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Oxygen Interaction with Space-Power Materials

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I. Introduction

Data from space shuttle flights have established that many materials experience relatively rapid degradation when exposed to the low earth orbit ambient atmosphere[1], which is predominantly atomic oxygen. While much has been learned from samples flown on the shuttle, laboratory simulations of the shuttle environment are necessary for a detailed understanding of the various interactions which contribute to the observed degradation. These laboratory experiments are particularly important for predicting the deterioration to be expected for materials aboard orbiting power systems, which will be exposed for long periods of time and could have components operating at very high temperatures.

For the past 4-1/2 years we have been conducting experiments on the interaction of low energy oxygen ions with surfaces, first with the support of NASA Grant NAG 3-426 and now with the support of NASA Grant NAG 3-696. By using a mass spectrometer to synchronously detect molecules emitted from the surface as a result of amplitude modulated oxygen ion bombardment, we have obtained quantum yields as functions of ion energy.[2]

II. Recent Accomplishments

During the last 1-1/2 years we have:

1) developed a technique to obtain preliminary yield data by slowly scanning the mass setting of the mass spectrometer,
2) extended our measurements down to zero modulation frequency,
3) obtained yield data for the insulating materials (Nomex, Kevlar, and Teflon) used in the construction of electrodynamic tether,

4) constructed a heated sample holder to investigate the effect of sample temperature on quantum yields,

5) developed the instrumentation necessary to observe the mass spectrometer signal as a function of time during and following bombardment of the sample by a brief (~ 1 millisecond) pulse of ions.

A - Mass Scanning

The nature and utility of the mass scanning technique can be seen by examining Figs. 1 and 2. These show the mass spectrometer signal (processed by a lock-in detector) as a function of mass number M in the range M = 26 to M = 46 amu. The target surface was Teflon from a sample of electrodynamic tether. The left-hand trace in each figure shows the signal strength S while the right-hand trace shows S $\sin\phi$, where ϕ is the phase shift of S relative to the lock-in reference. Figure 1 was obtained with the ion beam turned off, but with O_2 still flowing through the ion gun into the vacuum chamber. Figure 2 was obtained with the sample bombarded by a 0.1 μA, 30 Hz, 93 eV beam of oxygen ions. The signals in Fig. 1 at M = 28, 32, 34, 40, and 44 are noise peaks arising from statistical fluctuations in the dc mass spectrometer signals from background gases (CO, O_2, $O^{16}O^{18}$, A, and CO_2) in the vacuum chamber. For successive traces the sizes and shapes of these signals are random. Figure 2 shows the appearance of true ion bombardment induced signals at M = 28 and 31. The M = 28 signal is from CO produced by interaction of oxygen ions with carbon contamination on the Teflon surface. The M = 31 signal we attribute to CF molecules arising from the oxygen ion degradation of Teflon.

Traces such as those shown in Figs. 1 and 2 enable us to determine quite rapidly which mass spectrometer settings (M values) should be used in the detailed investigation of oxygen ion interactions with various target

surfaces. The signals at these particular M values can then be examined as functions of ion energy, target temperature, modulation frequency, etc.

B - Zero Frequency Signals

The principal reason for using amplitude modulation of the ion beam and synchronous detection of the molecules emitted from the target surface is to separate the ion-induced signals from mass spectrometer signals arising from background gases in the vacuum chamber with the same mass numbers (M values). An additional reason for using modulated beam bombardment and synchronous detection is that the variations in signal strength (S) and phase (ϕ) with modulation frequency are potential sources of information on the chemical kinetics of the surface interaction.[3] Therefore, the modulated beam technique is used extensively even when there is no appreciable background signal at the mass spectrometer setting (M value) of the detected molecule. However, if the ion-induced signal has a large slow component with a reaction time greater than ~ 10 milliseconds, the strength of the detected signal is substantially reduced at a modulation frequency even as low as 30 Hz. To check for the presence of such slow components, we have observed signals at zero frequency using the circuit shown in Fig. 3. The simple RC filter reduces the noise and the bucking circuit can be used to tune out any dc signal arising from the background gases in the vacuum chamber. Figure 4 shows the zero frequency CF signal from Teflon.

