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A STUDY OF THE OUTGASSING AND EVAPORATION PRODUCTS OF SOME MATERIALS UPON EXPOSURE TO REDUCED PRESSURE

By

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ENGINEERING MATERIALS BRANCH
PROPULSION AND VEHICLE ENGINEERING DIVISION

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SUMMARY

A technique has been developed which allows identification and differentiation of the outgassing and evaporation products resulting from the exposure of a material to reduced pressure. The experimental approach entails collection of the outgassing and vaporization products in a special chamber, then examination of the collected vapors with a mass spectrometer. Since the time of collection can be extended indefinitely, even materials with extremely low vapor pressures and/or outgassing rates can be studied.

The outgassing and evaporation products of two pure materials (glycerine and dibutyl phthalate), two lubricants (Fluorolube T-45 and Rockwell 950), two solid propellants (normal polybutadiene acrylic acid and Flexadyne, a modified polybutadiene acrylic acid), and seven elastomers (natural rubber, silicone rubber, Buna-N, Viton A, neoprene, butyl rubber, and Kel-F) were collected and analyzed.

All of the materials investigated released adsorbed moisture; the adsorption and subsequent release of other atmospheric constituents depend upon the chemical structure of the material. The two pure compounds, the lubricants, the solid propellants, and the natural rubber endured losses in weight from both outgassing and evaporation; the other elastomers examined lost only adsorbed atmospheric constituents.

Evaporation rates, determined by continuous weighing of the sample while exposed to reduced pressure, correlate with the results obtained from the mass spectrometric examination of the outgassing and vaporization products.

INTRODUCTION

In recent years, the behavior of materials when exposed to the conditions of pressure, temperature, and radiation which exist outside the earth's atmosphere has assumed a position of paramount importance. Several possible effects may result form this exposure: (1) adsorbed gases may outgas from the material; (2) the material may evaporate completely; (3) the more volatile constituents of a mixture may vaporize, leaving a residue of the less volatile components; (4) the material may undergo complete or partial decomposition or polymerization; (5) combinations of the preceding effects may occur. The extent to which these effects take place and the subsequent influence on the performance of an individual material depend upon such parameters as temperature, external radiation, the surface area exposed to the environment and the chemical and physical properties of the material under consideration.

From a practical standpoint, no material can be tested under all the possible combinations of environmental conditions. For this reason, test conditions must be selected which will provide information that can be used to determine the applicability of the material for its intended function. In many instances, the identification and the quantity of products from the evaporation and the outgassing of engineering materials when subjected to reduced pressure are indicative of the usefulness of the material in this environment. The investigation described herein was undertaken primarily for the purpose of distinguishing the outgassing and evaporation products from the selected materials upon exposure to a vacuum environment and correlating these results with those obtained from the determinations of rates of vaporization. With this knowledge, the performance of a material when incorporated into a component and subjected to environmental conditions similar to those imposed during the test can be predicted.

No effort was made to identify the vaporization products enamating from the various materials since the objective of the investigation was the differentiation of the products of outgassing from those of evaporation. Also, qualitative identification by mass spectrometry is a well established technique so that identification of the products of vaporization can be accomplished if the need arises.

THEORETICAL BACKGROUND

A material will evaporate in vacuum at a rate according to the relationship developed by Langmuir:

$$\mu = P(M/2\pi RT)^{\frac{1}{2}}$$

where:

μ = Evaporation rate in grams/cm^2/second

P = Pressure in dynes/cm^2

M = Molecular weight

R = Universal gas constant

T = Temperature, $^{\circ}$K

Experimentally, the evaporation rate is best determined by measuring continuously the weight of the material while under vacuum. With a pure substance, the material itself is converted without change in composition to the gaseous phase and these vapors can be detected as the unchanged compound or fragments therefrom. In a mixture, the components of the material evaporate at rates dependent upon the vapor pressures of the individual constituents as well as upon the exposed surface area. Most engineering materials of organic derivation (lubricants, plastics, rubbers, adhesives, etc.) are included in this category. Most inorganic materials, notably metals and their alloys, have extremely low vapor pressures, so that significant vaporization takes place only at elevated temperature even under the most severe conditions of vacuum that can be imposed.

In addition to the possible loss of one or more components through vaporization, all materials lose adsorbed gases when subjected to reduced pressure. These adsorbed vapors outgas from the surfaces of all materials and parts (including the vacuum chamber itself) which are exposed to the condition of reduced pressure. Gases which have been trapped or have diffused into the interior of a material or part migrate, sometimes violently, to the surface upon reduction of the environmental pressure and also are lost through the process of outgassing. With a "clean" vacuum system, the rate of outgassing can be controlled by controlling the temperature and is the basis of the bakeout procedure for rapidly achieving the ultimate pressure of which a vacuum system is capable.

From the above considerations, it is evident that at ambient temperature only the outgassing characteristics of a material with extremely low vapor pressure need be considered, whereas both evaporation rate and outgassing properties govern the usefulness of a material with relatively high vapor pressure.

When a mixture is evaporated, the ratio of the constituents in the vaporized fractions varies as the temperature is increased. However, if the decomposition temperature of any of the components in the mixture is not reached, the chemical identities of the outgassing and vaporization products are the same regardless of the temperature. Thus, the only effect on the material produced by elevated temperature is an increase in the outgassing and evaporation rates. From the standpoint of this investigation, the only advantage to be gained by conducting the experiments at elevated temperature was a decrease in the time needed to collect sufficient sample for analysis. Offsetting this advantage and perhaps introducing further complications into the measurements was the necessity for designing and constructing a means of producing, controlling and measuring the elevated temperature. For these reasons and because the procedure and apparatus adopted for the investigation affords an almost unlimited time for sample collection, all experimental work was done at ambient temperature.

DESCRIPTION OF EQUIPMENT

Since the operating conditions of a mass spectrometer require a pressure of 10^{-5} mm Hg or lower, this instrument was ideally suited to fulfill the purpose of the investigation, namely, the study of the outgassing and evaporation products of selected materials upon exposure to reduced pressure.

For a mass spectographic analysis, vapors of the sample are admitted into an ionization chamber where a stream of electrons is emitted between a hot filament and a positively charged plate. The molecules of the vapor are bombarded by these electrons and are converted into ions. The electron current has sufficient energy to fragmentize some molecules, especially those of the higher molecular weight organic compounds. In the cycloid tube mass spectrometer, the positive ions resulting from the electron bombardment are accelerated by a high D. C. potential into a magnetic field. Here the ions, following a cycloidal path, are separated into individual ion beams according to their ratio of mass to charge (m/e). Each positive ion beam is focused through a slit onto a plate by varying the accelerating ion beam voltage. The impingement of these ions on the plate produces a current; this current is amplified and recorded as peaks on a strip-chart recorder.

The mass spectrum of an element or compound consists of the masses (m/e) of the ions and ion fragments produced in the ion beam. For a specific sample pressure, the resulting peak heights are related to the abundance of the ions present, i.e., the peak heights are proportional to the concentration of the molecules present in the original sample. No two compounds will fragmentize and ionize in the same manner; therefore, every compound has its unique mass spectrum. For this reason, the mass spectrogram indicates the relative abundance of any component of a homogeneous material, regardless of the sample pressure. The mass spectrum can be used for qualitative identification, for quantitative determination and for molecular structure studies. In this investigation, the spectrometer was used to identify the gases emanating from materials in vacuum and to distinguish outgassing from actual vaporization of the material under examination.

To carry out the experimental investigation, a special sample chamber was designed and constructed from type 303 stainless steel. The cross-sectional diagram of this chamber is shown in FIG. 1. The O-ring seal is soft, 1/8 inch diameter solid wire solder. The ability of the O-ring to form an effective seal after repeated use was tested by evacuating the system to the lowest pressure attainable (10^{-5} mm Hg), holding the system at this pressure for several minutes, raising the internal pressure back to atmospheric conditions, then breaking the seal. The O-ring was removed, then again placed in position and the system carried through the evacuation, holding, pressurization, breaking cycle. The ultimate internal pressure and the ability of the seal to maintain the differential in pressure was checked during each cycle. After twelve cycles, the O-ring exhibited no evidence of air leakage since the ultimate pressure of the system and the effectiveness of the seal in retaining this pressure were the same during the twelfth cycle as had been determined during the first. Besides the obvious advantage of permitting repeated usage of the same O-ring, standardization of the outgassing from the system itself was rendered much easier, since the multiple determinations necessary to establish this value were not complicated by insertion of a new O-ring of unknown history for each test. For tests at elevated temperature, the solder O-ring could not be used.

The chamber was designed to fit the inlet system of a Consolidated Electrodynamics Corporation Model 21-620 mass spectrometer. Also, the chamber was constructed so that a sample could be placed at the bottom in a suitable container, thus allowing only vapor to enter the mass spectrometer. This arrangement minimizes possible contamination of the instrument from mechanical ejection of liquid or semi-solid particles of sample upon initial reduction in pressure. A schematic diagram of the system is given in FIG. 2. Aluminum cups 5/8 inch in inside diameter by 3/4 inch in depth were used as containers for liquid and semi-solid samples.

MATERIALS INVESTIGATED

Two pure liquids, glycerine and dibutyl phthalate, were selected for the initial investigation. Both of these materials were studied extensively in the development of techniques for determination of the rates of evaporation of materials in vacuo, so that reliable data concerning their behavior when subjected to reduced pressure were available. Also, the study of these compounds aided in the interpretation of data obtained from more complex materials. Both glycerine, which has a vapor pressure of 2.5×10^{-4} mm Hg at 25°C, and dibutyl phthalate, with a vapor pressure of 1.8×10^{-4} mm Hg at 25°C, are relatively stable under normal conditions and do not evaporate appreciably at room temperature and under atmospheric pressure. Curves depicting the evaporation rates of glycerine and dibutyl phthalate in vacuum at ambient temperature are given in FIGS. 3 and 4, respectively. As is characteristic of all pure materials, the evaporation rates are constant at a specific temperature.

During vacuum compatibility testing, two materials, a lubricating oil (Fluorolube T-45) and a grease (Rockwell Lube 950), were observed to outgas violently upon initial reduction in pressure. In some instances, this outgassing was so vigorous that most of the sample was lost from the container by foaming, with consequent ejection of material. These two materials were investigated to ascertain the cause of the violent outgassing.

Two samples of polybutadiene acrylic acid (PBAA), a solid propellant, were examined. Although the materials were reputed to be of the same chemical composition, they differed in appearance and in some of their physical properties, i.e., hardness, elongation and tensile strength. These materials were examined to determine if their behavior differed in the vacuum environment and if the outgassing and evaporation products would give an indication of why the physical properties tested were different.

Since rubber and elastomeric materials are used widely as sealants and gaskets, their outgassing and evaporation characteristics are of special interest. To determine the effectiveness of a material as a sealant, the outgassing and evaporation products originating from the material itself must be differentiated from the gases permeating the sealant or leaking around it. Seven commonly used elastomers, including natural rubber, Buna-N, a silicone, Viton A, neoprene, butyl and Kel-F, were examined.

EXPERIMENTAL

A. DETERMINATION OF SYSTEM BACKGROUND

Prior to exploration of the outgassing and evaporation phenomena associated with the materials selected for investigation, it was necessary to identify the gases and to determine the rates of evolution of these gases from the clean, empty system. To accomplish this, the interior of the chamber was washed thoroughly with detergent and warm water, rinsed and air dried. The chamber then was attached to the mass spectrometer. With Valve 2 closed (cf FIG. 2), Valve 1 was opened and the chamber pumped down for five minutes. Because of the small volume of the chamber, a pressure of less than 10^{-4} mm Hg could be attained in approximately 30 seconds. After the five minutes of pumping, the chamber was isolated by closing Valve 1, and the system was allowed to remain static for a definite time interval until sufficient sample was collected for analysis. From a clean, empty system, the quantity of gas collected over a period of several hours was too small to be detected by the thermocouple pressure gauge; however, the mass spectrometer was capable of detecting and quantitatively analyzing this minute amount of gas. With Valve 2 open, the collected sample was introduced into the analyzer tube and a mass spectrogram obtained with an ionization current of 20 microamperes. From the spectrogram, the identities and quantities of the various gases comprising the outgassing product from the system itself during the chosen period of time were established. Without opening the system and with the chamber again isolated (Valve 2 closed), a second sample of the outgassed vapors was collected. When sufficient sample had been collected and with the time required for collection definitely known, Valve 2 was opened, thus introducing the sample into the mass spectrometer for analysis.

Three additional samples were collected and analyzed in this manner. After analysis of these five samples, the chamber was opened to the atmosphere and allowed to re-adsorb gases for at least 16 hours. Identification and quantitative determination of the outgassing products was repeated, with the chamber isolated and the outgassing vapors collected over five definite periods of time as before. In all, the chamber was opened and reexposed to the atmosphere five times. Following each re-adsorption of atmospheric gases, five portions of the outgassed vapors were collected over definite time intervals and complete mass spectrometric analyses made of the system background. Data representing five determinations of each gas over five different time intervals were compiled. For simplicity, the outgassing rates of the various gases were calculated as chart divisions per second; if desired, this quantity may also be expressed as the change in pressure per second or as the change in concentration (gram - moles) of gas per second. The values of outgassing rate in chart divisions per second thus obtained for each gas were plotted versus the total time required for collection of the sample. The outgassing rates of the various gases desorbed from the chamber are given in FIG. 5. Precision of the method for measuring these rates is ±5 percent. The sensitivity of the instrument for the more common atmospheric gases (hydrogen, helium nitrogen, oxygen, argon, water and carbon dioxide) is given in Table 1.

Table 1. Instrument Sensitivity for Common Atmospheric Gases

Gaseous Component	Mass/Charge Ratio	Sensitivity (Chart Divisions/Micron Pressure)
Hydrogen	2	26
Helium	4	10
Water	18	--
Nitrogen	28	110
Oxygen	32	76
Argon	40	116
Carbon dioxide	44	92

By knowing the rates of outgassing of the various gases desorbed from the system, the outgassing and evaporation characteristics of a sample can be determined by measuring the spectral differences between the mass spectrogram produced by the sample and that originating from the clean, empty system. The spectrum from the outgassing products of the system is always superimposed on the spectrum of the outgassing and vaporization products actually removed from the sample, so that the instrument "blank", i.e., the background spectrum, must always be considered. With this technique, any desired length of time may be allotted for sample collection since the outgassing rates from the system itself are known. Materials of low vapor pressure and, consequently, slow evaporation rate can thus be analyzed.

B. DETERMINATION OF OUTGASSING AND EVAPORATION PRODUCTS FROM TEST MATERIALS

To study the outgassing and evaporation from a particular material, a sample of the material was placed in the special chamber. The system was evacuated for five minutes with Valve 1 open and Valve 2 closed (cf FIG. 2). This evacuation removed the air trapped in the chamber upon closure and established a steady state condition in the system. Following the five minute pumping interval, Valve 1 was closed, thus isolating the chamber and permitting the outgassing and evaporation products from the system and from the sample to collect. The time required to collect sufficient vapor for analysis depended on the outgassing and evaporation rates of the test material and varied from five to twenty minutes. Since outgassing and evaporation are continuous processes, the collection time for each mass (ion or ionized fragment) was measured from the closing of Valve 1 to the first detection of the particular mass in the spectrum. After adequate sample had been collected, Valve 2 was opened to admit the sample into the analyzer tube. All spectra were obtained with an ionization current of 20 microamperes.

From the mass spectrogram, an interpretation was made of the outgassing products as distinguished from the evaporation products originating from the sample. The appearance in the spectrum at mass 18 of a peak of much greater intensity than that produced by the outgassing from the system indicates that water (molecular weight = 18) was present in the sample. Ionization of a molecule containing the hydroxyl radical, e.g., an alcohol, does not produce a significant quantity of mass 18, but rather of mass 17. Similarly, the appearance at mass 32 of a peak indicates that molecular oxygen (O_2, molecular weight = 32) was evolved. If the intensity of the peak at mass 32 is greater than that of the instrument blank, the molecular oxygen must have outgassed from the sample.

The measurement of outgassing for any mass, m/e, is expressed arbitrarily as chart divisions/second of collection time. Then, the

$$\text{quantity of mass m/e outgassing} = \frac{\text{chart divisions/second}}{\text{sensitivity of the instrument}}.$$

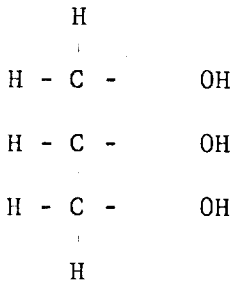
Sensitivity of the instrument is expressed in chart divisions/micron of pressure (Table 1), so that the quantity of mass m/e outgassing becomes

$$\frac{\text{chart divisions/second}}{\text{chart divisions/micron pressure}} = \text{microns pressure/second.}$$

Since the rate of outgassing depends on the surface area exposed, the outgassing rate is expressed as microns pressure/second/square centimeter surface area. From this relationship, the quantity of gas of mass m/e outgassing/second/square centimeter surface area can be determined in any appropriate unit, e.g., gram-moles, cubic centimeters, etc.

