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Analysis of the Residual Gases in Several Types of High-Vacuum Evaporators

Abstract: A mass spectrometer study is made of the residual gases in several types of vacuum evaporators ranging from oil-diffusion-pumped, conventional systems to an oil-free, ultra-high-vacuum chamber. Partial pressures of water vapor, hydrogen, carbon monoxide, carbon dioxide, nitrogen, oxygen, argon and hydrocarbon vapors varied appreciably in the evaporators studied.

The performance of a conventional system was improved by using special low-vapor-pressure gasket materials to minimize hydrocarbon contamination, a liquid-nitrogen trap to reduce water vapor, titanium gettering for oxygen and nickel-iron gettering for hydrogen. For thin-film deposition, the importance of thoroughly outgassing the source materials is pointed out.

The composition and magnitude of the residual gases in a vacuum chamber play an important role in determining the characteristics of an evaporated film. In bulk tantalum, for example, 0.01 at.% nitrogen can readily be detected by a shift in superconducting properties,[1] and similar effects are thought to exist in thin films of other superconducting materials. In magnetic films, Heidenreich predicts that oxygen concentrations as low as 10 ppm may be the source of uniaxial magnetic anisotropy.[2] Three points, therefore, are of interest: first, the role played by specific gases in determining the physical properties of evaporated films; second, the gases present in the evaporation chamber during the deposition; and, third, the concentration of these gases in the evaporated film.

Since the opportunity for a specific gas to react with a film during its deposition is proportional to the partial pressure of that gas in the chamber, films deposited in better vacuum are expected to contain less gas, all other parameters being equal. However, because high vacua require more complex vacuum apparatus and an increased cycle time for producing a film device, it is important to know the merits of different vacuum systems with respect to such important gases as oxygen, nitrogen, hydrogen, and the various hydrocarbons. The objective of this paper is to give such a comparison in order that one may select a suitable evaporator for his application. Mass-spectrometer data on the residual gases in vacuum systems ranging from a conventional bell-jar evaporator with an oil diffusion pump to a liquid-helium-pumped, ultra-high-vacuum evaporator will be presented and compared.

Experimental apparatus

- *Mass spectrometer*

The mass spectrometer employed in this investigation is a small, 180° deflection type instrument with high sensitivity and adequate resolution for analysis of residual gases in vacuum systems. The mass-spectrometer tube is a Diatron 20 manufactured by Consolidated Electrodynamics Corporation and is shown in Fig. 1 together with its deflection magnet. The tube is mounted directly on the vacuum system under study with gold or teflon O-ring seals. One tube has been modified for bakeout by replacing teflon gaskets with gold O-rings and soft soldered electrical inputs with kovar-to-glass feedthroughs. An Applied Physics Model 31 vibrating-reed electrometer is used as the ion detector. The sensitivity for nitrogen is $(3.8\pm0.2)\times10^{-6}$ amp/mm Hg with an ionization current of 91 microamps. A partial pressure of 2×10^{-10} mm Hg of nitrogen is detectable. The Diatron 20 is capable of resolving adjacent mass peaks of equal amplitude up to mass number 35. However, hydrocarbon peaks to mass number 240 may be observed.

A mass spectrometer provides a great deal more information than an integrating pressure measuring device such as an ionization gauge. Whereas an ionization gauge

collects ions of all gas species, the Diatron 20 measures only ions of mass-to-charge ratio m/q satisfying the equation $m/q=2R^2B^2V^{-1}$, where V is the potential difference through which the ions are accelerated and R is the radius of the ion path in the magnetic field B. By varying V, ions of different m/q may be collected.

A mass spectrometer, of course, does not give a direct analysis of the partial pressures of the residual gases in the chamber. The following problems are encountered when an attempt is made to convert mass spectrometer peak amplitudes to partial pressures:

(1) Several gas species may form ions of the same mass-to-charge ratio so that it is not immediately obvious which gas is responsible for a specific peak. For example, mass number 28 could result from nitrogen, carbon monoxide, or ethylene. However, it is possible to determine the composition of a multiple-gas peak on the basis of the amplitudes of other key peaks. With nitrogen, the mass 14 peak due to N_2^{++} and N^+ is 5.8 percent, as is shown in Table 1. Carbon monoxide, on the other hand, has smaller 12, 14 and 16 peaks associated with it, while ethylene has an appreciable 27 peak. In general, if the j^{th} gas has an amplitude a_{ij} at the i^{th} mass to charge peak, the total amplitude of the i^{th} peak A_i is $A_i=\sum_j a_{ij}$. However, $a_{ij}=K_{ij}a_{jj}$, where the K_{ij} are constants dependent on the operating conditions of the mass spectrometer. The values for the K_{ij} used to date are those reported by the manufacturer of the Diatron 20 (with the exception of values for nitrogen and argon, which were measured directly).[3] Substitution yields $A_i=\sum_j K_{ij}a_{jj}$, and a set of simultaneous equations that are solvable for a_{jj}. The accuracy of the solution depends on the complexity of the spectrum but is estimated to be within a factor of two for the work reported in this paper.

In some instances a secondary peak provides a better measure of the concentration of a gas than the principal peak. For example, methane is often masked by a contribution from water vapor. However, the mass 15 peak due to CH_3^+ is 85% as large as the CH_4^+ peak and a good measure of the methane partial pressure.[3] Similarly, argon at mass 40, a mass where the spectrometer resolution is reduced, is often hidden by a large, broad C_3H_6 peak. In this case, the argon peak amplitude may be estimated by multiplying the 20-peak amplitude by a factor of four, as shown in Table 1. These points should be kept in mind while interpreting the data presented in Tables 1 to 3.

Table 1 **Mass spectrum for reagent grade nitrogen bled into a Vac Ion, ultra-high-vacuum system.**

Mass-to-charge ratio	*Element*	*Peak amplitude*
4	He^+	5.5×10
14	$N_2^{++}N^+$	3.5×10^3
20	A^{++}	3.8×10^2
28	N_2^+	6.0×10^4
40	A^+	1.5×10^3
Ratio $N_2^{++}+N^+$ to N_2^+		5.8%
Ratio A^{++} to A^+		25%
N_2 sensitivity for 91 μamp ionizing current		3.8×10^{-6} amp/mm of Hg
Gauge pressure (corrected for N_2[17])		1.6×10^{-5} mm of Hg

