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ALUMINO-SILICATE ALKALI ION SOURCES :
COMPATIBILITY WITH ULTRAHIGH VACUUM AND APPLICATION
TO THE ISR PRESSURE - SURFACE PROBLEMS

by

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Introduction

The emission of positive ions from heated bodies is a comparatively well known phenomena, discussed as long ago as 1916 by O.W. Richardson in his text "The emission of electricity from hot bodies". Sources of positive ions based on this idea were investigated by many experimentalists in the first half of the present century and amongst the more significant contributions is the work of Blewett and Jones (1936). These authors established as the most copious source, a source of ions of the alkali metals produced by heating synthetic alkali alumino-silicate of β -eucryptite form. This compound $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, taking the case of lithium alumino silicate, has basically a silica structure in which during formation a certain proportion of the Si^{4+} ions are replaced by Al^{3+} ions. The electric field caused by the deficiency of positive charge is locally neutralised by the addition of alkali ions. These ions can be quite mobile within the structure, which provides a key to the mechanism of thermionic ion emission (Johnsen 1962).

Alkali ion sources of this kind have found many applications in gas discharge studies, in particular as ion sources in experiments of the drift and diffusion of low energy ions in gases (Crompton and Elford 1959, Davies, Dutton, Llewellyn-Jones and Williams 1966). Under the conditions of these experiments the sources operate typically at a dull red heat and emit a few micro-ampère of ion current which can be sustained over many hundreds of hours of operation.

Our interest in these ion sources was motivated by the importance of phenomena of ion bombardment with respect to the operation of the ISR (see Jones, Jones and Williams 1973 and references therein), with the desire to develop a facility to simulate the process of ion bombardment of surfaces at base pressures $\approx 10^{-11}$ torr. The difficulties of utilising a gas discharge ion source in conditions of UHV are clearly apparent. An alumino silicate source could offer a far simpler alternative; however, a key question remained as to the compatibility of the source with UHV. For this reason we set out to manufacture an alumino silicate ion source and to investigate its operation at pressures $< 10^{-10}$ torr. One may

note that the level of emission of ion current of interest in applications as a surface monitor for the ISR should be $\approx 10^{-9}$ A - at this value of current the bombardment of surfaces, under typical conditions, would give rise to pressure increments $> 10^{-12}$ torr, while ≈ 30 h of continuous operation would be necessary to form a monolayer of alkali metal at the surface. Such layers can be removed by bakeout at 300°C if necessary. The vapour pressure of Li at 300°C is $\sim 10^{-6}$ torr, while at 20°C it reduces to $\sim 10^{-14}$ torr.

Construction and testing of the source

We set out to manufacture a lithium aluminosilicate ion source by heating a mixture of lithium carbonate, aluminum nitrate and powdered quartz in the proportion 2.50 : 7.36 : 2.00 by weight. The fusion temperature of around 1400°C was attained by heating the mixture in a carbon crucible with an oxy-acetylene flame. It may be stressed that the conditions of manufacture were quite non-clinical with no special precautions being taken to safeguard a high level of purity. The chemicals used in manufacture were of reagent grade.

The aluminosilicate was formed as a vitreous bead which, on cooling, was ground to a fine powder and made into a paste by mixing with a few drops of distilled water. The paste was subsequently coated on to a tungsten helix filament, 8 mm long and 2 mm diameter formed of wire of diameter 0.2 mm. By again heating the assembly to the fusion temperature of the silicate a bead was formed around the tungsten wire. After this formation process the source was mounted in a rough vacuum (pressure $\approx 10^{-6}$ torr) and heated to around 800°C by resistive heating of the tungsten helix. The object at this stage was, firstly, to remove any gross contamination, and, secondly, to provide some preliminary ageing of the source. It was observed that currents \approx micro-ampère of positive ions could readily be drawn from the source. Thereafter use was made of two vacuum systems for assessing the performance of the source.

In the first system (system A) the pump unit was a 70 l s^{-1} turbomolecular pump with the source unit contained in a 38 mm diameter standard vacuum T-piece; the pumping speed at the source was some 43 l s^{-1} . The system

was provided with normal facilities for total and partial pressure analysis. The source was mounted some 8 mm distant from an anode with facilities for biasing either the source or the anode to any given potential. After bakeout at 300°C the limit pressure obtained in this system was 4×10^{-10} torr.