C. EXPERIMENTAL RESULTS

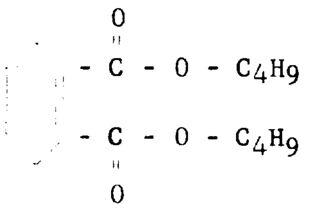
A sample of glycerine was placed in an aluminum container 5/8 inch ID x 3/4 inch deep, inserted in the special chamber and the outgassing and vaporization products collected and analyzed as described previously. The curve depicting the evaporation rate of glycerine at ambient temperature and 10^{-6} mm Hg is given in FIG. 3; the relative peak heights in chart divisions of the masses detected in the outgassing and evaporation products are presented in FIG. 6. The relative peak heights given in the figures for the various samples pertain only to a particular sample and are not comparable from material to material. Thus, the values given in FIG. 6 are not indicative of sample pressure or evaporation rate. From the mass spectrogram, it is evident that much of the initial outgassing from glycerine is due to vaporization of water (mass 18). As indicated by its relative peak height, mass 17 is present in exceptionally high concentration. This, of course, is to be expected from the structure of the glycerine molecule:



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & OH \\ H & - & C & - & OH \\ H & - & C & - & OH \\ & & | & & \\ & & H & & \end{array}$$

When the vaporized gylcerine enters the analyzer tube, many of the molecules are ionized as indicated by the dotted lines, i.e., hydroxyl ions of mass 17 are formed. Since the molecular weight of glycerine is 92, the peak of very weak intensity appearing at m/e 92 indicates that virtually all of the parent molecules were fragmentized into ions. The intensity of the peak at mass 92 can be increased substantially, if desired, by lowering the ion current to a value near the ionization potential of glycerine.

The outgassing and evaporation products from a sample of dibutyl phthalate were collected and analyzed. The curve representing the evaporation rate of dibutyl phthalate at a pressure of 10^{-6} mm Hg and room temperature is given in FIG. 4; the masses detected and their relative peak heights obtained from this compound are given in FIG. 7. From the structural formula of dibutyl phthalate,



it is to be expected that the fragments resulting from ionization of the molecules are numerous and the mass spectrum rather complex. Again, water (mass 18) is the chief outgassing product as indicated by the relative intensity of the peak. Although the primary purpose of this study was not the identification of complex molecules, the ability of the instrument to detect very easily a material of low vapor pressure and to determine if the material itself is evaporating in vacuo is illustrated from the spectrum obtained with dibutyl phthalate.

The determination of the evaporation rate of Fluorolube T-45 from an open container was difficult because the sample outgassed so violently upon initial exposure to vacuum that the bulk of the material was lost mechanically from the container. However, the outgassing and vaporization characteristics of Fluorolube T-45 were studied by the mass spectrometer collection technique with no difficulty. Violent outgassing is not critical when the material is exposed to reduced pressure in the special collection chamber, since the products of the outgassing and only that portion of the material which actually vaporizes are collected and held until analyzed.

Examination of the mass spectrum obtained from this material indicates that the desorption of moisture (mass 18) is the cause of the violent outgassing. From the mass spectrum, it is also apparent that a component (or components) of the oil itself evaporates during the vacuum exposure. The masses detected and the relative peak heights originating from Fluorolube T-45 are given in FIG. 8. To determine the rate of evaporation of the lubricant, a quantity of the material was outgassed by exposure to vacuum in a large container until no further evolution of gas was evident. The outgassed sample then was subjected to reduced pressure (10^{-6} mm Hg) at ambient temperature with continuous monitoring of the loss in weight. The evaporation rate thus obtained (FIG. 9) verifies the results from the mass spectrometer; i.e., a component of the oil itself is vaporized during the vacuum exposure.

Rockwell 950, a petroleum base grease, behaves similarly to Fluorolube T-45 with respect to its violent outgassing characteristic. The mass spectrum obtained from Rockwell 950 is given in FIG. 10. Again, water (mass 18) is indicated as the cause of the tremendous expansion in volume occurring upon initial exposure to vacuum. The mass spectrum also indicates that a volatile component of the grease itself is lost during the exposure to reduced pressure. No detectable weight loss was recorded when a sample of Rockwell 950 was subjected to reduced pressure (10^{-6} mm Hg) at ambient temperature for 12 hours. Since the sensitivity of the microbalance used for determining rates of vaporization is ±0.02 milligram, the quantity of volatile component lost from the sample during the evaporaation rate determination was less than 0.02 milligram. The fact that this volatile component was readily detected by the mass spectrometer points out one of the advantages of this approach; i.e., loss of an amount of a volatile constituent so small that the electronic microbalance is incapable of its detection can be discerned easily with the mass spectrometer.

The two solid propellants, normal polybutadiene acrylic acid (PBAA) and a modified polybutadiene acrylic acid (Flexadyne), both obtained from Rocketdyne, were cut into blocks of three square centimeters surface area. Each of the samples was examined by the previously described procedure. The detected masses and relative peak heights from the two materials are given in FIG. 11. Since a comparison of the outgassing and evaporation products from the two propellants was desired, the relative abundances of all masses (other than those originating from air and water) appearing in the spectra of the two materials were calculated. The relative abundance is determined by assigning a value of 100 percent to the most intense peak in the spectrum and relating all other peaks in the spectrum to it. The relative abundances determined for the two propellants are given in FIG. 12. From the mass spectrograms and calculated relative abundances of m/e, it is apparent that a component (or components) evaporated from the normal PBAA which was not lost by the Flexadyne. In addition, considerably more moisture (about 7.5 to 1) was outgassed from the PBAA than from the Flexadyne. The rates of evaporation also were determined for these two materials by exposing samples three square centimeters in surface area to a pressure of 10^{-6} mm Hg at room temperature with continuous weighing. The evaporation rate curves are given in FIGS. 13 and 14. From their mass spectrograms and evaporation rates, it is evident that the two propellants are different in chemical structure. This difference is probably due to cross-linking of the polymer chain in the case of Flexadyne, likely promulgated through use of an additive when the polymerization was carried out.

Samples of natural rubber, silicone rubber, Buna-N, Viton A, neoprene, butyl rubber, and Kel-F elastomer, measuring two centimeters by two centimeters by 0.16 centimeter thick, were prepared and examined. The mass spectrum obtained from the outgassing and vaporization products of natural rubber is given in FIG. 15. A comparison of the masses detected and the relative peak heights obtained from outgassing the other elastomers is given in Table 2.

Table 2. Masses Detected and Relative Peak Heights of Outgassing Products from Various Elastomers

Mass/Charge Ratio	Relative Peak Heights					
	Silicone	Buna-N	Viton A	Neoprene	Butyl	Kel-F
14	9	51	12	243	26	12
16	104	27	20	89	32	21
17	1395	167	195	476	264	240
18	5800	775	777	1956	1056	962
20	-	7	-	-	-	-
28	60	2352	220	3456	285	199
32	57	551	91	753	159	90
40	3	41	8	51	9	8
44	6	6	5	9	6	5

All of the materials released adsorbed moisture (mass 18); however, only neoprene and Buna-N released nitrogen and/or carbon monoxide (mass 28) and oxygen (mass 32). The quantities of the various gases outgassed from each material are indicated in FIGS. 16 through 22. These quantities represent the difference between the total amount of each gas collected from the outgassing of the sample and the amount of each gas desorbed from the clean, empty system. FIG. 23 gives a comparison of the quantities of water (mass 18) outgassed from the different rubber specimens; FIGS. 24 and 25 compare the amounts of nitrogen and/or carbon monoxide (mass 28) and oxygen (mass 32), respectively, which were desorbed from neoprene and Buna-N. The results of the mass spectrographic analysis indicate that the adsorption of atmospheric constituents, with respect both to identity and to quantity, is dependent upon the chemical composition of the elastomeric polymer.

Of the elastomeric materials examined, only natural rubber lost a component other than the adsorbed atmospheric gases. The complexity of the mass spectrum of natural rubber (FIG. 15) proves conclusively that a constituent evaporated from the rubber itself rather than being outgassed from the surface of the sample. Identification of this product was beyond the scope of this investigation; however, it is speculated that the volatile plasticizer or residual solvent used in formulating the rubber was the material vaporized.

The evaporation rates of the seven rubber materials under a pressure of 10^{-6} mm Hg at ambient temperature were determined. Changes in weight were recorded continuously during the vacuum exposure. Of the seven materials, only natural rubber exhibited a detectable loss in weight after 12 hours exposure to the imposed conditions. These results verify those obtained from the mass spectrographic analyses of the materials. The curve representing the evaporation rate of natural rubber is given in FIG. 26. As indicated by this curve, the evaporation rate of natural rubber is contrary to that usually obtained from a homogeneous material. It is speculated that the initial evaporation takes place when the volatile constituents at the surface are lost. During this initial vaporization, the volatile components trapped in the interior of the specimen are migrating to the surface. Upon reaching the surface, these components are vaporized, giving an accelerated evaporation rate.

CONCLUSIONS

From the results of this investigation, it is evident that water is the most readily adsorbed of the atmospheric constituents and is, therefore, the most likely source of difficulty when problems caused by outgassing are presented. Also, it is apparent that all atmospheric components are not adsorbed by all materials, the identity and quantity of the adsorbed molecules being governed by the chemical structure of the substrate.

Of the elastomeric materials examined, only natural rubber lost components other than adsorbed atmospheric gases. This observation, however, cannot be construed as all-encompassing since the loss of constituents other than adsorbed atmospheric components likely is dependent upon the kind and quantity of additives and the curing treatment the material has experienced.

The procedures used for determination of the rates of evaporation of materials upon exposure to reduced pressure are limited by the sensitivity of the balance employed to detect losses in weight. The mass spectrographic method of examining the products from outgassing and evaporation affords a means of estimating and identifying quantities of vaporized material which escape detection in the usual evaporation rate determinations. Also, the products of desorption can be distinguished from those of evaporation of the material itself with the mass spectrometer technique. When the mass spectrographic examination is made in conjunction with the determination of evaporation rate, a complete history of the vaporized products emanating from the material under investigation is available.

The mass spectrographic method of examining materials is recommended as a supplement to existing procedures for determining rates of vaporization in those special instances where knowledge of the identity and quantity of outgassing and evaporation products, and their differentiation,is essential.

FUTURE STUDIES

To ascertain the feasibility of the mass spectrographic approach, all of the results from the investigation were obtained at room temperature. However, the potential of this technique is by no means limited to ambient temperature. The interest in the behavior of materials under conditions of reduced pressure quite often coincides with an interest in the effect of temperatures above and below 25^{o}C; consequently, efforts will be directed toward the design, construction, and incorporation into the system of a means to attain, control, and monitor temperatures from -60^{o} to 200^{o}C.

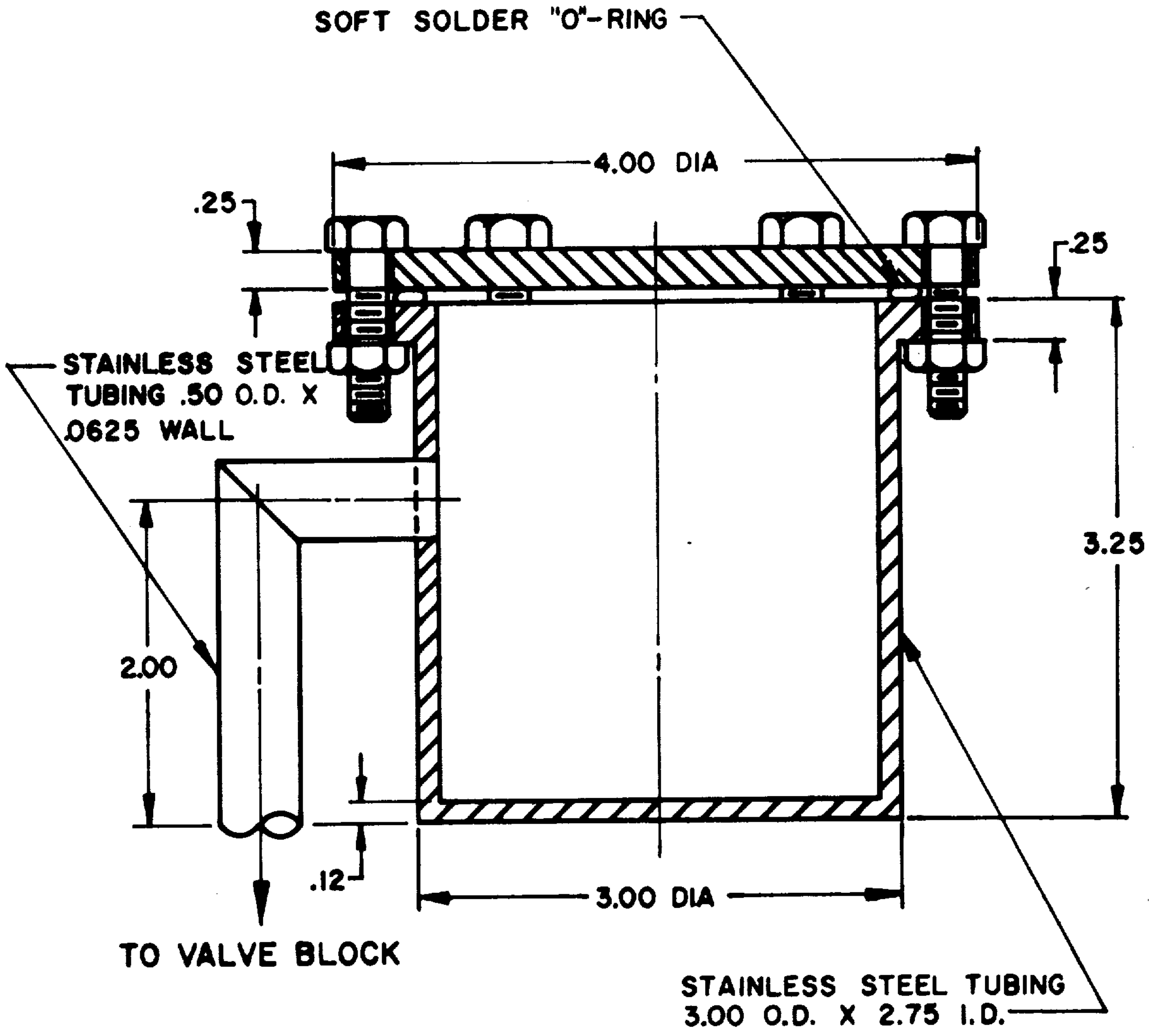


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FIGURE 1. CROSS SECTIONAL VIEW OF SAMPLE COLLECTION CHAMBER

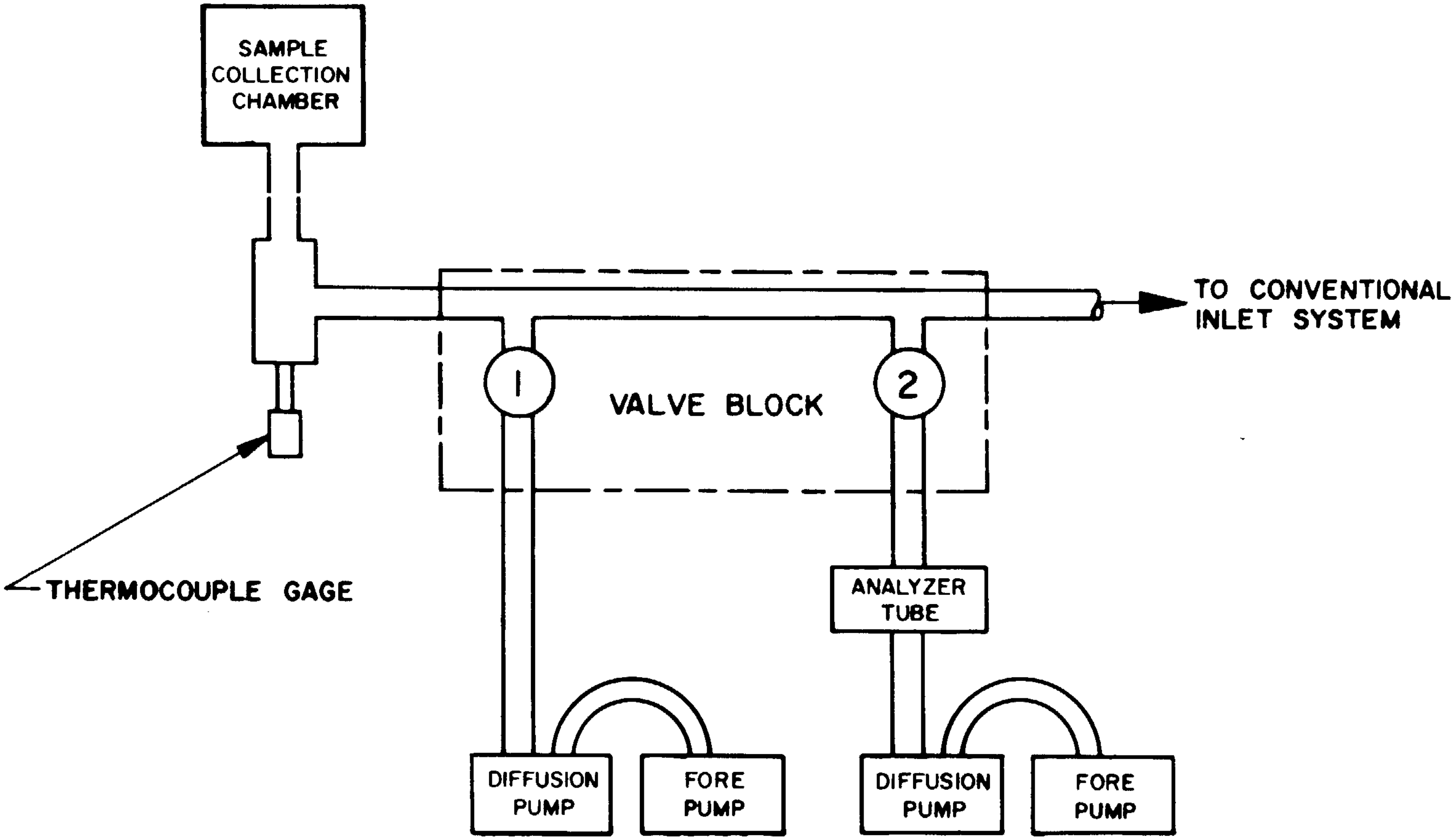

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FIGURE 2. SCHEMATIC DIAGRAM OF SAMPLE COLLECTION AND PUMPING ASSEMBLY

