Presented at the 23rd National Vacuum Symposium, 9/21-24/76, Chicago, Ill.

Behavior of Titanium Sublimation and Sputter Ion Pumps in the 10^{-11} Torr Range*

BNL-21615

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CONF-760921-2

Abstract

In the proposed Intersecting Storage Accelerator, ISABELLE, 1200 pumping stations will be used to keep two 3 km long rings at a pressure of 1×10^{-11} Torr. It is clear that in such a large system, price and simplicity are very important. We have therefore undertaken a study on a well instrumented room temperature vacuum system with a surface area of 6000 cm^2 and a volume of 17 ℓ, pumped by a Ti-ball and an ion pump. Total pressure and residual gas composition were measured by a Helmer gauge and a quadrupole mass spectrometer. The final pressures of $\sim 1 \times 10^{-11}$ Torr were reached with Ti films and a 20 $\ell\ s^{-1}$ sputter-ion pump. The main residual gas components were hydrogen and methane. The ultimate pressure was determined primarily by the ability of Ti films to pump H_2 and depend on the method of laying down the film and the surface temperature. Previous surface preparation seemed relatively unimportant. Two methods of pumping CH_4 were investigated, namely, a) cracking the molecules on hot tungsten filament and b) conventional sputter-ion pumping. Sputter-ion pump was found to be more efficient and preferable.

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*Work performed under the auspices of the U.S. Energy Research and Development Administration

CONTRACT NO. E(30-1)-16

DISCLAIMER

I. Introduction

The Intersecting Proton Storage Accelerator Facility ISABELLE[1] will consist of two rings having a circumference of 3 km each. To insure proper operation of colliding beam experiments, the pressure in the vacuum chamber of the rings should be about 1×10^{-11} Torr (N_2 equivalent).[2] For the vacuum system[3] we have selected an 8 cm diameter tube of aluminum alloy Al 6061 pumped every 5 m by a pumping station which contains a titanium sublimator and an ion pump. Extensive surface treatment and outgassing tests have been made on pipes of this Al alloy.[4] It has been found that a surface treatment consisting of chemical polishing and a glow discharge cleaning in argon and oxygen followed by $\sim 200^{\circ}$ C bake-out resulted in a hydrogen outgassing rate of 1×10^{-13} Torr liter cm^{-2} s^{-1}. The content of other residual gases was negligible. It is clear that this low outgassing rate will produce a pressure rise of only $\sim$ 2×10^{-12} Torr above the pressure attained in the pumping station. Since more than 1200 of these units will be required, the main task becomes to design a simple inexpensive pumping station having a large pumping speed for hydrogen and operating routinely below 3×10^{-11} Torr hydrogen pressure.

Only a modest pumping speed is required for non-getterable gases (helium, methane and argon). A combination of a titanium sublimator and a small sputter ion pump satisfies the criteria of both economy and simplicity. A vacuum system to investigate these two methods of pumping was therefore constructed. Extensive data obtained in the 10^{-11} Torr range confirmed that a small ion pump and a Ti-ball can routinely achieve the required pressures.

During the course of this work, which started as an engineering study of well understood phenomena,[5-7] it was realized that both titanium films and ion pumps behave differently at 1×10^{-11} Torr than at higher pressures. In fact, hydrogen pumping by Ti films was sufficiently different to warrant more funda-

mental experiments on Ti - H_2 systems at very low pressures which are now in progress. I will, however, limit my discussion to a description of how to achieve a nitrogen equivalent pressure of 1×10^{-11} Torr and what precautions have to be taken in the construction of such a system, in the selection of its components and in the interpretation of the results.

II. Experimental Apparatus

The main factors which determined the achievement of 1×10^{-11} Torr in our experimental set-up were:

1. The ability of Ti films to pump hydrogen.
2. The ability of ion pumps to pump methane without introducing helium back into the system.

The apparatus in which this study was conducted is shown schematically in Fig. 1. It consists of a standard Varian 15 cm cross and a stainless steel cylinder of the same diameter containing a titanium sublimator. The surface area and the volume of the system are 6000 cm^2 and 17ℓ respectively. The entire system can be covered with an oven and baked out up to 360° C.

The total and partial pressures were measured by a Helmer gauge, G, and UTI quadrupole mass spectrometer, MS. It is essential that both measuring devices, but especially the mass spectrometer, be mounted directly inside the main vacuum volume. The mass spectrometer when connected to the cross through a N_2 conductance of 30ℓ s^{-1} gave completely erroneous results. In order to reduce the heating of the walls of the apparatus and to extend the operation to 1×10^{-13} Torr, the Helmer gauge was operated with thoriated tungsten filament[8] which runs at a temperature < 1200 K for the rated emission of 10 mA. Altogether three sputter ion pumps, S_1, (Varian 20ℓ s^{-1} and 30ℓ s^{-1} triode pumps and Vecco 30ℓ s^{-1} Mag-Ion pump) were tested during this experiment. They were connected either directly or through a 7 cm Varian all metal valve, V_1, having N_2 conductance of $\sim$ 32ℓ s^{-1}, to the cross (Fig. 1).