Amplitude unit $=10^{-15}$ amp

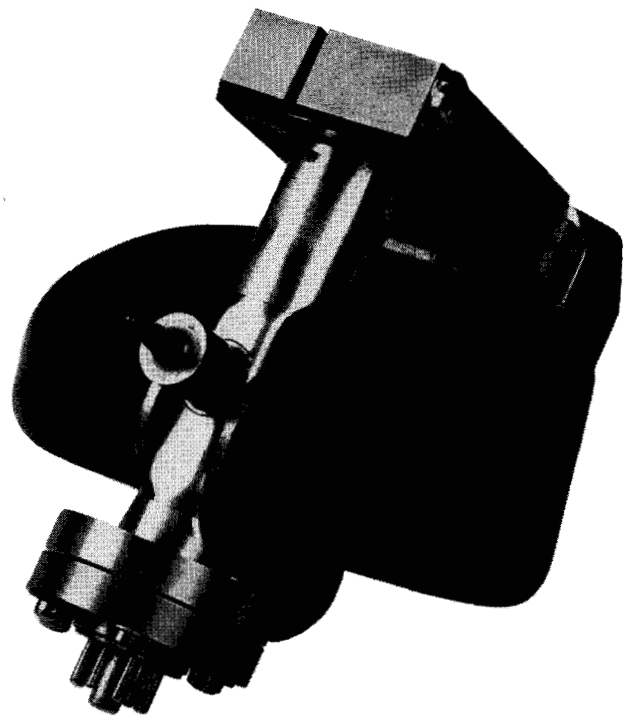


Figure 1 **Diatron 20 mass spectrometer tube.** *Approximately one-half actual size.*

(2) The conversion of peak amplitudes to partial pressures is subject to error. The positive ion current for a gas, a_i, is given by $a_i=\Gamma_i L I_e Q_i N_i$, where Γ_i is the percentage of ions collected which are formed by the electron beam I_e, N_i is the concentration of gas molecules in the ionization chamber, Q_i is the ionization cross section, and L is the length of the electron beam parallel to the mass spectrometer slit system. Assuming Γ_i not to be a function of mass number, and substituting for N_i in terms of the partial pressure P_i results in

$$a_i=KI_eQ_iP_i$$

and

$$K=9.66\times10^{18}T^{-1}\Gamma L,$$

where T is the absolute temperature. Table A lists the values for Q_i of various gases for slow electrons as reported in the literature.[4,5] The constant K may be evaluated from the data in Table 1, giving $a_i=(1.6\times10^{14})I_eQ_iP_i$.

The experimental value for K indicates that only 4 percent of the N_2^+ are being collected, the others not

Table A **Ionization cross sections.**

Gas	*Cross section*	*Gas*	*Cross section*
H_2	0.80×10^{-16} cm^2	C_2H_4	6.9×10^{-16} cm^2
He	0.24	C_2H_6	7.7
A	3.0	C_3H_6	5.4
N_2	2.6	C_3H_8	6.2
O_2	2.3	C_4H_8	7.3
H_2O	1.9	C_4H_{10}	8.0
CO	2.7	C_5H_{10}	8.8
CO_2	3.4	C_5H_{12}	9.9
CH_4	4.8		

being suitably oriented with respect to the slit system. The last equation for a_i is estimated to be accurate within a factor of four.

Because of the large errors in converting from mass peak amplitudes to partial pressures, the majority of the data is presented in terms of peak amplitudes which afford a direct comparison of the relative partial pressures in the different systems. An exception is Table 4, where partial pressures are presented. The values are estimated to be accurate within a factor of five.

(3) Reactions occurring at the hot filament used as an electron source may distort the analysis one obtains with a mass spectrometer.[6-9] For example, oxygen reacts with carbon on the surface of the filament to produce appreciable quantities of CO and CO_2. The relative amplitudes depend on the surface area, temperature, and previous history of the filament. In some cases the CO peak may be larger than the O_2 peak. Since the vacuum conductance from the filament to the evaporation chamber is limited, one may measure a lower oxygen concentration than actually exists in the evaporation chamber proper. Similarly, heavier oil molecules "crack" on the hot filament and the hydrocarbons of the lower mass number may be more concentrated in the immediate vicinity of the mass spectrometer.

In summary, a mass spectrometer is a very powerful tool with which to study vacuum chambers and reactions occurring within them. For many applications where an order of magnitude determination of partial pressures or relative partial pressures will suffice, the limitations of a mass spectrometer become relatively unimportant.

• *Conventional vacuum system*

In this study we will define a "conventional evaporator" as a large bell jar system employing an oil diffusion pump, liquid-nitrogen baffle, and organic vacuum seals. Such systems are readily available from most equipment manufacturers. The liquid-nitrogen trap is a simple thimble design which requires a minimum of one collision with a cold surface in order for an oil molecule to pass the trap. Contrary to good design, a room temperature path along which oil may "creep" to the evaporation chamber does exist.[10] The liquid-nitrogen trap in the roughing line serves to minimize diffusion of forepump oil into the bell jar chamber during roughing operations and also to maintain the forepressure of the diffusion pump at approximately one micron. The high-vacuum portion of the system is constructed of welded, stainless-steel sections.

Pressures of 5×10^{-6} to 2×10^{-5} mm of Hg are typical operating values for these evaporators. Readings are usually made on an ionization gauge located in the pumping line. Since evaporators are dynamic systems, these readings may differ by a factor of ten from readings obtained on an ionization gauge located in the bell jar. The mass spectrometer located in the base plate is in a favorable position for analysis of residual gases in the bell jar.

Measurements were made on two conventional evaporators: one equipped to fabricate multilayer cryogenic devices of tin, lead, and SiO, and the second to evaporate magnetic films. These will be referred to as Evaporators A and B, respectively. These systems are operated on a day-to-day basis in accord with accepted vacuum procedures.

• *Modifications of conventional systems*

Evaporator B has been equipped with a radiant tungsten heater for baking the substrates prior to deposition and holding them at elevated temperature during evaporation. Two graphite rods that radiate up to one kilowatt of power are employed to give the vacuum chamber a mild bake. A liquid nitrogen trap in the bell jar, or a Meissner trap, has been constructed from 36′ of ⅜″ copper tubing through which liquid nitrogen is circulated continuously.[11] This amount of tubing provides 3×10^4 cm^2 of cold surface. Titanium may also be evaporated in the top of the bell jar from a tungsten wire around which has been wrapped a titanium wire. An approximate surface area of 2×10^4 cm^2 is coated nonuniformly at an evaporation rate of several milligrams per second. The titanium evaporation is shielded from the Ni-Fe evaporation, enabling both to be performed simultaneously. A photograph of this chamber is shown in Fig. 2.

With these modifications the evaporator is able to obtain pressures in the range of 10^{-7} mm of Hg, as read on the ionization gauge. This is at the expense of one hour spent baking, 30 minutes cooling the Meissner trap, and 15 minutes in bringing the titanium getter to temperature.

• *Special high-vacuum evaporator*

This evaporator was designed to minimize contamination from oil and its decomposition products and is shown diagrammatically in Fig. 3. A mechanical forepump, trapped with liquid nitrogen, is employed to initially evacuate the system to a pressure of 10 microns at which point the 280 liters/second, Varian Associates "Vac Ion Pump" may be started. The forepump is then isolated from the chamber, eliminating this source of oil. Gold O-ring seals are used for all demountable joints with the exception of the bell jar and valve gaskets which are made from Viton, an elastomer having a low vapor pressure. There is also a substrate heating and cooling device

Figure 2 **Modification of a conventional evaporator.**

(A) titanium shield; (B) titanium getter; (C) substrate heater; (D) Ni-Fe on W wire; (E) graphite heater; (F) Meissner trap.

which for this investigation was used as a Meissner trap, presenting a cold surface of 2×10^3 cm^2.

