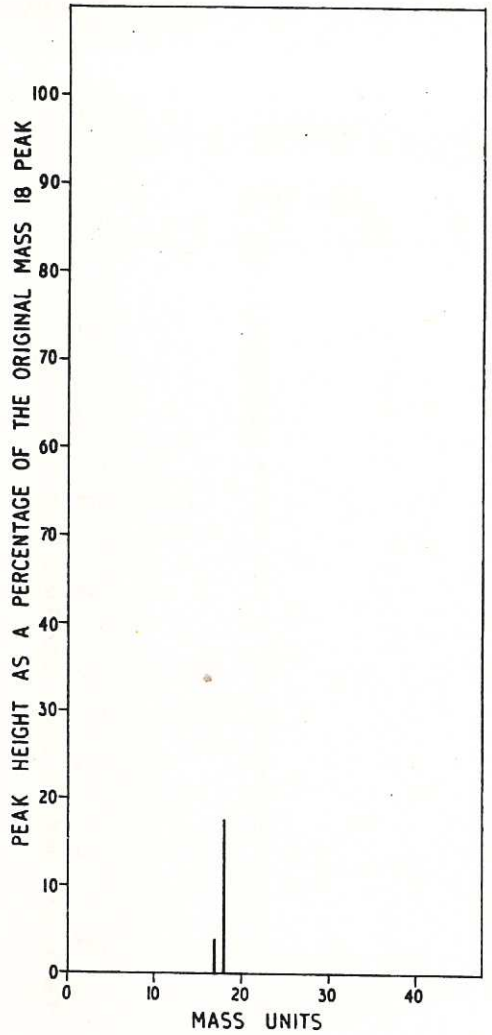


Fig. 5A

CLM - R 23

Araldite A.T.1. after exposure to atmosphere of 53% humidity for 24 hrs. followed by 51 hrs. pumping.

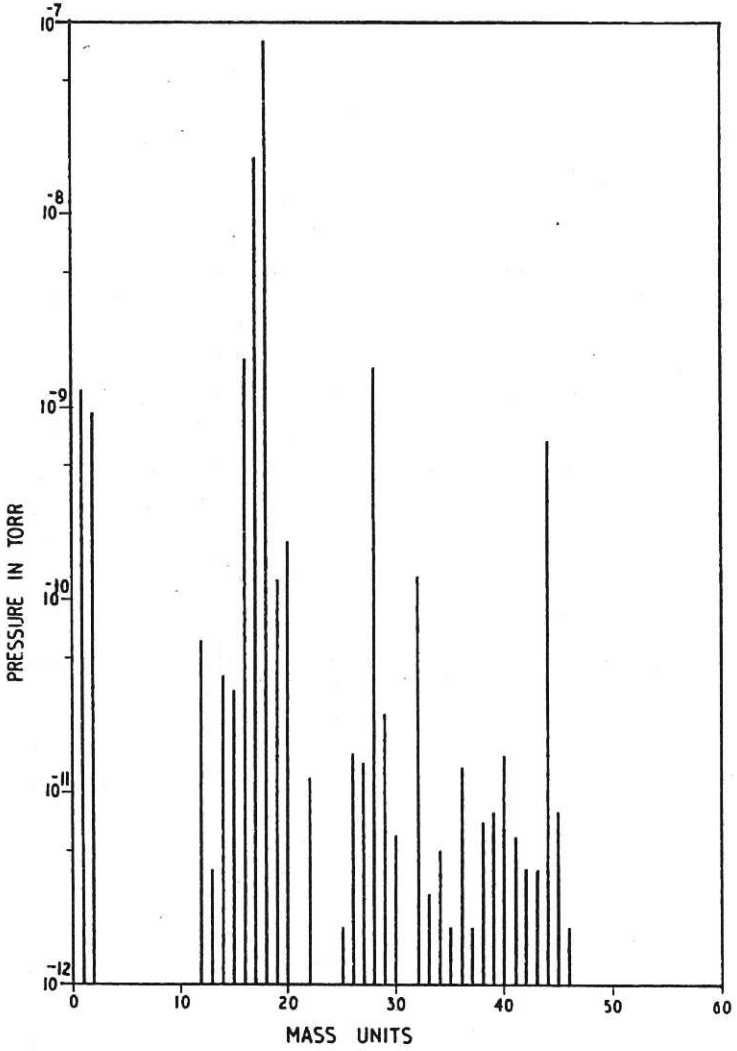


Fig. 6

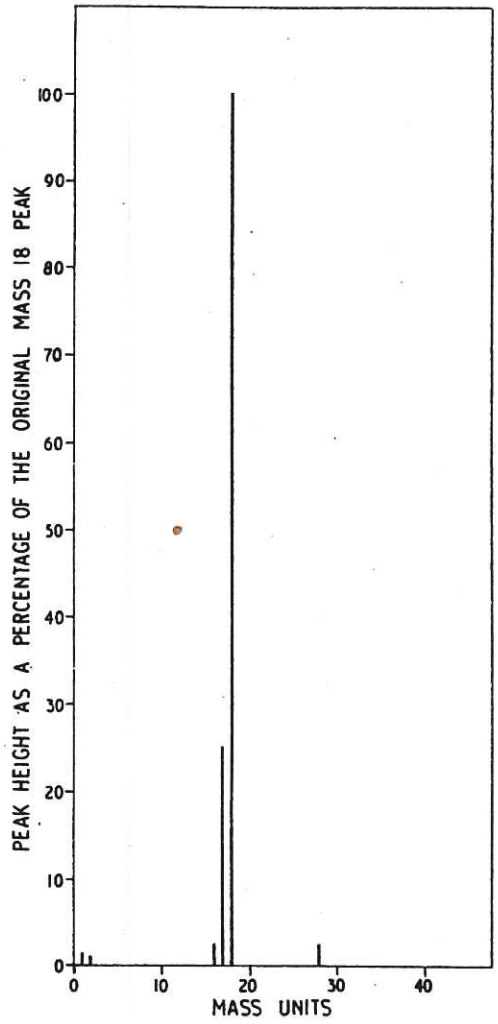
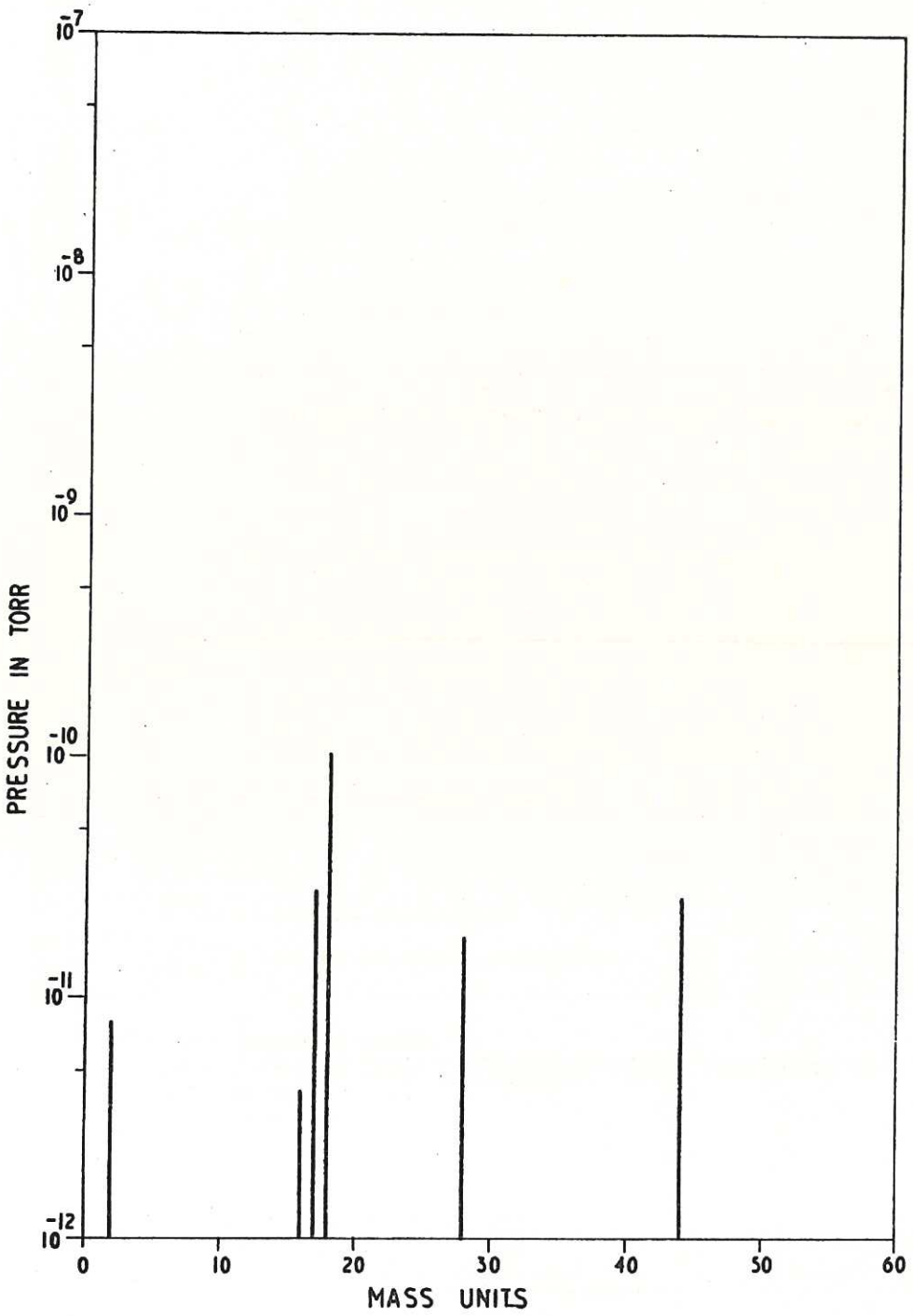


