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The goal of this project was to produce a source which is compact, durable and mounts on a standard UHV flange for the generation of hyperthermal oxygen atoms. This has been accomplished. In this source oxygen atoms permeate through a Ag membrane held at 500°C and are then emitted toward the target from the vacuum side of the membrane by electron stimulated desorption (ESD). The current prototype model generates usable O-atom fluxes of about 10^{12} atoms/cm²-s, and future modifications should increase this flux by 1 to 3 orders of magnitude. Based on the O⁺ energy distribution, the average O neutral energy is about 5 eV with a fairly broad distribution (FWHM $\approx$ 3.6 eV). The information required for the development of this source and a design of the source are presented.

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ABSTRACT:

The goal of this project was to produce a source which is compact, durable and mounts on a standard UHV flange for the generation of hyperthermal oxygen atoms. This has been accomplished. In this source oxygen atoms permeate through a Ag membrane held at 500°C and are then emitted toward the target from the vacuum side of the membrane by electron stimulated desorption (ESD). The current prototype model generates usable O-atom fluxes of about 10^{12} atoms/cm²-s, and future modifications should increase this flux by 1 to 3 orders of magnitude. Based on the O⁺ energy distribution, the average O neutral energy is about 5 eV with a fairly broad distribution (FWHM $\approx$ 3.6 eV). The information required for the development of this source and a design of the source are presented.

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INTRODUCTION

A source of hyperthermal (several eV) oxygen atoms with a significant flux ($>10^{12}$ atoms/cm²-s) would be useful in many application areas including corrosion studies of materials on space vehicles, growth of compound semiconductor materials by molecular beam epitaxy (MBE), and synthesis of new organic and inorganic materials. The upper orbital envelope contains a high concentration of O atoms due to dissociation of O₂ by photons and is even the predominant species at certain altitudes. These remain as O atoms because a ternary collision is required to form O₂ and a hot species which carries the energy of bond formation away. Such ternary collisions occur with a low frequency because the total pressure is low. When orbiting spacecraft strike these O atoms, severe corrosion damage to some of the materials occurs which limits the lifetime of the spacecraft (1). A typical speed of a spacecraft is about 8 km/s so the collision with thermal O atoms is equivalent to a 5 eV atom striking a stationary surface. It would be desirable to carry out O-atom corrosion studies in terrestrial laboratories to test the performance of various materials utilized for long-term space missions. During the growth of compound semiconductors, it is often required to produce insulating oxide layers. This may be difficult or impossible using O₂ because the sticking coefficient of O₂ on III-V semiconductors and other materials is often very low. This problem could be overcome by using O atoms, which most likely have a sticking coefficient near 1, to form the oxide layers. Studies of spacecraft materials after flight testing show that even fully oxidized oxides are susceptible to corrosion by O atoms (1). This fact suggests that chemical reactions which have not been observed previously may occur between high-energy O atoms and certain materials. Therefore, it may be possible to synthesize new organic and inorganic materials using hyperthermal O atoms.

Unfortunately, the development of a hyperthermal O-atom source has proven to be exceedingly difficult, and most efforts over the last decade have been unsuccessful. This paper describes the development of a functioning hyperthermal O-atom source. Many different studies relating to the processes involved in the O-atom source have been carried out by the authors over the last five years, and these form the basis for the development of this source. The purpose of this paper is to

summarize the findings of these studies and to present the most recent design of the gun and some of its performance characteristics.

DESIGN APPROACH

The original concept of the source shown in figure 1 is to allow oxygen to permeate through a metal membrane at elevated temperature from a high pressure region to the UHV side and then to produce hyperthermal O atoms by electron stimulated desorption (ESD). Many processes have to function simultaneously in series at sufficiently high rates for the system to work. These include dissociative adsorption of O₂ on the metal surface, diffusion of oxygen through the membrane and formation of a flux of O neutrals by ESD. It is also necessary to minimize the rates of other processes such as the thermal evaporation of Ag and the thermal desorption of molecular oxygen from the membrane.

Permeation Studies

An important consideration is the permeation rate of oxygen through the metal membrane. If this cannot be made large enough by manipulation of several variables including membrane composition, membrane microstructure, temperature, membrane thickness, upstream oxygen pressure, etc., then it would not be possible to obtain reasonable fluxes. High purity, polycrystalline Ag has been chosen for the membrane material due to its high permeation rate for oxygen. This permeation rate has been measured over the temperature range of 400 to 800°C (2), and the resulting permeability and diffusivity data are shown in figures 2a and b. The permeability was found to be linear, repeatable and virtually independent of microstructure. A break occurs in the Arrhenius plot of diffusivity at 630°C which is due to thermal desorption of O₂ above 630°C from the surface and subsurface regions. Using this data, it was determined that a temperature of 500°C gives an acceptable permeation rate of oxygen through the Ag membrane ($2 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$). Furthermore, loss of Ag by sublimation is not significant at this temperature, and a stable chemisorbed layer of O atoms is maintained since the thermal desorption rate of O₂ is low.

Surface Characterization Studies

The adsorption of oxygen on large-grain polycrystalline Ag surfaces is of importance with regard to the initial adsorption on the Ag membrane surface and the O/Ag surface formed at the UHV side of the membrane. These surfaces have been examined in two characterization studies (3,4). Davidson et al. (3) have studied the adsorption of oxygen on polycrystalline Ag during exposure to 75 Torr of O₂ for 1 hour at temperatures ranging from 75 to 250°C using ion scattering spectroscopy (ISS) and angle-resolved Auger electron spectroscopy (ARAES) (5) in order to obtain the near-surface region compositional information shown in figures 3a and b. The purity of the Ag is critical because small amounts of impurities can segregate to the surface and dictate the chemical behavior of the surface. Regardless of the cleaning procedure used, it was impossible to remove all of the subsurface O. According to the ISS data, the O concentration in the outermost atomic layer increases monotonically from 0 to 50 at.% for the 250°C exposure. The total amount of subsurface O also increases monotonically with dosing temperature and reaches a uniform concentration level of 14 at.% over the region probed by AES. A model of the O concentration as a function of depth has been constructed based on these data which is shown in figure 3b. The O-rich surface layer and subsurface region are separated by an O-depleted region due to a contraction relative to the bulk between the first two Ag layers and an expansion between the second and third layers. This model is consistent with the surface reconstruction observed by Kuk and Feldman (6) for Ag(110) and predicted by Ning et al. (7) for Ag(111).

ESD Studies

The information regarding the ESD process and related experimental techniques contained in a review by Hoflund (8) forms the basis of the ESD studies and was responsible for the initial collaboration between Outlaw and Hoflund on this research project. Consequently, an electron stimulated desorption-ion energy distribution (ESDIED) study of oxygen-exposed Ag(110) (9) was carried out in order to determine the desorbing energies of the species produced in ESD. Even

though the sample was cleaned extensively, the prominent desorbing peaks were due to H^+ and OH^+ . The O^+ signal emerged with continued dosing and grew with respect to the H^+ and OH^+ signals. The relative sizes of the O^+ , H^+ and OH^+ signals vary with sample history, dosing conditions and primary beam energy.

In another study by Davidson et al. (10), 0.5 weight percent Zr was added to the Ag membrane for two reasons. The first was to inhibit grain growth at elevated temperatures in order to maintain small Ag grains. This results in a lower diffusivity but a higher permeation rate because the solubility is higher and the activation energy for dissociative adsorption is lower. The second was to obtain a higher ESD O^+ flux based on the fact that ZrO_2 is a maximal valency oxide (11-13). The O^+ ESDIED spectra obtained from oxygen-exposed (a) Ag and (b) Ag/0.5% Zr are shown in figure 4. The Ag yields a distribution with a maximum at about 5.7 eV and a FWHM of about 3.5 eV. The O^+ ESD signal from Ag-0.5-Zr is several times larger than that from Ag and shows contributions at approximately 5 and 6.7 eV possibly due to desorption from Ag-rich and ZrO_2 -rich regions (12) respectively. Furthermore, the neutral-to-ion ratio has been determined to be about 1.1×10^7 .