The base pressure of this evaporator is in the low 10^{-7} mm of Hg range. The improvement in vacuum has been at the expense of roughly doubling the time required to obtain operating pressures.

- *Ultra-high-vacuum evaporator*

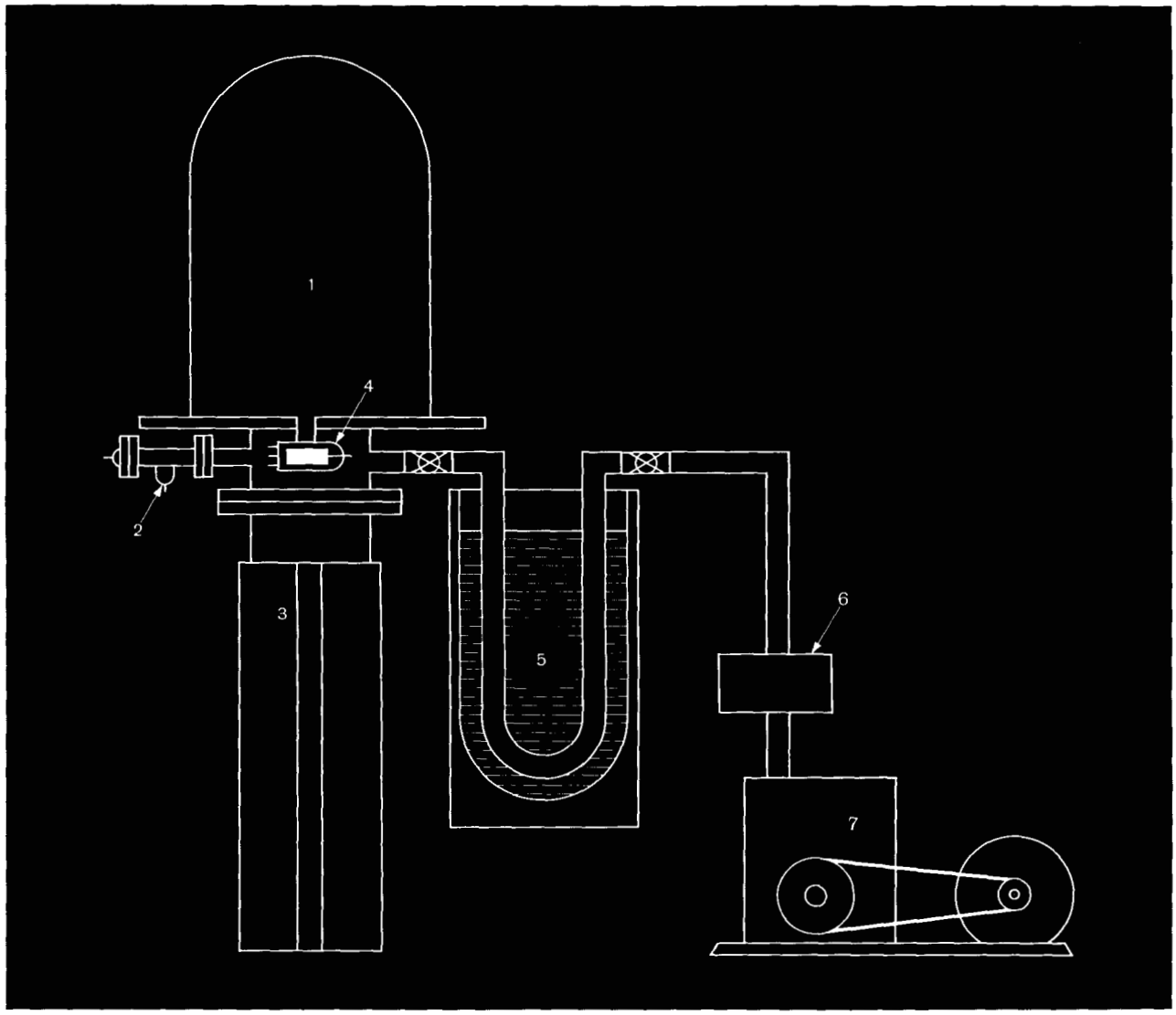
This small two-liter evaporator, which has been described previously, is shown diagrammatically in Fig. 4.[12] No oil or mercury pumps are utilized, but a combination of a water aspirator, liquid-helium traps, and Vac Ion pump serve to reduce the pressure initially to the low 10^{-10} mm range and to maintain pressures below 10^{-9} during evaporations.

To obtain these pressures, the system must be baked at 430°C for several hours. This baking temperature introduced numerous problems in the design of mask and substrate handling equipment required for the fabrication of multilayer devices. Materials anneal at these temperatures, making it difficult to hold tolerances on components. Baking removes any oil or air film on surfaces, resulting in extreme galling between sliding parts. Restrictions on motion in the chamber are introduced by the limitations of bakeable mechanical inputs such as bellows and magnetic drives. The construction of a large ultra-high-vacuum evaporator for complex device fabrication will be a formidable problem.

One also sacrifices time to obtain this improved vacuum. Roughly three days are required to evaporate a

Figure 3 **Special high-vacuum evaporator.**

(1) bell jar 12″ diameter, 18″ high; (2) mass spectrometer tube; (3) 280-liter/second Vac Ion pump; (4) ionization gauge; (5) liquid nitrogen trap; (6)P_2O_5 trap; (7) mechanical forepump.



