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ABSTRACT

The impurity ions in an r.f. discharge have been directly extracted and then both energy and mass analysed. A variety of surfaces have been exposed to the plasma including borosilicate glass, alumina and carbon. In each case a large variety of species were produced initially, due to desorption of impurities from the surface. After some hours exposure to the plasma many of these species decayed away and relatively simple ion mass spectra were observed. The principal species with oxide surfaces were OH^+, OH_2^+ and OH_3^+ and the corresponding OD^+, OD_2^+, OD_3^+ in a deuterium plasma. Two other major impurities were mass 28 and 29. These are attributed to CO^+ and COH^+. When the carbon sample was exposed to the plasma the main species observed were CH_3^+, CH_4^+ and the series $C_2H_2^+$ to $C_2H_6^+$.

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INTRODUCTION

Processes leading to impurities in plasmas have become of great importance in the study of plasmas for thermonuclear fusion devices,as the energy loss by radiation increases rapidly with atomic number and therefore small concentrations of impurities can have a significant cooling effect.

The chemical interaction of hydrogen atoms and ions with insulator surfaces has been known for many years. In an early investigation of the reaction between hydrogen atoms and glass, Hickmott[1] showed that atomic hydrogen was much more reactive than molecular hydrogen. Various reactions result in the production of CO, CH_4 and H_2O. The production of H_2O by an r.f. discharge of H_2 in a pyrex bottle was demonstrated by Blauth and Meyer[2].

The interaction of hydrogen, both atomic and molecular, with carbon, has also been extensively investigated[3,4]. In most of the investigations however the analysis of the impurity has been indirect. Either simply the erosion rate has been measured or else the analysis of species produced has been done after collision with another surface. Since it is possible that radicals will be formed,an experiment has been carried out in which the species in the discharge have been directly extracted and analysed with a quadrupole mass spectrometer.

EXPERIMENT

The plasma used is that of a conventional r.f. ion source[5]. Hydrogen or deuterium flows into a borosilicate glass bottle via a palladium/silver leak. An r.f. discharge is formed by a coil 70mm long wound round the bottle which is connected to a self-excited oscillator operating at about 30 MHz. The total power dissipation is typically 100 watts. A sample of the ions in the discharge emerge through a canal 1mm diameter and 10mm long. The ion beam is electrostatically focussed, energy analysed using a conventional 90° cylindrical electrostatic analyser and then mass analysed with a quadrupole mass spectrometer. The experimental arrangement is shown schematically in Figure 1. Samples are introduced into the discharge tube before evacuating, but are initially kept out of the discharge. They are subsequently moved into the discharge by means of a small magnet attached to one end of the sample.

The gas flow from the discharge region into the main vacuum chamber is $\sim 10^{-3}$ t 1 s^{-1} and a pressure of about 2×10^{-5} torr of H_2 can be maintained in the chamber in the presence of the discharge. The system is pumped by a mercury diffusion pump, using a liquid nitrogen trap with a speed of 7.6 1 s^{-1} for nitrogen. Ultimate pressures in the range 5×10^{-8} torr are obtained after a bake to 100°C; metal gaskets are used throughout the vacuum system. The residual gas in the main chamber is analysed with a 180° magnetic mass spectrometer (V.G. Micromass II). Thus both the ion species in the discharge and the resultant stable neutral species can be analysed. In the following discussion the results from the quadrupole mass spectrometer will be referred to as the "ion spectra" and those from the magnetic mass spectrometer as the "gas spectra."