Fig. 6A

CLM-R 23

Araldite C.T.200, Hardener H.T. 901. After pumping for 51 hrs. September, 1962.



CLM-R 23 Fig. 7 Araldite C.T. 200, Hardener H.T. 901. After 98 hrs. pumping including 24 hrs. at 100°C. September, 1962.

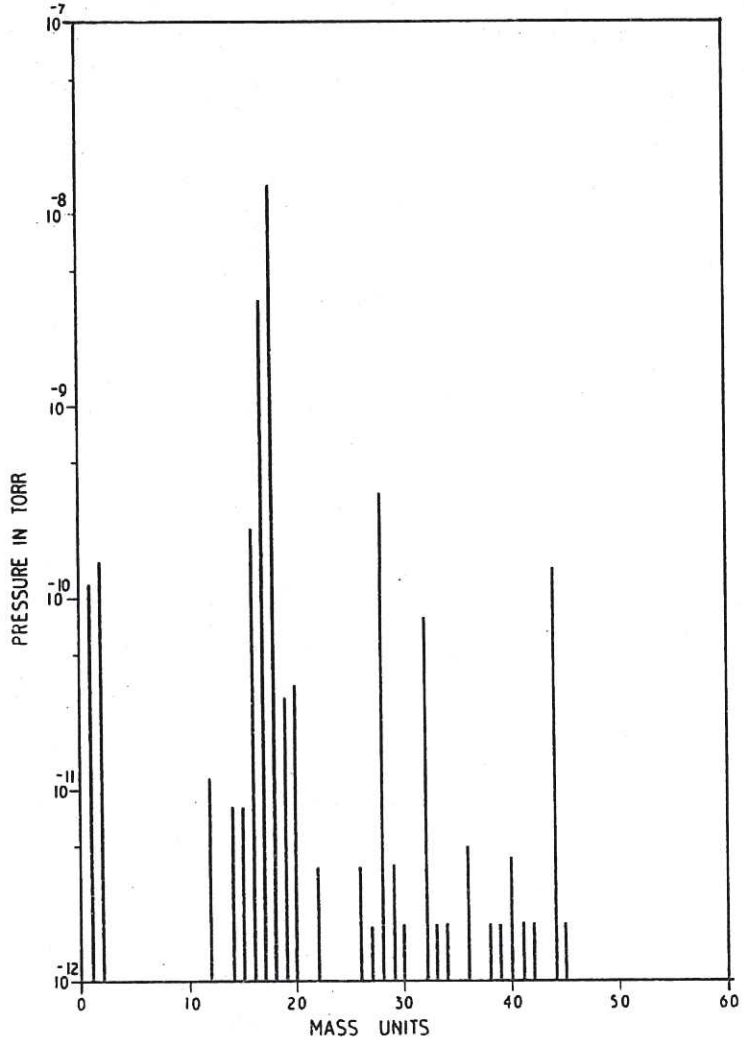


Fig. 8

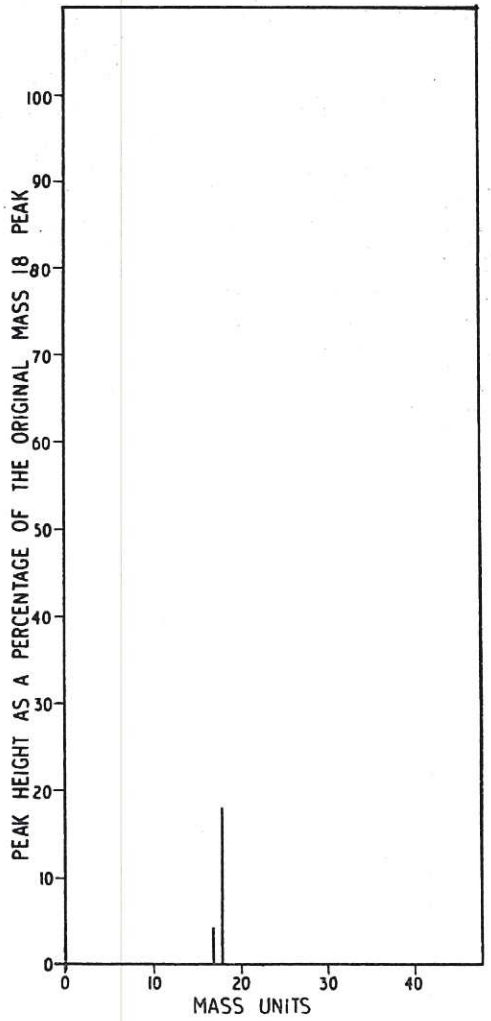


Fig. 8A

CLM-R 23

Araldite C.T.200, Hardener H.T. 901. After exposure to air for 24 hrs. at 59% humidity followed by 51 hrs. pumping. September, 1962.