Neutral O Detection

Neutral ESD species are difficult to detect so very few ESD studies of neutral species have appeared in the literature. Outlaw et al. (14) developed an experimental ESD system capable of detecting O atoms emitted from an oxygen-charged Ag wire (see the system schematic in figure 5). The O atoms are detected using a quadrupole mass spectrometer operated in the appearance potential (AP) mode to allow the O atoms to be distinguished from residual gases and background gas products formed by collisions of the O atoms with the walls of the system. In the AP mode the energy of the ionizing electrons is reduced below the first ionization potential of the background species which accentuates the O-atom signal. ESD mass survey spectra taken in the normal and AP modes after charging the Ag sample with $^{18}O_2$ are shown in figure 6a and b respectively. The difference in the spectra demonstrate the importance of using the AP mode. An ESD cross section

for O neutral desorption from polycrystalline Ag of $7 \times 10^{-19} \text{ cm}^2$ was determined for a sample temperature of 100°C and a primary beam energy of 100 eV. The accuracy of this cross section is not known since no surface analysis was performed on the Ag wire and impurities segregating to the surface (3) may control the ESD yield. Nevertheless, these experiments did serve as a proof of concept for hyperthermal neutral oxygen emission with the oxygen being supplied from the bulk of the Ag.

Continuous ESD

The feasibility of continuous ESD by permeation of oxygen through a zirconia-coated ($1000\text{\AA}$)/Ag membrane was first demonstrated using the system shown in figure 7 (15). The ESD-emitted species was O_2^+ . The O which permeated through the membrane probably reacted with contamination resulting in desorption of O_2^+ because cleaning the vacuum side of membrane was not possible. The steady-state O_2^+ ESD signal is shown as a function of membrane temperature in figure 8.

Hyperthermal Oxygen Atom Generator

A functioning hyperthermal oxygen-atom generator has been constructed, and a schematic of the source is shown in figure 9. The mass spectrum of the O-atom beam shown in figure 10 was taken by operating the quadrupole mass analyzer in the AP mode and using an ion extraction voltage of 0 V. This procedure minimizes the contribution of background gases to the O signal since background gases have thermal energies on the order of several tenths of an eV which is insufficient to pass through the quadrupole filter. The time response of the O signal to a change in upstream O_2 pressure is shown in figure 11. Initially, the upstream O_2 pressure was at 200 Torr. The O_2 was then pumped out, and the O signal decayed by a factor of 10 over a period of about 950 minutes. The O_2 was then reintroduced resulting in a rapid rise in the O signal. Efforts are underway to accurately quantify the flux from the O-atom source, to measure the kinetic energies of the neutral O atoms directly, and to determine the electronic states of the desorbing atoms.

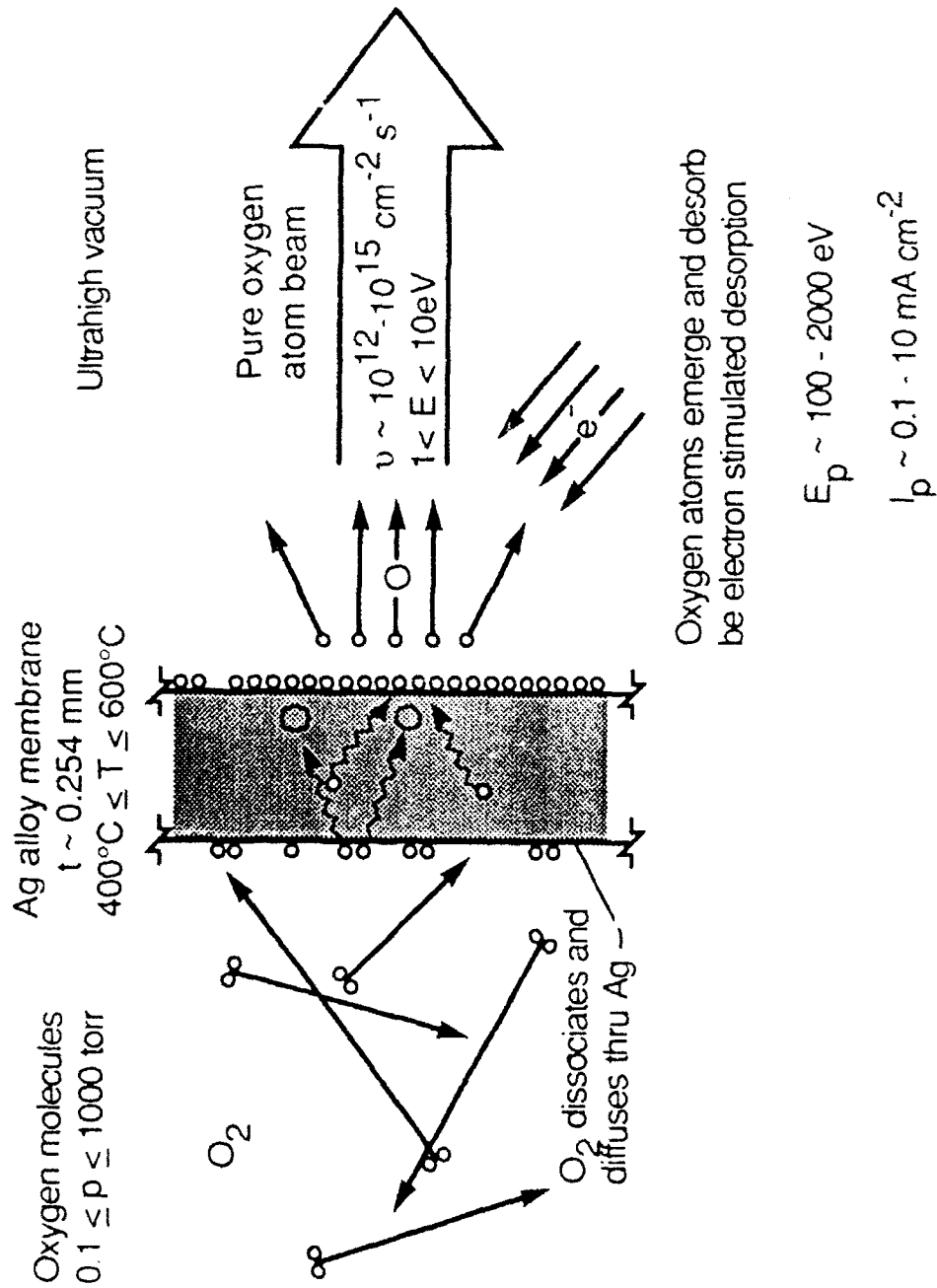
Efforts are also being made to increase the flux by changing the composition and microstructure of the membrane and by varying the source geometry and operating parameters.