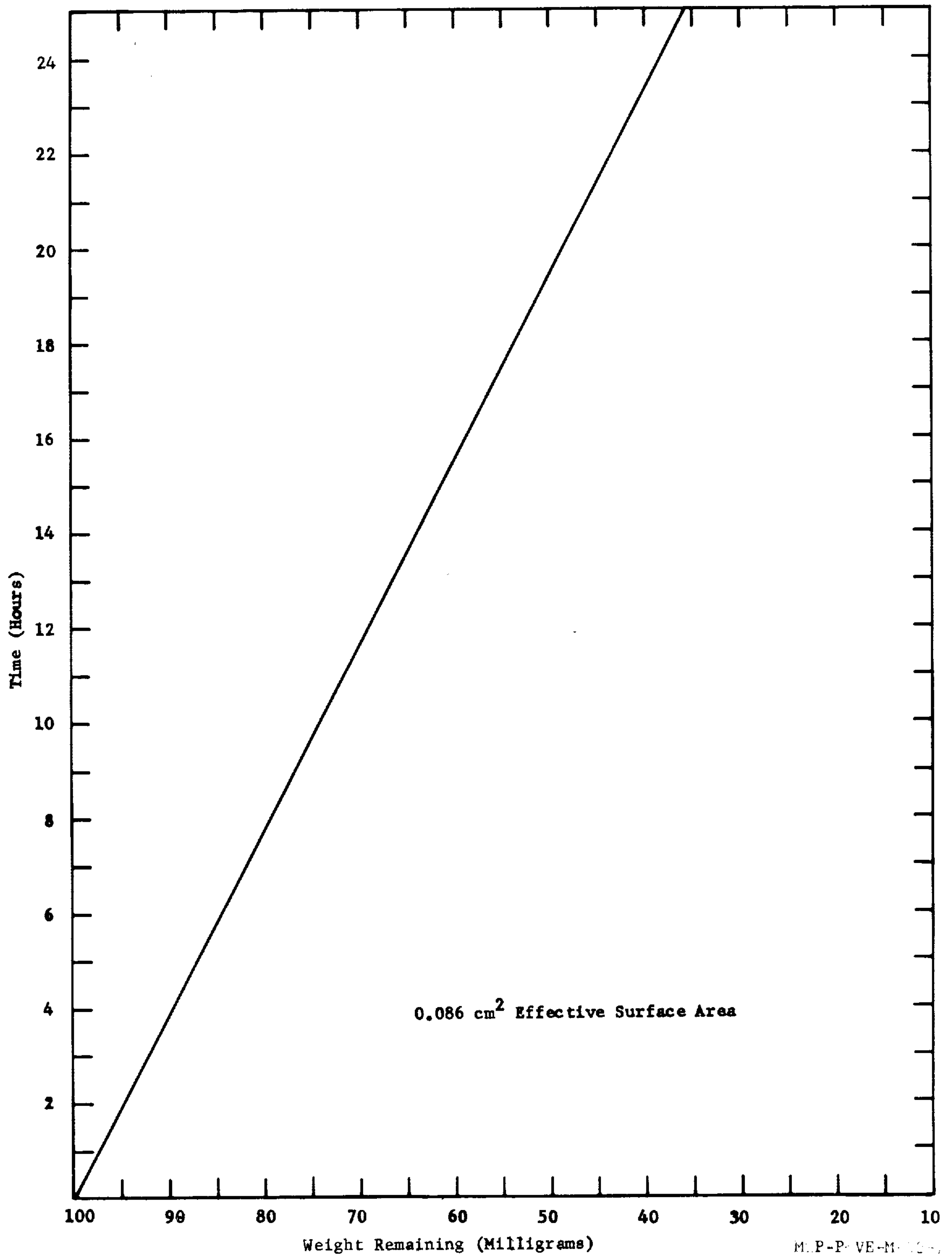

FIGURE 3. EVAPORATION RATE OF GLYCERINE AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