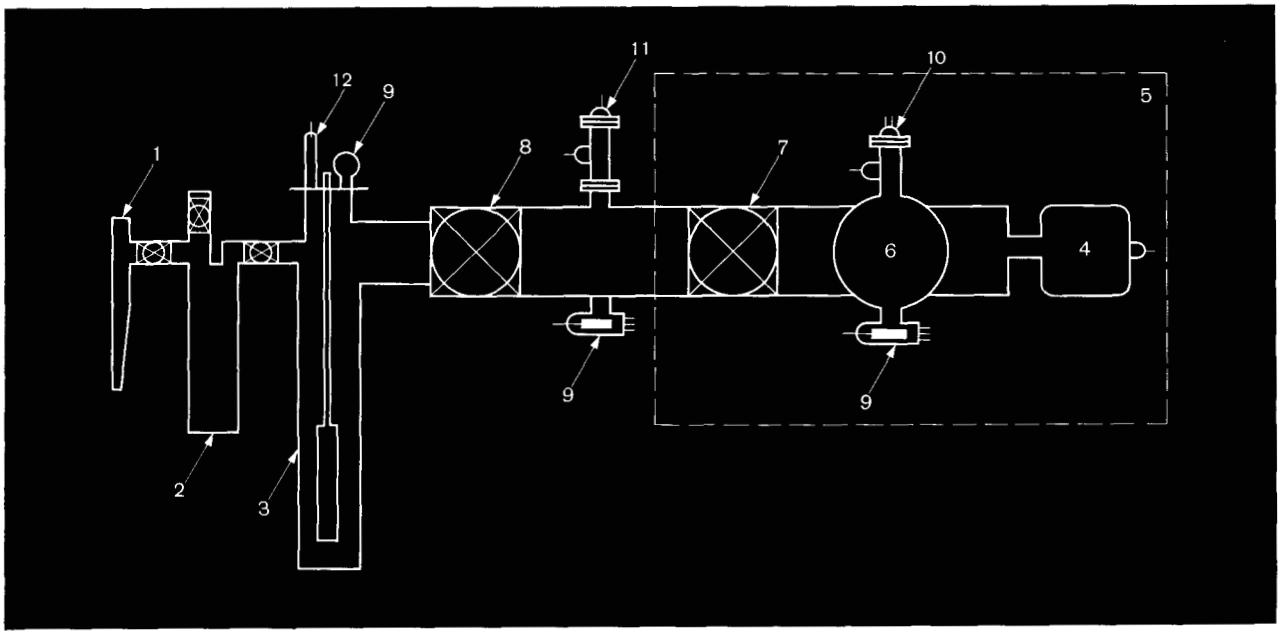


Figure 4 **Ultra-high-vacuum system.**

(1) water aspirator; (2) liquid nitrogen trap; (3) liquid helium trap; (4) 5-liter/second Vac Ion pump; (5) oven; (6) evaporation chamber; (7) 1" bakeable valve; (8) 2" ball valve; (9) ionization gauges; (10) bakeable mass spectrometer tube; (11) mass spectrometer tube; (12) Pirani gauge.

single-layer device which in a conventional system would require only three hours.

Experimental results

- *Conventional evaporators*

A typical spectrum, as it was recorded, is shown in Fig. 5. Since ten minutes are required to record the amplitude of all the masses in this manner, this method was limited to fairly long-term equilibrium conditions. For rapidly changing conditions such as exist during an evaporation, specific mass peaks were observed continuously or at frequent intervals. To facilitate comparisons, the data have been converted from graphical to tabular form.

Fig. 6 indicates the change in composition which occurs during five hours of continuous pumping on Evaporator A. The entire pressure change indicated by the ionization gauge results from a decrease in the water vapor peak. The various hydrocarbon peaks decrease slightly, but the concentration of hydrogen, oxygen, and nitrogen remains almost constant.

The residual gases in a conventional evaporator vary appreciably from day to day, as is shown in Table 2. The following characteristics were common to Evaporators A and B:

1) The major constituent is water vapor. The amount varies from day to day by as much as a factor of ten, depending on humidity, the length of time the system remains at atmospheric pressure, and the length of time the system has been under vacuum. To minimize contamination from water vapor, it is important to let the system down to atmospheric pressure with a dry gas such as nitrogen.

2) On a static system, the partial pressure of hydrogen was fairly constant at an estimated value of 5×10^{-7} mm of Hg.

3) The composition of the 28 peak, which is the summation of CO and N_2, is predominantly nitrogen.

4) The concentration of hydrocarbons varies appreciably as a function of time. This is anticipated since the back diffusion of pump oil and its decomposition products depends on heater power, liquid level in the nitrogen trap, length of time the oil has been used, and numerous other factors. Inadvertent handling of chamber components is another variable source of hydrocarbons.

The two evaporators differed in the amounts of nitrogen and oxygen they contained; Evaporator B was lower by a factor of seven. Although this is indicative of a leak in Evaporator A, none was found, and the difference is thought to be characteristic of the operating procedures followed in the two cases. Although both are operated on a daily cycle basis, Evaporator B is outgassed more thoroughly by the mild bake previously described.

An interesting effect was observed during rotation of a mechanical input whose shaft was sealed with a Buna-N O-ring. A blip occurred on the hydrogen background each time the shaft was rotated. The hydrogen probably results from hydrocarbons released by the O-ring being cracked on the mass spectrometer filament. This is supported by the presence of smaller blips on the mass 28