C - Heated Sample Holder

Our heated sample holder is a thick copper plate with holes drilled to accommodate coiled tungsten wire heating elements insulated from the plate by ceramic tubes. This holder has been used to search for MoO_3 molecules

emitted from a Mo surface as the result of oxygen ion bombardment. With an ion energy of 93 eV, we have seen no MoO_3 signal above noise up to a sample temperature of 570°C. The noise level was ~ 1% of the signal strength which we observe for the CO signal from surface carbon contamination.

While we should be able to modify the present heated sample holder to reach temperatures in the 600-700°C range, we have decided to use direct resistive heating of a thin sheet of Mo (2 cm long, 0.5 cm wide, and 2.54×10^{-3} cm thick) to reach a temperature of at least 1000°C. At this high a temperature there should be an appreciable dc MoO_3 signal from the mass spectrometer due to interaction of Mo with the O_2 background gas in our vacuum chamber, since with the ion gun in operation the O_2 pressure in the chamber is ~ 5×10^{-5} Pa (4×10^{-7} torr). This dc signal can be used to determine precisely the mass spectrometer settings corresponding to MoO_3 for the various isotopes of Mo. We will then proceed to investigate enhancement of the MoO_3 signals by oxygen ion bombardment of the Mo surface.

D - Pulse Signals

The most exciting of our results since the beginning of this research are the signals we have obtained when samples are bombarded by a brief pulse of oxygen ions. These pulse measurements were undertaken initially as a result of the frustration we experienced in our attempts to interpret modulation data (signal strength and phase versus modulation frequency). Analysis of this data has been limited by the need to correct the phase data for instrumental phase shifts arising from the transit times of the ions and molecules involved. It is particularly difficult to estimate the time required for molecules to travel the 3 cm distance from the target surface to the ionizer of the mass spectrometer since the velocity distribution of the molecules emitted from the surface is unknown.

The modulation technique yields data in the frequency domain from which surface reaction times can be extracted,[3] at least in principle. The pulse technique, which observes the buildup and decay of the ion-induced signals during and after bombardment of the sample by a brief pulse of ions, gives the same information in a more direct manner.

For the pulse measurements the ion beam is cut off by biasing the extract electrode of our ion gun and then turned on for a brief time by applying a square voltage pulse to this same electrode. This produces a square ion pulse with rise and fall times less than 5 μsec. The signal from the mass spectrometer is sent, via a current to voltage preamp, to a signal averager (PAR Model 4202), which has 1024 memory channels. The averager is triggered by the onset of the pulse which extracts the ion beam and scans through its channels, dwelling in each for a time which is adjustable down to 5 μsec. To recover the weak ion-induced signals (corresponding to electron currents of ~ 10^{-8} amps or less at the output of the mass spectrometer's multiplier) from statistical and amplifier noise, the signals from a large number of pulses (and subsequent scans) are averaged.

Figures 5, 6, and 7 are representative of the data we have obtained. The first shows the CF (M=31) signal from Teflon for a 0.25 msec pulse width and a 5.12 msec scan time (5 μsec/channel times 1024 channels). The sharp spike on the rising portion of the trace signals the cutoff of the voltage pulse which gates the ion beam on and off. Its presence in the trace is the result of a small ground-loop coupling between the pulser and signal averager. The time interval by which this spike precedes the peak of the trace is a direct measure of the time required for the CF molecules to travel the 3 cm distance from the target surface to the ionizer of the mass spectrometer.

Figures 6 and 7 show the CO (M=28) signal from carbon contamination on the surface of a copper plate for a 2.5 msec pulse width and a 30.72 msec scan time (30 μsec/channel times 1024 channels). The first is for an oxygen ion energy of 93 eV and the second for an energy of 4.5 eV. These traces illustrate the ease with which one can extract semi-quantitative information on chemical kinetics from data in the time domain. The steep initial rise of the trace in Fig. 6 and corresponding steep fall from the peak shows the presence of a very fast component for the signal at an ion energy of 93 eV. Figure 7 shows that this component is much slower at 4.5 eV.