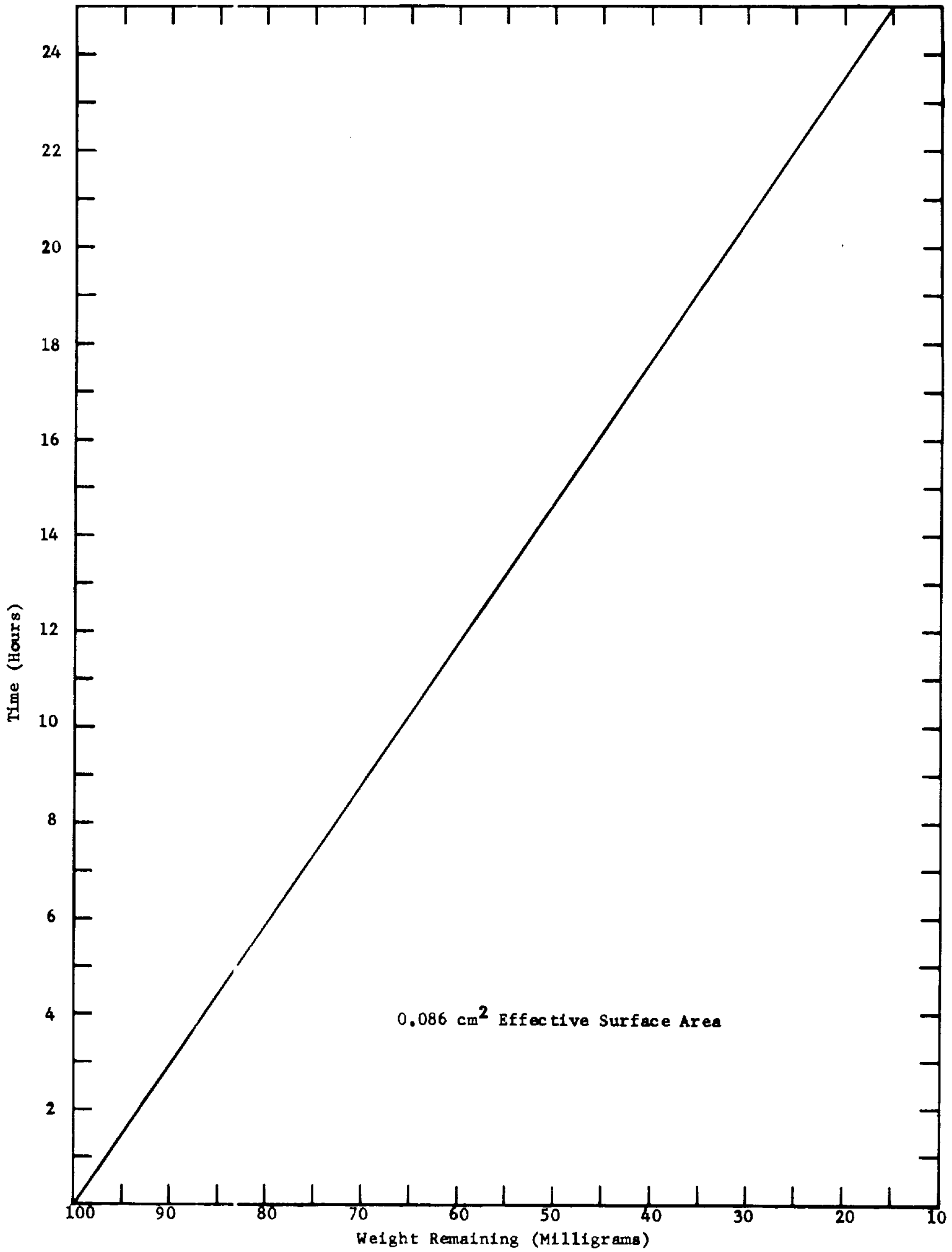

FIGURE 4. EVAPORATION RATE OF DIBUTYL PHTHALATE AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

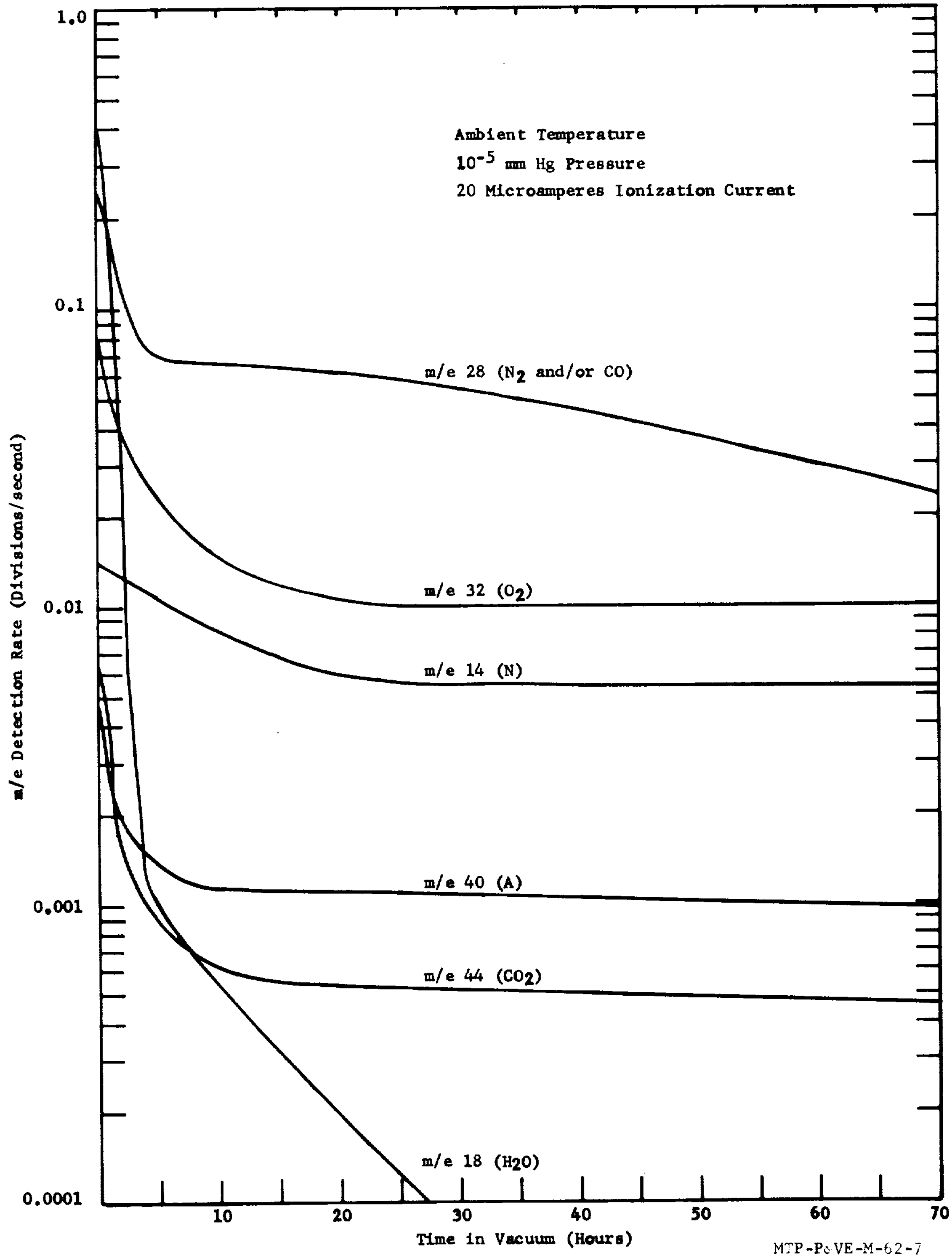

FIGURE 5. OUTGASSING RATES OF ATMOSPHERIC COMPONENTS DESORBED FROM EMPTY CHAMBER

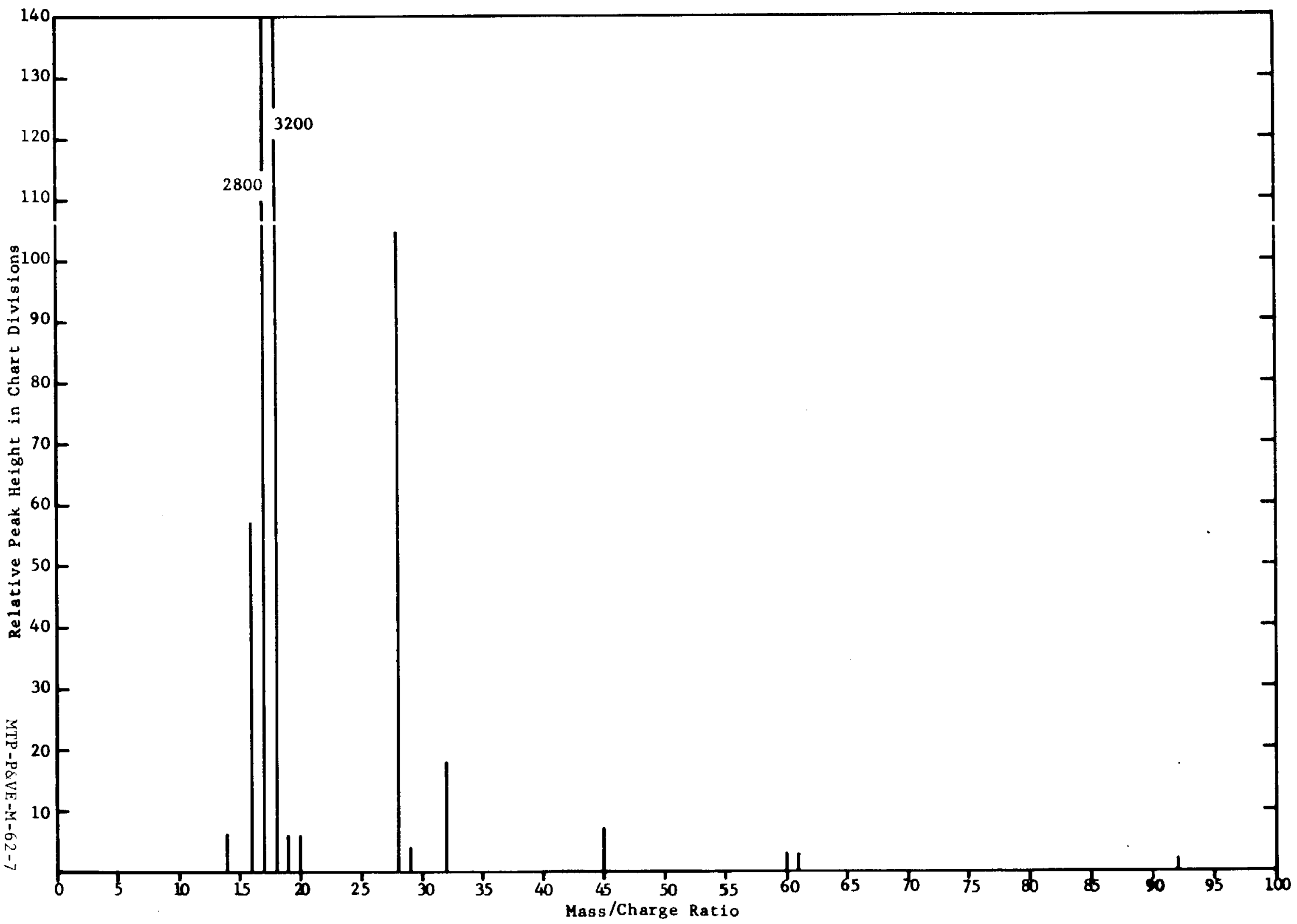

FIGURE 6. MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM GLYCERINE

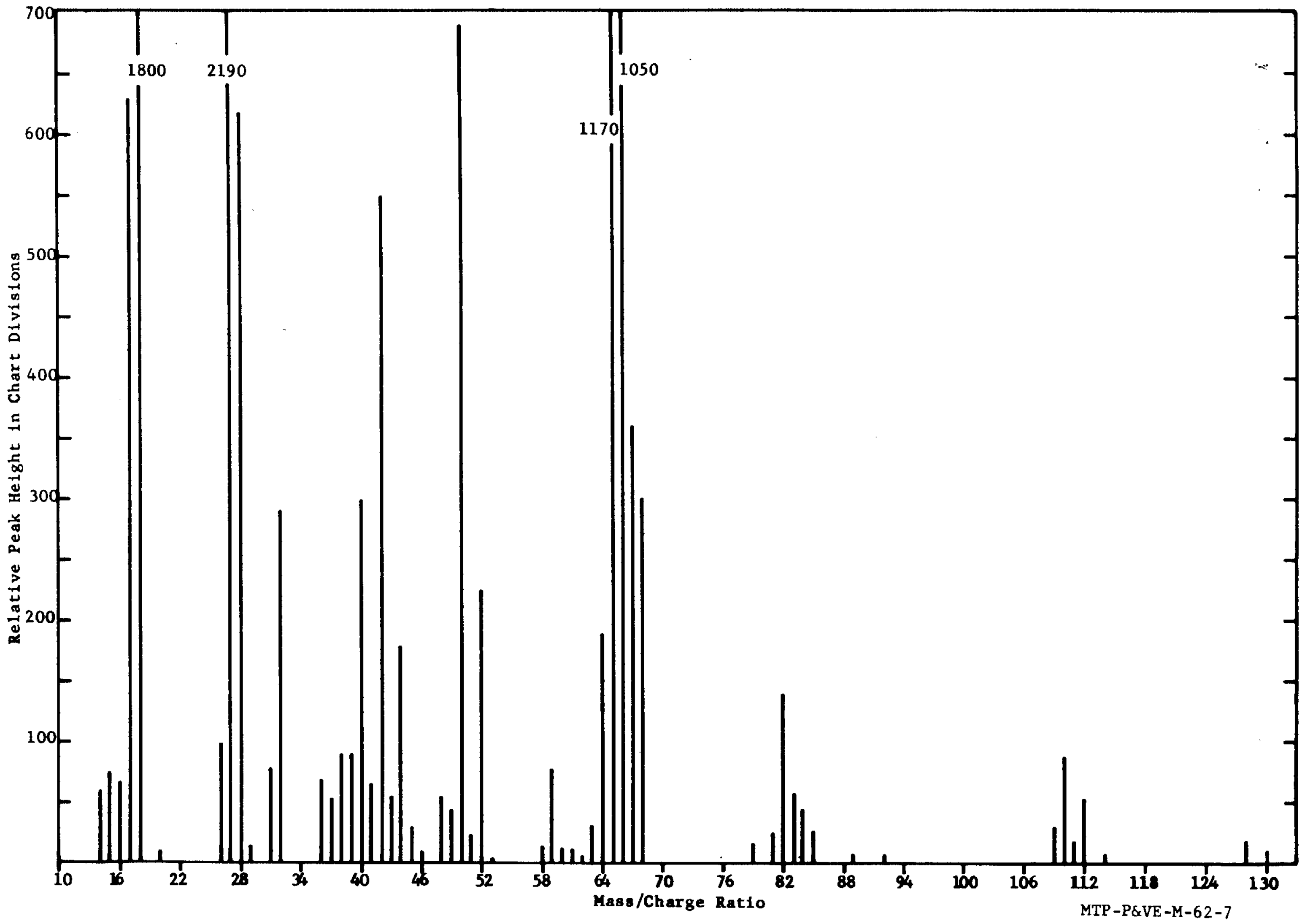

FIGURE 7. MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM DIBUTYL PHTHALATE

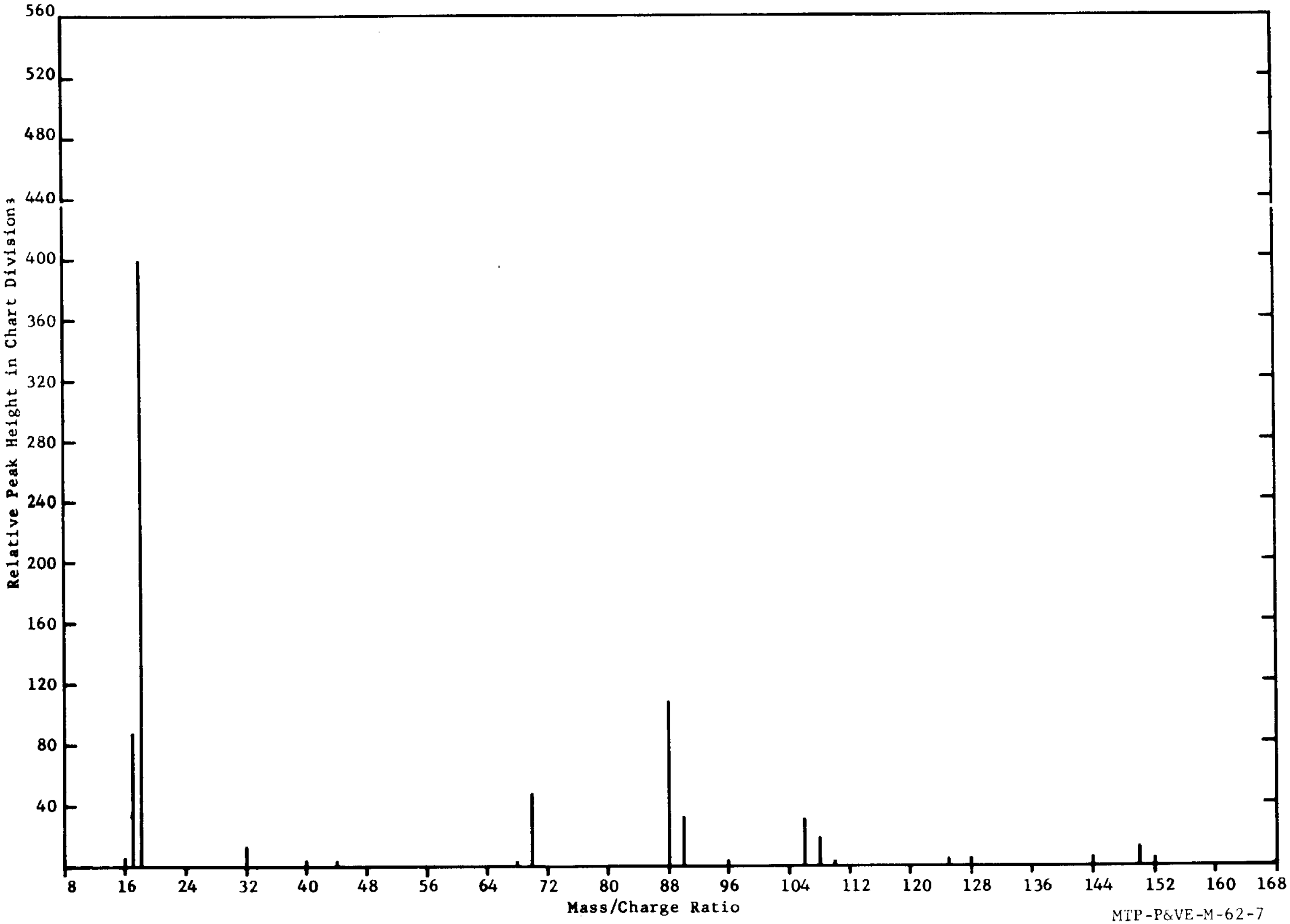

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FIGURE 8. MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM FLUOROLUBE T-45

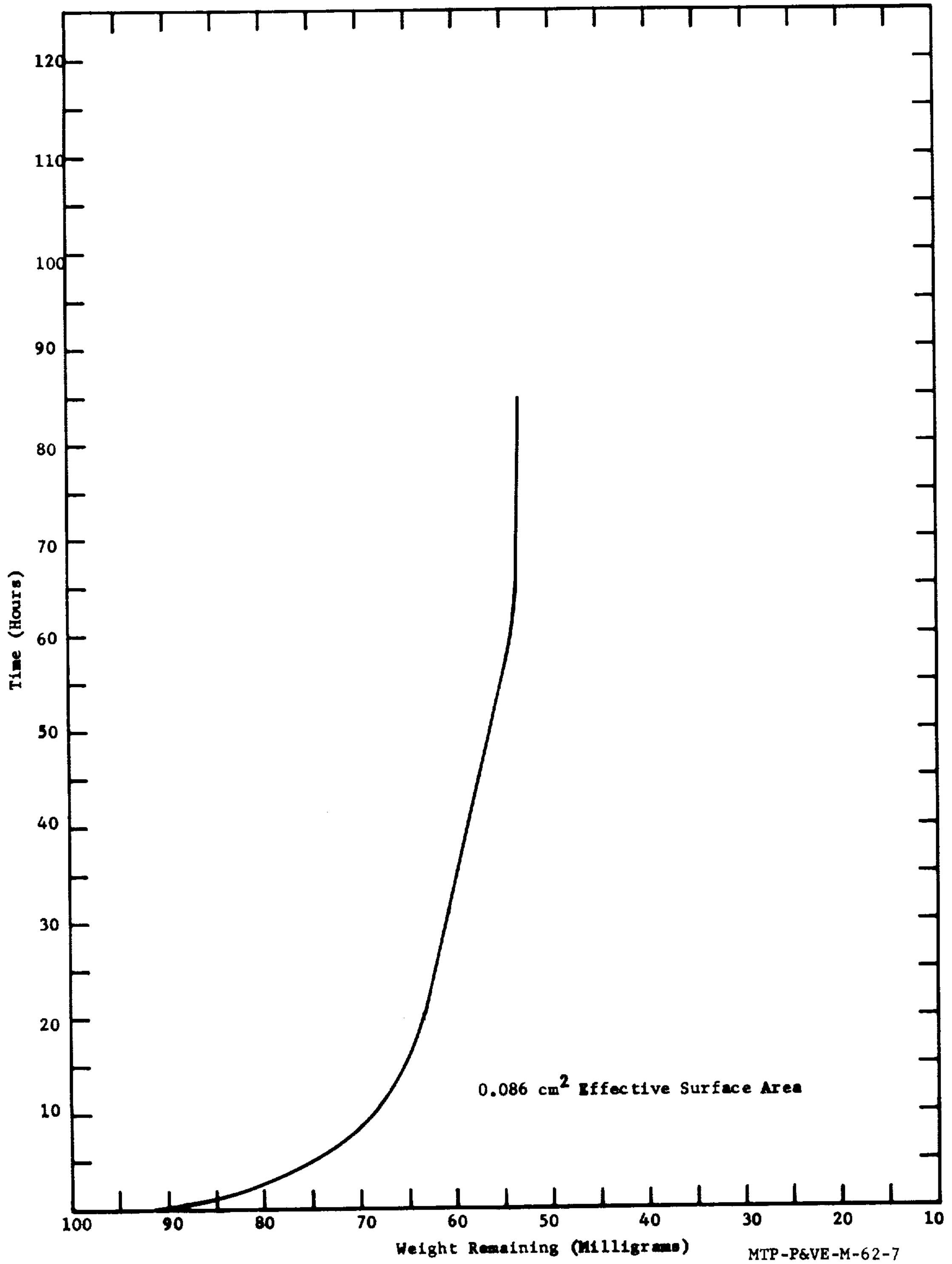

FIGURE 9. EVAPORATION RATE OF FLUOROLUBE T-45 AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

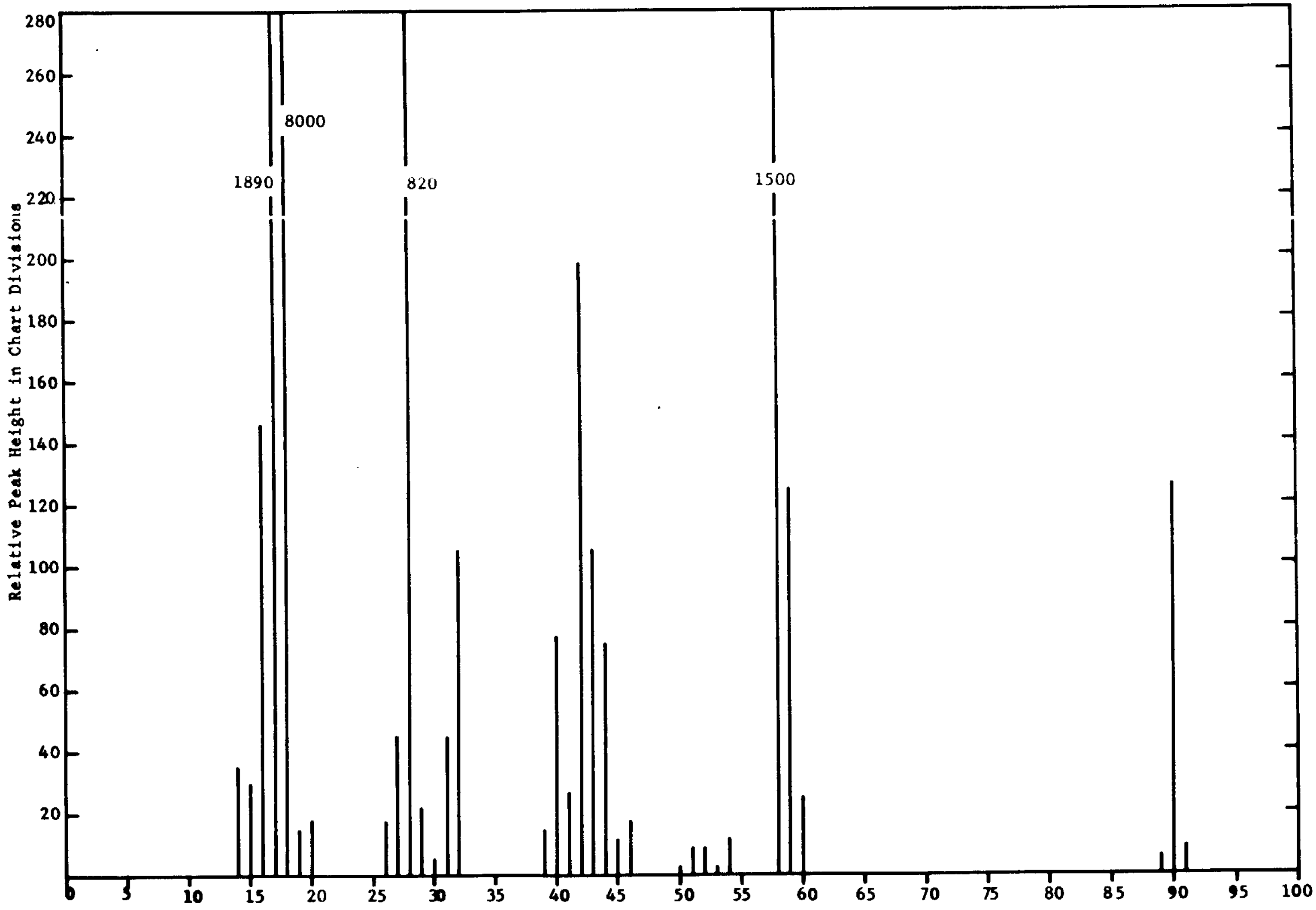

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FIGURE 10. MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM ROCKWELL 950

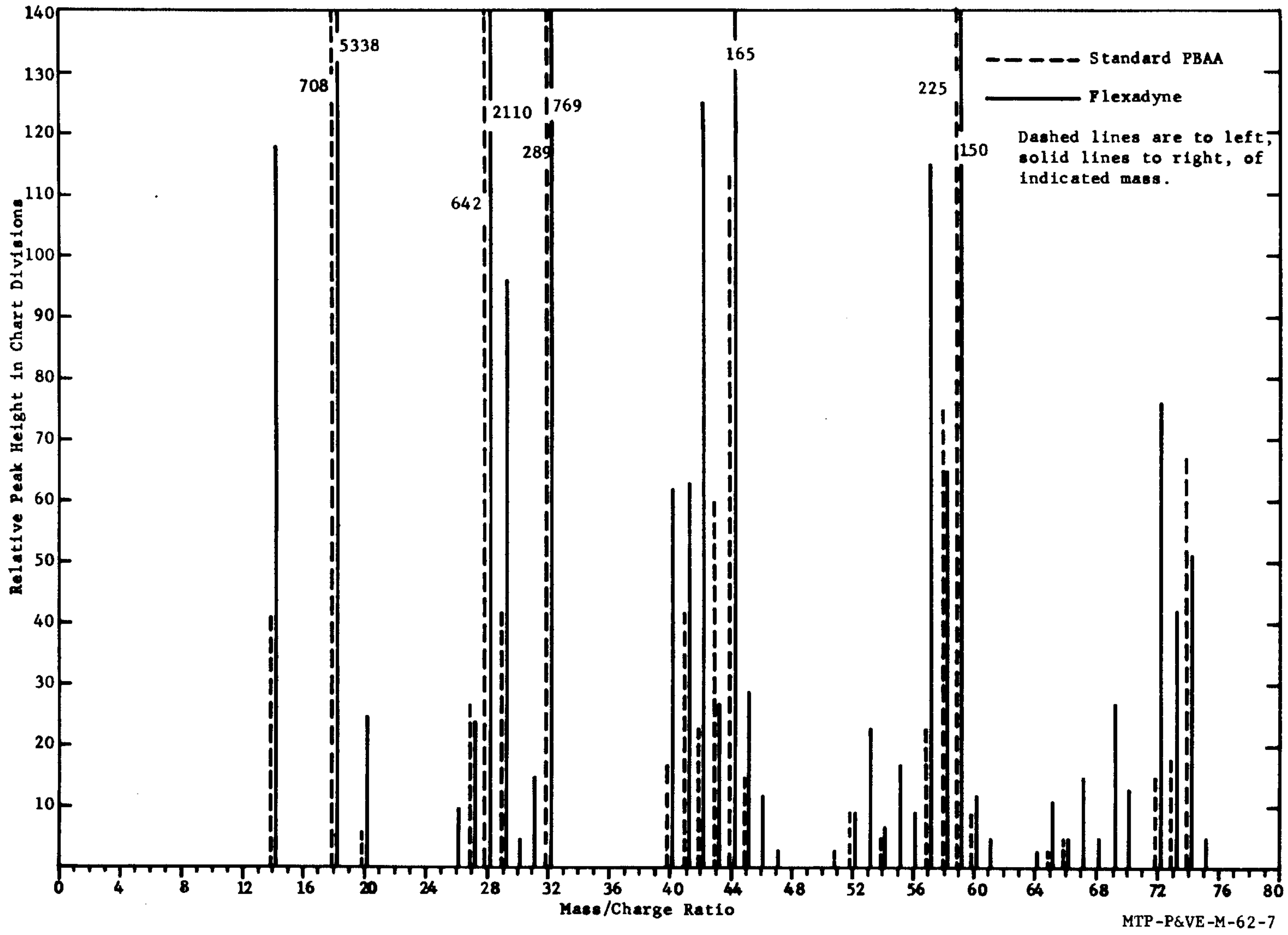

FIGURE 11 (PART 1). MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM STANDARD POLYBUTADIENE ACRYLIC ACID (PBAA) AND FROM FLEXADYNE