For every experimental run the system is first pumped out by a sorption pump and leak checked. This is followed by a 150° C bake to transfer most of the water and other easily removable gases into the sorption pump. After about 8 hours at this temperature, V_3 in Fig. 1 is closed and V_4 opened. The bake out continues into a 100ℓ s^{-1} ion pump, S_2, for a time at the temperature required by the various experimental schedules. During this bake out the Helmer gauge and the mass spectrometer are degassed and the Ti-ball is operated at standby power for 15 minutes. At the end of each bake out cycle, S_1 is switched on. Thirty minutes later V_2 is closed and the system is cooled down. In addition to the above cycle the Ti-ball was initially conditioned by being operated at its standby power for 50 hours while the system temperature was held at 200° C. During the cool down, the Helmer gauge and the mass spectrometer were again outgassed.

III. Measurements

Total and partial pressures were measured as a function of three surface treatments.

1. Chemical cleaning in an acid solution of 33 percent hydrofluoric, 33 percent nitric, remainder distilled water for 10 minutes, followed by a thorough rinse in distilled water plus vacuum bake in a temperature range from 200 to 350° C.

2. 16 hour bake in oxygen-air at 200° C + vacuum bake at 260° C for 24 hours.

3. Glow discharge in 2.5×10^{-2} Torr oxygen, (flow rate 5×10^{-2} Torr liters s^{-1}, current density 50μA cm^{-2}, total dose 1.1×10^{18} ions cm^{-2}) + 260° C vacuum bake for 24 hours.

Furthermore, the methane pumping speed of 2 different gauges, three ion pumps and a hot tungsten filament were also investigated.

A. Total Pressure

The total pressures were measured in N_2 equivalent on the Helmer gauge with the mass spectrometer switched off, because it was found that even with many outgassing cycles the mass spectrometer contributed 3 to 6 times more gas than the rest of the system. The Helmer gauge was compared by D. Edwards with the calibrated Varian nude BA gauge and the Balzer modulated BA gauge type IMR 105. All three gauges agreed with one another to within 17 percent. Hydrogen sensitivity was previously determined to be 2.8 (Ref. 9).

Equilibrium pressures were reached in about two days after bake out termination and the values read 50 hours after the bake out are tabulated in Table I. At this point the Ti-ball was turned on and 3 mg were deposited over an area $\sim 2000 cm^2$. A few hours later, the Helmer gauge and the mass spectrometer were degassed and operated for about 8 hours, after which MS was switched off. With only the Helmer gauge on, the Ti-ball was flashed again to lay down 6 mg of titanium. Figure 2 shows a typical pressure behavior with time from the end of titanium sublimation. The pressures read 5 days after the second Ti flash are listed in Table I. In several cases the final pressures were reached in < 3 days.

It is apparent from Table I that with the exception of a 200° C bake and possibly the oxygen-air bake, all pressures are the same within our measuring tolerances for the surface treatments and the pumps investigated. Longer times (Fig. 2) and additional degassing of gauges produced negligible decreases in the final equilibrium pressures. The temperature of the surface on which titanium is deposited as well as its deposition rate seemed on the other hand to be critical in reaching these low pressures quoted. Raising the surface temperature to $\sim 120^{\circ}$ C almost doubled the lowest equilibrium pressure achieved. Upon cooling a small area of the cross to 77 K, the pressure was reduced slightly

indicating still some CH_4 present in the system.

Unfortunately below 1.5×10^{-11} Torr pressures, the Helmer gauge is often noisy which makes the exact measurements difficult. It is, therefore, not clear whether pressures below 1×10^{-11} Torr were reached in our system.

B. Partial Pressure

Quantitative determination of residual gases in the vacuum system under study was the most difficult task due to the considerable outgassing of the mass spectrometer and the low CH_4 pumping speed of the ion pumps in the 10^{-11} Torr range. Even with repeated degassing and filament conditioning the MS contribution to the residual pressure was several times the amount of the gas load from the wall of the system. The Helmer gauge on the other hand raised the partial pressures of H_2 and CH_4 by 4 and 2 percent respectively. Its contribution to other gases was immeasurable.

Before sublimation the pressure in the system was limited by the H_2 pumping speed of the ion pump S_1. With bake out temperatures $> 250^{\circ}$ C the main components of residual gas for most experimental runs fell within these limits

H_2	85 - 93 percent
CH_4	4 - 8 percent
CO	3 - 8 percent
CO_2	1 - 2 percent

After titanium sublimation sufficient pumping speed was provided for all gases by the titanium film except for CH_4. Noble gases were absent in our system with the exception of He in 2 runs which originated in the ion pump and was eventually almost eliminated.