Quantitative analysis of the pulse signal traces is relatively straightforward. Semi-log plots of the signal versus time show a sequence of straight-line segments, provided the reaction times of the component signals are sufficiently different. From these straight-line segments of the semi-log plots one can extract the reaction times and the strengths of the individual component signals.

III. Plans for the future

For the immediate future we plan to

(1) pursue, vigorously, the pulse signal measurements, including examination of signals induced by argon-ion bombardment of Teflon and surface carbon contamination,

(2) investigate the effect of surface temperature on the pulse signals,

(3) continue our investigation of the interaction of oxygen with Mo (see discussion in Sec. II-C).

References

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2. C.C. Horton, T.G. Eck, and R.W. Hoffman, "Carbon Monoxide Production in Low Energy Oxygen Ion Bombardment of Pyrolytic Graphite and Kapton Surfaces", J. Vac. Sci. Technol. A4, 1236 (1986).

3. R.H. Jones, D.R. Olander, W.J. Siekhaus, and J.A. Schwarz, "Investigation of Gas-Solid Reactions by Modulated Molecular Beam Mass Spectrometry", J. Vac. Sci. Technol. 9, 1429 (1972).

Figure Captions

Figure 1. Mass scan at ~ 40 sec/amu for a modulation frequency of 30 Hz and a lock-in time constant of 4 sec. No ion beam is incident on the target surface. This trace shows the noise peaks from the background gases in the vacuum chamber.

Figure 2. The same as Fig. 1, except that a 0.1 μA, 30 Hz, 93 eV oxygen ion beam is incident on the Teflon target surface.

Figure 3. Circuit used to observe ion bombardment induced signals at zero frequency.

Figure 4. The zero frequency M = 31 (CF) signal from Teflon for a 0.1 μA, 93 eV oxygen ion beam incident on the sample surface, an RC time constant of 4 sec, and an inverse chart speed of 30 sec/cm.

Figure 5. Recorder trace of the CF signal induced by a 0.1 μA, 93 eV square pulse of oxygen ions incident on a Teflon target. This trace shows the average of 131,072 repetitions with a pulse width of 0.25 msec, scan time of 5.12 msec, and repeat time of 6 msec.

Figure 6. Recorder trace of the CO signal from surface carbon contamination on a copper plate for a 0.1 μA, 93 eV incident ion pulse. Average of 32,768 repetitions with a pulse width of 2.5 msec, scan time of 30.72 msec, and repeat time of 32 msec.

Figure 7. Same as Fig. 6, except for an ion energy of 4.5 eV.