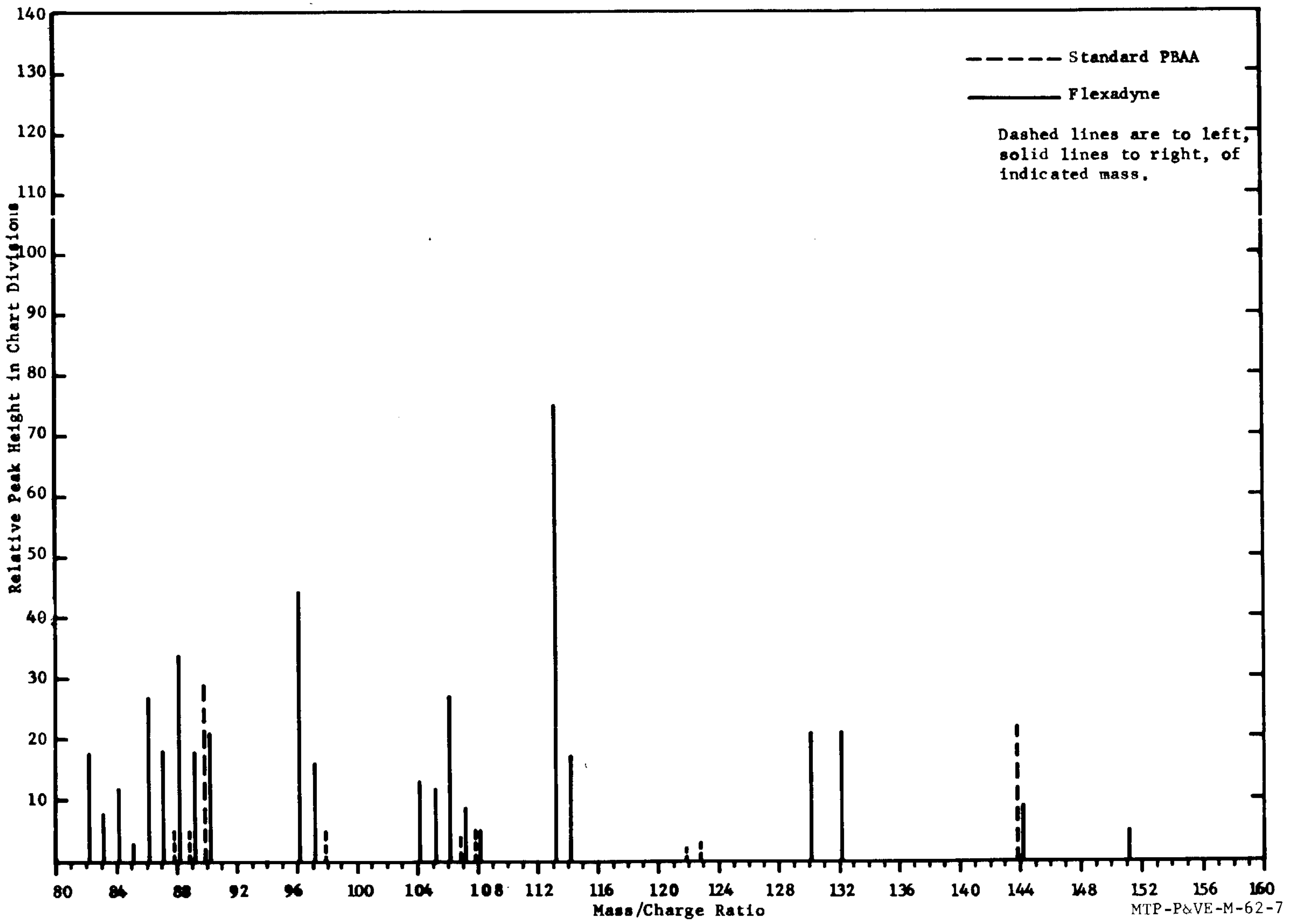

FIGURE 11 (PART 2). MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM STANDARD POLYBUTADIENE ACRYLIC ACID (PBAA) AND FROM FLEXADYNE

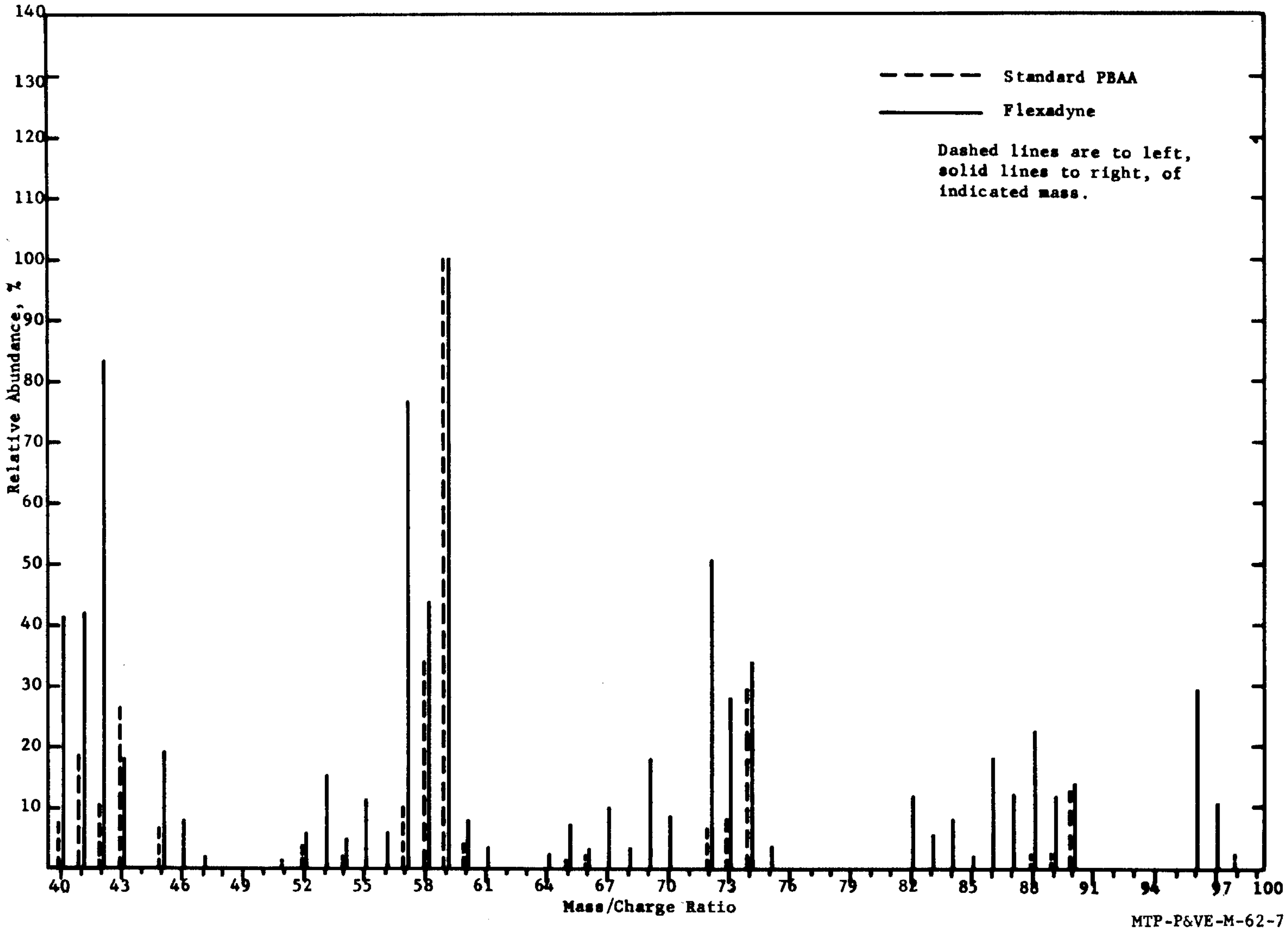

FIGURE 12 (PART 1). RELATIVE ABUNDANCES OF MASSES DETECTED IN SPECTRA OF STANDARD POLYBUTADIENE ACRYLIC ACID (PBAA) AND FLEXADYNE

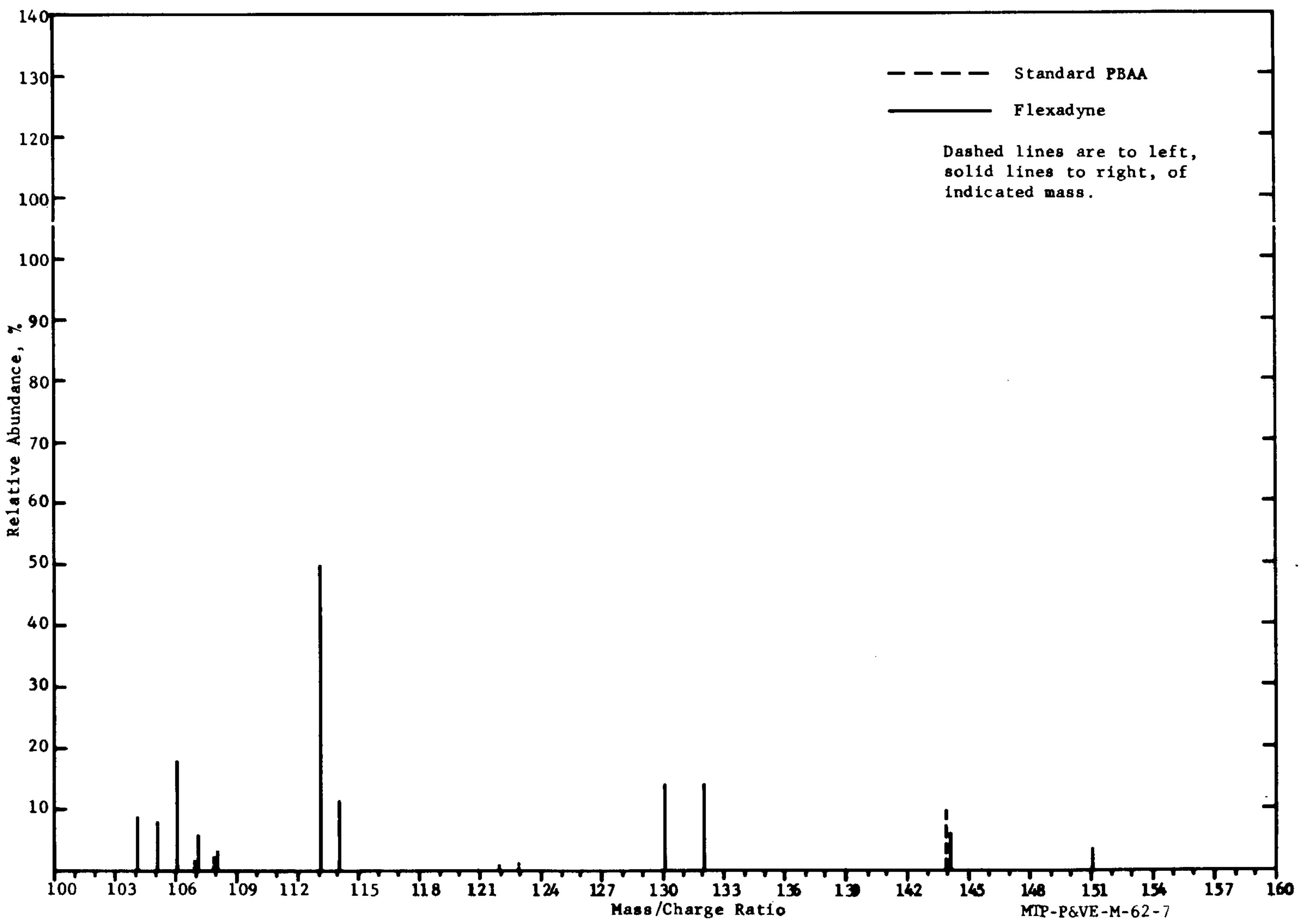

FIGURE 12 (PART 2). RELATIVE ABUNDANCES OF MASSES DETECTED IN SPECTRA OF STANDARD POLYBUTADIENE ACRYLIC ACID (PBAA) AND FLEXADYNE

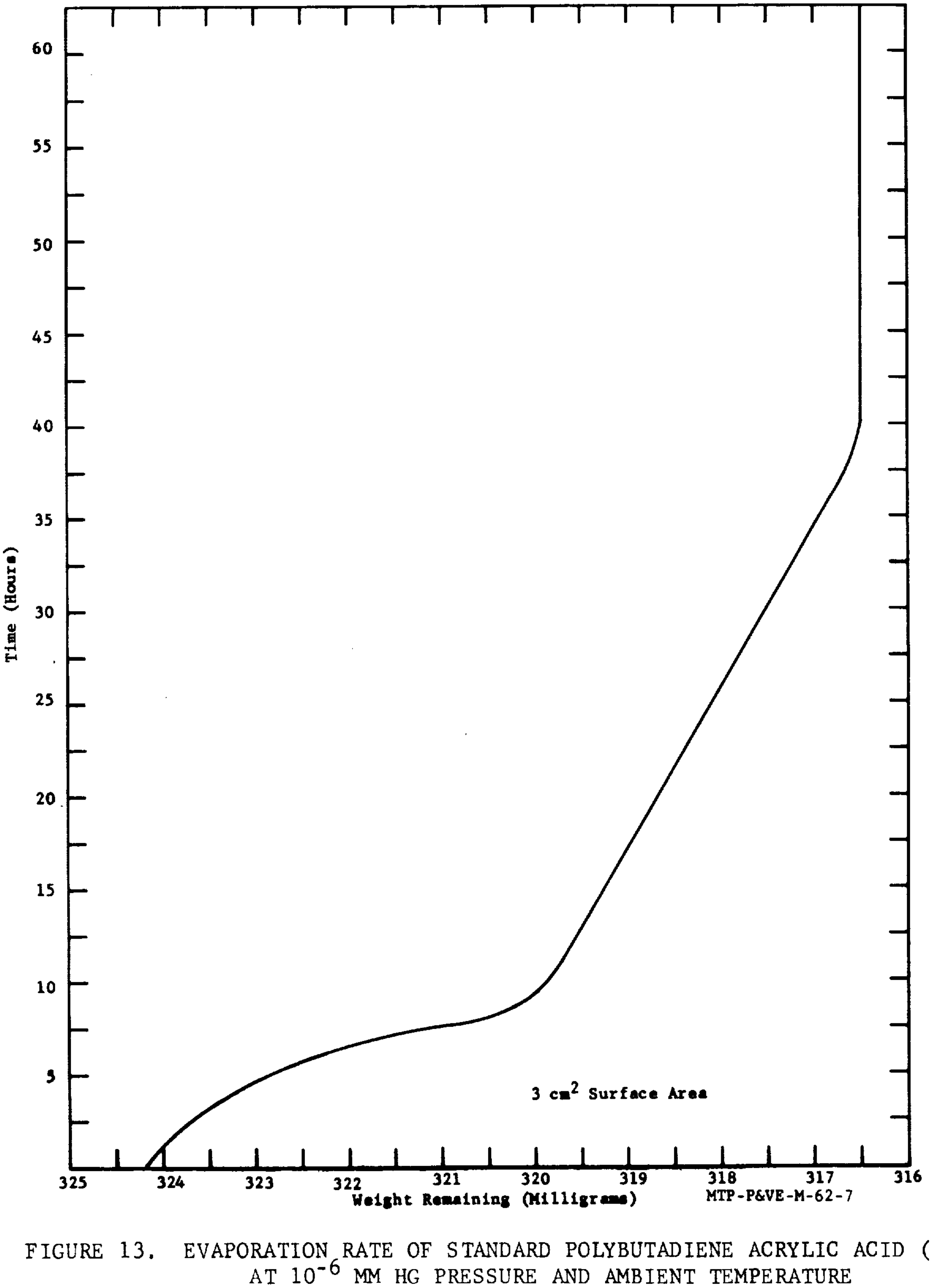

FIGURE 13. EVAPORATION RATE OF STANDARD POLYBUTADIENE ACRYLIC ACID (PBAA) AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