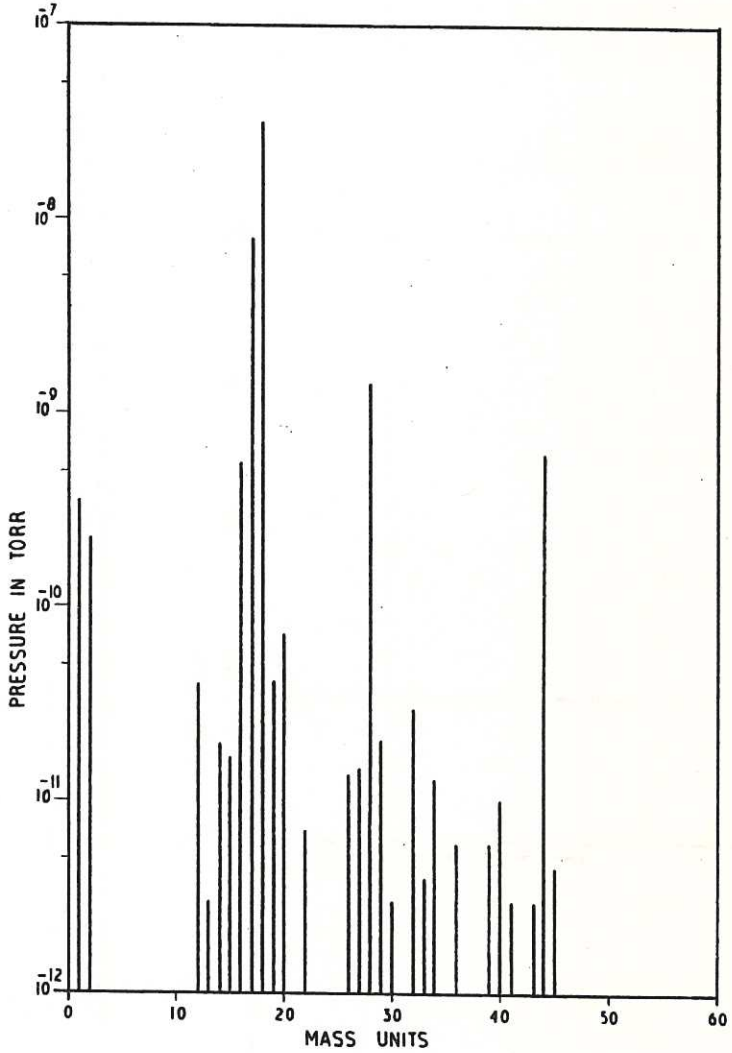


Fig. 9

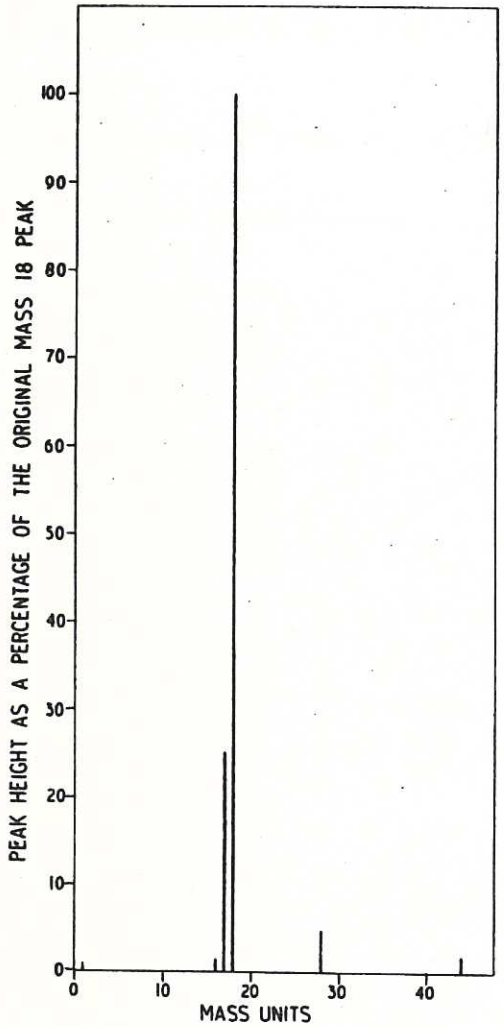
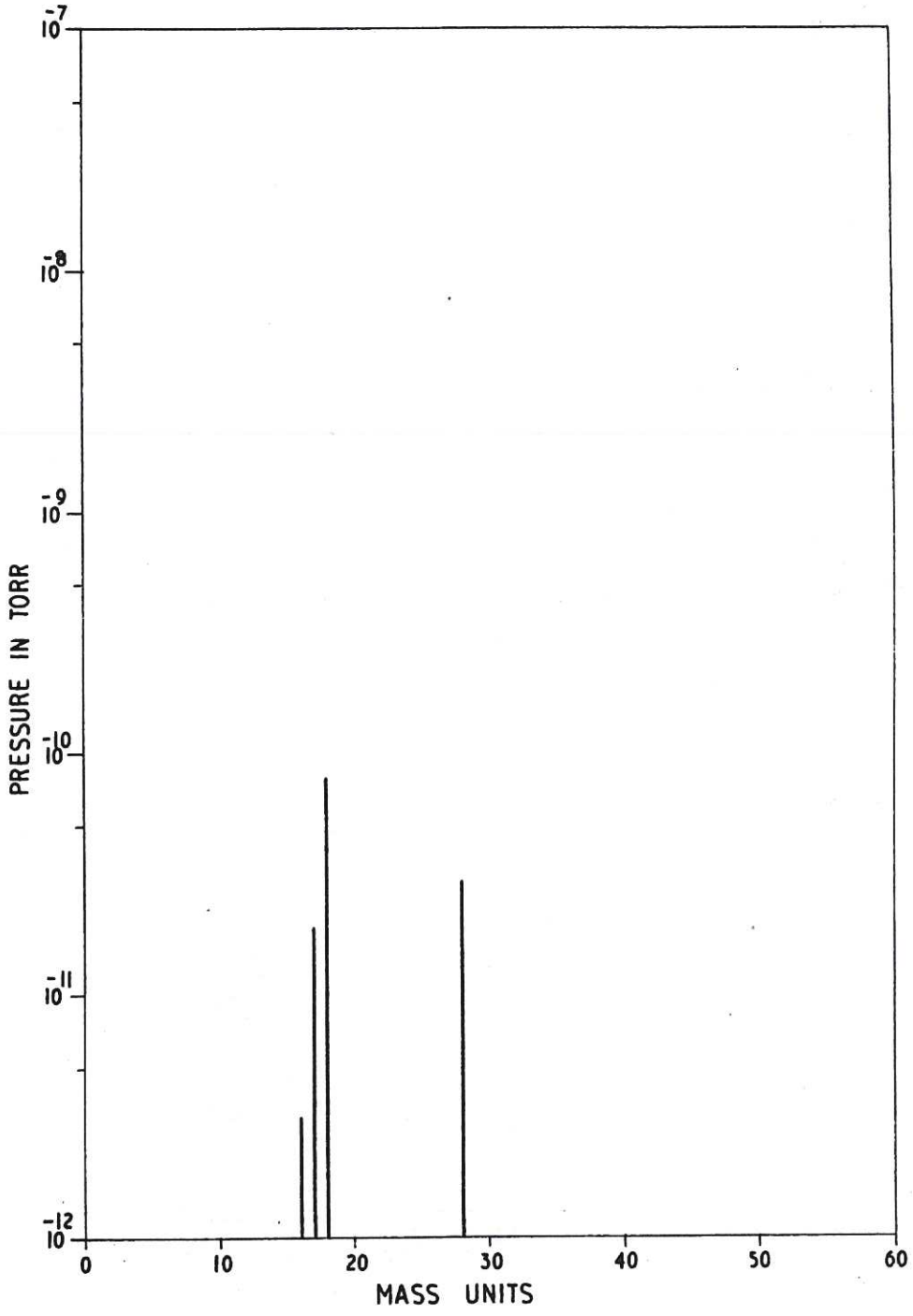


Fig. 9A

CLM-R 23

Araldite C.T.200, Hardener H.Y. 906. Accelerator X33/1266-
After 51 hrs. pumping. August, 1962.