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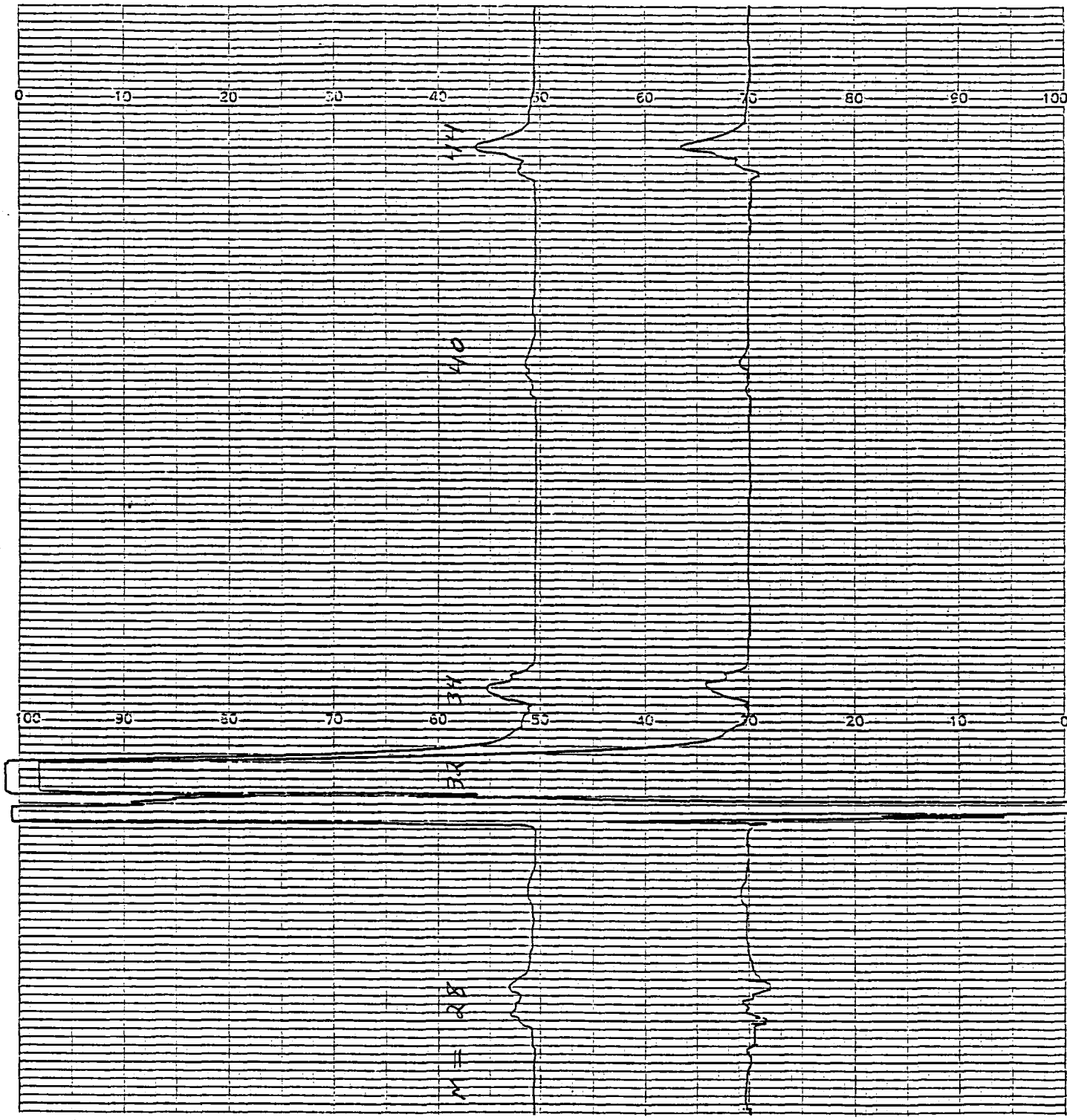

Figure 1

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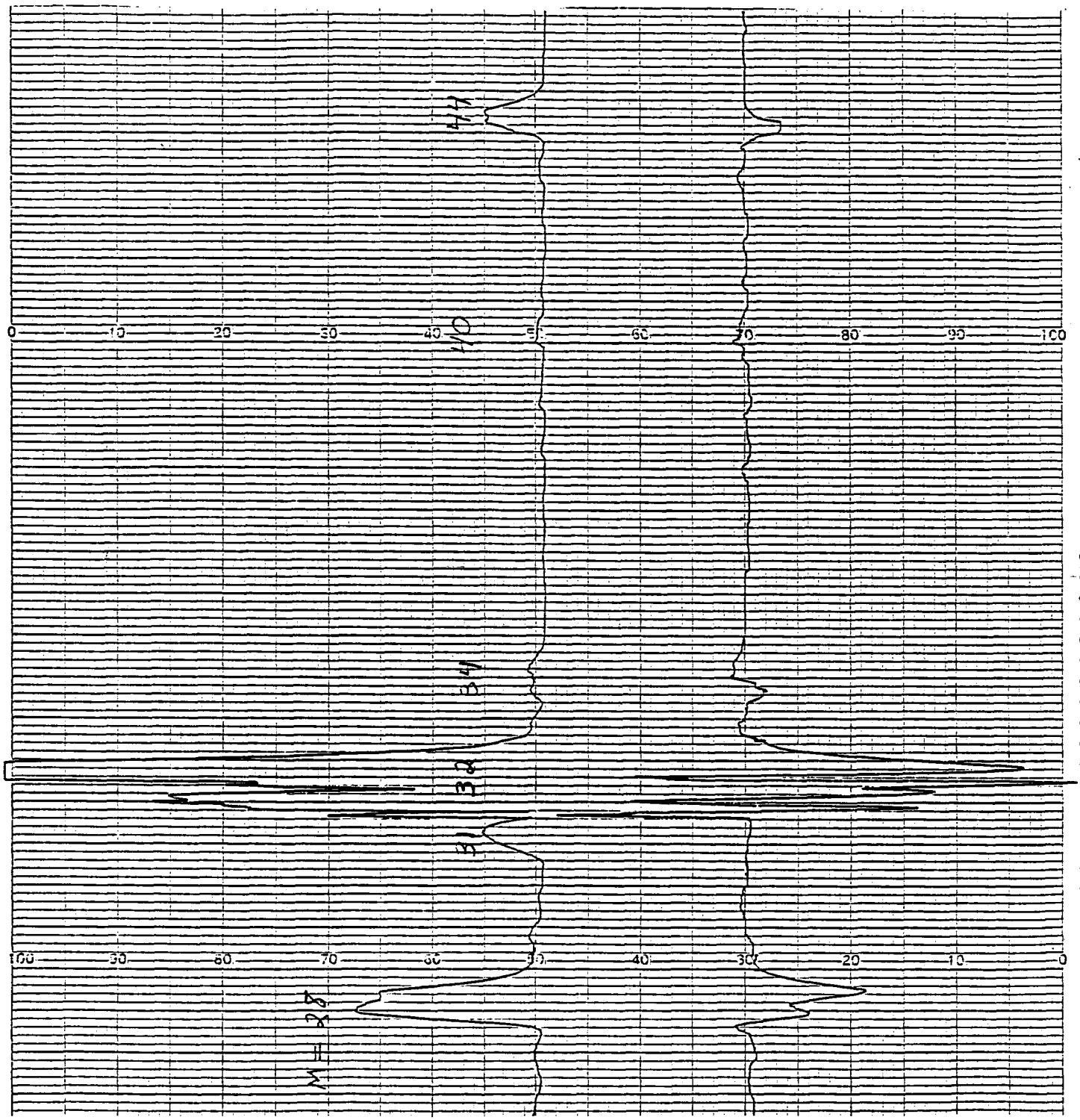