The ions can be extracted from the discharge at any energy depending on the potential applied to the extractor electrode A; but in general both the quadrupole mass analyser and the extractor have been operated at ground potential. With the extractor at ground potential the ions still emerge from the canal with an energy in the range 30-80eV due to the space charge sheath potential at the walls of the discharge tube. The ions of a given species are monoenergetic but this energy varies depending on the discharge conditions and is frequently significantly higher for the impurity ions than for the hydrogen ions. All ions above mass 12 are normally of the same energy and these are focussed by the lenses B, C and then deflected by the energy analyser into the mass spectrometer. The yield of ions is very dependent on the pressure in the discharge tube. This pressure can be inferred from the pressure in the main chamber and the known conductance between the two. Ion currents can be observed for pressures between

5×10^{-3} torr and 10^{-1} torr (H_2). However there is an optimum pressure for maximum ion current which is normally in the range 1 to 2×10^{-2} torr. The ion currents are also dependent on the power absorbed by the discharge. Thus the direct analysis of the ion species is a rather uncertain tool for quantitative analysis. The information which it provides is the type of species removed from the surface and the resultant radicals formed in the discharge in the presence of hydrogen. These should give an indication of the type of species present near the wall in larger plasma physics experiments.

RESULTS

(a) Glass discharge tube

Measurements were first made with a normal borosilicate glass tube (Corning 7740) 40mm in diameter. As is well known, when the glass tube is new an r.f. discharge can be induced without introducing any gas into the system. Gas desorbed from the surfaces is sufficient to produce a discharge. Part of this desorption is thermal as the temperature of the glass tube rises to about 150°C. Over a period of about an hour the wall concentration decreases and the discharge goes out. On introduction of hydrogen however the discharge is by no means pure and it is clear that further impurities are being desorbed from the wall. This is seen both from the ion spectra and from the colour of the discharge which starts a blue-white colour and only gradually changes to the deep magenta colour characteristic of a pure hydrogen discharge. Ion spectra observed at the start of the discharge in deuterium are shown in Figure 2a, and after 6 hours in Figure 2b. The principal impurity ion species in Figure 2b are masses 18, 20, 22 and 30, whereas at the start of the discharge many odd mass numbers are present as well. The latter are explained by the release of hydrogen from the walls both directly and in water molecules. The many gas phase as well as surface reactions such as ionisation, charge exchange, dissociation and isotopic exchange will lead to molecules and radicals of the type OH_nD_m and CH_nD_m. As the surfaces clean up only deuterated species resulting from reactions with the injected gas occur.

Possible interpretation of the simpler species in Figure 2b are given in Table 1. The COD_2^+, COD^+, OD_3^+ and CD_5^+ radicals are well known in other gas discharges as charged species[6,7] although they are of course not stable when neutral. A proposed reaction for the formation of CH_5^+[7] is $H_3^+ + CH_4 \rightarrow CH_5^+ + H_2$. Carbon species are expected because carbon is so universally present as an impurity in solids. The ambiguity between carbon and oxygen containing species is partially

removed when hydrogen is used rather than deuterium, as shown in Table 1. A spectrum using hydrogen is shown in Figure 3a and the presence of masses 18 and 19, corresponding unambigously to OH_2^+ and OH_3^+ indicate that oxygen species predominate. The cracking patterns are of course very different to those expected in conventional mass spectrometry because the electron temperature in the discharge is very low, probably $\lesssim$ 5eV.

The higher masses can be identified in a similar way. The predominant mass in the hydrogen spectra is 29 and in the deuterium spectra 30. These are attributed to COH^+ and COD^+. All these identifications are confirmed by the gas spectra obtained on the magnetic mass spectrometer, Figure 3b. In these spectra we expect only to see stable species and their conventional cracking patterns. The presence of masses 28 (CO), 17 and 18 (H_2O), 15 and 16 (CH_4) confirm the diagnosis of the ion spectra. The large proportion of CO is evidence that the identification of 29 and 30 as COH and COD is correct. In some glass samples larger amounts of hydrocarbons were detected and found to persist for considerable times. The spectra were similar to those observed for carbon, shown in Figure 5.