CLM-R 23 Fig. 10 Araldite C.T.200, Hardener H.Y. 906. Accelerator X33/1266. After 95 hrs. pumping including 22 hrs. at 100°C. August, 1962.

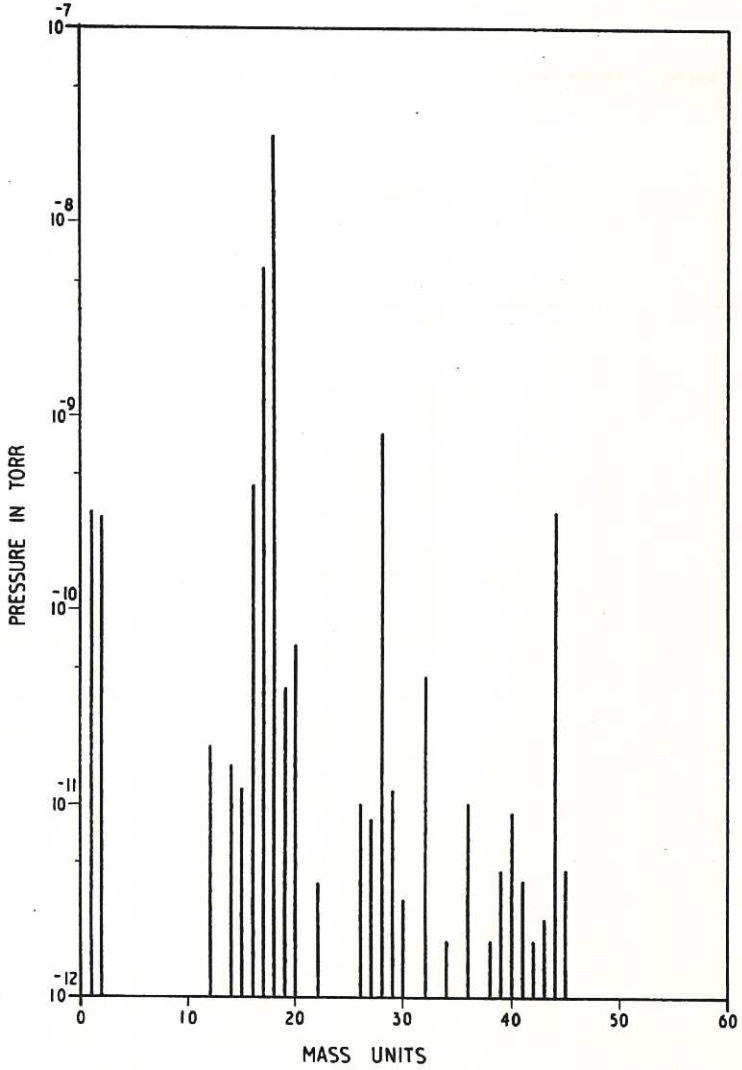


Fig. 11

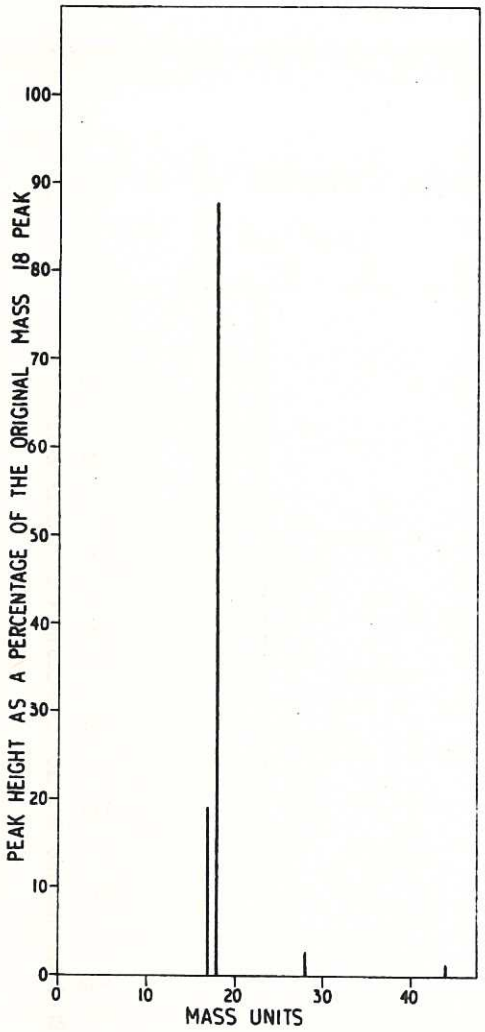


Fig. 11 A

CLM-R 23

Araldite C.T.200, Hardener H.Y.906, Accelerator X33/1266.
After exposure to atmosphere of 61% humidity for 24 hrs.
followed by 51 hrs. pumping. August, 1962.