It can be seen from Table I that the total pressures dropped below 2×10^{-11} Torr after sublimination. However, when the MS was switched on, the pressure (predominantly CH_4) rose initially to 1.5×10^{-10} Torr (Fig. 3)

and was finally lowered after a few weeks of operation and extensive degassing to $< 1 \times 10^{-10}$ Torr. It was suggested by J. P. Hobson that methane might originate in the filament. The filament was subsequently operated overnight (15 hours) at its maximum allowable temperature without affecting the CH_4 content.

The principal factors which limited the achievement of low pressures in our vacuum system are best appreciated from Figs. 3 through 5. It should be pointed out here that total pressures are read on the Helmer gauge and are therefore given in N_2 equivalent. To convert from partial pressure one must use the appropriate gauge sensitivity which is ~ 0.36 for H_2 and 1.5 for CH_4.[10,11] In cases where the total pressure is above 5×10^{-11} Torr, methane predominates and the pressure is limited by systems pumping speed for CH_4. Below 3×10^{-11} Torr the hydrogen pumping speed of titanium films determines the residual pressure. Not readily apparent from the spectra in Figs. 3 and 4 is the 1 amu mass peak (precursor of H_2 peak), associated with and comprising about 10 percent of the methane peak.[12] When methane is eliminated, atomic hydrogen disappears as well (Fig. 5). Better representation of H peak can be obtained by expanding the x-axis but its amplitude remains the same as that of the precursor. Methane partial pressure was lowered in Figs. 4 and 5 by cooling a small area of the cross to 77 K. Mass peaks 12 and 28 in Fig. 5 originate in the ionizer.

C. Methane Pumping Speed

It is obvious from the previous discussion that in titanium sublimation pumped systems, methane constitutes a major obstacle in maintaining the pressure in low 10^{-11} Torr range. Compared with the H_2 pumping speed, which can be increased by simply increasing the area of Ti film, the CH_4 pumping speed will to a large extent determine the price of the ISABELLE pumping station. We have, therefore, investigated two methods of pumping CH_4, namely ion pumps and

methane cracking on hot tungsten filament. In addition the pumping speed of the Helmer and BAG were found to be $\sim 0.06\ell\ s^{-1}$.

The pumping speeds of sputter ion pumps were measured in the following way: The ion pump voltage was switched off to let the pressure increase. Then at some point P_o, the voltage was turned back on, while the output of the Helmer gauge was plotted versus time, t, on a strip chart recorder. From this plot the pumping speed, S, was calculated according to

$$P = P_o\, e^{-(S/V)t},$$

where V is the volume of the vacuum system. The $30\ell\ s^{-1}$ Mag-ion pump has the following pumping speeds, S, at the pressures listed below:

1×10^{-10} Torr $S = 2\ell\ s^{-1}$

8×10^{-10} Torr $S = 1.8\ell\ s^{-1}$

4×10^{-10} Torr $S = 1.3\ell\ s^{-1}$

The range of all three pumps in many measurements at 4×10^{-11} Torr was estimated to be between 0.7 and $1.4\ell\ s^{-1}$. At lower pressures pumping speeds could not be measured by this method, but it seems reasonable to assume that at 1×10^{-11} Torr $S < 1\ell\ s^{-1}$ are to be expected. Taking into account the difficulties inherent in this method of measurement, we concluded that at 4×10^{-11} Torr all three pumps after conditioning had about the same pumping speeds namely $(1.0 \pm 30\%)\ell\ s^{-1}$. Their striking pressures, i.e. the pressures at which the pumping started once the voltage was turned off and back on, varied from 4×10^{-11} to 3×10^{-10}. The pumps exhibited a number of other peculiarities[13] such as extinguishing the discharge in low 10^{-11} Torr range and restarting again at higher pressure, gas liberation (mainly He and CH_4) upon turn off, and excessive dark current. These problems were, however, largely eliminated by bake out and hi-potting.

It was pointed out to me by Dr. W. Lange[14] that methane can be removed by cracking the molecules on hot tungsten filament. Carbon is chemisorbed by

tungsten and hydrogen is pumped by Ti films. A 16 cm long filament, 0.25 mm in diameter, and a view port for pyrometric temperature measurements were incorporated into the apparatus in Fig. 1. Since the filament has to be operated between 2400 - 2500 K for efficient methane pumping,[14] the pressure in the system was always higher with the filament on. This was probably due to wall heating by radiated power, which was $\sim$ 80 W. Even though methane pumping was observed, it was concluded that this method is not suitable for low pressure operation and was therefore abandoned.