(b) Alumina

A sample of re-crystallised Purox alumina (99.5%) in the shape of a cylinder 34mm in diameter, 2mm thick and 60mm long was placed inside the glass tube at the end away from the r.f. discharge coil. The discharge was then run to clean up the pyrex tube until major surface impurities had been desorbed. The alumina sample was moved into the discharge region and both ion and gas spectra recorded as a function of time.

The yield recorded in both the ion spectra and the gas spectra were significantly lower than for glass particularly for the methane and water production, Figure 4. The small quantity of these impurities which are produced may be due to interaction of the plasma with the surface of glass visible to it through the end of the tube rather than with the alumina. Thus the present yields should be considered as an upper limit. The amount of CO produced is still substantial and it is by far the most important impurity peak in both gas and ion spectra (though it appears as COH^+ at mass 29 in the ion spectrum.) The deuterium discharge spectra are again similar with the major peaks in the gas spectrum being at 18, 20 and 28. The methane and water production are about equal, the CO about 5 times greater.

(c) Carbon

The carbon sample was a graphite cylinder 28mm in diameter, 50mm long and 2mm thick with a density of 1.72 gm cm^{-3}.

It was moved into the discharge after the pyrex tube had been discharge cleaned as before. Due to its low resistivity compared with glass some of the r.f. power was induced in the carbon and its temperature rose to about 400°C as measured with an infra red pyrometer. Ion spectra and neutral gas spectra were taken as a function of time. Results using a hydrogen discharge after 13 hours are shown in Figure 5. In both spectra it is clear that there are 3 major groups of ions. In the gas spectra mass 15 and 16 are identified as methane as before. The group of peaks for masses 25 to 30 are due to molecules containing 2 carbon atoms, C_2H to C_2H_6 (although the mass 28 could also be due to CO) and the group from 39 to 41 as molecules with 3 carbon atoms, C_3H_3 - C_3H_5. The middle group is clearly the most intense. In the ion spectra a similar general pattern holds although due to the factors noted before such as low electron energy and ion molecule reactions the spectra within the different groups are not the same. The ion species observed are very much the same as those observed by Smolinsky and Vasile[7] in an r.f. discharge in methane. The mass 18 and 19 shown in the ion spectra cannot be due to hydrocarbons, as indicated in Table I, and so must be due to H_2O^+ and H_3O^+. It is again possible that the small amount of oxygen containing molecules could be due to some plasma interaction with the pyrex tube surrounding the carbon sample, which is not completely shielded.

The spectra of the species occurring in the deuterium discharge show a good correlation with the hydrogen. The methane group now appears at 18 and 20 (CD_3^+ and CD_4^+), the two carbon group previously appearing at masses 25 to 29 now appear from 26 to 34 and the three carbon group previously appearing from 39 to 41 now appear at 42, 44 and 46. In the ion spectra we have all the same peaks as the gas spectra and an additional peak at mass 22 (CD_5^+). In general the impurity production in deuterium was a factor 1.5 to 2.0 higher for deuterium species than for hydrogen.

DISCUSSION

If we consider the discharges in deuterium at the start of a run many hydrogen containing species are present e.g. mass 17 (OH^+) and 19 (OHD^+, OH_3^+). After about 6 hours running all the odd numbered masses disappear, presumably due to the desorption of the adsorbed gas originally on the surface. If adsorbed gas species have been removed then it follows that the oxygen present in OD^+, OD_2^+, OD_3^+ etc is being removed from the glass itself by interaction with the deuterium atoms and ions. This picture is consistent with the results obtained by Hickmott[1] using hydrogen atoms dissociated at a tungsten surface, and by Blauth and Meyer[2] using an r.f. discharge. A further indication that the interaction is a chemical one was that no water species were observed during

a discharge in helium. The lower yield of water production in alumina compared with glass can probably be explained in terms of the much higher heat of formation of the Al_2O_3 compared with the binding energy of oxygen in glass.