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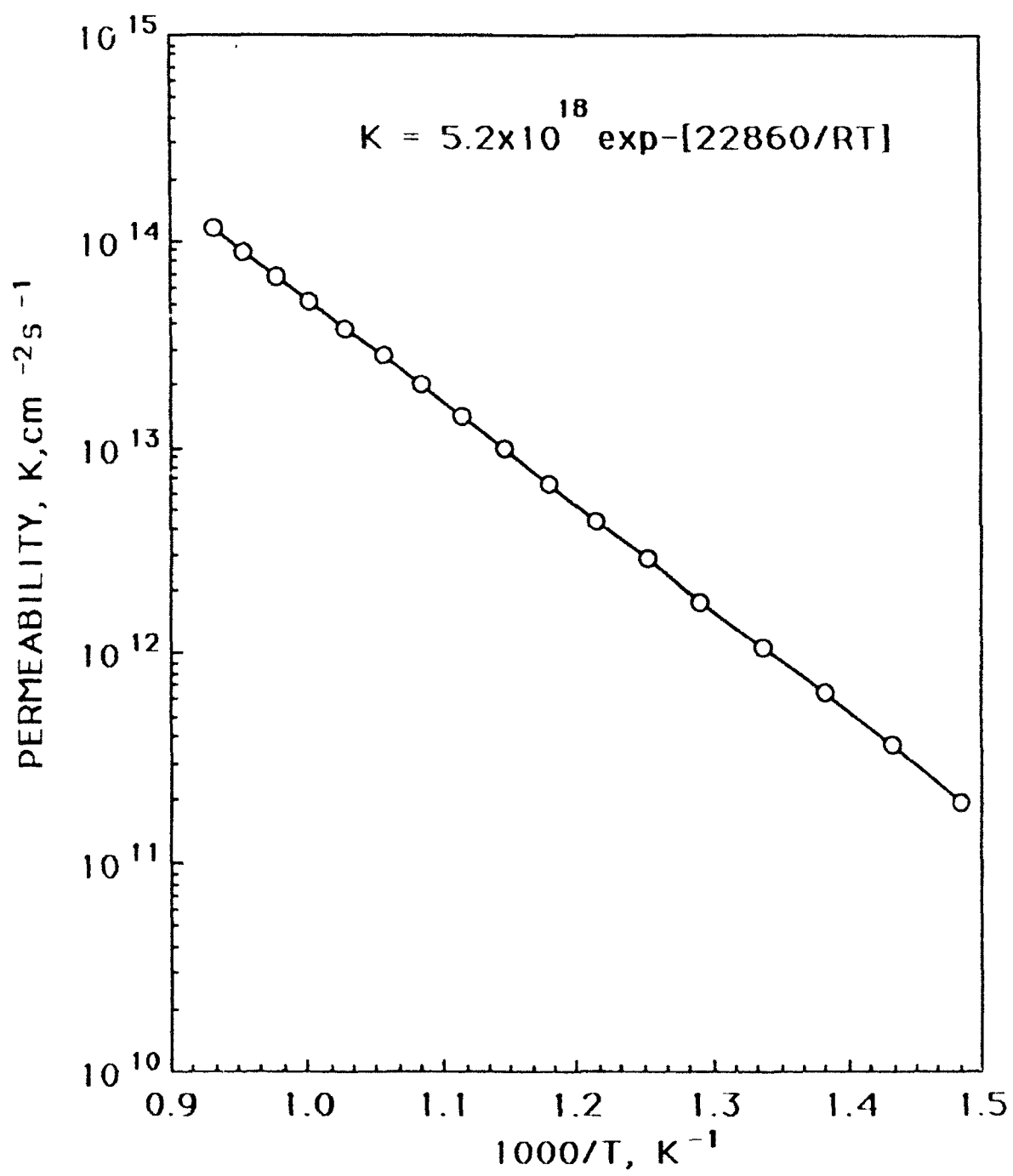
FIGURE CAPTIONS

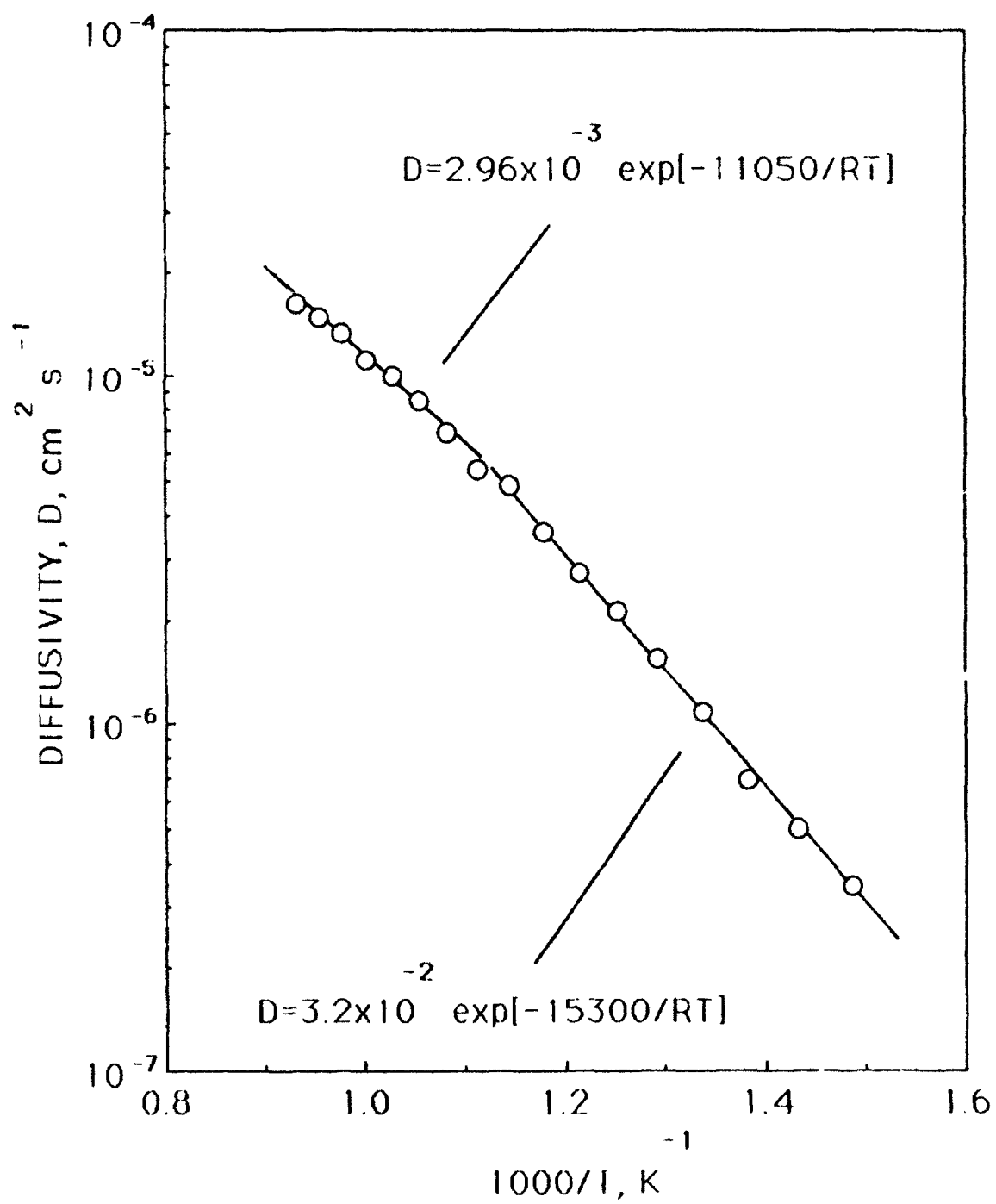
- Figure 1. Schematic showing the design concept of the hyperthermal oxygen atom gun.
- Figure 2. Arrhenius plots of oxygen (a) permeability and (b) diffusivity in large-grain, high purity Ag.
- Figure 3. (a) Oxygen concentrations (at.%) calculated from ISS and ARAES data obtained after dosing high-purity polycrystalline Ag for 1 hour in 75 Torr of O₂ at the temperatures indicated. (b) A schematic model of the O concentration profile after a 250°C dose obtained from the data shown in (a).
- Figure 4. ESDIED spectra obtained from oxygen-dosed polycrystalline (a) Ag and (b) Ag-0.5-Zr.
- Figure 5. Schematic diagram of the experimental system used to study ESD of neutral species.
- Figure 6. ESD mass survey spectra taken in the (a) normal and (b) AP mode from polycrystalline Ag at 450°C after charging with ¹⁸O₂.
- Figure 7. Schematic diagram of the first system used to demonstrate continuous ESD.
- Figure 8. O₂ QMS signal due to ESD of O₂ neutral species from ZrO₂ (1000Å coated on a Ag membrane) as a function of membrane temperature. The upstream O₂ pressure was 100 Torr, and the primary electron beam energy was 1 keV at a flux of 100 μA/cm².
- Figure 9. Schematic diagram of a functioning hyperthermal oxygen-atom generator. Ions produced by ESD are removed electrostatically.
- Figure 10. Mass spectrum of the O-atom beam produced by the HOAG.
- Figure 11. Time dependence of the O signal after pumping out the upstream O₂ at time = 0 and reintroducing O₂ at time = 950 min.