In the second and more sophisticated system (system B) pumping was supplemented by a 400 l s^{-1} ion pump and a titanium sublimation pump. The source was contained in a chamber of 70 l volume which was connected to the pump station via a moveable vane. In the closed position the vane provided a defined pumping speed of 27 l s^{-1} at the source, while in the open position the pumping speed was $\approx 300 \text{ l s}^{-1}$. During bakeout the vane was maintained in the open position and enabled an ultimate pressure of 2.8×10^{-11} torr to be attained in the chamber. With subsequent closure of the vane the pressure increased to around 5.8×10^{-11} torr. As with system A, the partial constituents of the residual gas could be examined - in particular in this case the analyser was arranged in direct line of sight with the ion source. A series of anodes were incorporated in the source chamber and the current from the source could be drawn to any anode by suitable biasing of potentials. The experience in operating the ion source in these two systems is summarised as follows :

i) with the attainment of low pressures in the above systems the initial heating of the source (not previously activated since exposure to room air) was found to give rise to a gas load which decreased with time of operation. The policy we followed was to increase gradually the power input to the source while maintaining the total pressure $< 10^{-9}$ torr. In this way the power input was increased to a final level of around 10 watts while the pressure decreased to $\approx 10^{-11}$ torr. For production of nano-ampères of positive ion current (extractor voltage ≈ 1 kV) the power input requirement was some 7 watts. At this power level no radiation was visible from the source; moreover the pressure difference between source-filament on and off fell to $< 10^{-12}$ torr, corresponding to a degassing rate of $\approx 10^{-11}$ torr l s^{-1} . This examination was carried out with the source biased 200 V negative and all other parts of the

system at ground potential - in this way no ions were emitted and the pressure difference was due entirely to the degassing of the source. We adopted in general the scheme whereby with the completion of the degassing programme the bias of - 200 V was permanently maintained, as was the normal input power to the source. For extraction of ion current, the source was switched to ground potential and a negative potential applied to the anode/collector electrode.

- ii) With the facilities of partial pressure determination available the opportunity was taken to examine the neutral gas produced from the source. Figure 1 shows the spectrum of gases during the action of degassing the source, while Figure 2 shows the analysis of residual gas carried out at a pressure 3×10^{-11} torr and with the source in direct line of sight with the ionisation cell of the gas analyser. The result of Figure 2 is typical of a "residual gas analysis" spectrum with a stainless steel system at low pressure. Figure 1 shows that the gases desorbed from the source are carbon, oxygen and hydrogen in the commonly occurring molecular forms.
- iii) By suitable biasing of the ion source with respect to the gas analyser it was possible to mass analyse the ions emitted from the source. Tests carried out in this way showed, rather surprisingly, the predominant species of emitted ion to be potassium K^+ ions, amounting to > 99% of the total of emitted ions. This result is attributed to the lack of purity of the constituents of the source, moreover, Elford (1962) has demonstrated the preferential emission of K^+ ions at low input power. Similar difficulties have been noted by other users of alumino-silicate ion sources (Davies 1962, Weber and Cordes 1966). Thus although we set out to produce a lithium ion source, because its mass is nearer to that of the hydrogen molecules predominantly found in stainless steel vacuum systems, the potassium source actually produced and used was just as useful for our purposes. The vapour pressure of solid potassium at $300^{\circ}C$ is 3×10^{-1} torr while at $20^{\circ}C$ it is 2×10^{-8} torr. Thus it should be easier to remove by bakeout but can also contribute to the residual gas pressure if enough of it is deposited on the stainless steel surface.

In all of the experiments described herein the potassium ion source was used. However, later attempts to produce a lithium source have succeeded. The major source of the potassium impurity was eventually traced to the tungsten filament. It appears that the production of tungsten filaments involves a considerable amount of treatment with potassium salts. The potassium can be expelled from the tungsten by simply degassing in a vacuum before attempting to fuse together the alumino-silicate bead to the filament.