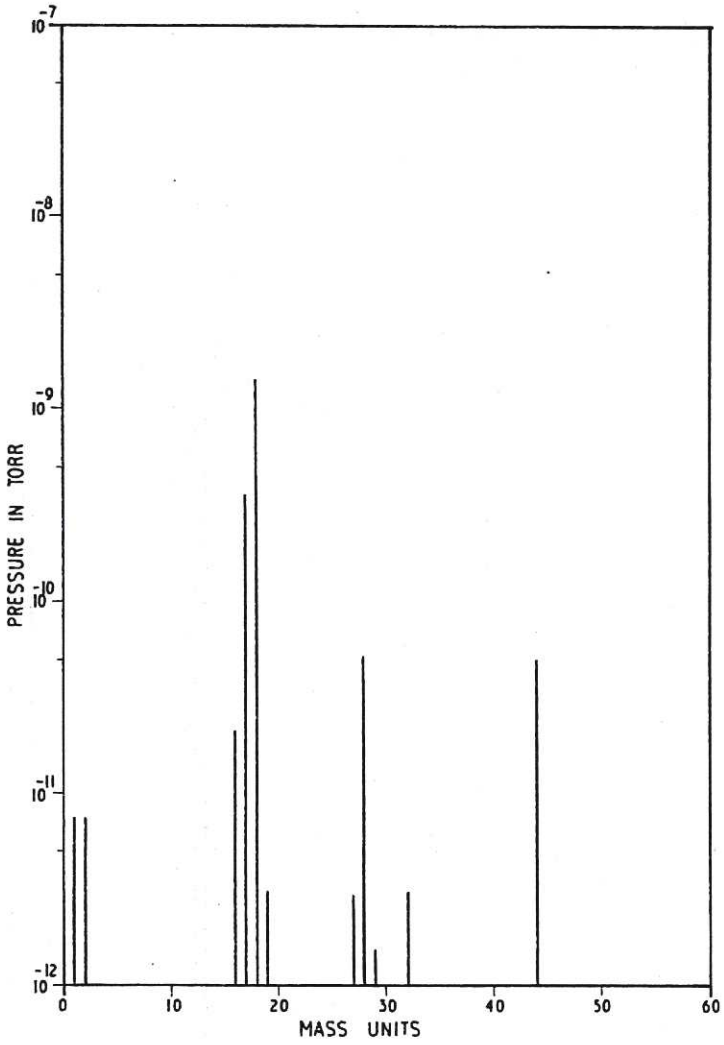


Fig. 12

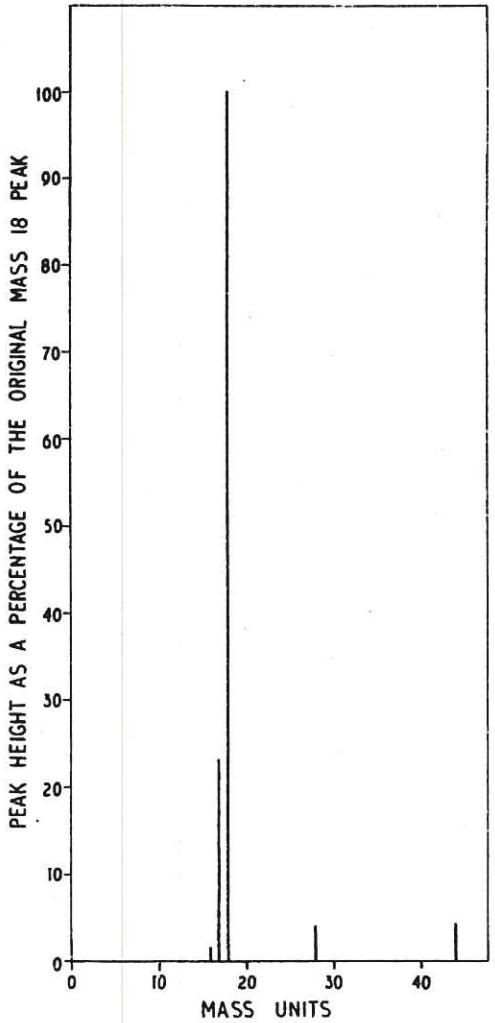


Fig. 12 A

CLM - R 23

Mycalex. After 52 hrs. pumping. July, 1962.

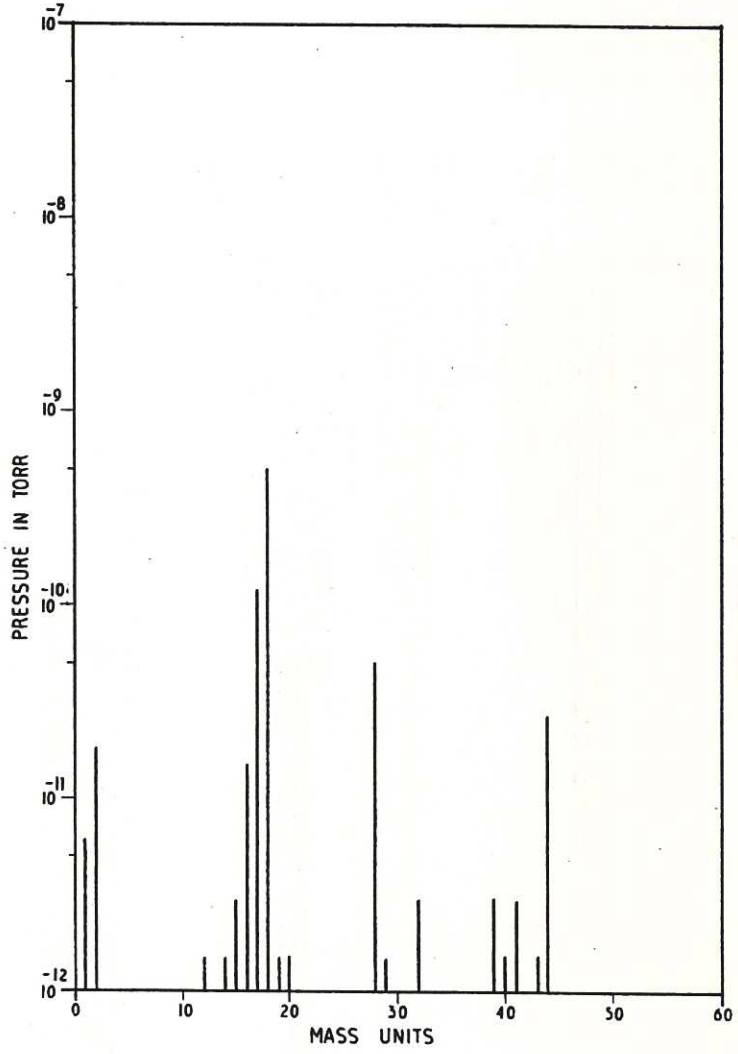


Fig. 13

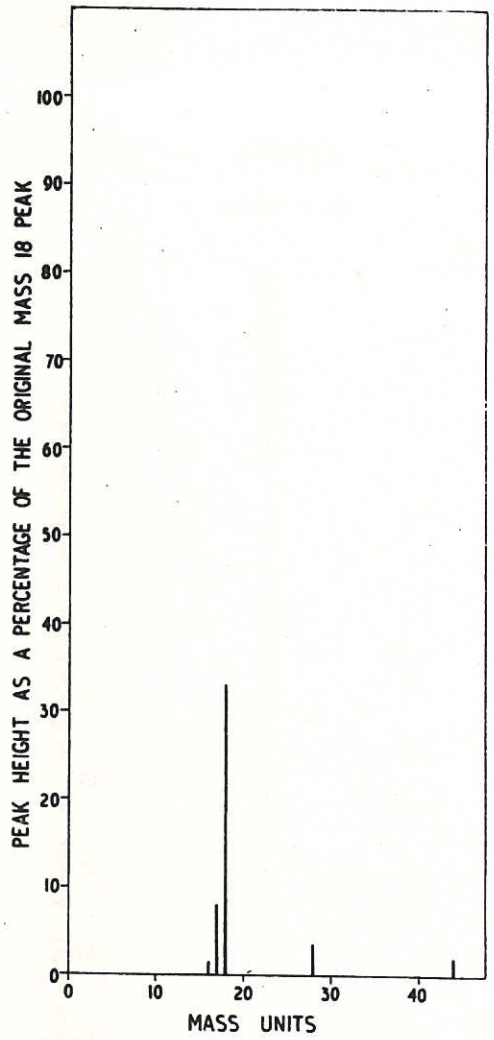


Fig. 13 A

CLM - R 23

Mycalex. After exposure to atmosphere of 64 % humidity for 24 hrs. followed by 51 hrs. pumping. July, 1962.