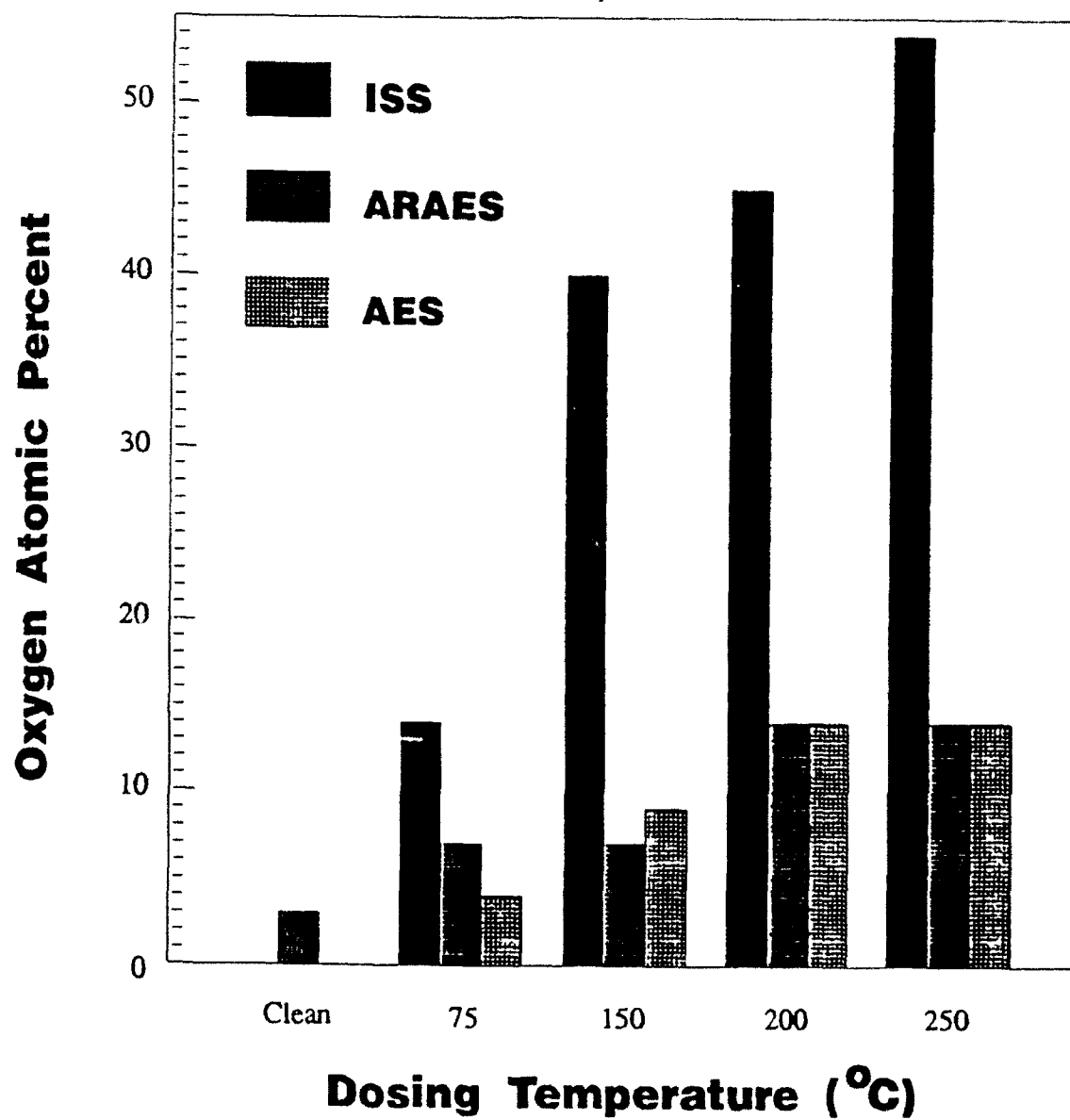


$$E_p \sim 100 - 2000 \text{ eV}$$

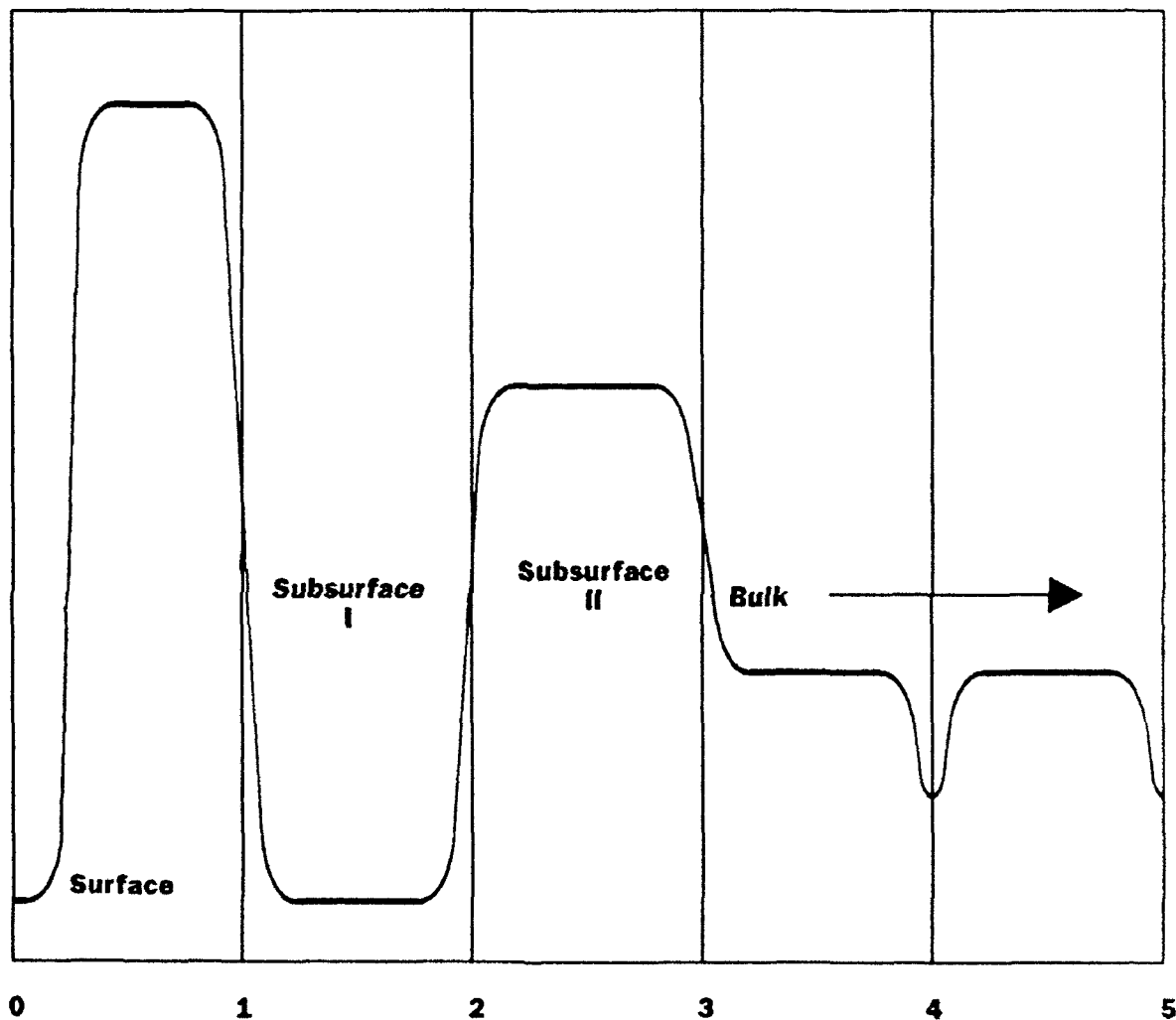
$$I_p \sim 0.1 - 10 \text{ mA cm}^{-2}$$