Large quantities of CO are observed in the gas spectra, with COH^+ and COD^+ in the ion spectra. These species are very often the most abundant impurity observed. Carbon monoxide was also observed by Hickmott using atomic hydrogen and explained as being due to the water cycle first proposed by Langmuir[8]. Atomic hydrogen interacts with glass to form water. The water is subsequently dissociated and the resultant radical O or OH reacts with impurity carbon atoms at the surface to form CO. In the present experiment it is also possible that ion or electron desorption could contribute to the production of CO as both mechanisms are known to have large cross sections for desorption[9,10]. In either case the presence of COH^+ and COD^+ in the ion spectra can be explained as gas phase collisions between CO and hydrogen.

The hydrocarbon species observed with all three samples CH_n, C_2H_n and C_3H_n all occur both as hydrogenated and deuterated series and therefore must be formed by the interaction of the ions or atoms in the plasma with carbon atoms in the surface. These reactions have recently been observed with atomic hydrogen beams,[11] ion beams[12,13] and in many earlier investigations using hydrogen discharges. The present experiments indicate the production of hydrocarbons when carbon is present only as an impurity on the surface (in the case of glass and alumina) as well as when using bulk carbon. In the case of glass the initial production rate was high but it decayed with time indicating that the carbon concentration on the surface was depleted.

The absolute yield of impurities as measured by the partial pressure in the main chamber using the gas spectrum is in the range 0.1 to 1.0% of the gas throughput of hydrogen. The integrated yield over 10 hours is of the order of 10^{16} molecules/cm^2. With the exception of the CO peak which normally decays by a factor of about 3 during a period of 10 hours, the yield from the other species is relatively constant.

The chief contribution of the present experiments is the direct analysis of the ions in the discharge. This gives a qualitative guide to the impurity ions existing in the low temperature region at the edge of a plasma. The fact that the impurities such as carbon and oxygen exist initially in hydrogenated molecules and that there is a relatively large fraction as ions such as OH_3^+ and CH_5^+ gives a starting point for the analysis of the atomic physics processes in the boundary layer.

The fact that the hydrocarbon and water molecules are produced in these materials indicates that these surface processes are a general phenomena. Preliminary results with electrical porcelain, silica and stainless steel have shown similar impurity species to be produced. In the case of the stainless steel both methane and water vapour production was comparable with glass. It must be due to reaction of hydrogen with impurities on the surface. Thus the yield of impurities will be expected to reduce with discharge cleaning, as is observed in many plasma confinement experiments.

No attempt has been made in the present experiments to measure the temperature dependence of these reactions. It has been shown previously[11,12,13] that the methane production rate from carbon has a maximum at a temperature of ∿ 900K. There have been no investigations into the temperature dependence of water formation. Some data on this would be valuable.

CONCLUSIONS

Chemical reactions between hydrogen atoms, ions and surfaces appears to be a general phenomenon leading to impurities in plasmas even at very low plasma temperatures. Four major species, methane, water, acetylene and carbon monoxide have been observed. Small quantities of carbon dioxide and higher hydrocarbons were also seen. The principal impurity in the case of glass was water, for alumina it was CO, and for carbon it was hydrocarbons. Although the absolute yields were rather irreproducible it appeared that the impurity yield for alumina was significantly lower than for pyrex glass, by a factor in the range 3 to 5. Carbon was slightly better than glass but as discussed above the carbon yield is very temperature dependent.

The presence of CO as the major impurity is consistent with previous data on the hydrogen atom reactions with glass, and with ion and electron stimulated desorption. From the present results it would be expected to be a major impurity at the boundary of a plasma.

The results illustrate that impurities are produced in significant quantities not only from bulk carbon and oxides but also from carbon and oxygen impurities on the surface of the bulk material exposed to the plasma. The results are consistent with the mass spectrometric observation of both CH_4 and CO production during a plasma pulse in Tokamak discharges. The importance of obtaining low impurity concentrations in metals is thus emphasised. It is well known to operators of plasma physics devices that discharge cleaning is effective

in reducing impurities. The present experiments together with recently reported data on the temperature dependence for chemical interactions indicate that there may be an optimum surface temperature for this cleaning process.