The "purity" of the lithium source was examined by mounting the ion source in place of the usual ion-gun of a residual gas analyser. In this way, and after degassing the source for two hours in vacua at a power of about 30% in excess of the operating power level (≈ 6 watts), one finds that the ions emitted consist of about 99% Li^+ and the other 1% about equally divided between Na^+ and K^+ ions. In fact the major impurity at the beginning of the degassing cycle is more likely to be Na than K as long as the tungsten filament was properly degassed to start with. Work is continuing on the Li source in order to examine its sensitivity to contamination by exposure to air and to prolonged operation in stainless steel and titanium vacuum chambers.

Application to surface investigation

The above considerations establish the suitability of the source as a generator of nano-ampères of K^+ ion current at pressures 10^{-10} torr. Results of application of the source to the determination of ion desorption efficiency η (i.e. the ratio of neutral gas particles desorbed to incident ions) are illustrated in Figure 3. The figure illustrates determinations of η performed simultaneously with three different anode samples and carried out at three different pressures during the course of evacuation of the source chamber.

The measurements were made in system B with a pumping speed at the source chamber of 27 l s^{-1} (i.e. vane in closed position). The anode materials were stainless steel and titanium (samples A and B). The stainless steel sample was not subject to any special preparatory treatment other than

degreasing and rinsing with alcohol. Both samples of titanium, on the other hand, were pretreated by baking at 700°C; sample A was incorporated into vacuum within a day of completion of the heat treatment, while sample B was left in room air for some 10 days prior to insertion in the vacuum system. Furthermore, sample A was consequently subjected to two bakeouts at 300°C while sample B was only subjected to one such bakeout.

The values of η were calculated from observations of the pressure increase accompanying the process of ion desorption according to

$$\frac{\eta I^+}{e} = \frac{\Delta p S}{a},$$

where e is the electronic charge,

I^+ is the ion current ($\approx 10^{-9}$ A)

Δp is the pressure increment

S is the pumping speed (27 l s^{-1}), and

a is a constant to interconvert torr litres and number of molecules.

Since each potassium ion is expected to "stick" to the bombarded surface and was not initially a constituent of the residual gas pressure, the value of η measured in this way is expected to be larger by an amount equal to unity than that value of η_{ISR} measured in the usual way at the ISR. In the latter each ion of H_2^+ which bombards (and presumably "sticks" to) the surface is thought to be removed from the residual gas pressure. Thus values of $(\eta-1)$ measured herein are thought to be equal to the values of η_{ISR} . This is borne out by the fact that "clean" titanium has values of $\eta-1 < 1$ and should therefore exhibit a pumping action in the ISR - as is found to be the case!

The ion current used was 5×10^{-9} A, and the pressure increments recorded were in the range $1 - 5 \times 10^{-11}$ torr. (The pressure increments as well as the pumping speed are expressed in nitrogen equivalents). The differences between the values of η for the three samples are quite evident as is the difference in behaviour amongst the samples of the dependence of η upon ion energy. Of particular concern to the ISR project is the strong dependence of η on ion energy for stainless steel.

A further very interesting aspect of utilisation of the source is with regard to what might be termed as "ion stimulated surface gas analysis" (ISSGA?). This is a technique in which one may use the source in conjunction with a partial pressure analyser to determine the composition of gases adsorbed at the surface. Essentially, a comparison is made of the gas spectrum both with and without ion bombardment. Figure 4 illustrates measurements obtained in this way with the stainless steel specimen at a pressure of 3×10^{-11} torr (system B - 300 l s^{-1} pumping speed at the source chamber). Figure 4 (a) shows the increase in the H_2 partial pressure accompanying bombardment while from a comparison of the two traces of Figure 4 (b) the increase in masses such as 44 (CO_2), 28 (CO), 26 (C_2H_2), etc. can be seen. In this way a spectrum of the surface gas can be obtained and in Figure 5 we illustrate the surface gas composition (i.e. the increase in pressures obtained upon ion bombardment of the surfaces) of stainless steel and of titanium at a base pressure of 3×10^{-11} torr. In Figure 5 we have not "corrected" for ionisation properties etc. but simply given the percentage as measured by the individual currents corresponding to the different masses. This method of analysis of surface gas could prove to be a very useful technique in the general field of surface research.

It should be noted also, that by examining the changes occurring in the gas phase components, the heavier masses, 44 CO_2 , 28 CO and 26 (?) desorb heavily whilst the lighter masses do not increase by more than a factor of two (see Figure 6).