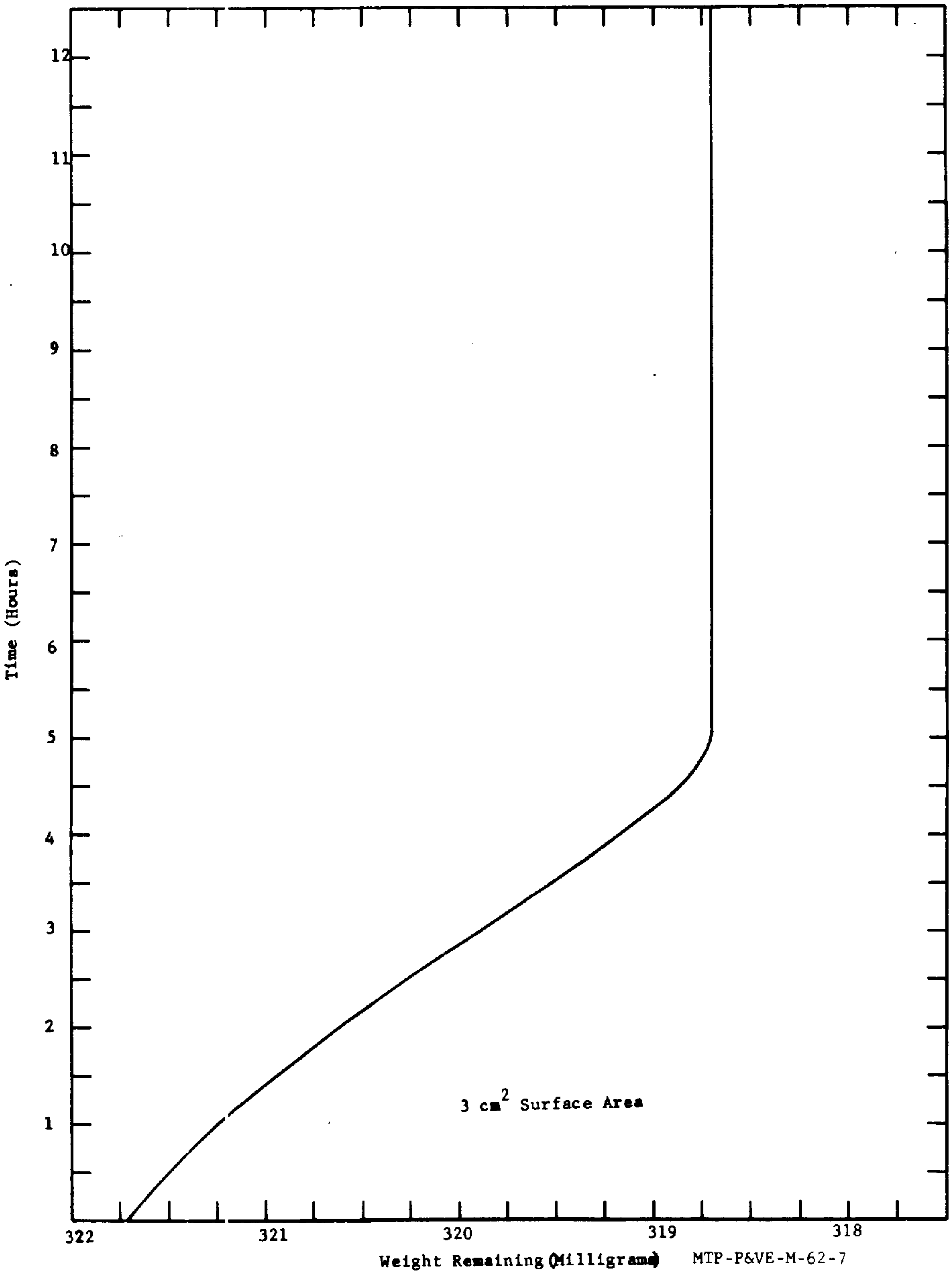

FIGURE 14. EVAPORATION RATE OF FLEXADYNE AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