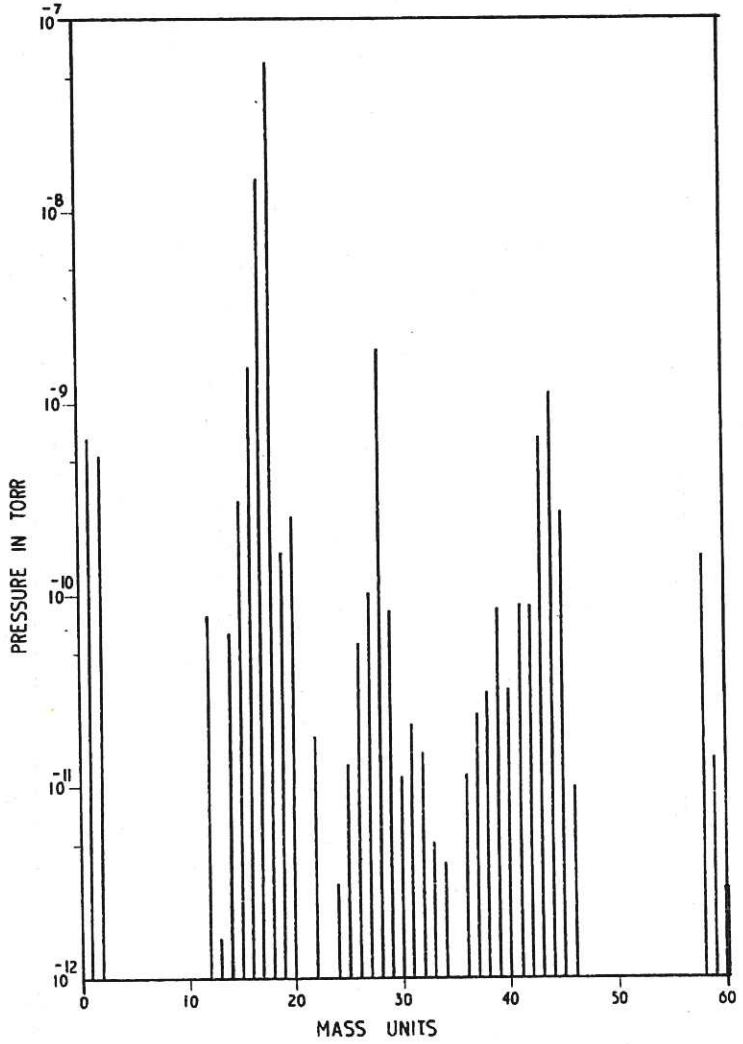


Fig. 14

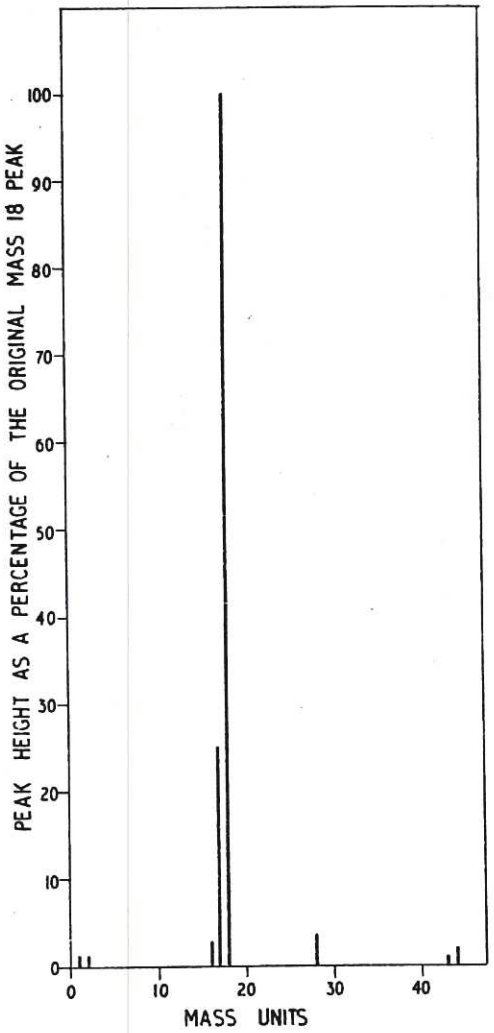
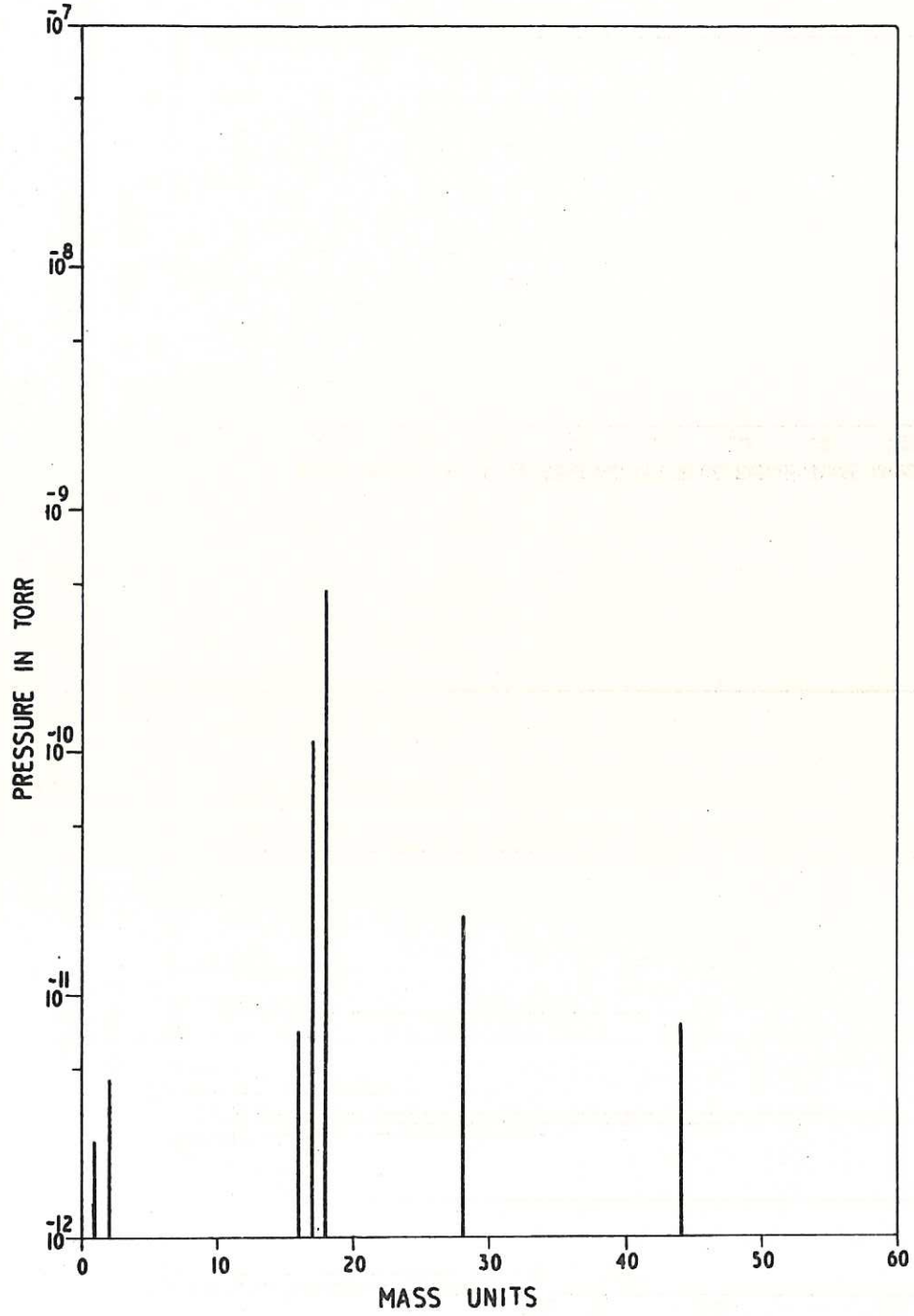


Fig. 14 A

CLM-R 23

Nylon 31 after 51 hrs. pumping. February, 1963.



CLM-R 23 Fig. 15 Nylon 31 after 80 hrs. pumping including 24 at 120°C. February, 1963.