The appearance of mass 26 is difficult to interpret but could be C_2H_2 (acetylene). It must be remembered that the source was produced by heating in an oxyacetylene flame; however, if one refers to Figure 2, mass 26 does not appear to be desorbing from the source and only appears when ions are emitted and the samples being bombarded.

Conclusions and discussion

Our findings with regard to the operation and application of alumino-silicate alkali ion sources illustrate :

- i) the suitability of the source as a generator of nano-ampères of positive ion current at pressures $\approx 10^{-11}$ torr, and
- ii) the usefulness of the source in determinations of ion desorption efficiency and in examining the composition of ad-layers. There remains further work to exploit fully the capabilities of the source, and to control the purity of the constituents of the source should a source of lighter Li^+ ions be desired.

Our conclusions on the low level of neutral emission from the source are corroborated by the findings of Weber and Cordes (1966) who investigated the operation of a number of alkali alumino-silicate ion sources at pressures $\approx 10^{-10}$ torr with ion emission in the micro-ampère range. On the other hand, Septier and Leal (1964) claim that in operating a lithium ion source at emission currents $>$ milli-ampères a significant portion of lithium (estimated as $< 50\%$) is emitted in the form of neutral vapour. This finding is most probably associated with the relatively high input power (600 W, source temperature $\approx 1300^\circ\text{C}$) employed by these workers in an endeavour to generate some tens of milli-ampères of Li^+ ion current.

Further support for our findings is found in the recent investigations of Tracy (1972) into the preparation of clean nickel surfaces. Traditionally, the problem of generating clean sample surfaces in surface research has been approached by ion bombardment, using inert gas ions, and by heating in oxygen to remove carbon impurities. Neither of these methods proved to be satisfactory in the case of Tracy's experiment, and as an alternative he employed heat treatment in oxygen combined with bombardment by a micro-ampère current of K^+ ions from an alumino-silicate ion source. The nickel surface generated in this way was found to be virtually free of impurities, as judged by in situ Auger analysis.

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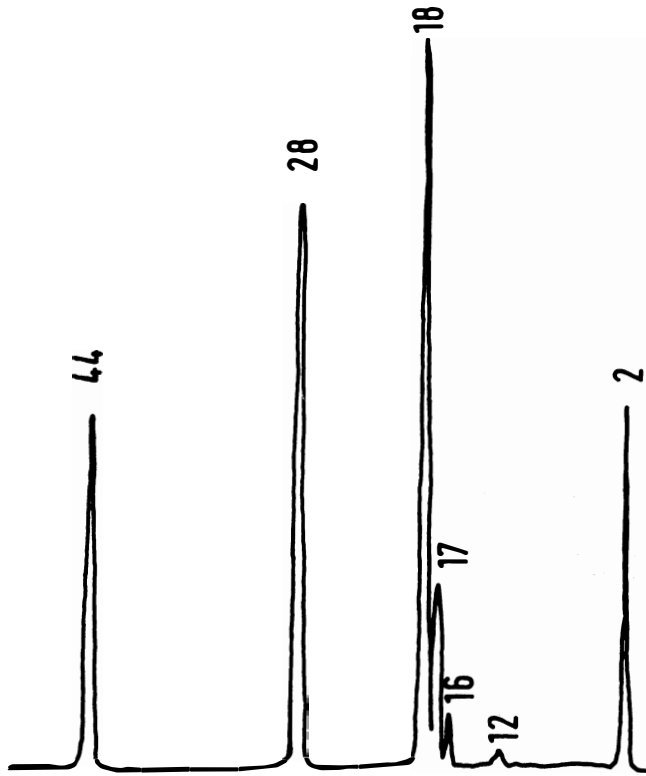


Fig.1. Spectrum of gas load, total pressure $\sim 10^{-9}$ torr, produced in the process of initial degassing of the source. Source biased — 200 V to suppress ion emission.