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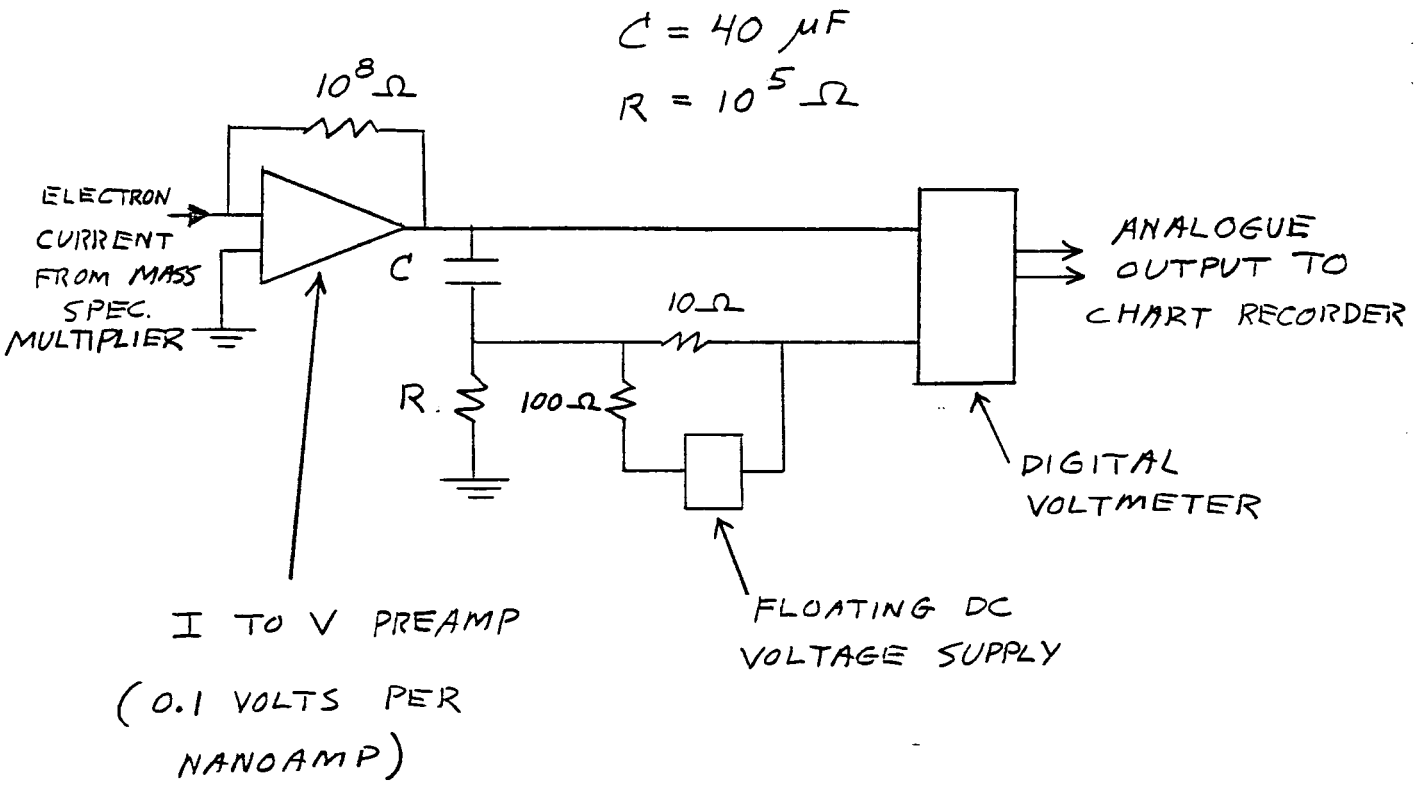
C = 40 μF
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ELECTRON CURRENT FROM MASS SPEC. MULTIPLIER
C
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ANALOGUE OUTPUT TO CHART RECORDER
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I TO V PREAMP
(0.1 VOLTS PER NANOAMP)
FLOATING DC VOLTAGE SUPPLY