IV. Conclusions

Based on the work presented, a few more general conclusions can be drawn:

1. Pressures of $1 - 2 \times 10^{-11}$ Torr can be achieved routinely in a vacuum system pumped by Ti films and a 20 ℓ s^{-1} ion pump.

2. In 10^{-11} Torr range the only residual gases present were H_2, He, and CH_4. Below $1 - 2 \times 10^{-11}$ the pressure was limited primarily by H_2 and more work is being done on Ti - H_2 system at these pressures.

3. Pumping speed of ion pumps drops drastically in 10^{-11} Torr range, probably because only a few Penning cells are operating. Pumps used previously in unclean systems have to be vacuum fired before they are suitable for this operation. Better measurements are badly needed and will be carried out using a cryopump capable of operating in 10^{-12} Torr range.

Acknowledgments

I would like to acknowledge many helpful discussions with Drs. J. P. Hobson and D. Edwards, Jr. I would also like to thank Mr. J. R. Aggus for his help in solving mechanical problems and Mr. Frank Timm for his able assistance throughout the experiments.

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TABLE I Comparison of Total Pressures in Torr N_2 Equivalent for Various Surface Treatments and Pumps.

	Before Ti Sublimation		After Ti Sublimation	
Pump ℓs^{-1}	20	30	20	30
Treatment	Torr	Torr	Torr	Torr
1 + 200°C	9×10^{-10}		3×10^{-11}	
1 + 250°C	6×10^{-10}	5×10^{-10}	1.5×10^{-11}	2×10^{-11}
1 + 300°C	5×10^{-10}	5.5×10^{-10}	1.5×10^{-11}	1.5×10^{-11}
1 + 350°C		5×10^{-10}		$< 1.5 \times 10^{-11}$
2		6.5×10^{-10}		2.5×10^{-11}
3	5.5×10^{-10}		$< 1.5 \times 10^{-11}$	

Figure Captions

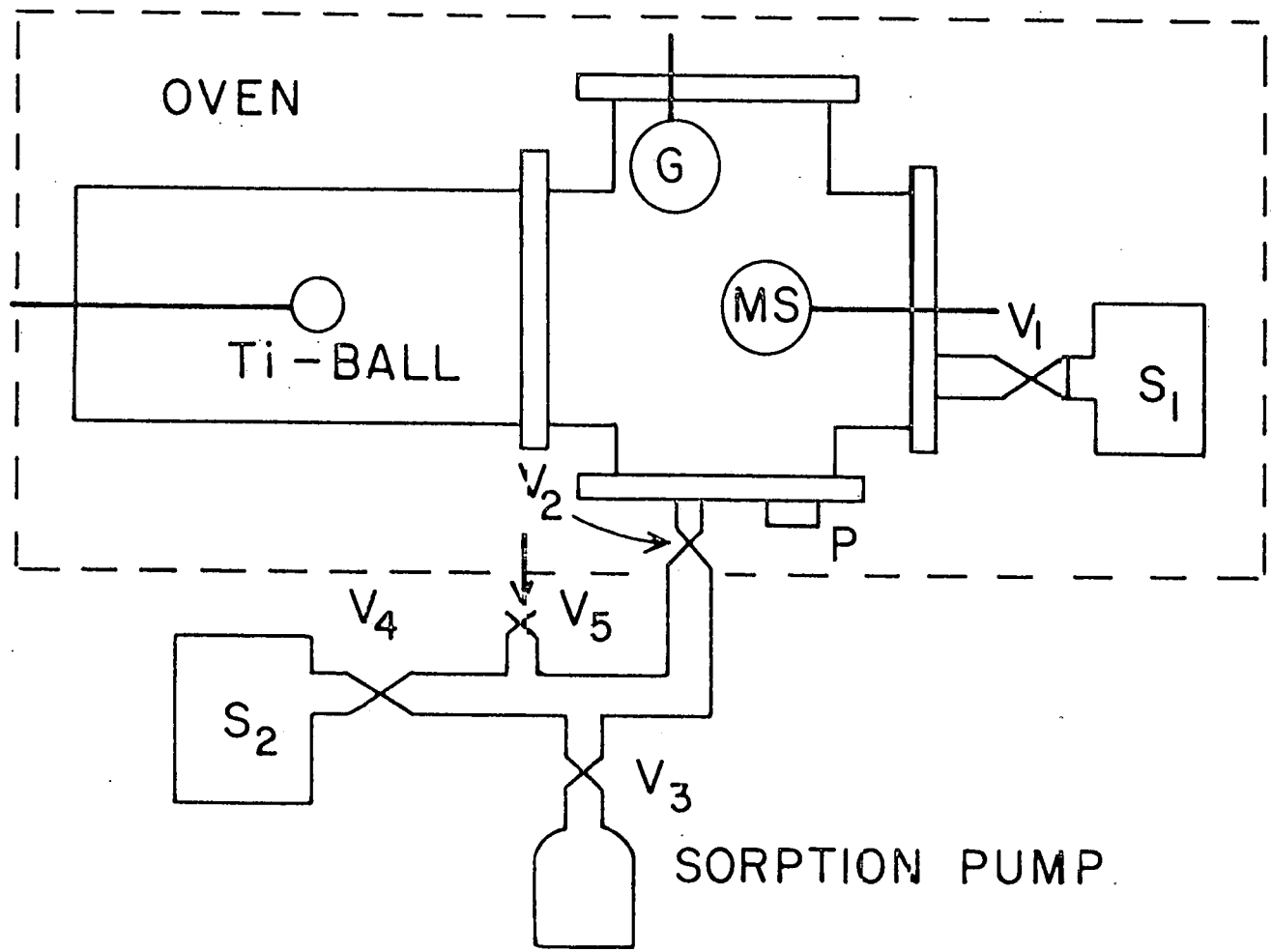
Fig. 1. Schematic diagram of the experimental vacuum system. G: Helmer gauge; MS: UTI Quadrupole mass spectrometer; S_1: Ion pump under test; V_1, V_2, V_3, V_4: Varian 7 cm all metal valves; V_5 variable bleed valve; P: Viewing port; S_2: $100\ell.s^{-1}$ pump. Neg. #7-80-76