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TABLE I

Identification of ion spectra

Hydrogen species		Mass	Deuterium species	
	C^+	12		
	CH^+	13		
	CH_2^+	14		
	CH_3^+	15		
O^+	CH_4^+	16	CD_2^+	O^+
OH^+	CH_5^+	17		
OH_2^+		18	CD_3^+	OD^+
OH_3^+		19		
		20	CD_4^+	OD_2^+
		21		
		22	CD_5^+	OD_3^+
		23		
		24		
	C_2H^+	25		
	$C_2H_2^+$	26	C_2D^+	
	$C_2H_3^+$	27		
CO^+	$C_2H_4^+$	28	$C_2D_2^+$	CO^+
COH^+	$C_2H_5^+$	29		
COH_2^+	$C_2H_6^+$	30	$C_2D_3^+$	COD^+
		31		
		32	$C_2D_4^+$	COD_2^+
		33		
		34	$C_2D_5^+$	
		35		
		36	$C_2D_6^+$	

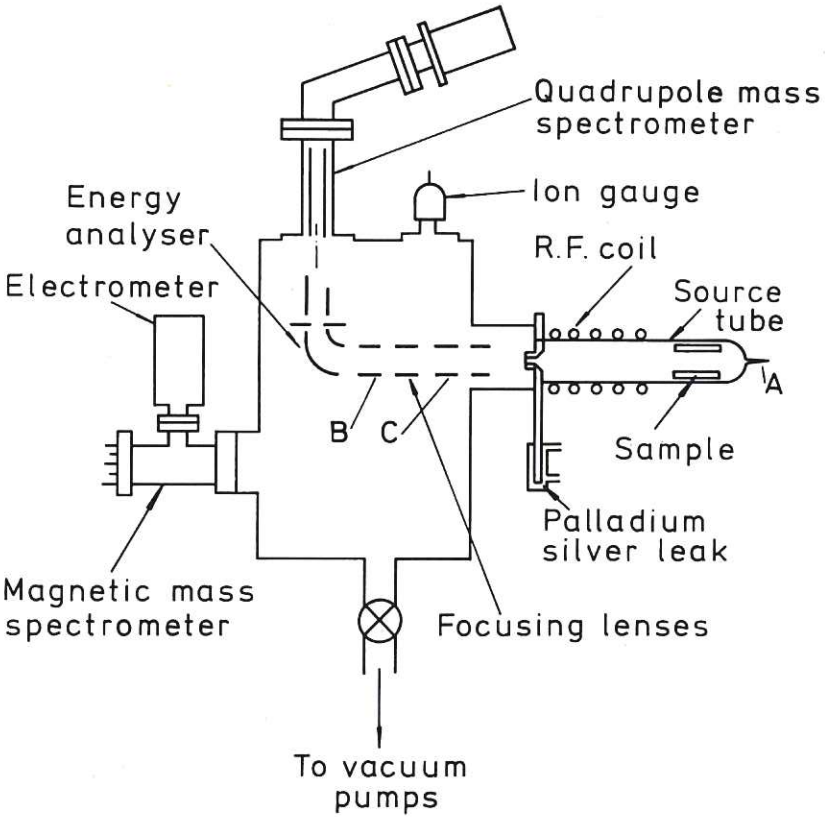

Fig.1 Schematic diagram of experiment.