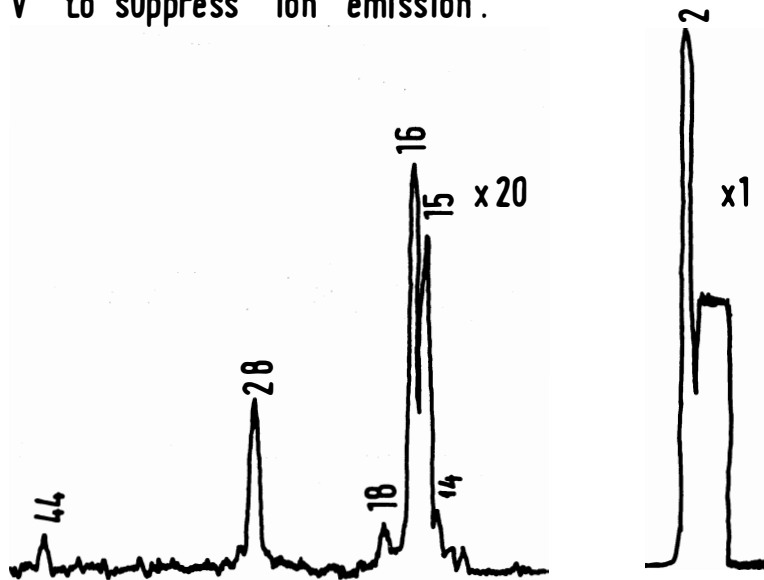


Fig.2. Spectrum of residual gas at total pressure of 3×10^{-11} torr with normal heating power applied to source, but biased — 200 V to suppress ion emission.