Fig. 2. Total pressure versus time plot. Conditions: Second entry in Table I, $20\ell\ s^{-1}$ pump. Neg. #7-81-76

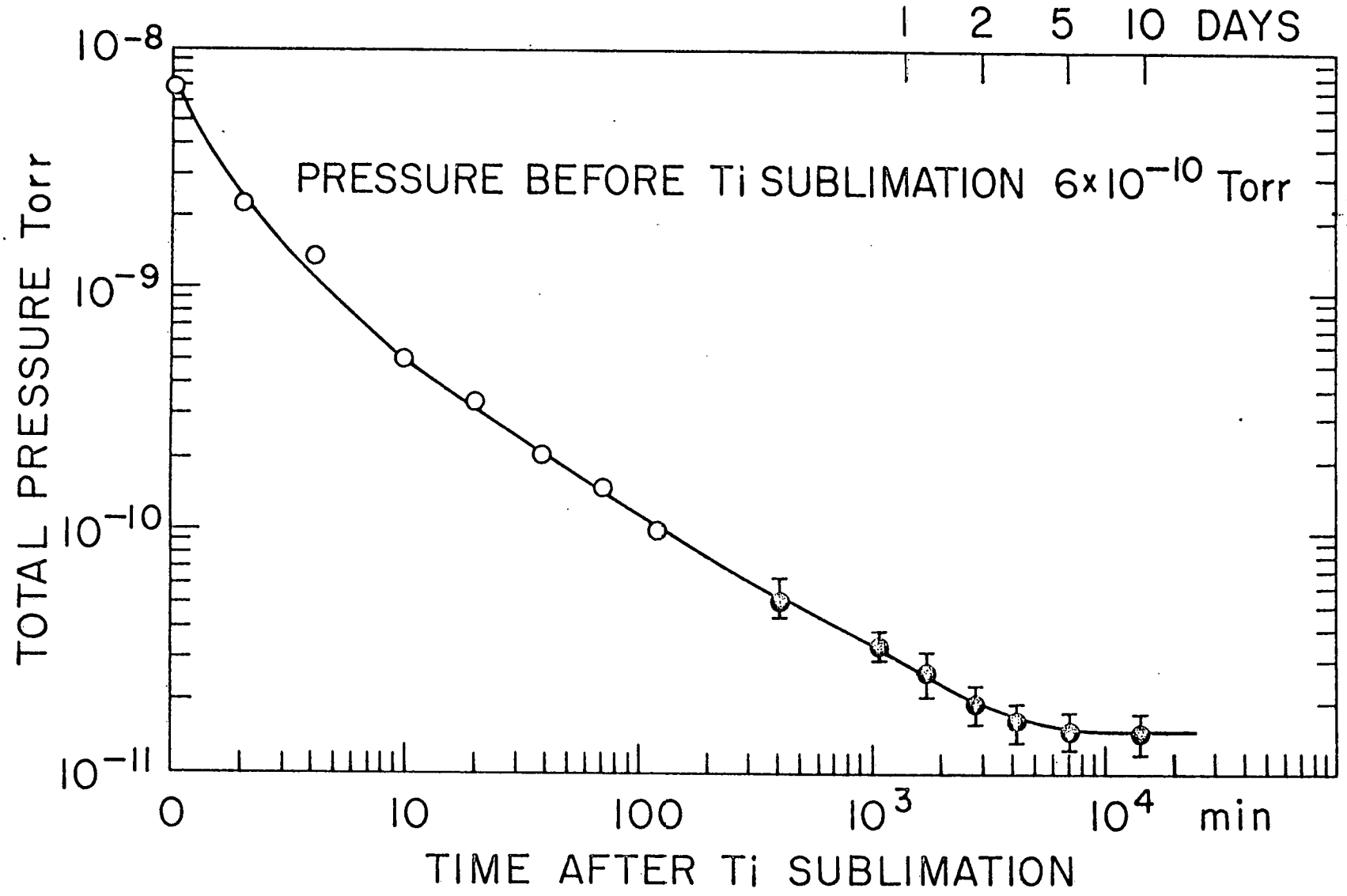
Fig. 3. Mass spectrum for 4th entry in table I. Partial pressures of H_2 and CH_4 are 6.5×10^{-11} Torr and 7×10^{-11} Torr. Total pressure before MS turn on 2.5×10^{-11} Torr. Neg. #7-83-76