Figure 3

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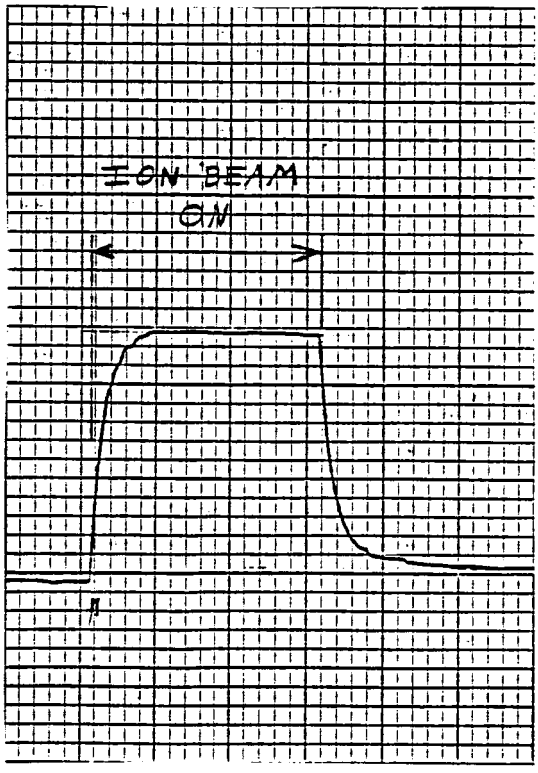