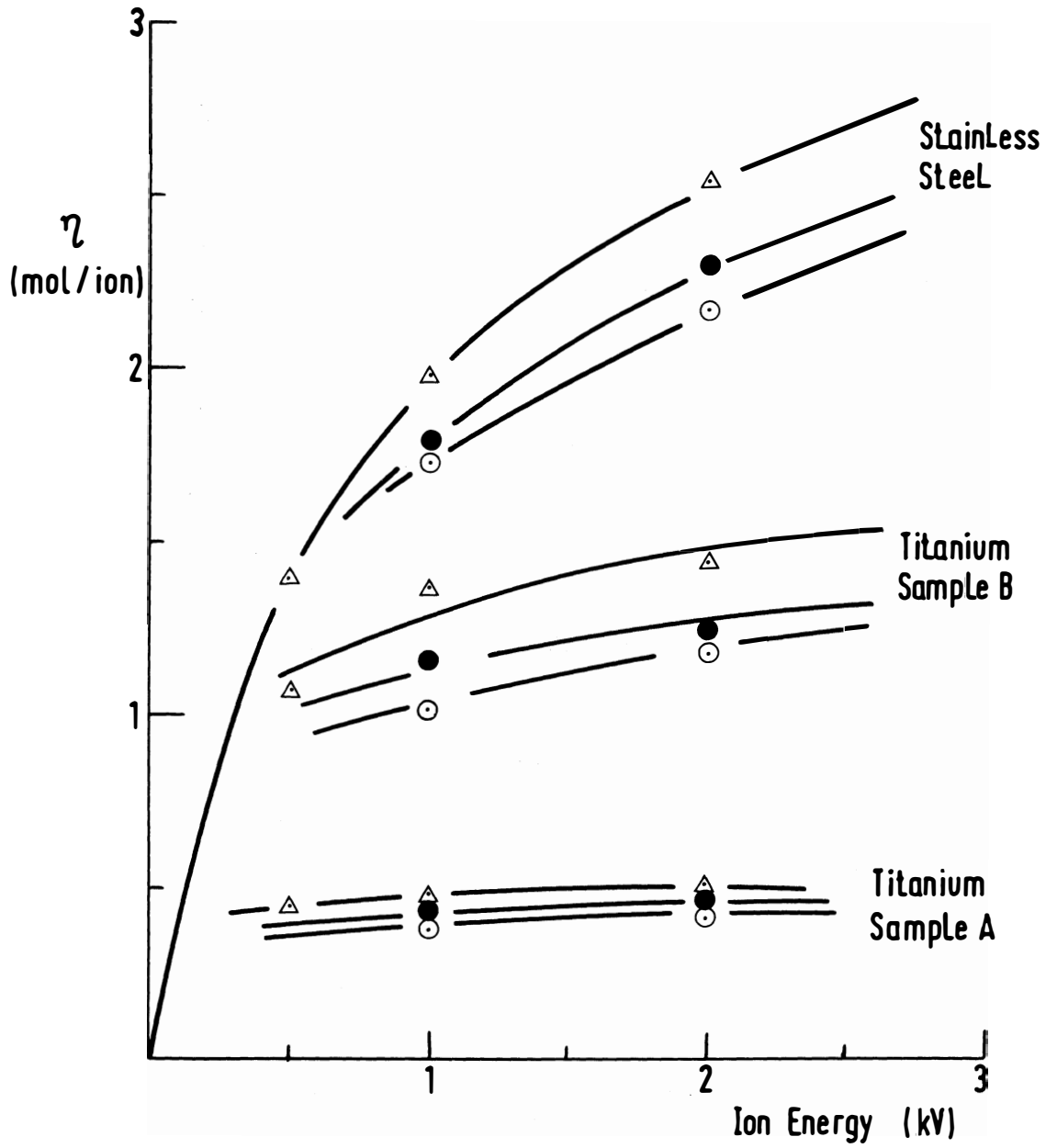


Fig.3. Measurements of ion desorption efficiency η
 Δ - 1.1×10^{-10} torr ; \bullet - 7.7×10^{-11} torr ; \odot - 5.8×10^{-11} torr