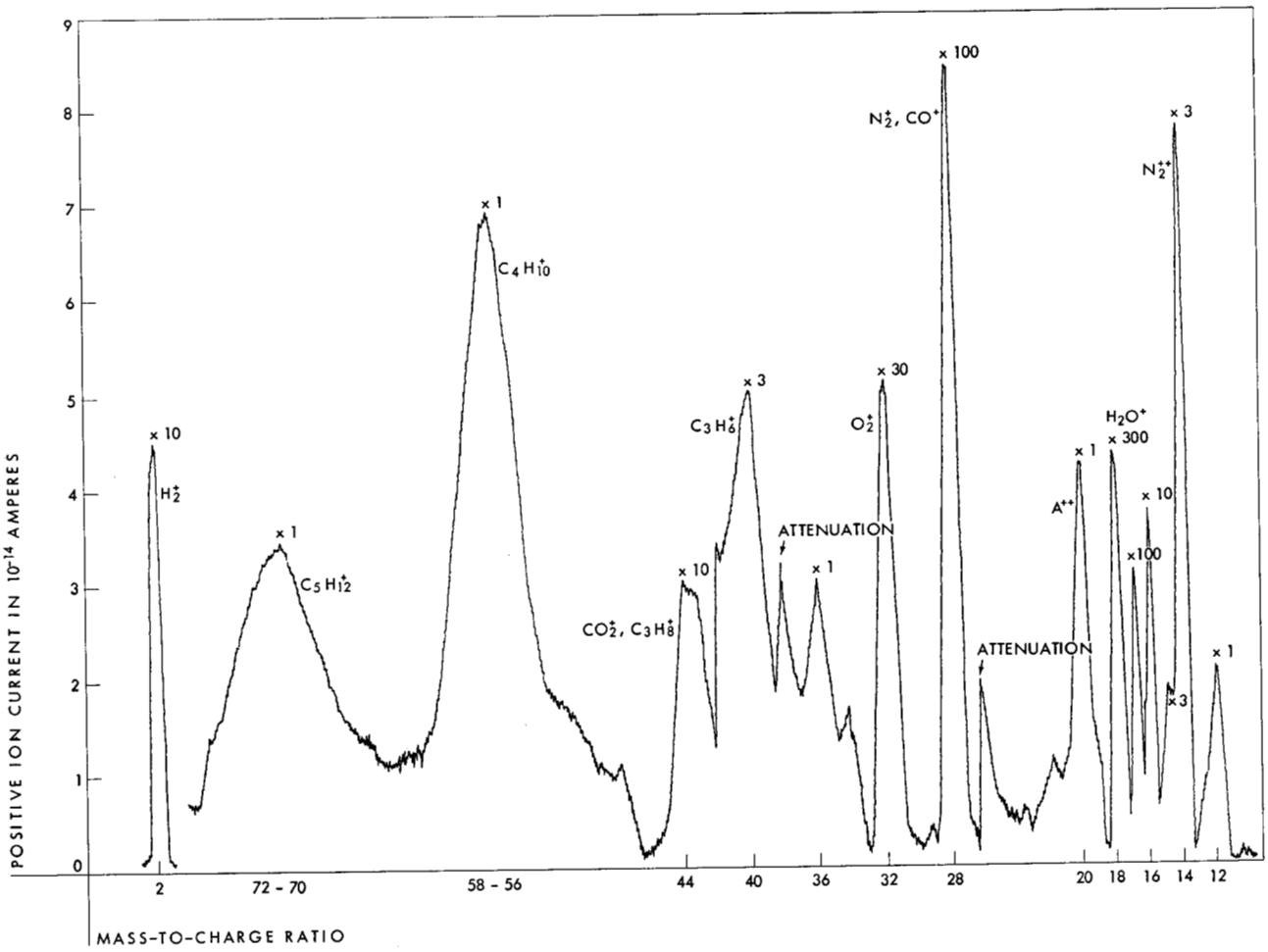


Figure 5 **Typical mass spectrometer spectrum of a conventional evaporator.**

Table 2 **Day-by-day operation of evaporator A.**

		1st Day	*4th Day*	*5th Day*	*6th Day*	*11th Day*
	Gauge pressure	8.0×10^{-6}	8.3×10^{-6}	1.0×10^{-5}	1.6×10^{-5}	8.5×10^{-6}
Mass-to-charge ratio	*Element*					
2	H_2^+	3.6×10^{2}	4.5×10^{2}	4.6×10^{2}	5.4×10^{2}	3.0×10^{2}
12	C^+	2.9×10	2.0×10	1.1×10	2.4×10	0.4×10
14	N_2^{++}, CH_2^+	1.8×10^{2}	2.4×10^{2}	1.8×10^{2}	4.7×10^{2}	4.8×10^{2}
15	CH_3^+	4.8×10	5.7×10	2.0×10	2.3×10^{2}	1.8×10
16	O^+, CH_4^+	4.8×10^{2}	3.6×10^{2}	1.8×10^{2}	7.8×10^{2}	1.9×10^{2}
17	OH^+	3.0×10^{3}	3.2×10^{3}	1.6×10^{3}	1.05×10^{4}	1.6×10^{3}
18	H_2O^+	1.11×10^{4}	1.30×10^{4}	7.4×10^{3}	4.5×10^{4}	6.7×10^{3}
20	A^{++}	2.6×10	3.2×10	2.0×10	1.32×10^{2}	3.3×10
28	N_2^+, CO^+	6.9×10^{3}	8.4×10^{3}	5.3×10^{3}	8.5×10^{3}	8.6×10^{3}
32	O_2^+	1.05×10^{3}	1.53×10^{3}	8.9×10^{2}	1.74×10^{3}	1.40×10^{3}
41-42	$C_3H_6^+$	1.7×10^{2}	—	—	1.2×10^{2}	1.3×10^{2}
43-44	$CO_2^+, C_3H_8^+$	5.5×10^{2}	3.0×10^{2}	4×10	2.5×10^{2}	5×10
56-58	$C_4H_{10}^+$	1.02×10^{2}	6.9×10	1.8×10	1.5×10	3.5×10
70-72	$C_5H_{12}^+$	5.0×10	3.4×10	0.6×10	0.8×10	1.7×10

Amplitude unit $=10^{-15}$ amp

and 44 peak backgrounds. Evidently a fresh portion of the O-ring is exposed to the vacuum chamber upon rotating the shaft. The effect is less noticeable after the shaft has been turned several revolutions.

In Fig. 7, the changes which occur in the residual gas spectrum during a tin evaporation from a tantalum source are shown. The inadequacies of an ionization gauge are clearly exemplified here. The oxygen concentration drops by a factor of two, although the ionization gauge reading increases. Evidently the oxygen reacts with carbon on the surface of the hot tantalum source to produce carbon monoxide and dioxide, as indicated by increases in these peaks. There is no evidence that the tin film is gettering the oxygen, since an empty source is just as effective at producing the same effect. The tantalum is also responsible for the tremendous increase in the hydrogen content during the evaporation. The initial peaked behaviour of the hydrogen outgassing is caused by raising the source to temperature in steps rather than continuously. A slight increase in the water vapor content is noted as the radiant energy from the source heats up adjacent areas. The hot source also offers heavier oil molecules a means of decomposing into lighter fractions so that an increase in the lighter hydrocarbons results in the manner illustrated by the curve for butane.

Interesting effects with hydrogen are observed during the evaporation of nickel-iron films from a tungsten wire wrapped with a 76%-24% nickel-iron wire. As shown in Figs. 8 and 9, raising the source to temperature releases large quantities of hydrogen. The nickel-iron film clearly getters the hydrogen, as is seen by the sharp drop in hydrogen content upon evaporation, the levelling off when the source temperature was reduced just below the evaporation point, as shown in Fig. 8, and a further decrease when a film was again evaporated. Outgassing data on nickel-iron films indicate these films do contain large quantities of hydrogen.[13] The source of hydrogen proved to be the tungsten wire, which had not been degassed, rather than the vacuum-melted nickel-iron wire.

These results emphasize the importance of using thoroughly outgassed source materials. Since stock refractory metals contain tremendous quantities of gas, vacuum-melted or degassed materials must be used. In either case a source should be thoroughly outgassed at a tem-

Figure 6 **The effects of extended pumping on a conventional evaporator.**

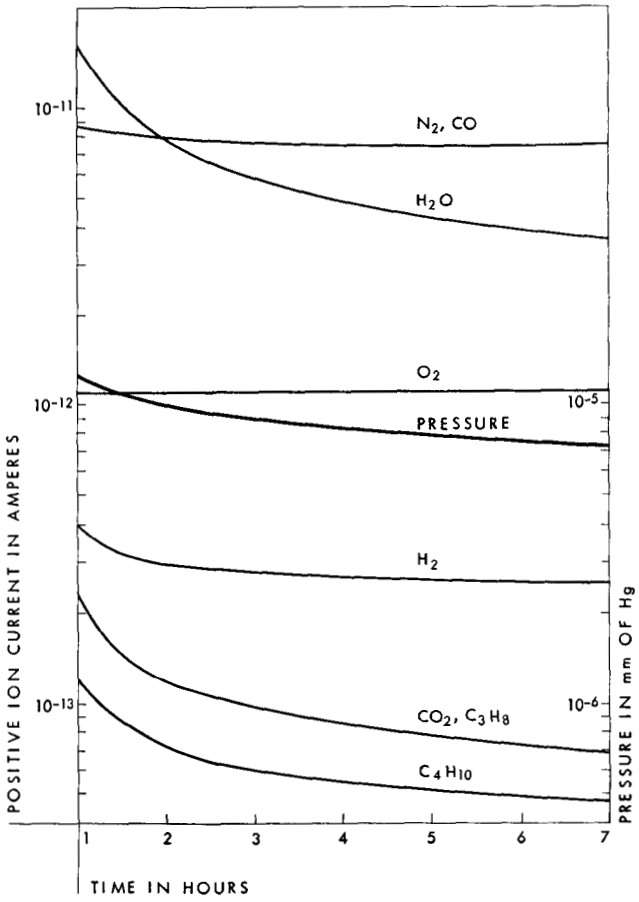
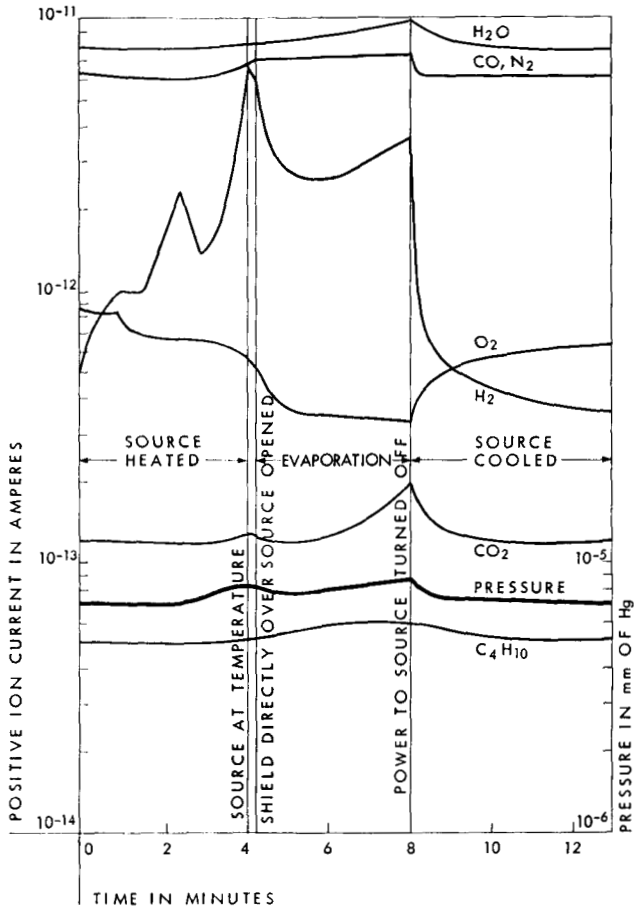