Figure 4

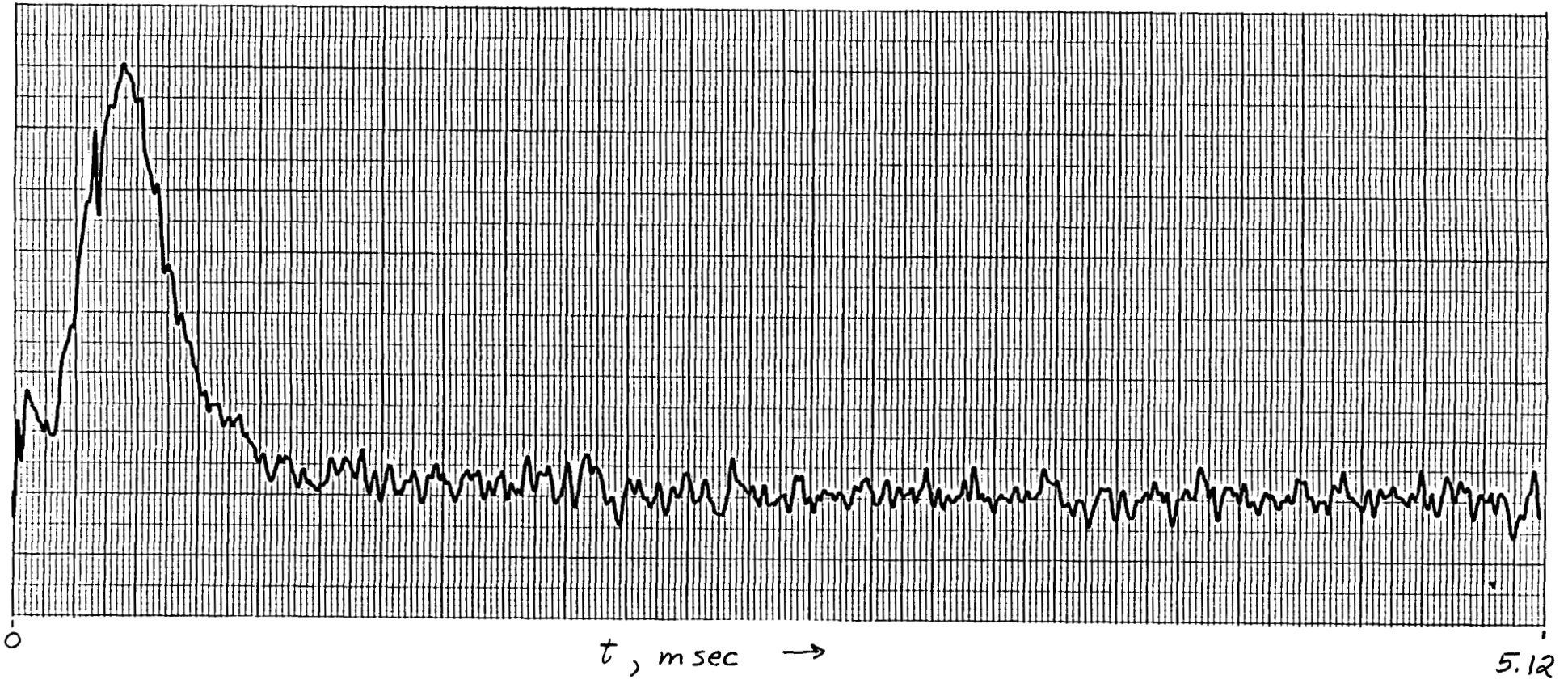

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Figure 5

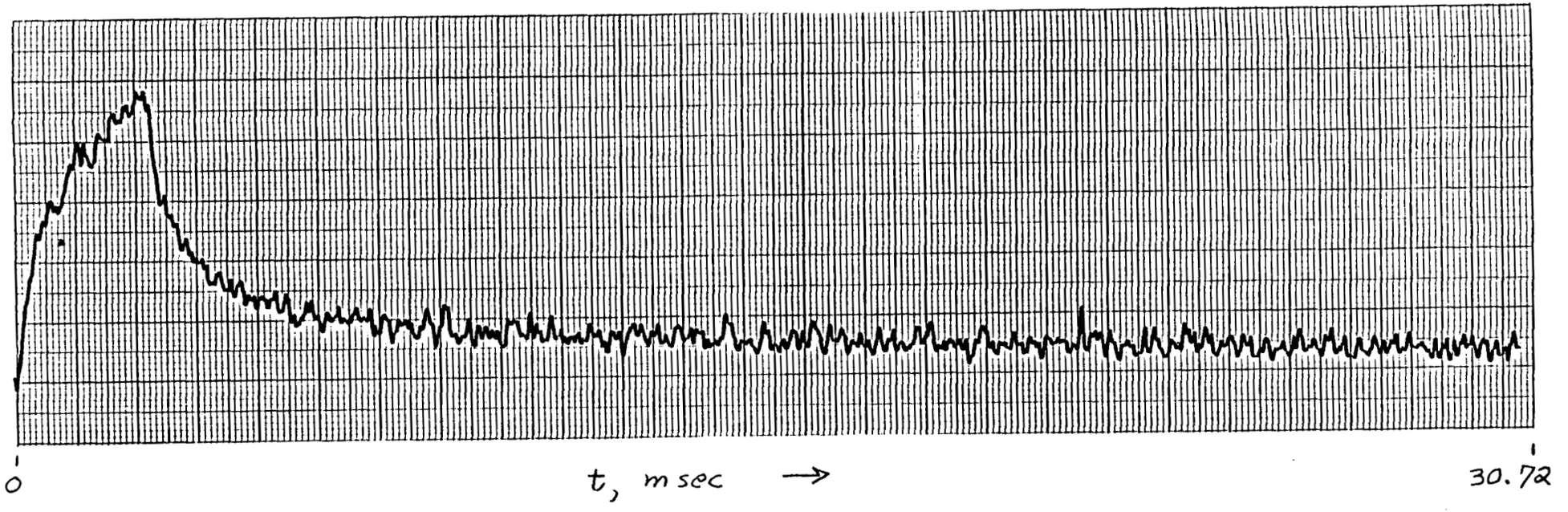