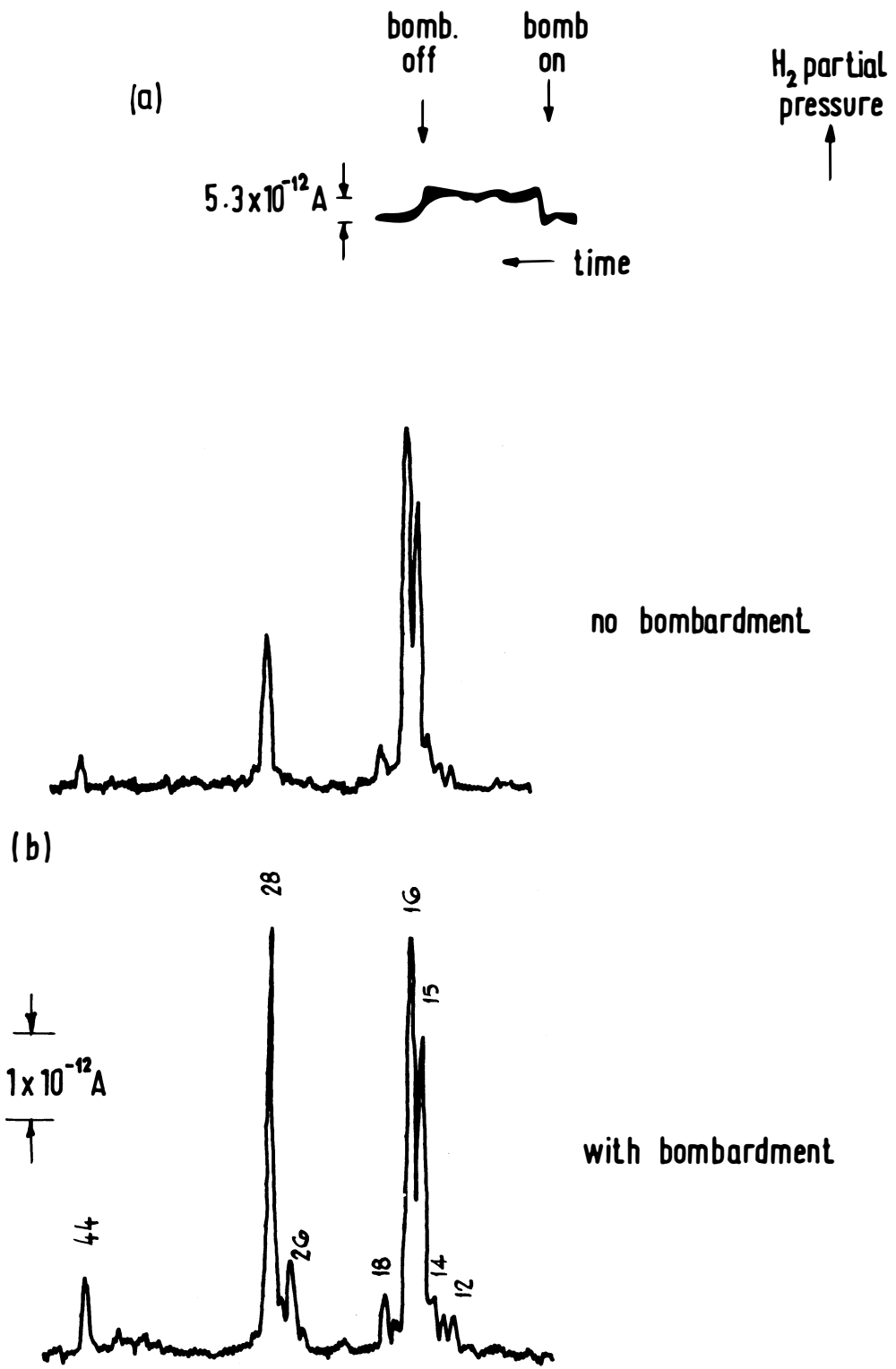


Fig.4. Ion stimulated surface gas analysis. Pressure 3×10^{-11} torr
 (a) Trace of H_2 partial pressure with intermittent bombardment.
 (b) Spectrum of masses >2 with and without bombardment.
 (identical sensitivity)