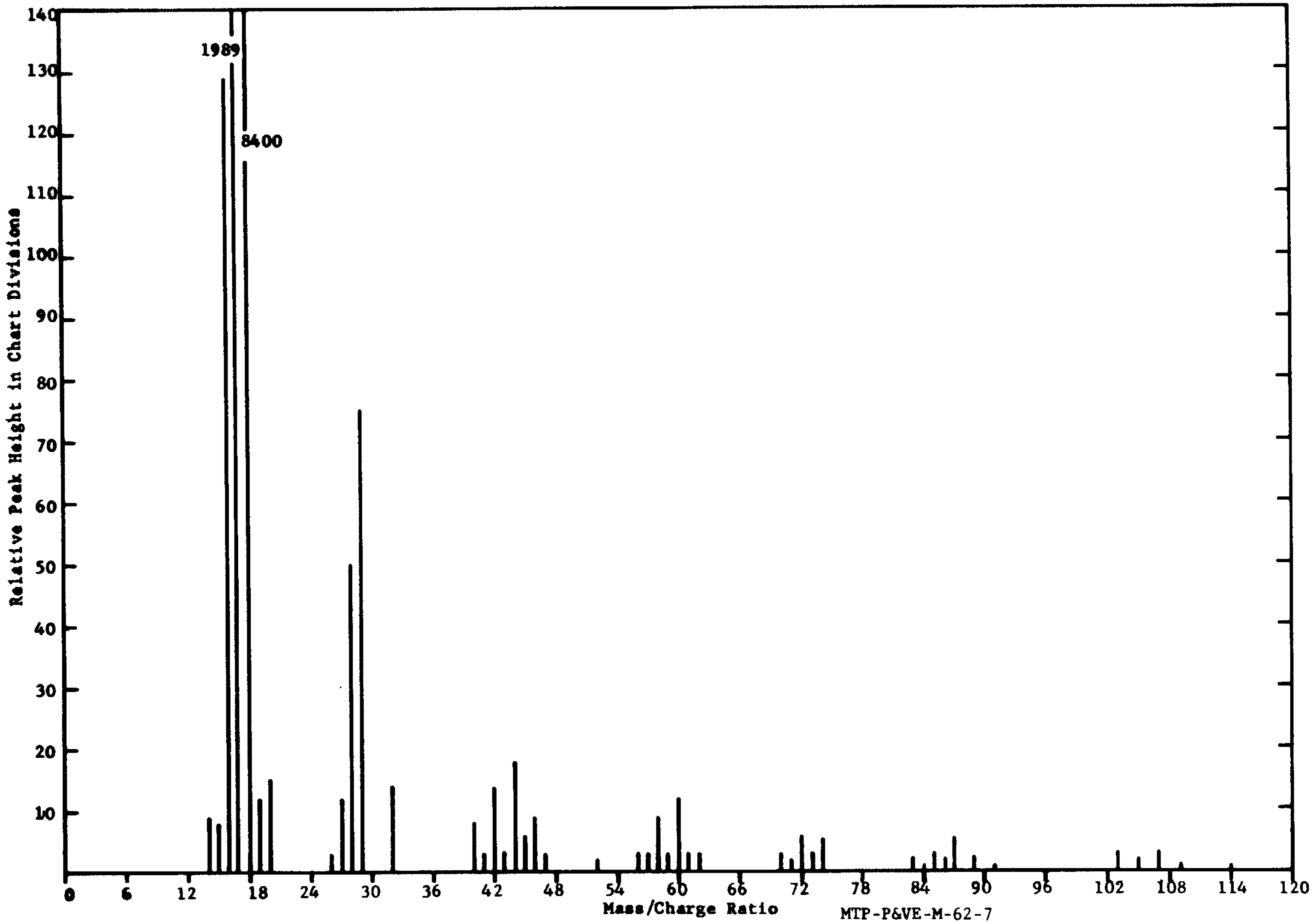

FIGURE 15. MASSES DETECTED AND RELATIVE PEAK HEIGHTS OF OUTGASSING AND EVAPORATION PRODUCTS FROM NATURAL RUBBER

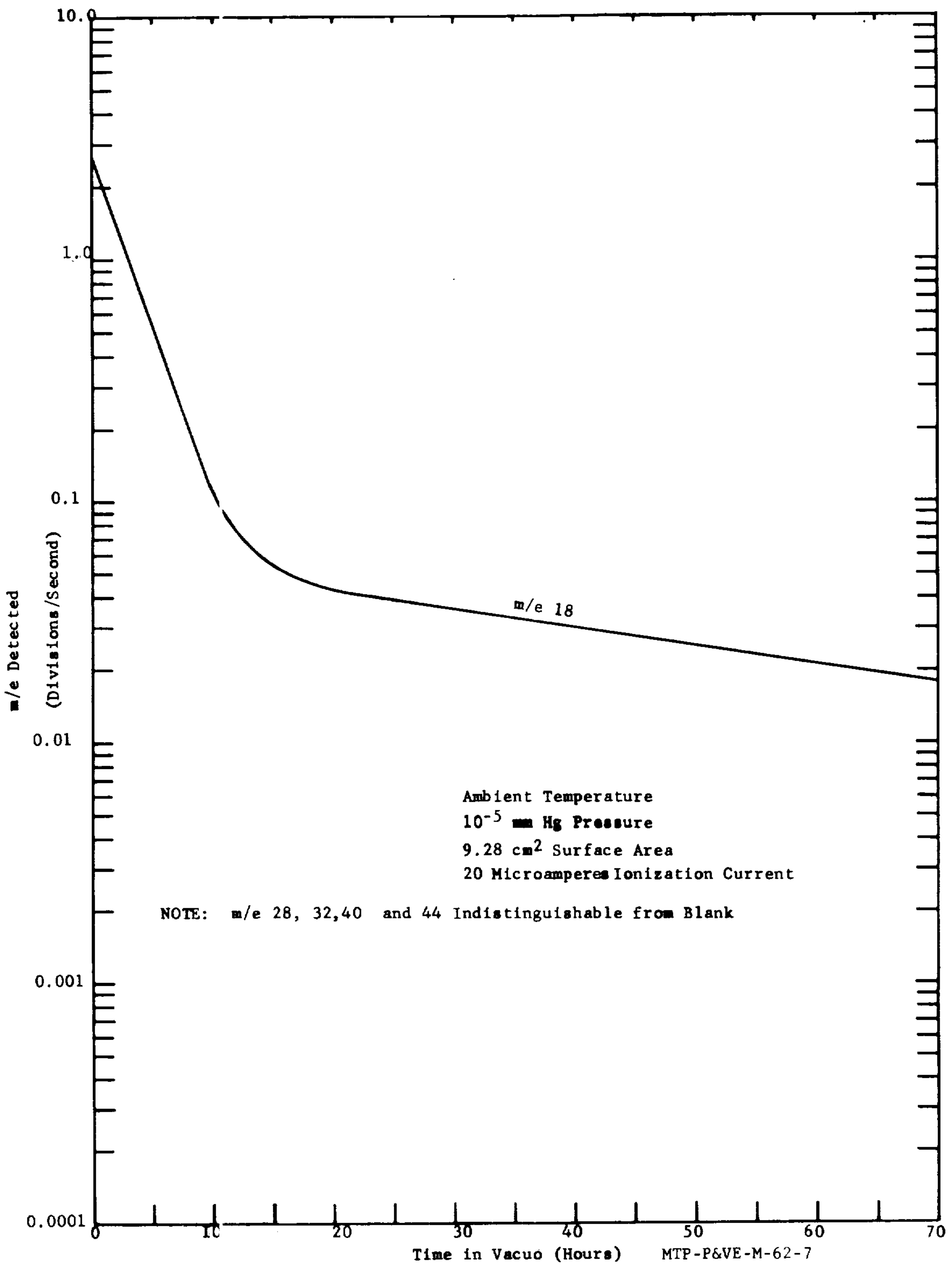

FIGURE 16. OUTGASSING RATE OF ADSORBED MOISTURE FROM NATURAL RUBBER

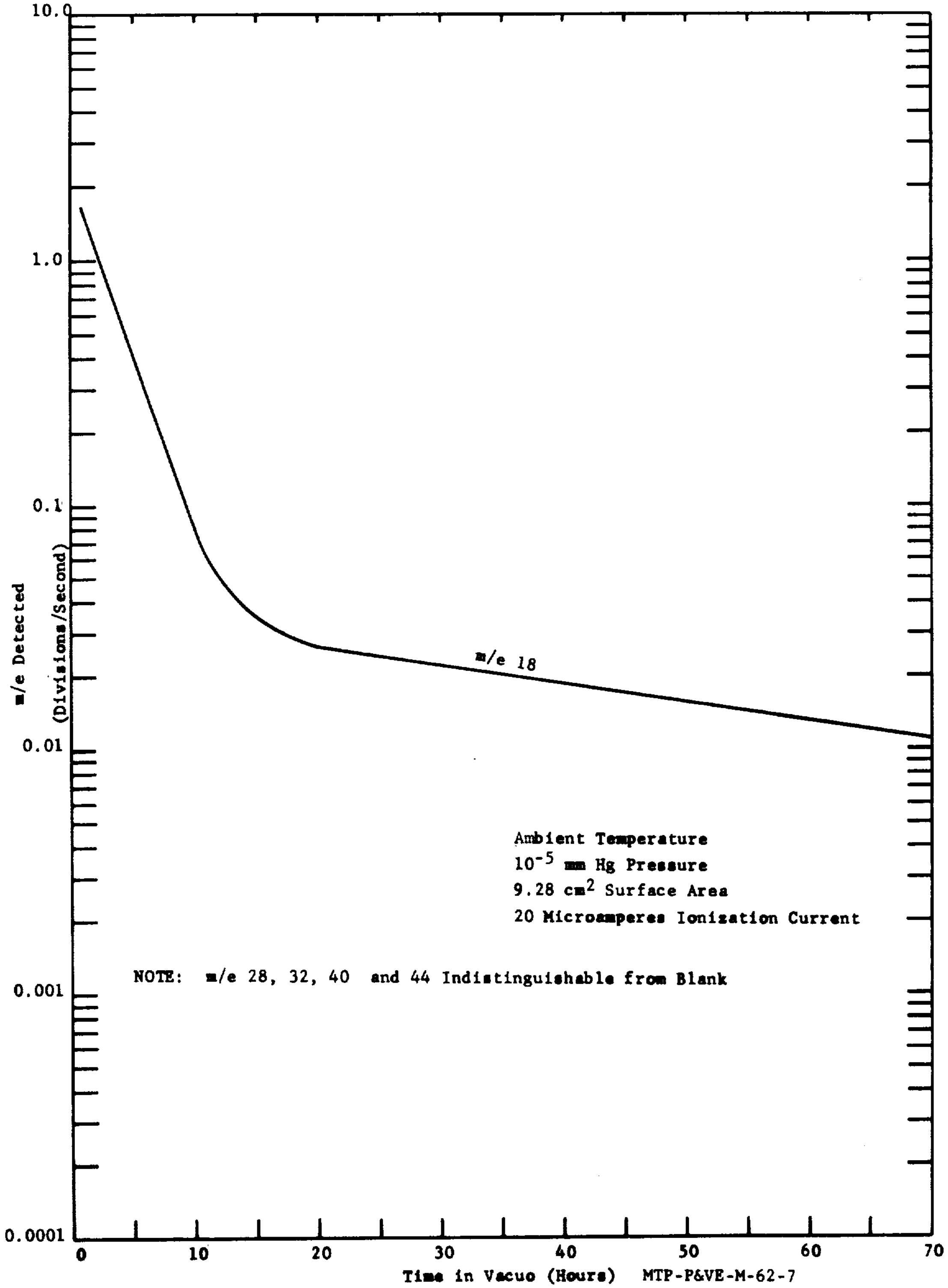

FIGURE 17. OUTGASSING RATE OF ADSORBED MOISTURE FROM SILICONE RUBBER

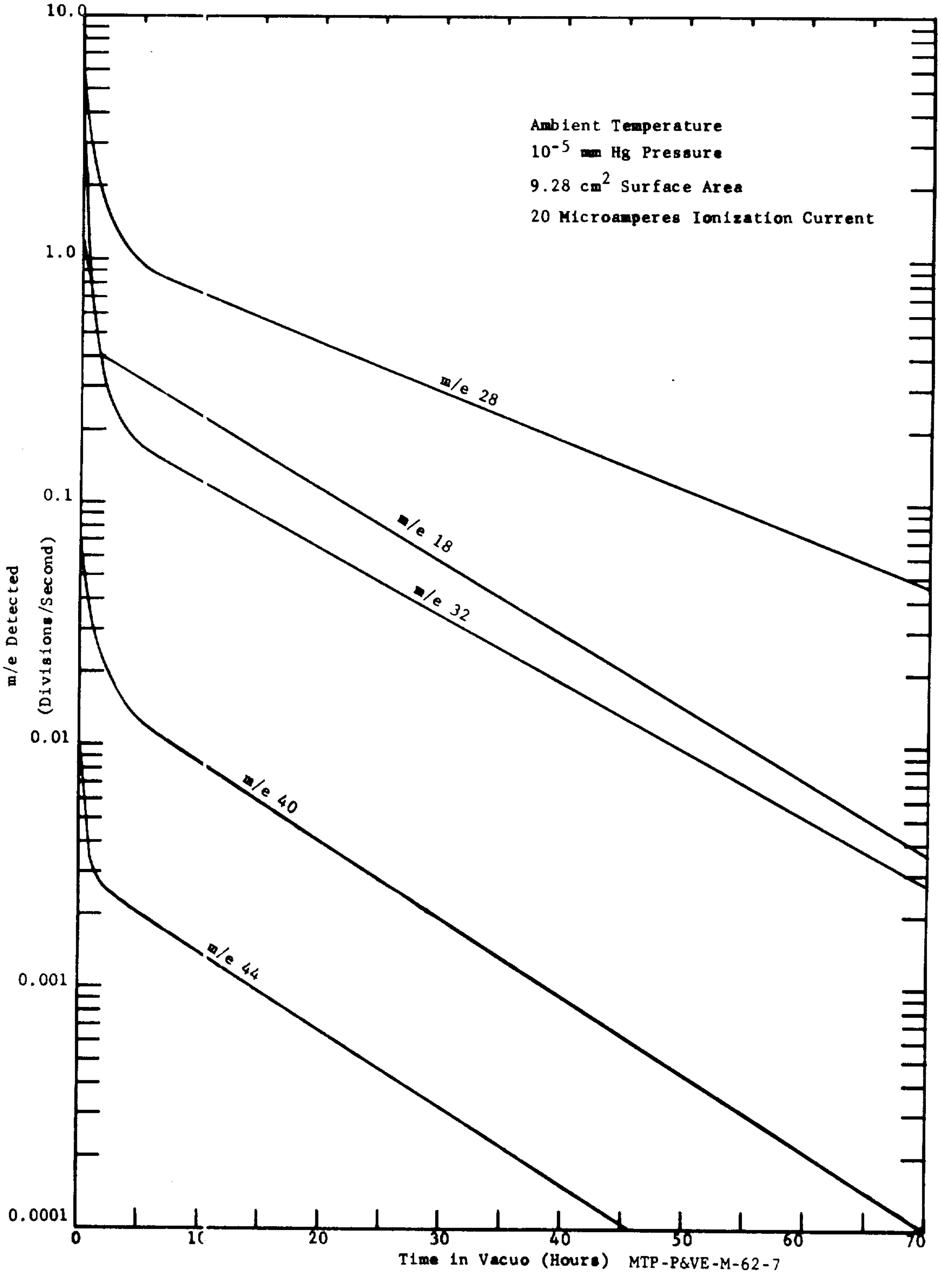

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FIGURE 18. OUTGASSING RATES OF ADSORBED ATMOSPHERIC COMPONENTS FROM BUNA-N