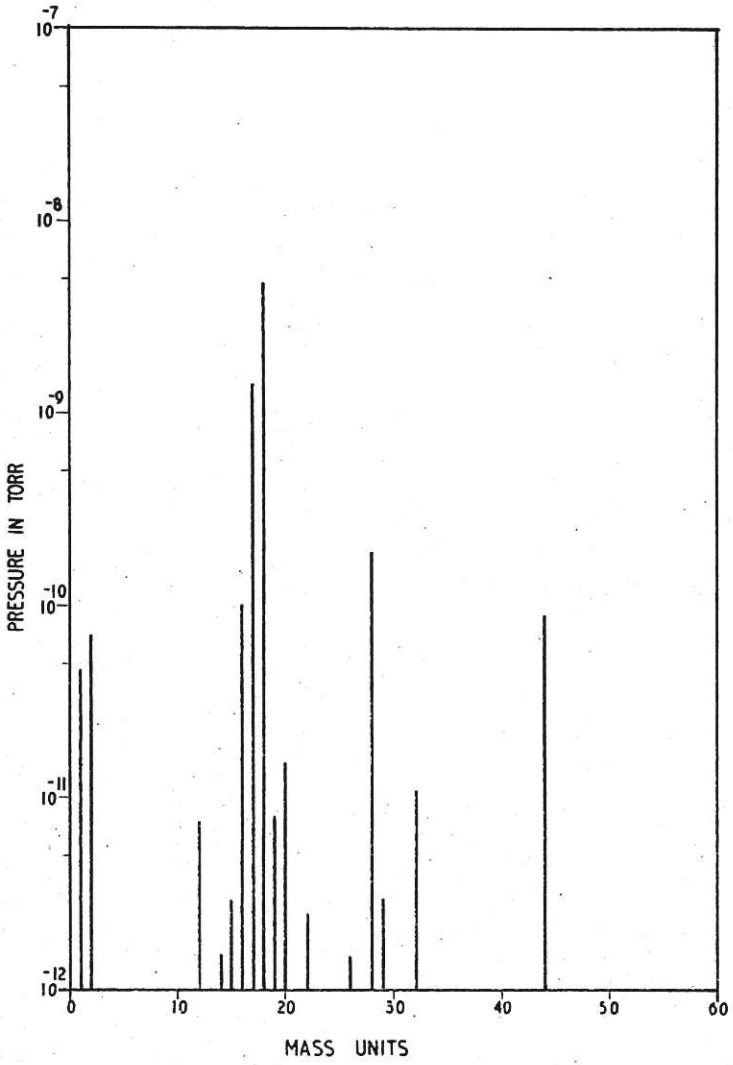


Fig. 16

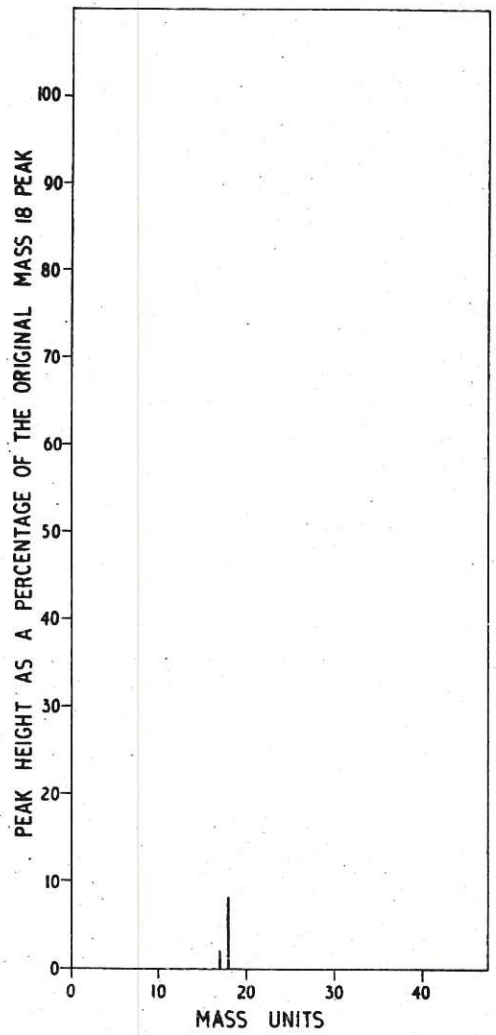


Fig. 16 A

CLM-R 23

Nylon 31 after exposure to atmosphere of 55% humidity for 24 hrs. followed by 51 hrs. pumping. February, 1963.