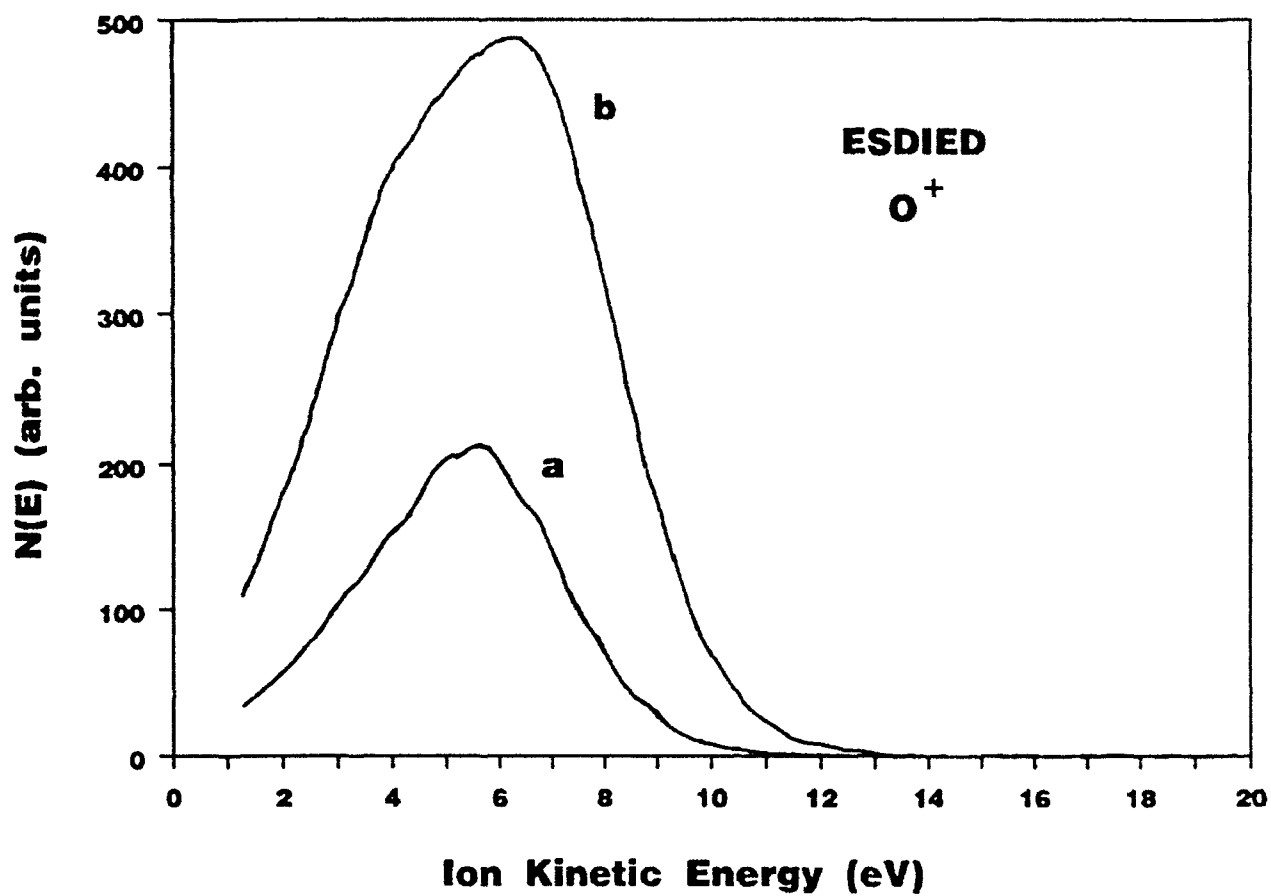


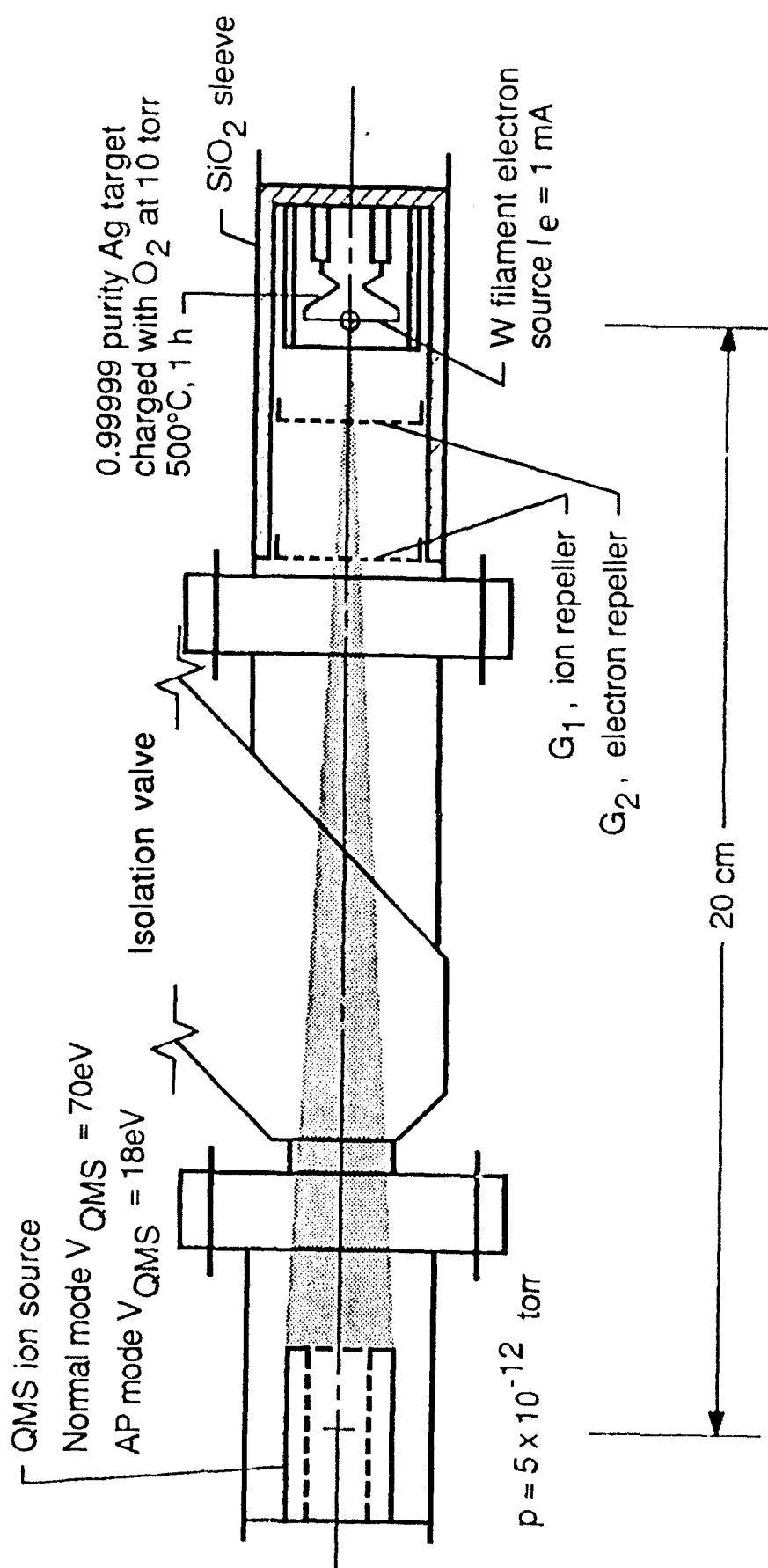


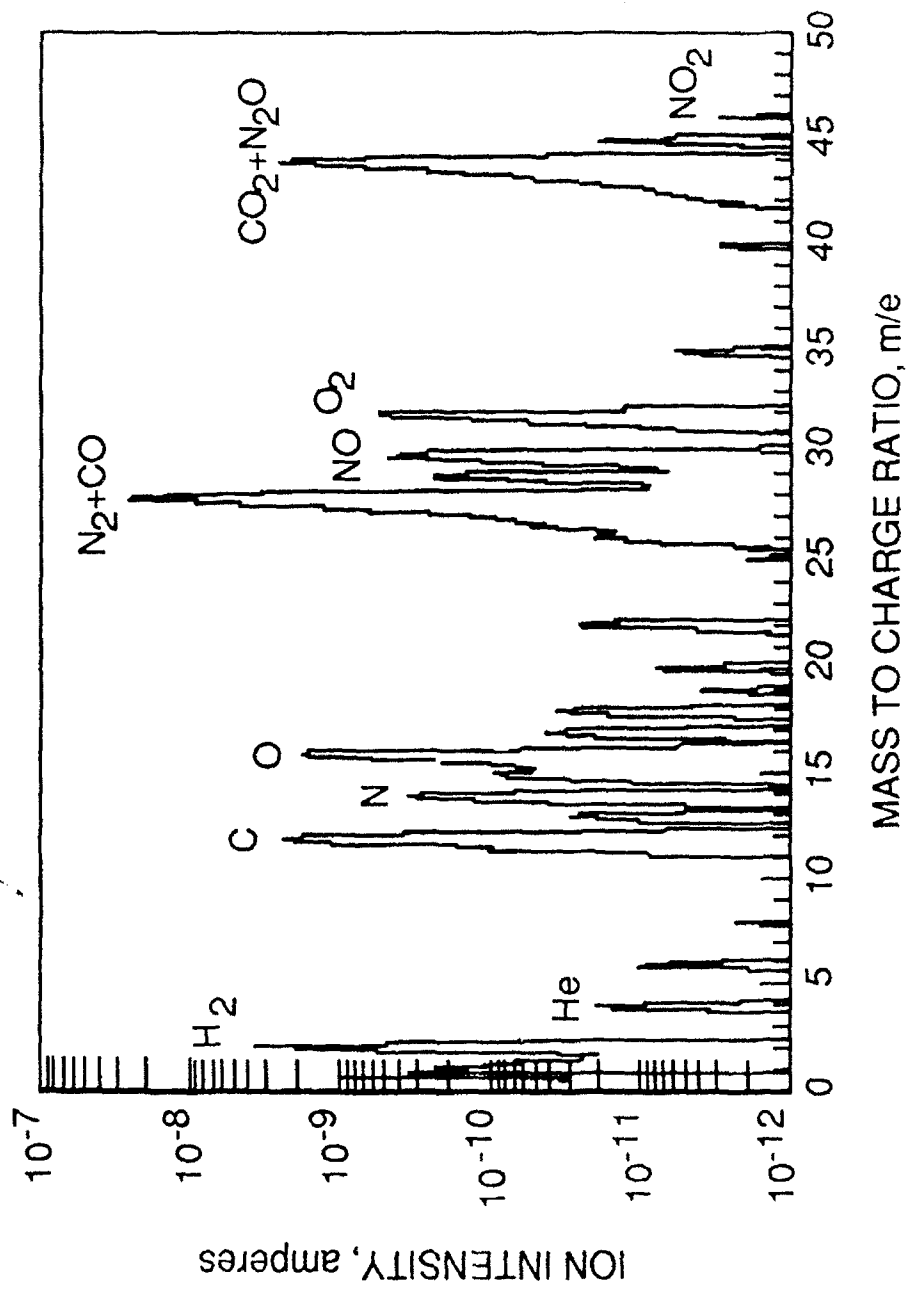
**Final Schematic Oxygen
Conc. Profile (arb. units)**