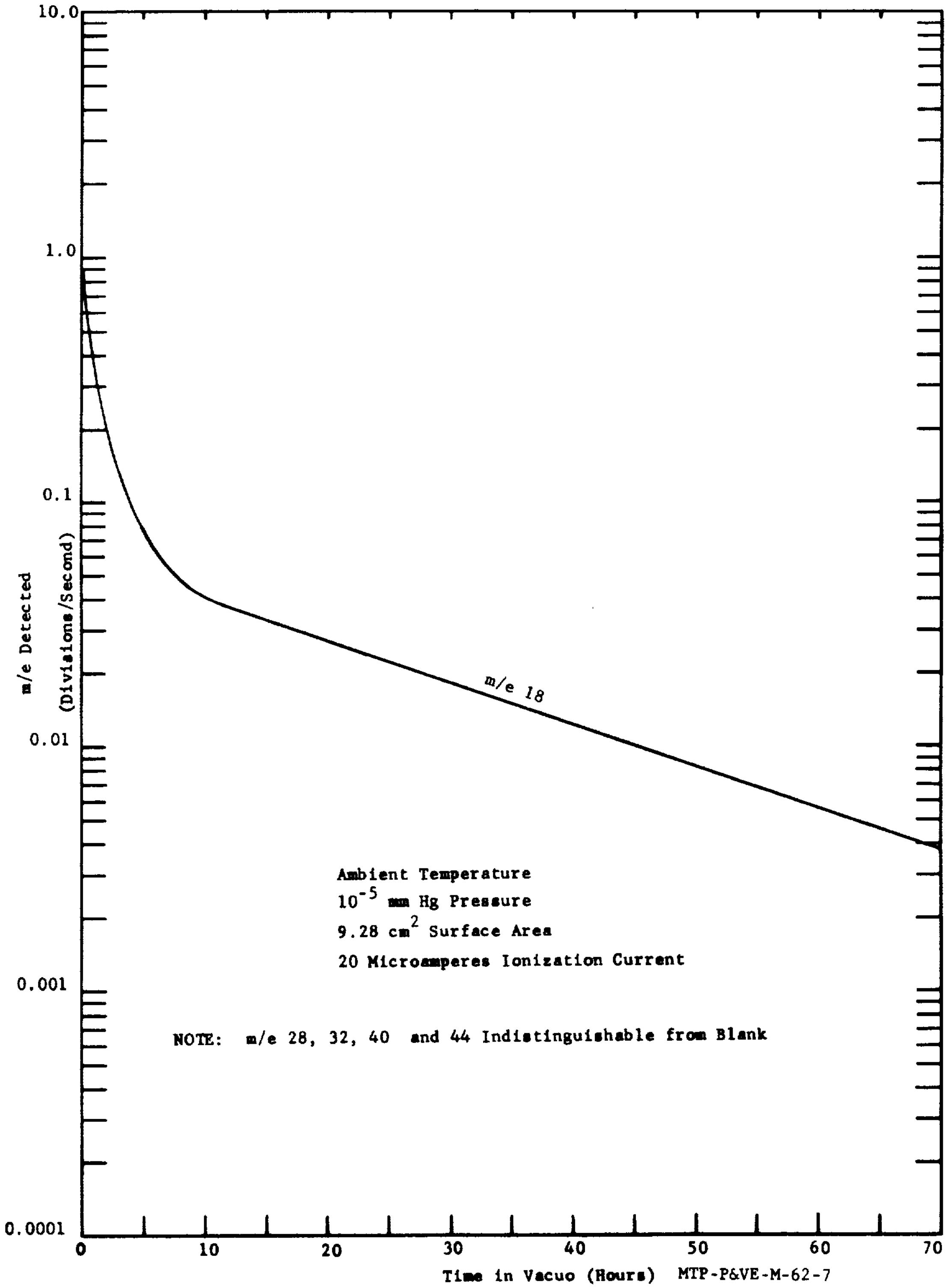

FIGURE 19. OUTGASSING RATE OF ADSORBED MOISTURE FROM VITON A

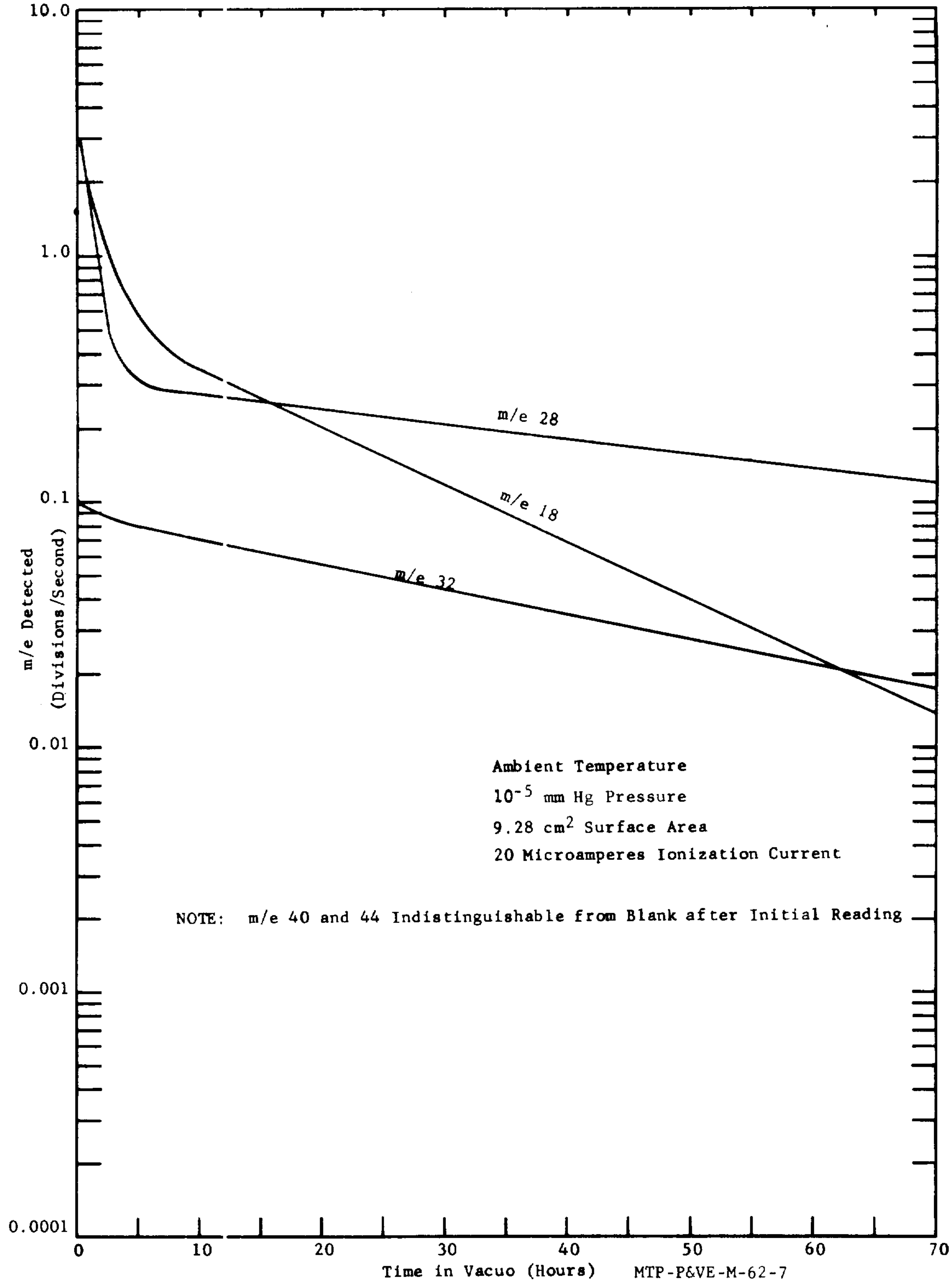

FIGURE 20. OUTGASSING RATES OF ADSORBED ATMOSPHERIC COMPONENTS FROM NEOPRENE

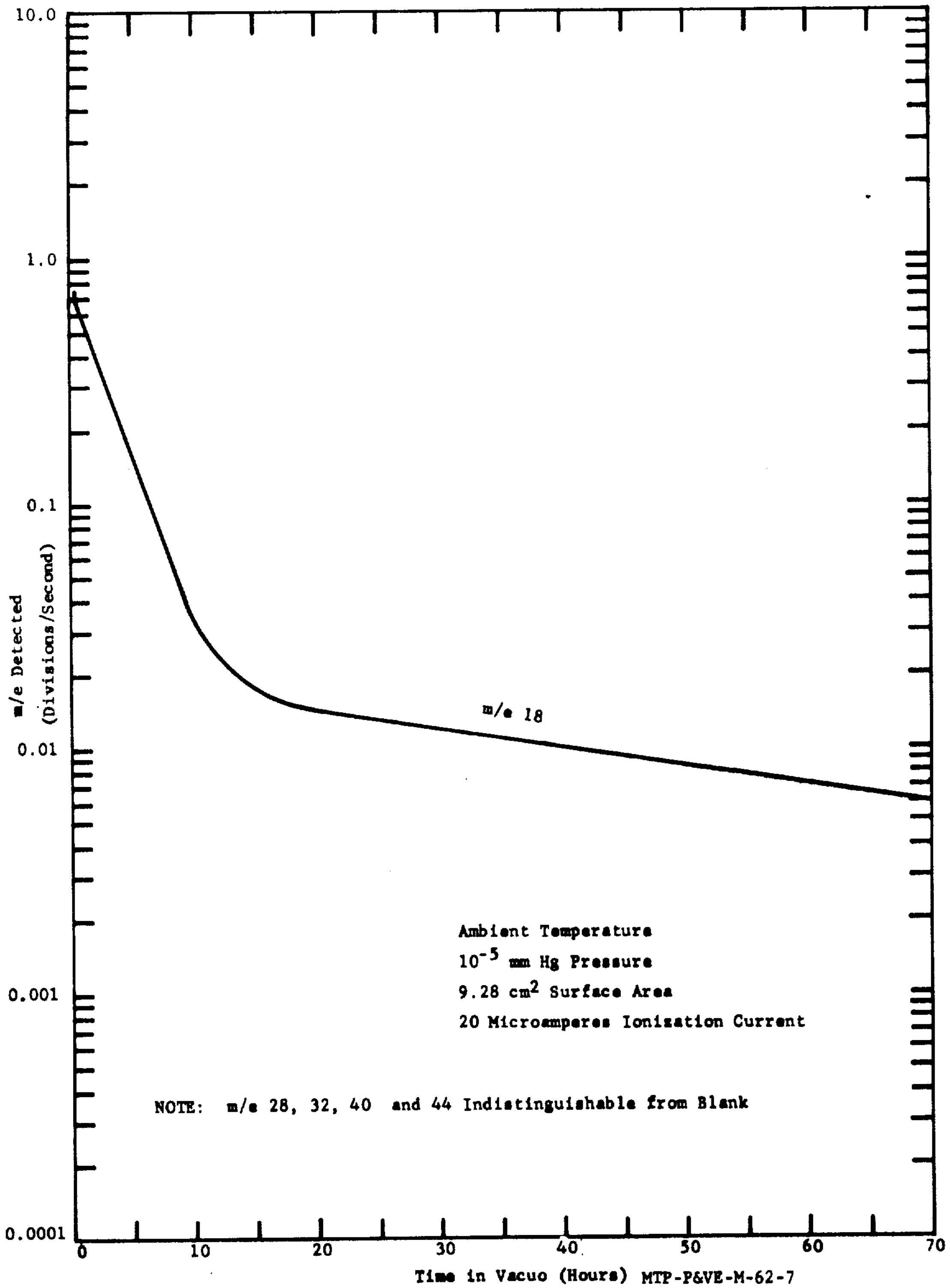

FIGURE 21. OUTGASSING RATE OF ADSORBED MOISTURE FROM BUTYL RUBBER

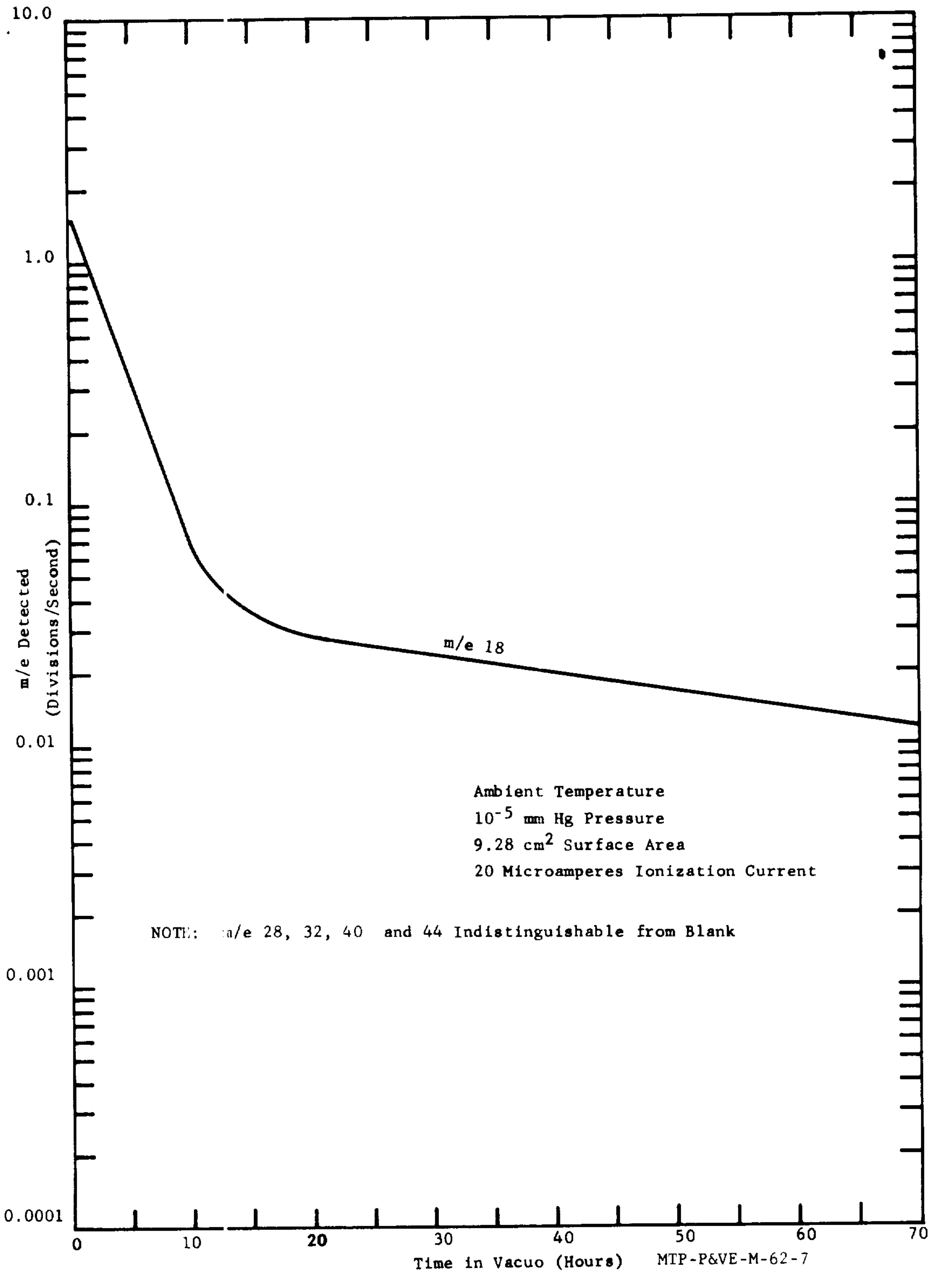

FIGURE 22. OUTGASSING RATE OF ADSORBED MOISTURE FROM KEL-F ELASTOMER

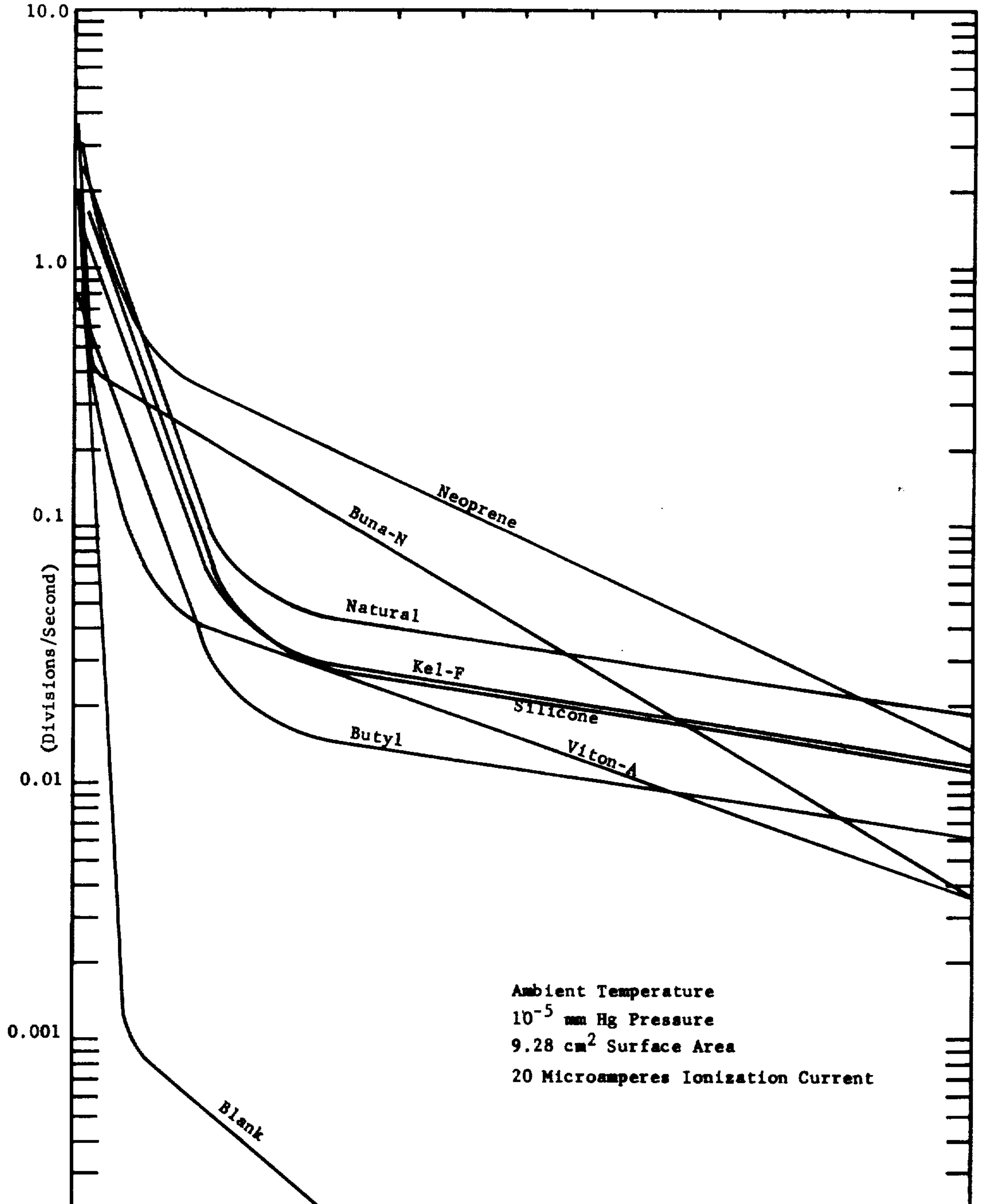

FIGURE 23. OUTGASSING RATE OF ADSORBED MOISTURE (m/e 18) FROM VARIOUS RUBBER MATERIALS

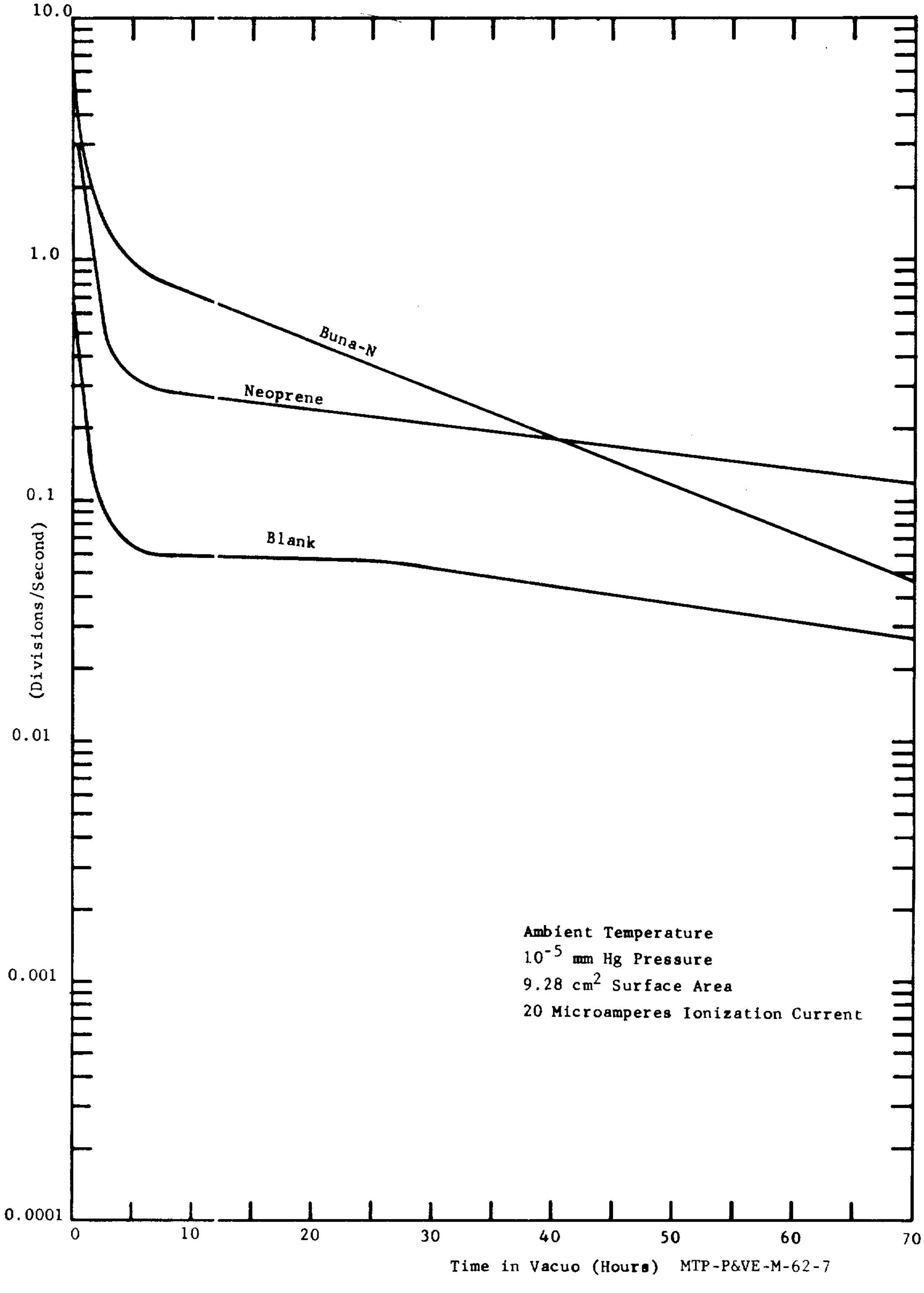

FIGURE 24. OUTGASSING RATE OF ADSORBED NITROGEN (m/e 28) FROM BUNA-N AND NEOPRENE

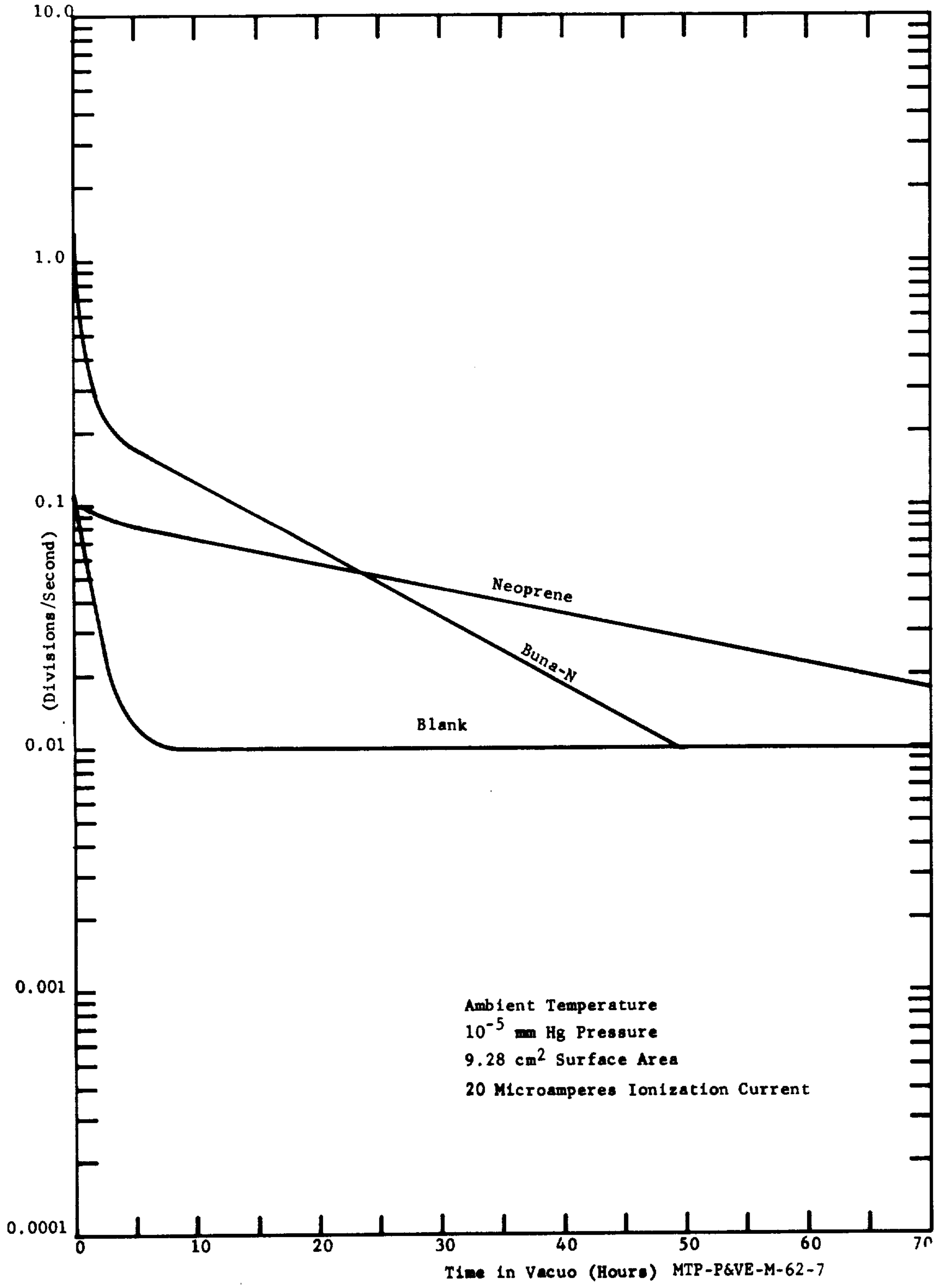

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FIGURE 25. OUTGASSING RATE OF ADSORBED OXYGEN (m/e 32) FROM BUNA-N AND NEOPRENE

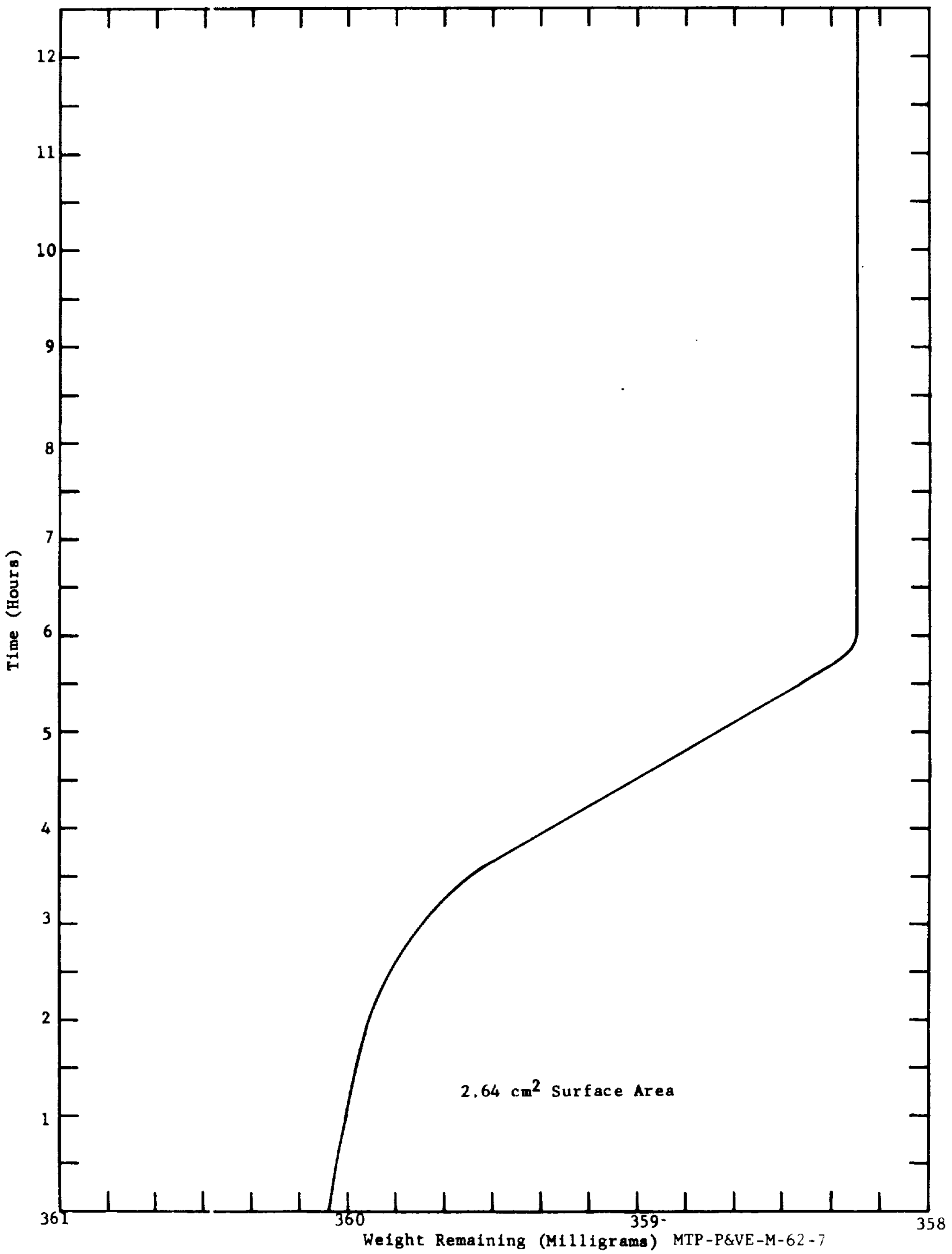

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FIGURE 26. EVAPORATION RATE OF NATURAL RUBBER AT 10^{-6} MM HG PRESSURE AND AMBIENT TEMPERATURE

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A STUDY OF THE OUTGASSING AND EVAPORATION PRODUCTS OF SOME MATERIALS UPON EXPOSURE TO REDUCED PRESSURE

By S. V. Caruso and W. C. Looney

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