Figure 7 **The residual gases during a tin evaporation.**

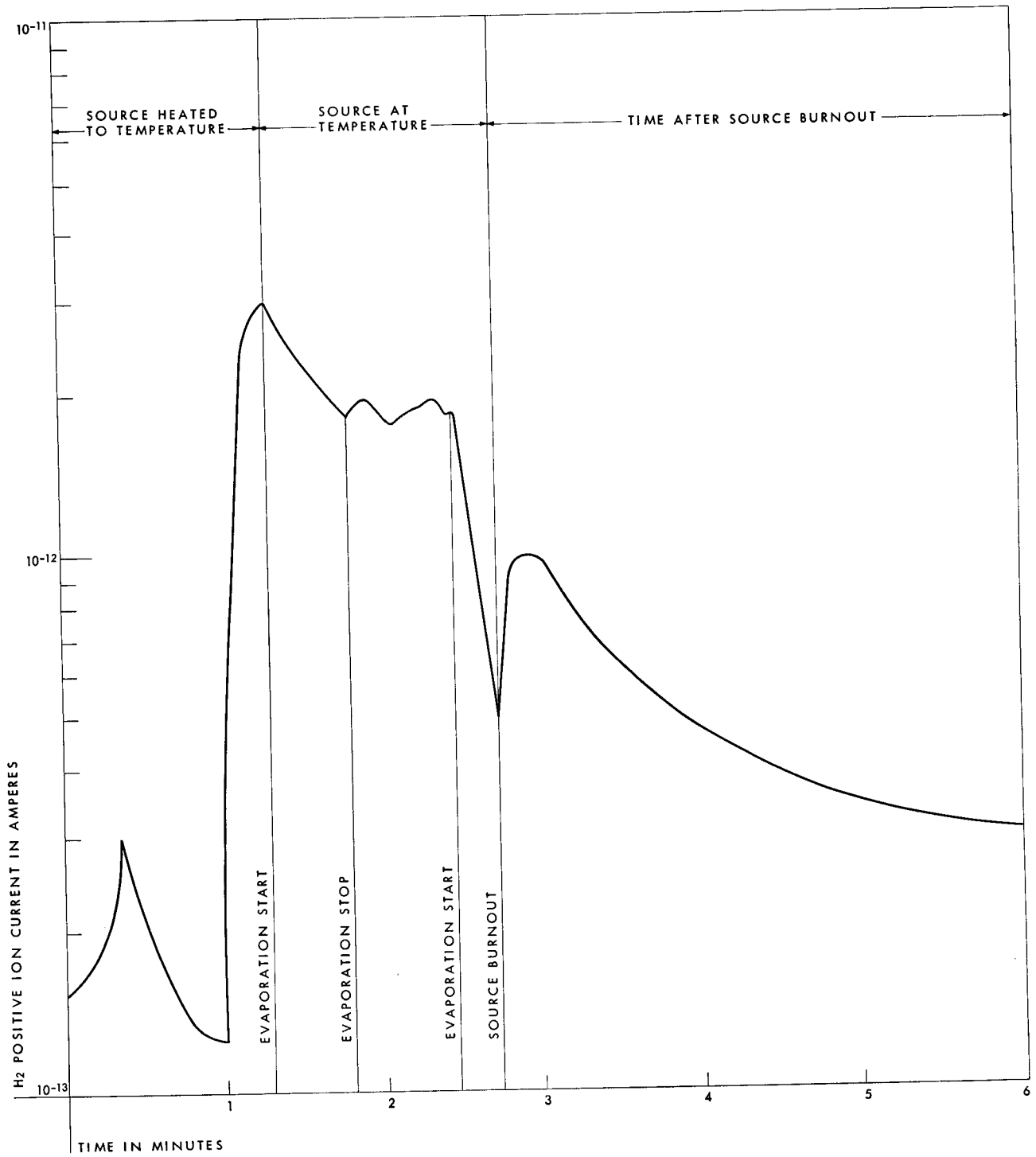


perature well above its normal operating point prior to its use in evaporating films. Although this is accepted vacuum practice, it is relatively easy to become lax in this regard when an ionization gauge indicates no further significant outgassing. However, a mass spectrometer will usually show this is not the case since its results are not masked by a dominant water vapor concentration.

• *Modifications of conventional systems*

The residual gases in a conventional evaporator may be altered significantly by some rather simple methods. A sequence of operations was performed in Evaporator B and their effect on the residual gases is illustrated in Table 3. The low-temperature bake, indicated in Column II, was made at temperatures ranging from 370°C on

Figure 8 **The variation in the hydrogen partial pressure during a Ni-Fe evaporation.**