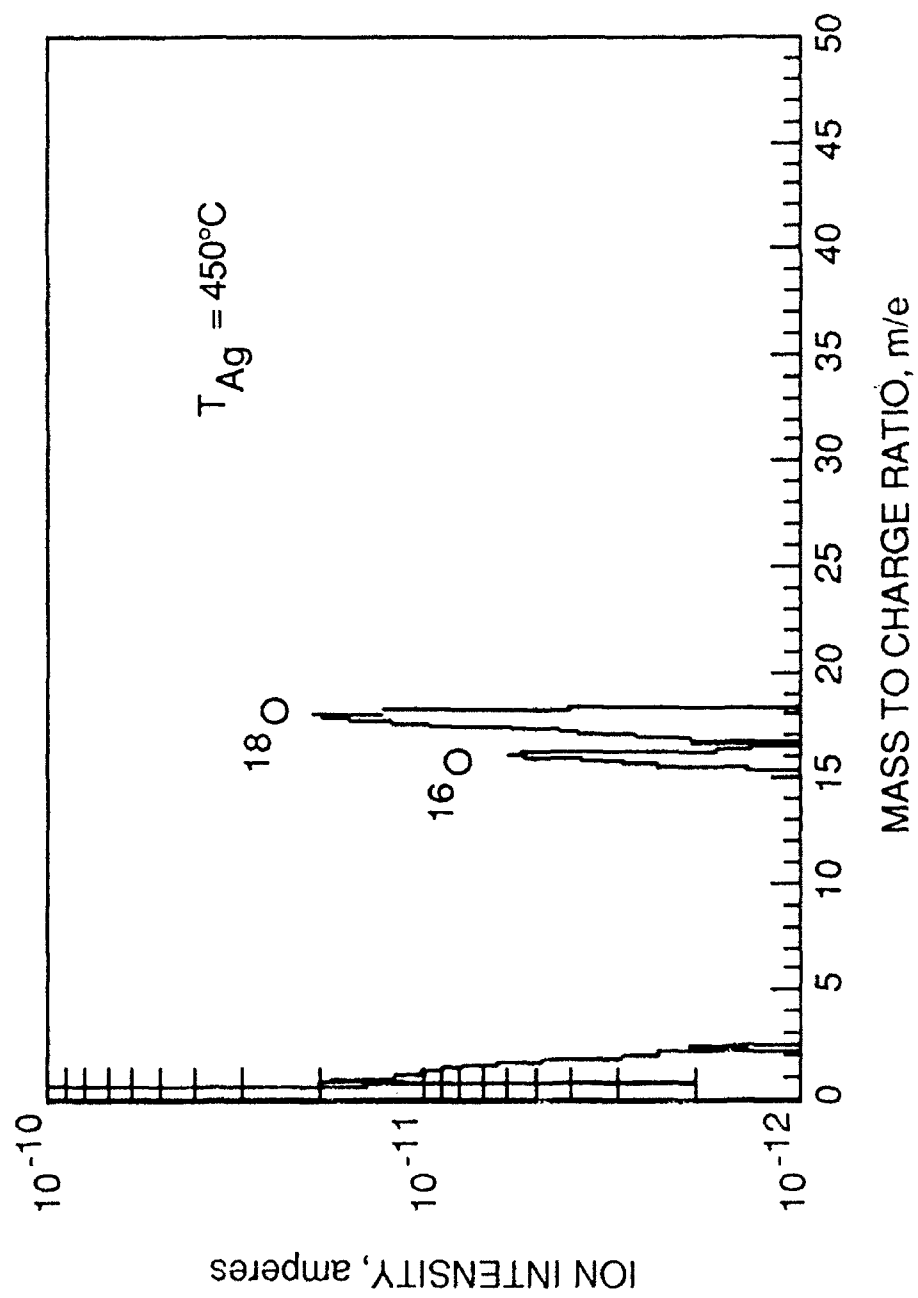


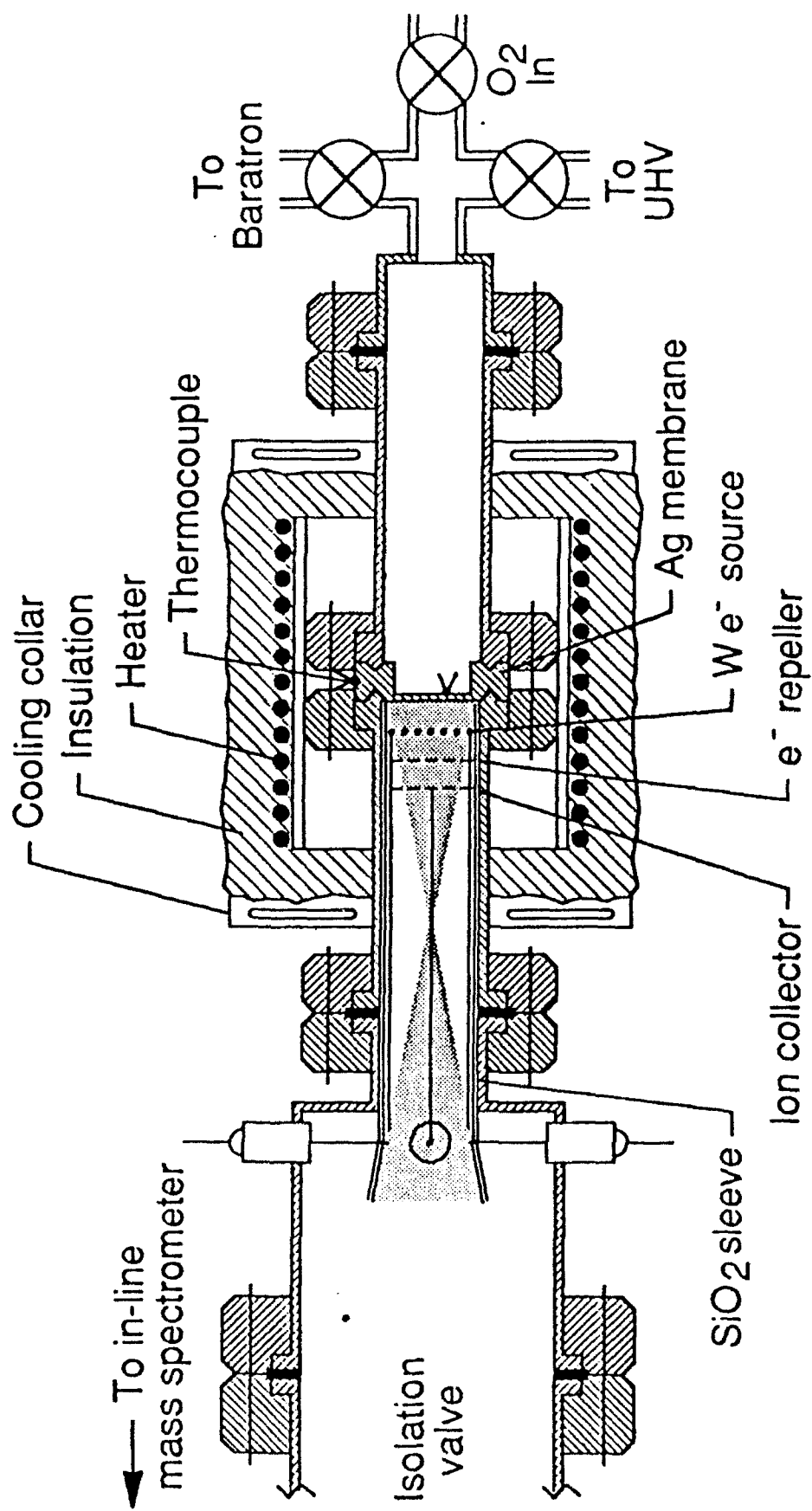