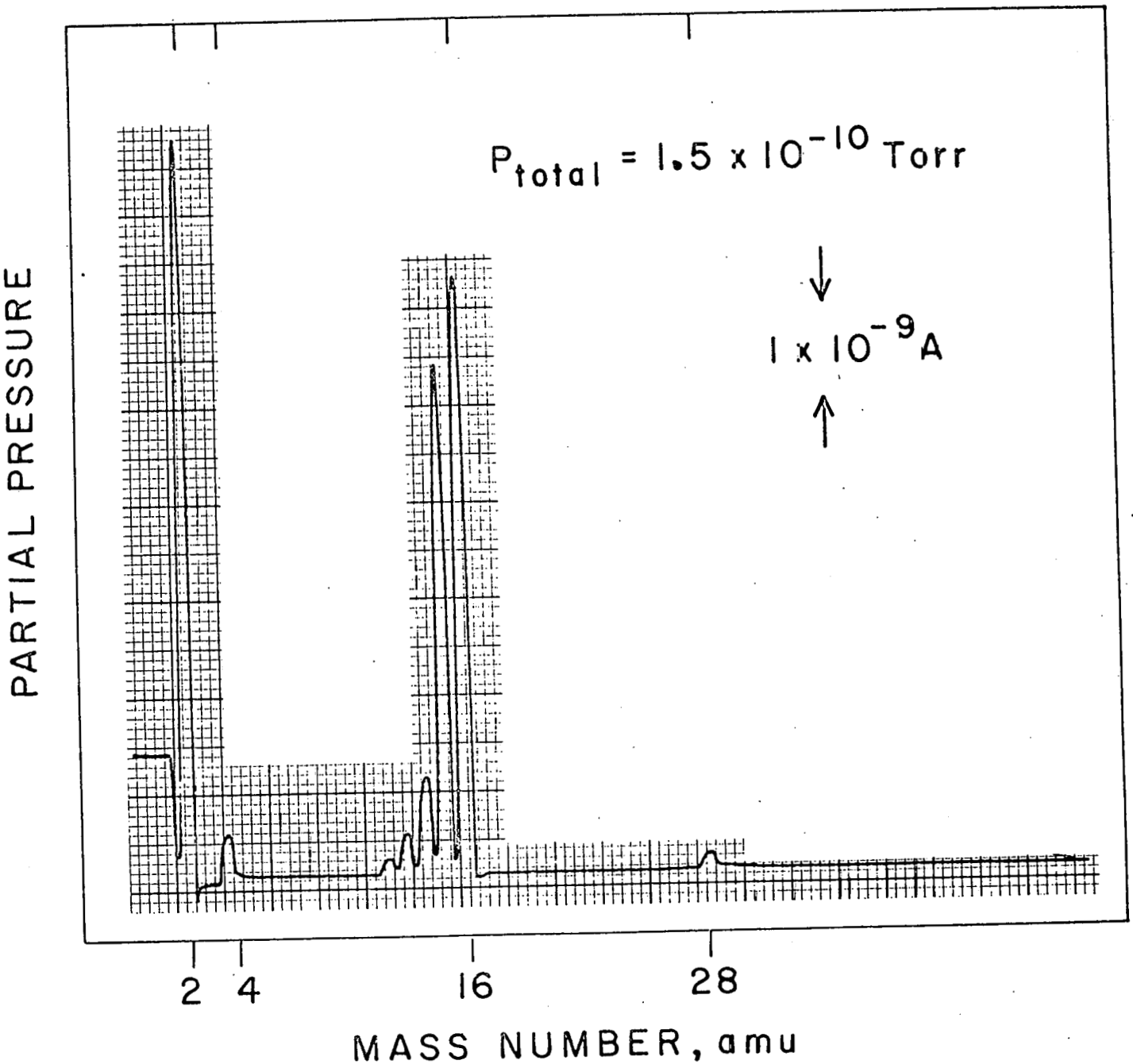
Fig. 4. Mass spectrum for 4th entry in Table I. Partial pressures of H_2 and CH_4 are 4.5×10^{-11} Torr and 1.5×10^{-11} Torr. Total pressure before MS turn on 1.5×10^{-11} Torr. Neg. #7-84-76