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Figure 6

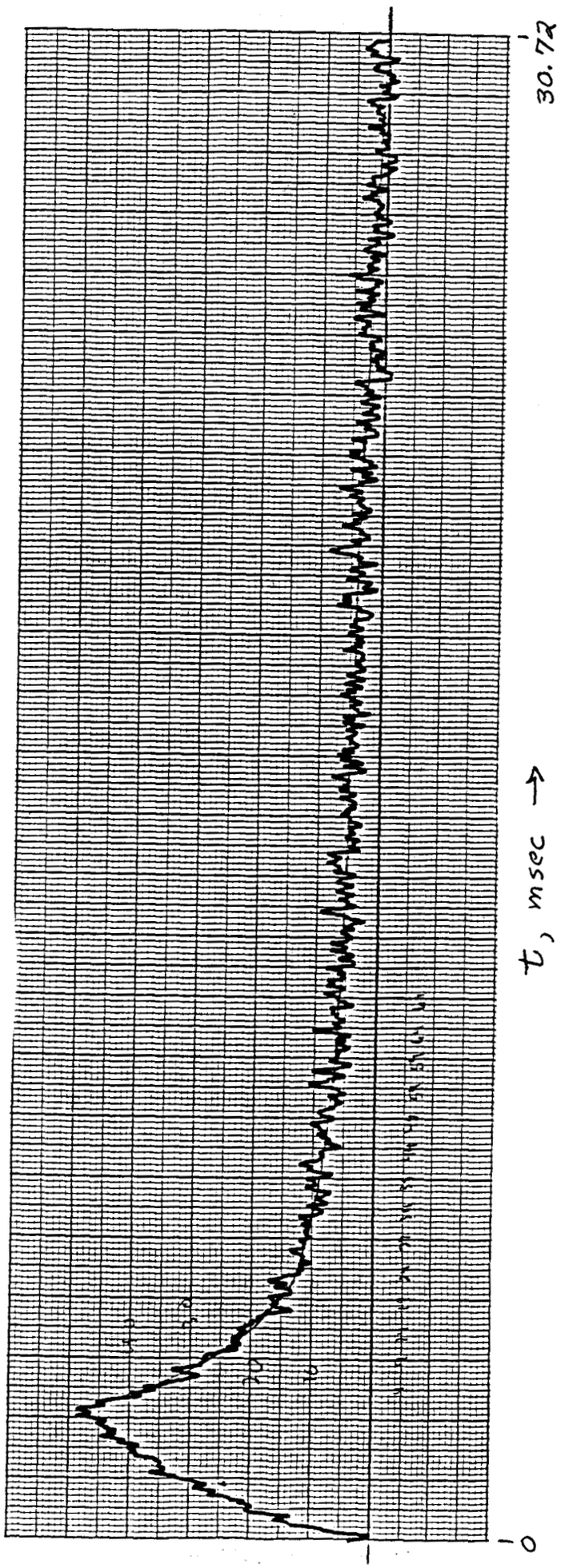

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Figure 7