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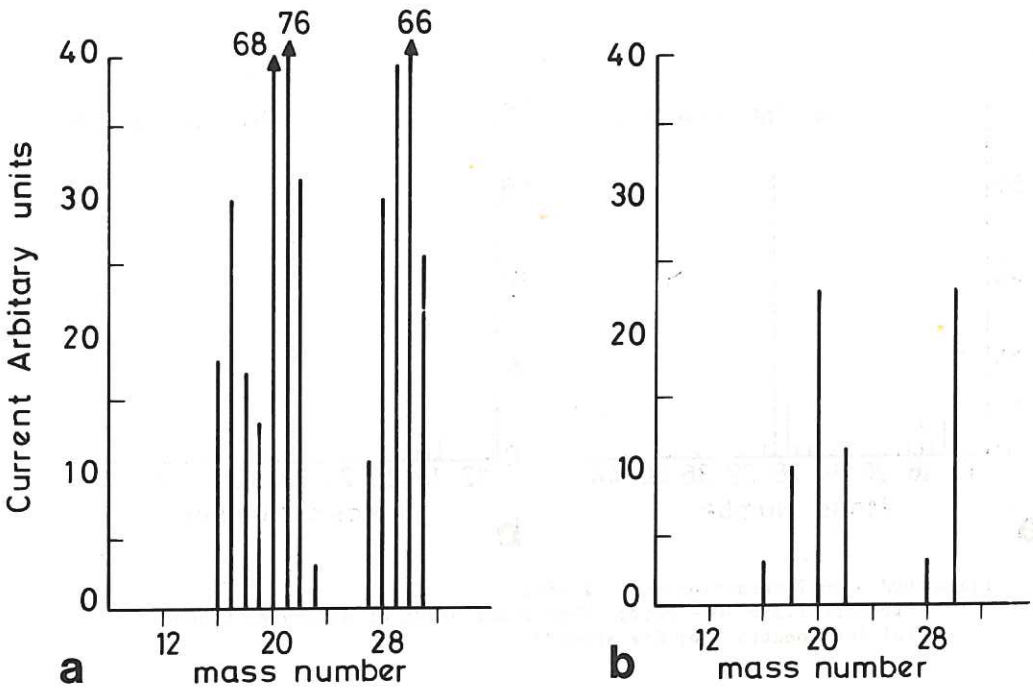

Fig.2 Deuterium interaction with borosilicate glass
Source pressure 2.1 x 10^{-2} torr; Ion spectra
(a) ½ hour after start of discharge
(b) 6 hours after start of discharge

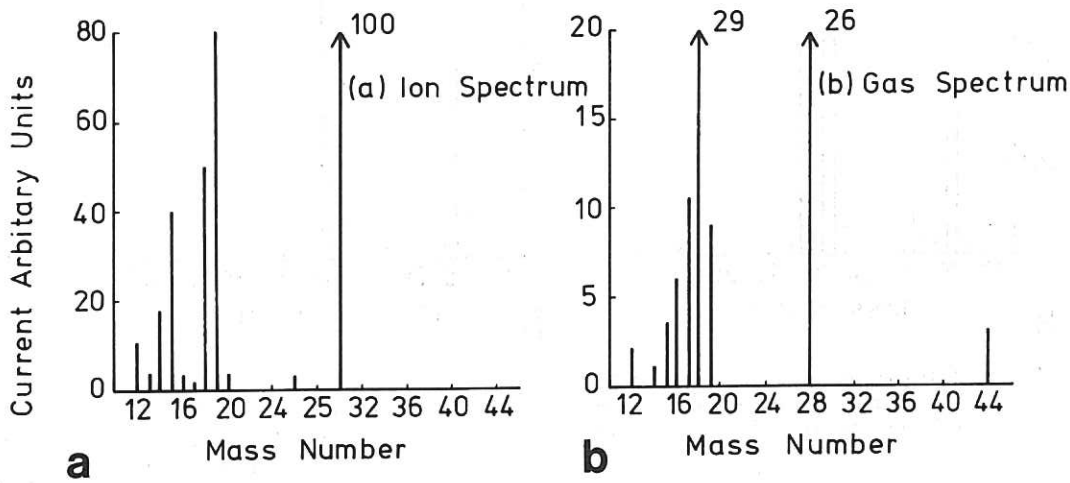

Fig.3 Hydrogen interaction with borosilicate glass
Pressure 2.1 x 10^{-2} torr; Time after start of discharge 9 hours
(a) Ion spectra (b) Gas spectra