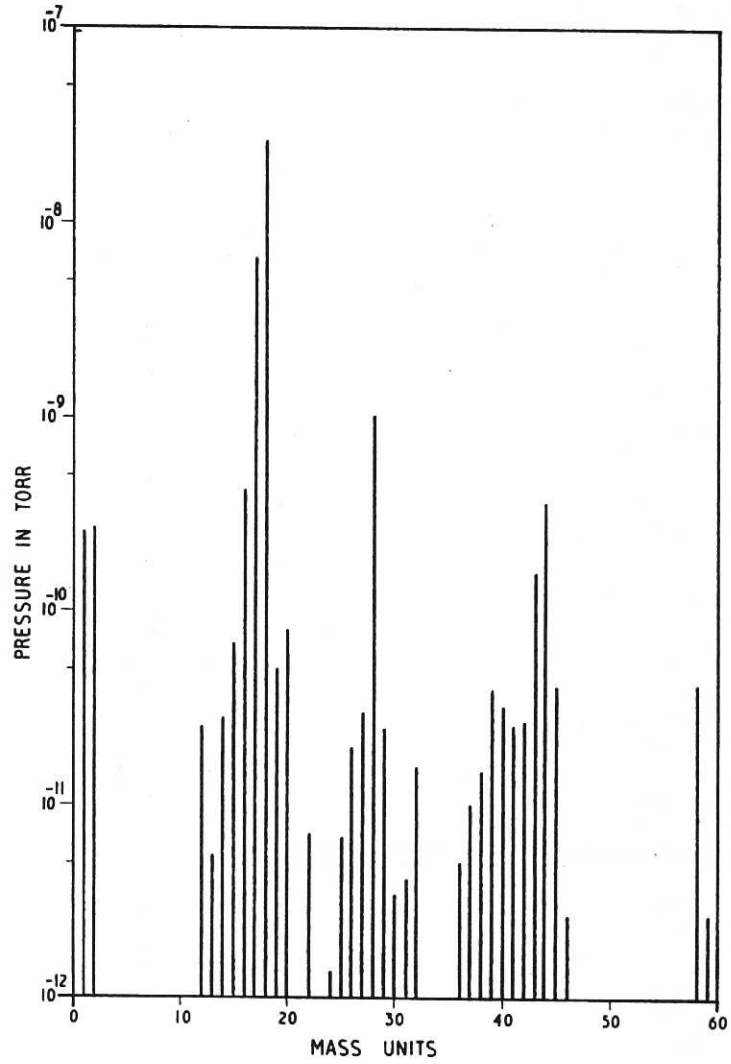


Fig. 17

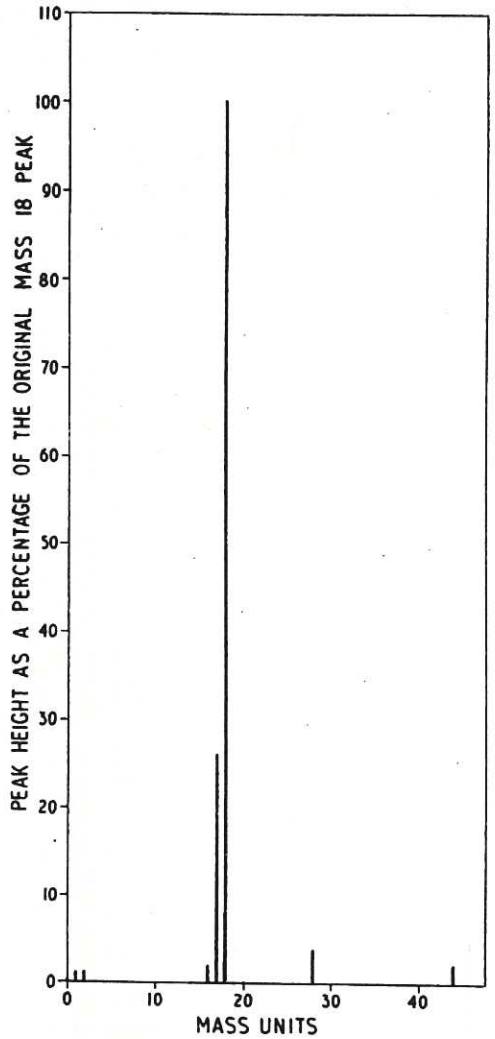


Fig. 17 A

CLM-R 23

Nylon 51 after 51 hrs. pumping. February, 1963.

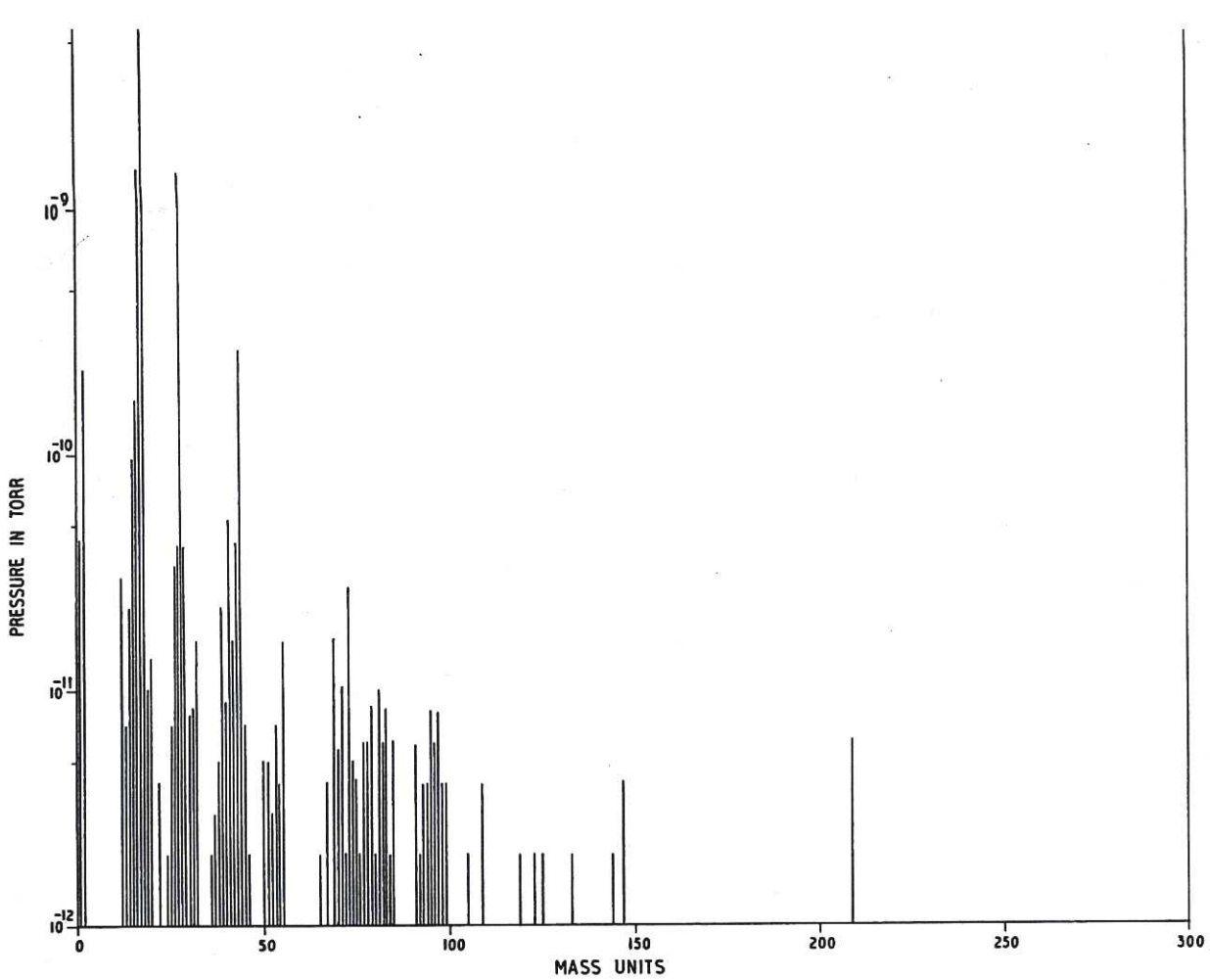


Fig. 28

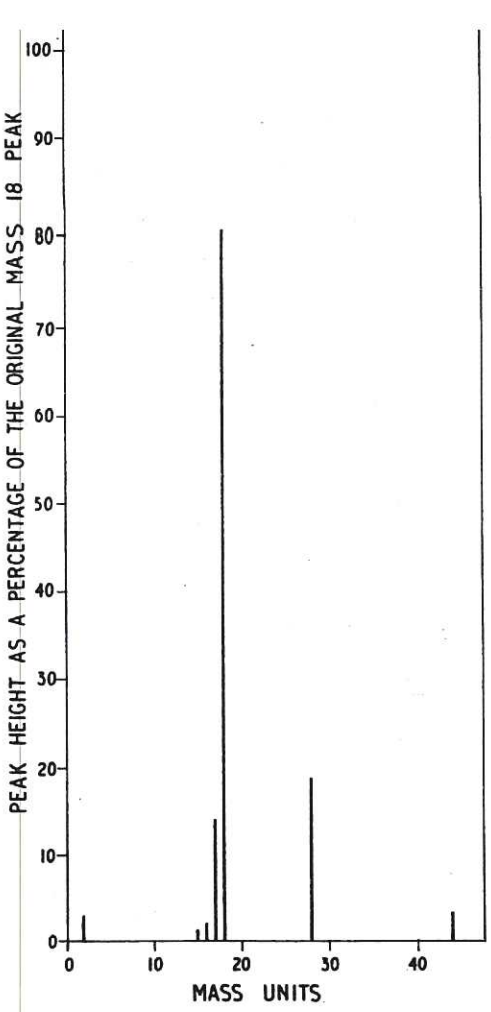


Fig. 28 A

CLM-R 23

Silastomer 80 after exposure to atmosphere of 47% humidity for 24 hrs. followed by 51 hrs. pumping. April, 1963.

Available from
HER MAJESTY'S STATIONERY OFFICE
York House, Kingsway, London W.C. 2
423 Oxford Street, London W. 1
13a Castle Street, Edinburgh 2
109 St. Mary Street, Cardiff
39 King Street, Manchester 2
50 Fairfax Street, Bristol 1
35 Smallbrook, Ringway, Birmingham 5
80 Chichester Street, Belfast
or through any bookseller.

Printed in England

S.O. Code No. 91-3-14-25