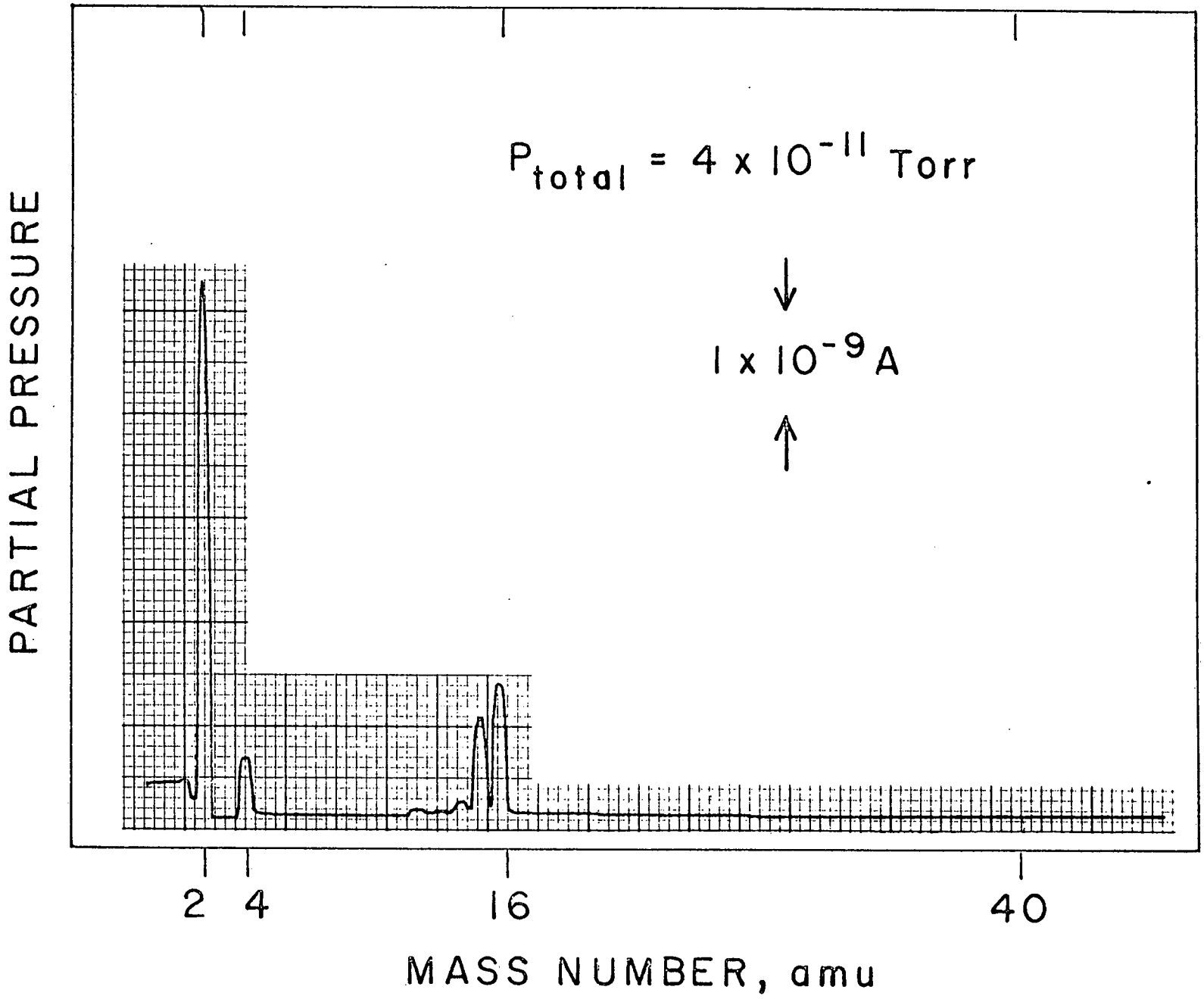
Fig. 5. Mass spectrum for 4th entry in Table I. H_2 partial pressure is 3.3×10^{-11} Torr. Total pressure before MS turn on $< 1.5 \times 10^{-11}$ Torr. Neg. #7-82-76