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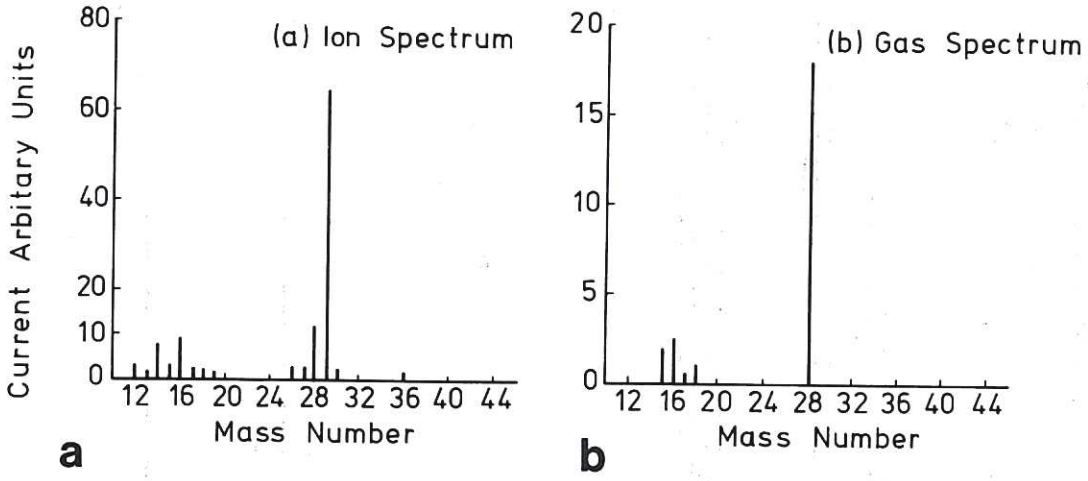

Fig.4 Hydrogen interaction with alumina
Pressure 1.5 x 10^{-2} torr; Time after start of discharge 9 hours
(a) Ion spectra (b) Gas spectra

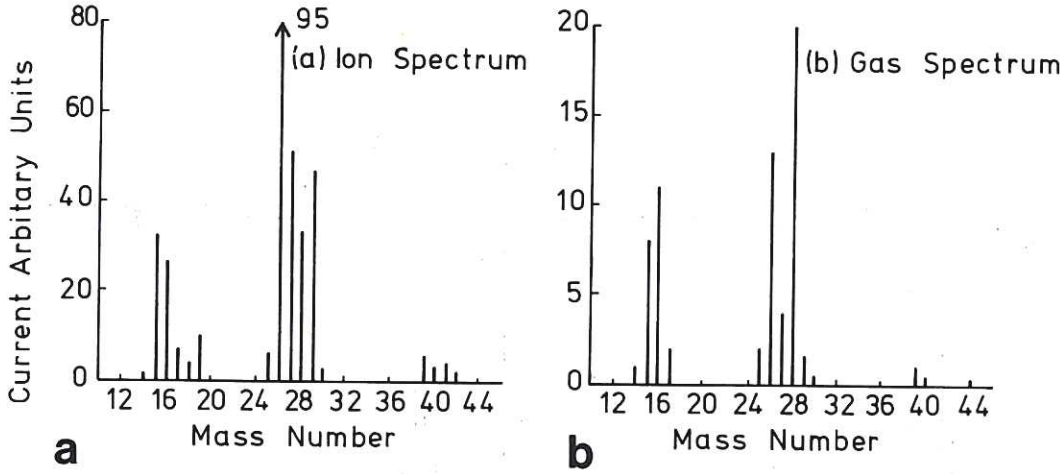

Fig.5 Hydrogen interaction with carbon
Pressure 2.1 x 10^{-2} torr; Time after start of discharge 13 hours
(a) Ion spectra (b) Gas spectra

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