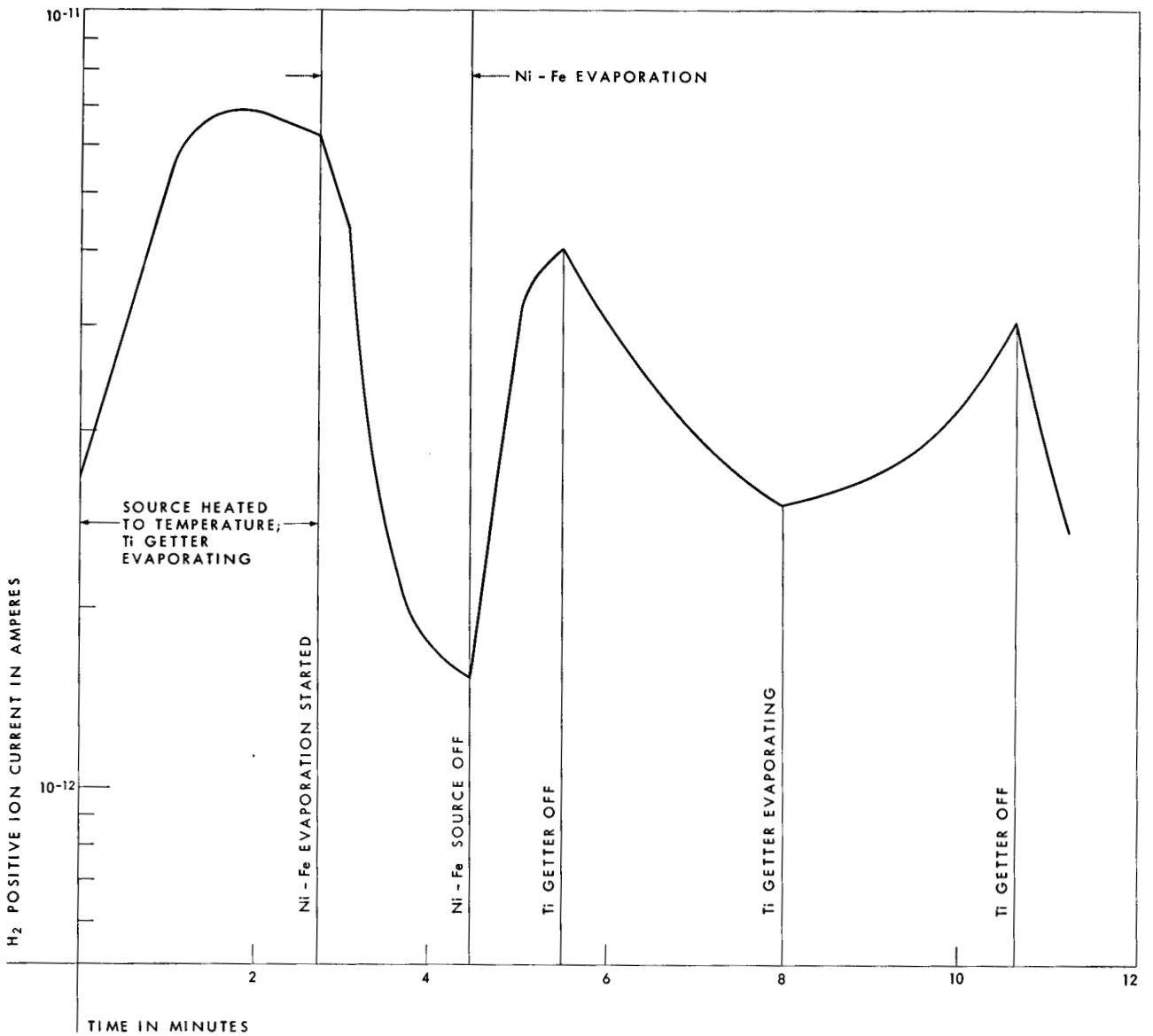


the substrate holder to 50°C on the bell jar wall. The hot filaments of tungsten and carbon offer additional pumping speed for oxygen and a decrease in the 32 peak by a factor of five was observed after a two hour bake. They also afford heavier oil molecules a method of decomposing into lighter fractions, and an increase in the lighter hydrocarbons was noted. The water-vapor peak decreases by a factor of two, but a decrease of this magnitude would have been expected solely by pumping on the chamber for this period of time. An increase in hydrogen was observed due to outgassing of the tungsten heaters.

The effect of modifying Evaporator B with a Meissner trap is shown in Column III of Table 3. A Meissner trap has a very high pumping speed for water vapor whose vapor pressure at 80°K is less than 10^{-22} mm of Hg. For example, the trap used in this experiment has a calculated speed of 5×10^4 liters/sec assuming a sticking probability of unity on the cold surface. A decrease by a factor of twelve in the partial pressure of water vapor was recorded by the mass spectrometer mounted on the bell jar base plate.

Carbon dioxide, which has a vapor pressure of 10^{-7} mm of Hg at 80°K is another gas which is effectively pumped by the Meissner trap. The hydrocarbons are also trapped to some degree; especially the heavier ones, since their vapor pressure decreases with increasing molecular weight. Decreases in the concentrations of nitrogen, car-

Figure 9 **The effect of a titanium getter on the hydrogen partial pressure during a Ni-Fe evaporation.**



bon monoxide, and hydrogen which occur are probably due to physical absorption on the cold surface, since vapor pressure data would not predict appreciable condensation of these gases on a liquid-nitrogen cooled surface.

The effect of using a titanium getter is shown in Column IV of Table 3. A titanium getter provides a convenient method of reducing the oxygen concentration in a system. For example, in a non-baked system with no Meissner trap, a getter fired from a tungsten wire reduced the partial pressure from 2×10^{-7} mm of Hg to less than 4×10^{-9} mm of Hg. A decrease by a factor of three to five also occurs in the 28 peak. On the other hand, the tungsten wire liberated large quantities of hydrogen, as shown in Fig. 9. The gettering action of the nickel-iron film for hydrogen is also illustrated. Proper outgassing of the wire would remedy this situation.

Hydrocarbons present a problem in vacuum systems. They enter the evaporation chamber through backstreaming of diffusion pump oil, handling of evaporation components, and outgassing of organic gaskets. Well-designed liquid nitrogen baffles or substitution of a mercury for an oil-diffusion pump can reduce diffusion of hydrocarbons from the pumps, and improved handling techniques can reduce the human source of contamination. Similarly, better gasket materials exist than the conventional neoprene or Buna-N seals which are widely used. The outgassing characteristics of a wide range of materials has been measured, but mass spectrometer data on outgassing is limited.[14-16] Therefore, tests were made on a number of materials placed in one of the conventional evaporators. Because of the limitations of the evaporator these results are not quantitative, but only serve to indicate the types of gases one may expect from these materials. The samples, approximately 60 sq. in. in area, were cleaned in detergent followed by an alcohol rinse and outgassing in vacuum for several hours. Each sample was then tested by calibrating the empty system, inserting the sample, pumping for one hour, and noting significant differences between the sample and reference spectrums. Viton was excellent, water vapor being the only detected desorbed material. Kel-F was good, emitting somewhat more water vapor and a trace of methane. Teflon, on the other hand, had still more water vapor and detectable propane, butane and pentane peaks. Neoprene and Buna N had six and thirty times respectively as much butane and pentane as teflon and appreciably more water vapor. An experimental silicone rubber which looked promising on the basis of outgassing data obtained in the conventional manner with an ionization gauge was found to desorb one hundred times more butane and pentane than teflon and to have detectable hydrocarbon peaks from methane to mass 238. This data indicates that a suitable choice of gasket material may significantly reduce the hydrocarbon contamination in a conventional evaporator.