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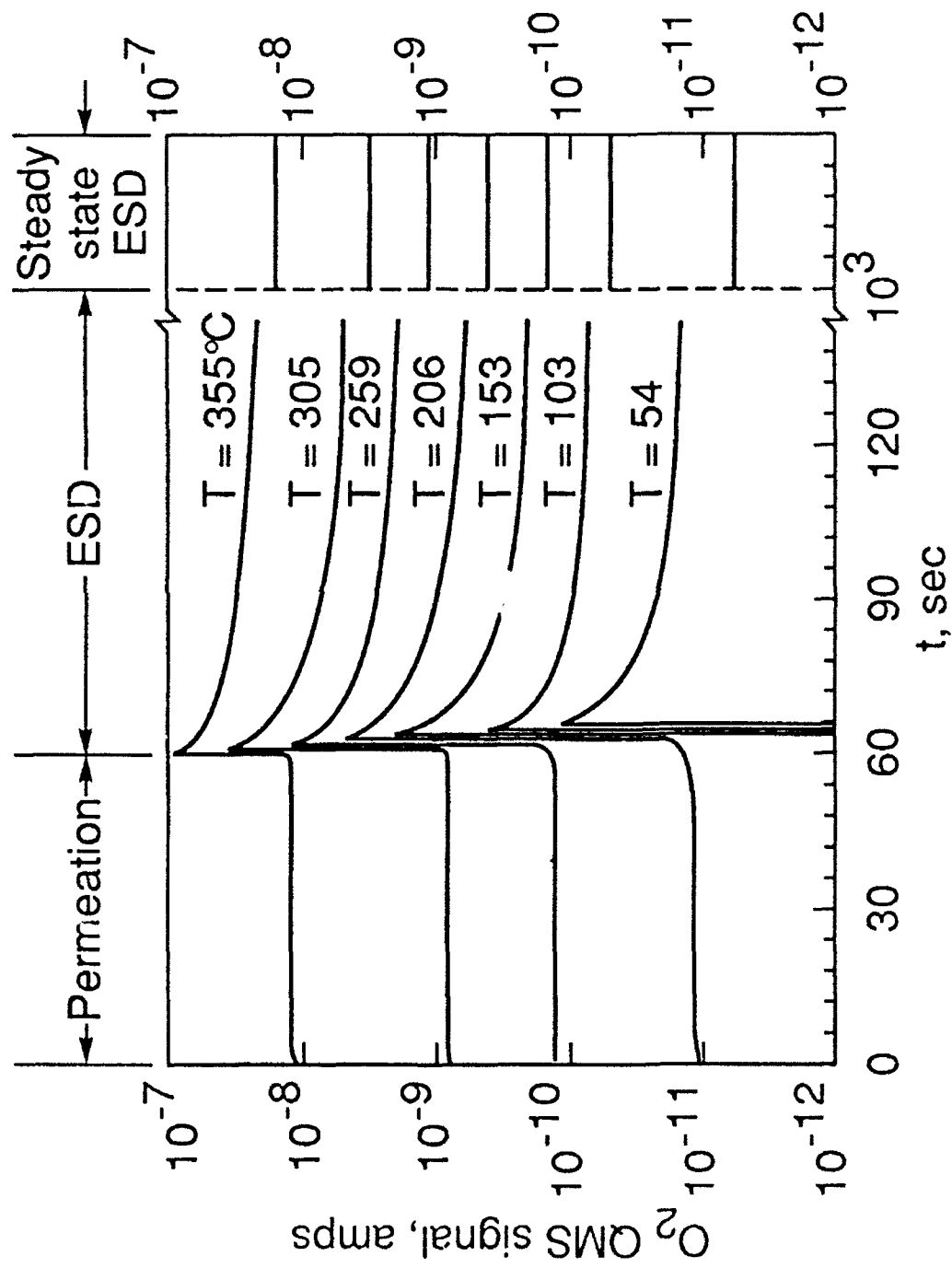