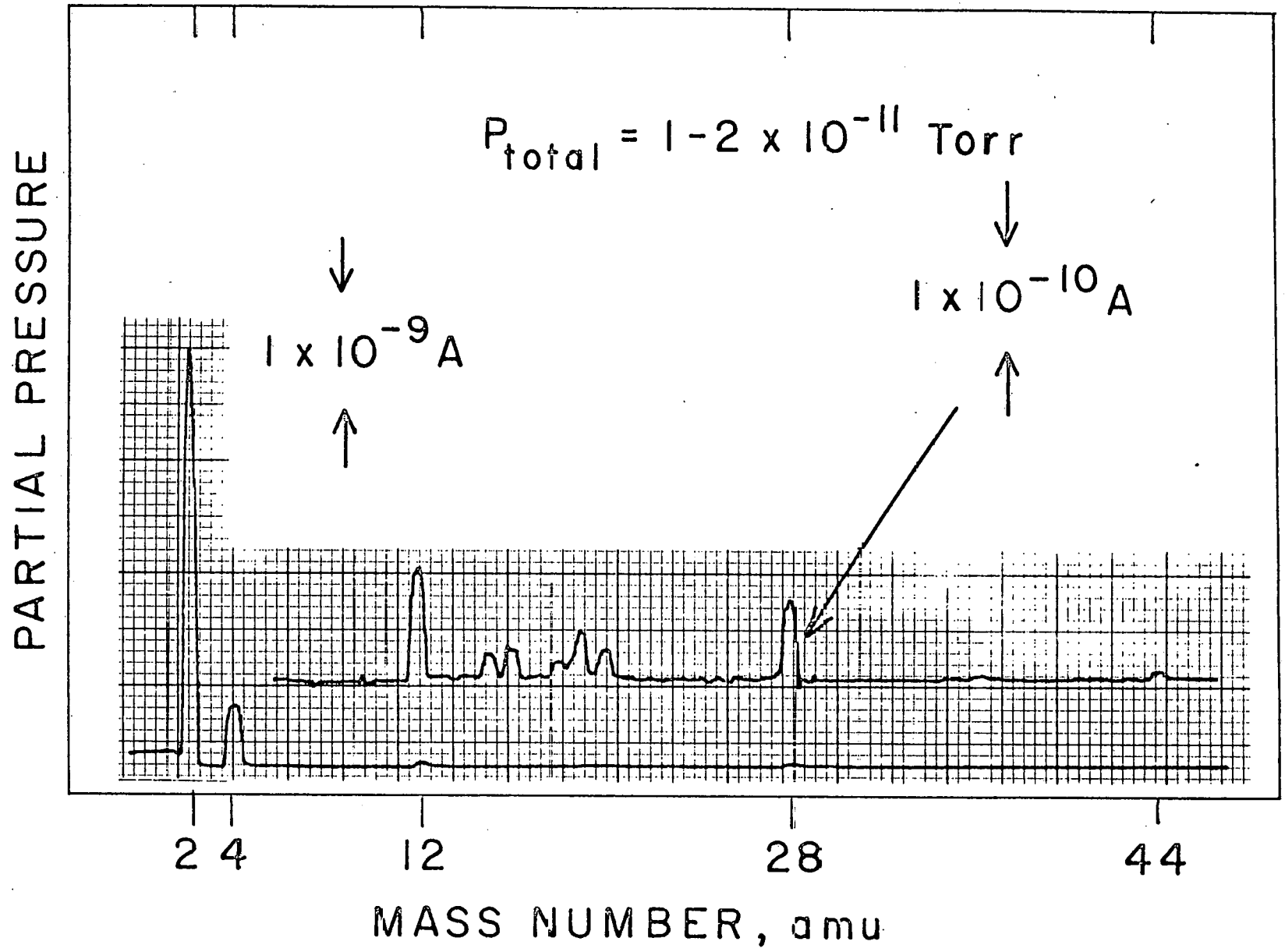


VACUUM SYSTEM


1 2 5 10 DAYS
PRESSURE BEFORE Ti SUBLIMATION 6×10⁻¹⁰ Torr
TOTAL PRESSURE Torr
10⁻⁸
10⁻⁹
10⁻¹⁰
10⁻¹¹
0
10
100
10³
10⁴ min
TIME AFTER Ti SUBLIMATION


$P_{total} = 1.5 \times 10^{-10}$ Torr
1×10^{-9} A
PARTIAL PRESSURE
2
4
16
28
MASS NUMBER, amu


$P_{total} = 4 \times 10^{-11}$ Torr
1×10^{-9} A
PARTIAL PRESSURE
2
4
16
40
MASS NUMBER, amu


P_{total} = 1-2 x 10^{-11} Torr
1 x 10^{-9} A
1 x 10^{-10} A
PARTIAL PRESSURE
2
4
12
28
44
MASS NUMBER, amu