Table 3 **The effect of various modifications on a conventional evaporator.**

Mass-to-charge ratio	*Element*	*Amplitude unit* $=10^{-15}$ amp				
		I	*II*	*III*	*IV*	*V*
2	H_2	4.0×10^{2}	7.2×10^{2}	5.0×10^{2}	1.65×10^{3}	?
12	C^+	1.1×10	2.2×10	—	—	—
14	N_2^{++}, CH_2^+	9.9×10	7.5×10	3.5×10	9.0×10	0.7×10
15	CH_3^+	2.3×10	4.5×10	—		2.8×10
16	O^+, CH_4^+	5.0×10^{2}	2.1×10^{2}	1.7×10	1.2×10^{2}	4.1×10
17	OH^+	8.7×10^{3}	2.9×10^{3}	2.2×10^{2}	2.2×10^{2}	2.1×10^{2}
18	H_2O^+	3.8×10^{4}	1.23×10^{4}	1.1×10^{3}	1.0×10^{3}	1.0×10^{3}
20	A_2^{++}	7.8×10	2.4×10	0.5×10	—	—
22	CO_2^{++}	1.0×10	1.2×10	—	—	—
28	N_2^+, CO^+	1.6×10^{3}	1.3×10^{3}	7.8×10^{2}	1.6×10^{2}	1.3×10^{2}
32	O_2^+	2.9×10^{2}	5.8×10	1.0×10	0.3×10	0.1×10
41-42	$C_3H_6^+$	3.0×10	6.6×10	3.3×10	3.7×10	3.7×10
43-44	CO_2^+, $C_3H_8^+$	1.3×10^{2}	2.2×10^{2}	3.6×10	4.1×10	4.3×10
56-58	$C_4H_{10}^+$	0.9×10	4.5×10	3.2×10	?	3.5×10
70-72	$C_5H_{12}^+$	—	1.7×10	1.6×10	?	2.0×10
Gauge pressure in mm Hg		7.7×10^{-6}	3.1×10^{-6}	2.4×10^{-6}	2.4×10^{-6}	2.0×10^{-6}

Column I : Normal operation of evaporator B
Column II : After a mild two-hour bake
Column III : After cooling a Meissner trap
Column IV : While evaporating a titanium getter
Column V : After evaporation of Ni-Fe Film; Ti getter off, Meissner trap on

Table 4 **The partial pressures of residual gases in various types of vacuum systems.**

Gas	Pressure in mm of Hg					
	I	*II*	*III*	*IV*	*V*	*VI*
H_2	4×10^{-7}	4×10^{-7}	2×10^{-7}	2×10^{-7}	4×10^{-8}	2×10^{-9}
O_2	5×10^{-7}	4×10^{-8}	4×10^{-8}	3×10^{-9}	5×10^{-10}	$<10^{-10}$
A	3×10^{-8}	2×10^{-8}	5×10^{-9}	2×10^{-8}	8×10^{-10}	$<10^{-10}$
N_2	1×10^{-6}	2×10^{-7}	2×10^{-7}	5×10^{-8}	1×10^{-8}	8×10^{-10}
CO	9×10^{-7}	5×10^{-8}	5×10^{-8}	1×10^{-7}	2×10^{-8}	
CO_2	6×10^{-8}	1×10^{-8}	3×10^{-9}	5×10^{-9}	2×10^{-9}	$<10^{-10}$
H_2O	5×10^{-6}	6×10^{-6}	5×10^{-7}	3×10^{-7}	7×10^{-8}	$<10^{-10}$
CH_4	1×10^{-8}	8×10^{-10}	$<10^{-10}$	6×10^{-9}	7×10^{-9}	$<5\times10^{-11}$
C_3H_8	2×10^{-8}	4×10^{-9}	2×10^{-9}	6×10^{-9}	2×10^{-9}	$<5\times10^{-11}$
C_4H_{10}	6×10^{-9}	2×10^{-9}	1×10^{-9}	1×10^{-9}	1×10^{-9}	$<5\times10^{-11}$
C_5H_{12}	2×10^{-9}	4×10^{-10}	4×10^{-10}	6×10^{-10}	5×10^{-10}	$<5\times10^{-11}$
ΣP_j	8×10^{-6}	6×10^{-6}	1×10^{-6}	7×10^{-7}	2×10^{-7}	3×10^{-9}
P*	8×10^{-6}	4×10^{-6}	2×10^{-6}	8×10^{-7}	6×10^{-8}	6×10^{-9}

*Uncorrected ionization gauge readings.

Column I : Conventional evaporator A
Column II : Conventional evaporator B
Column III : Evaporator B with Meissner trap, titanium getter not used
Column IV : Special high-vacuum evaporator
Column V : Special high-vacuum evaporator with Meissner trap
Column VI : Vac Ion, ultra-high-vacuum system

• *Special high-vacuum evaporator*

As shown in Table 4, the composition of the residual gases in this system is not radically different from that in a conventional evaporator although the partial pressures are considerably smaller. The major constituent is again water vapor, the quantity being a function of the previous history of the system. Hydrogen, nitrogen and carbon monoxide are the other principal gases, with oxygen, argon, methane, propane, butane, and other hydrocarbons present in lesser quantities.

A Meissner trap, cooled for several hours, reduces the gauge pressure from the mid-range of 10^{-7} mm of Hg to the mid-range of 10^{-8} mm of Hg, largely through a reduction in the water-vapor concentration. Trapping of oxygen, nitrogen, carbon monoxide, and hydrogen also occur to a lesser degree. This is illustrated in Column V of Table 4.

• *Ultra-high-vacuum system*

The residual gases in this system after baking are nitrogen, carbon monoxide, and hydrogen. Column VI of Table 4 presents a gas analysis obtained at a gauge pressure of 5.5×10^{-9} mm of Hg. Water vapor, oxygen, carbon dioxide, and the hydrocarbons are not detectable, which implies their vapor pressures are less than 10^{-10} mm of Hg. Prior to an evaporation, a liquid-helium finger in the vacuum chamber is cooled to reduce the chamber pressure to the low 10^{-10} mm Hg range. Hydrogen was the predominant gas. Even with the high pumping speed of this trap, very thorough outgassing of the source prior to and after inserting the tin charge is necessary in order to maintain pressures below 10^{-9} mm of Hg during evaporations.[18]

Conclusions

The systems described in this paper operate at pressures of 10^{-5} to 10^{-10} mm of Hg during evaporation of thin-film specimens. A comparison of the residual gases in these systems is given in Table 4. However, the complexity of the apparatus and the time required for deposition increase with decreasing pressure. It is advantageous, therefore, to determine what gases are detrimental to the physical characteristics of interest and to pump these gases preferentially rather than attempt to reduce the total pressure. Examples of preferential pumps are a liquid-nitrogen-cooled surface for water vapor, a titanium film for oxygen, and a nickel-iron film for hydrogen.

A considerable improvement may be made over a conventional evaporator by substituting an electromagnetic pump for the diffusion-forepump combination, and low vapor pressure seals for conventional rubber gaskets. A high-temperature bake, however, remains the most reliable method of reducing water vapor, oxygen, and hydrocarbon partial pressures below 10^{-10} mm of Hg.

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