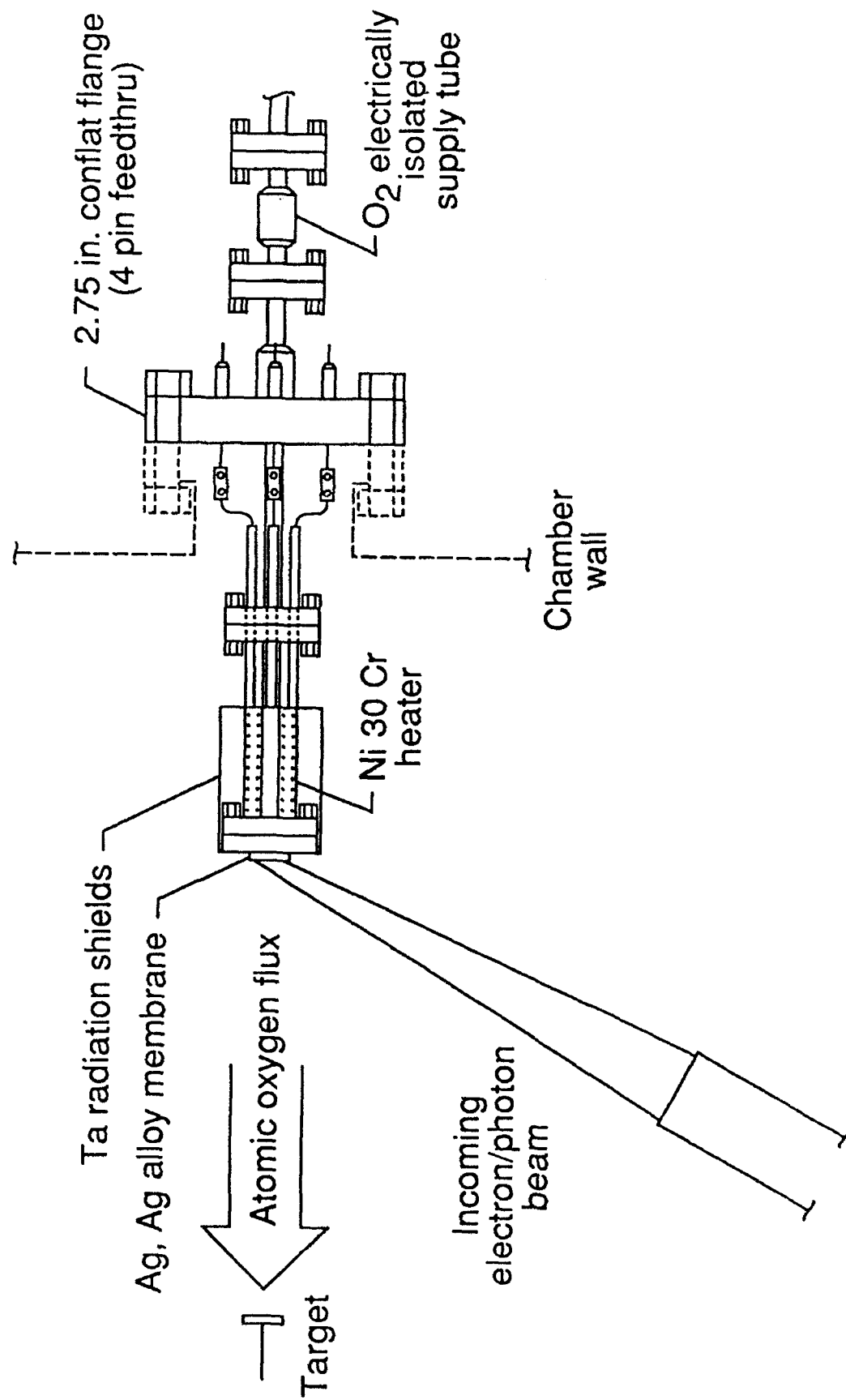




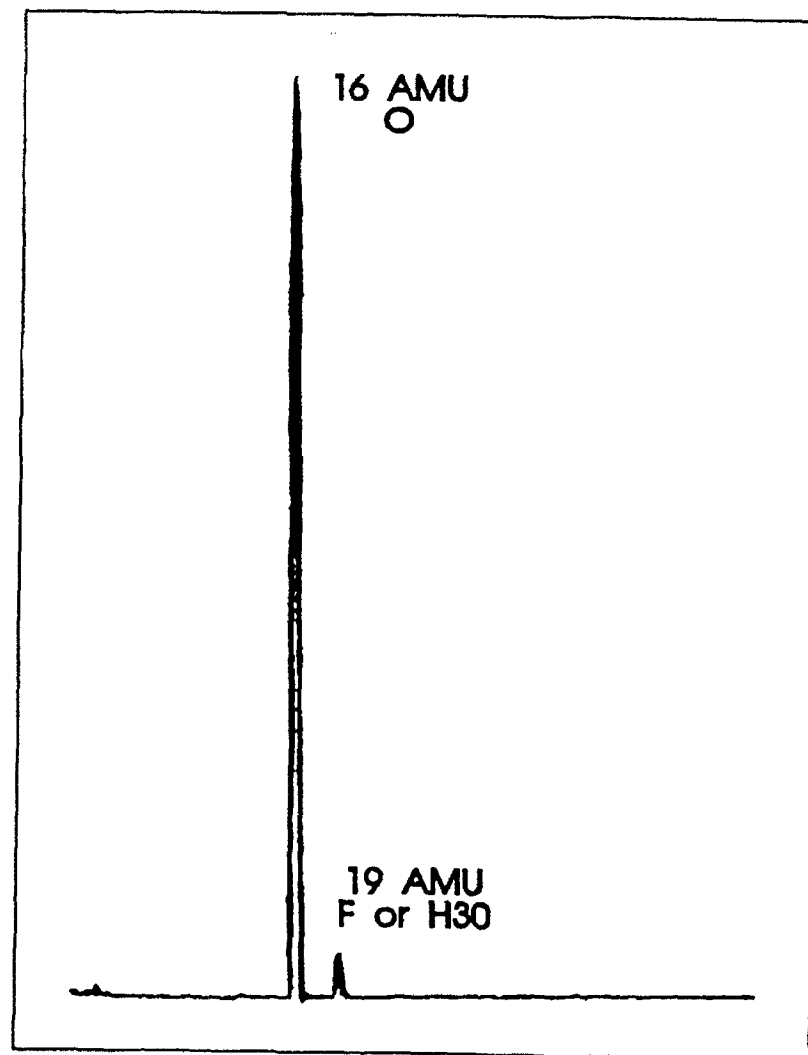








QMS Signal (arb. units)



Mass/Charge

F10