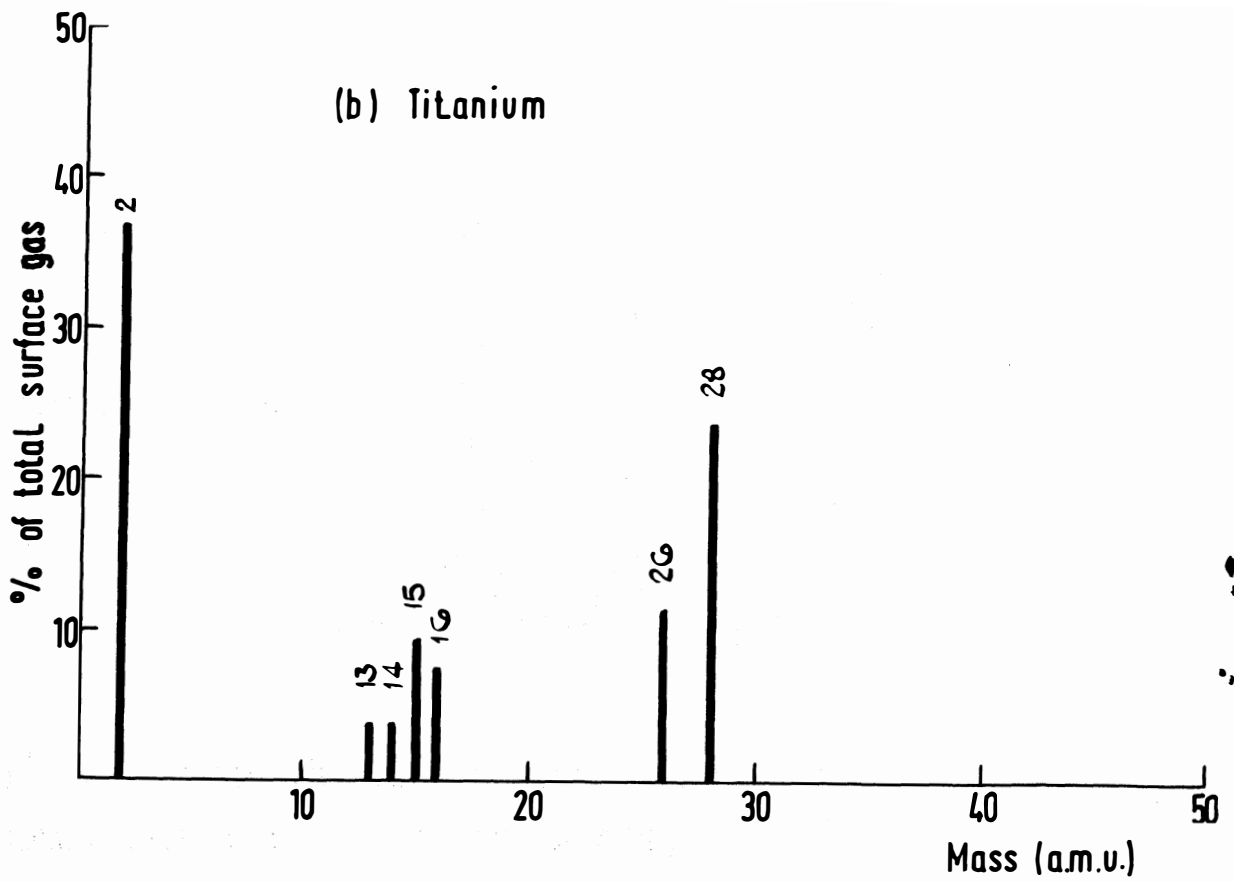
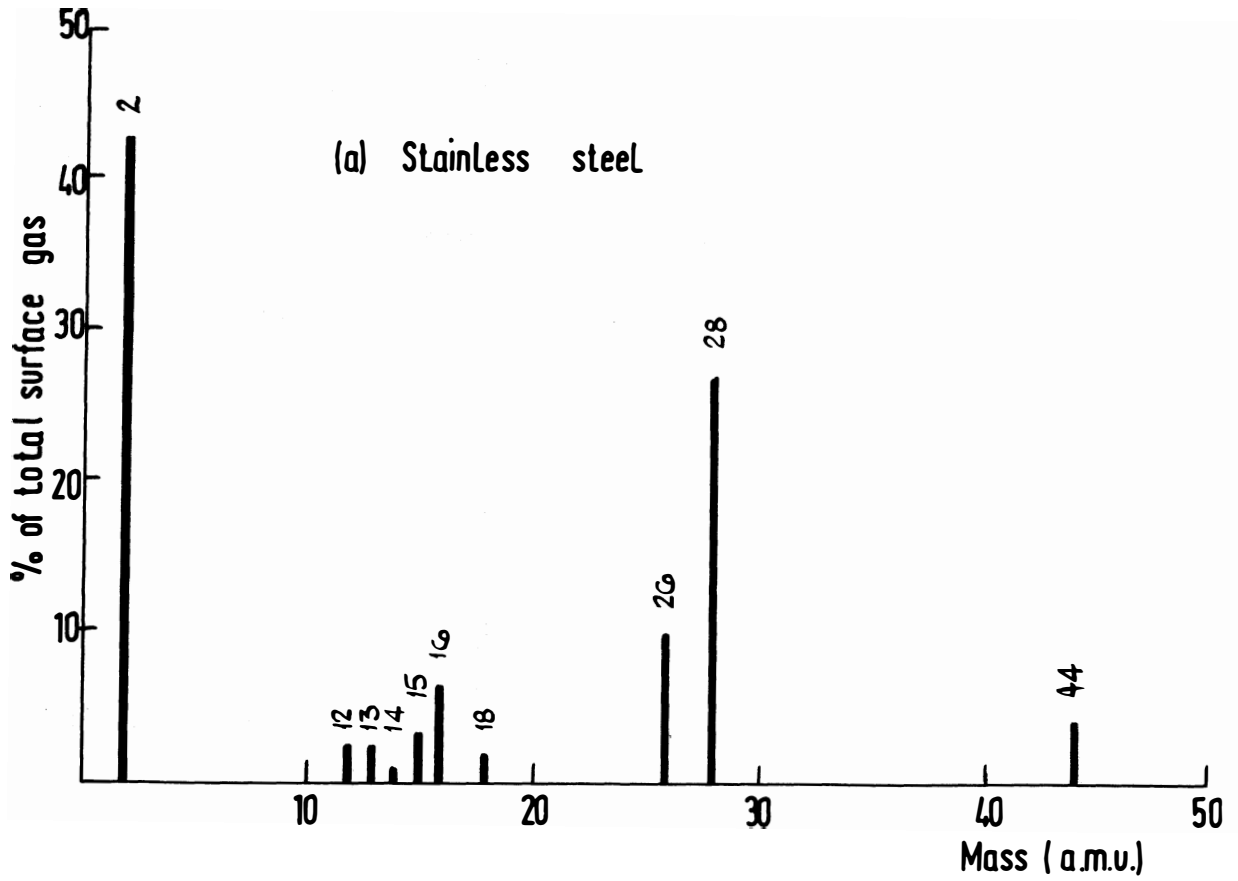


Fig. 5. The composition of surface gas at total pressure of 3×10^{-11} torr with (a) stainless steel and (b) titanium surfaces.

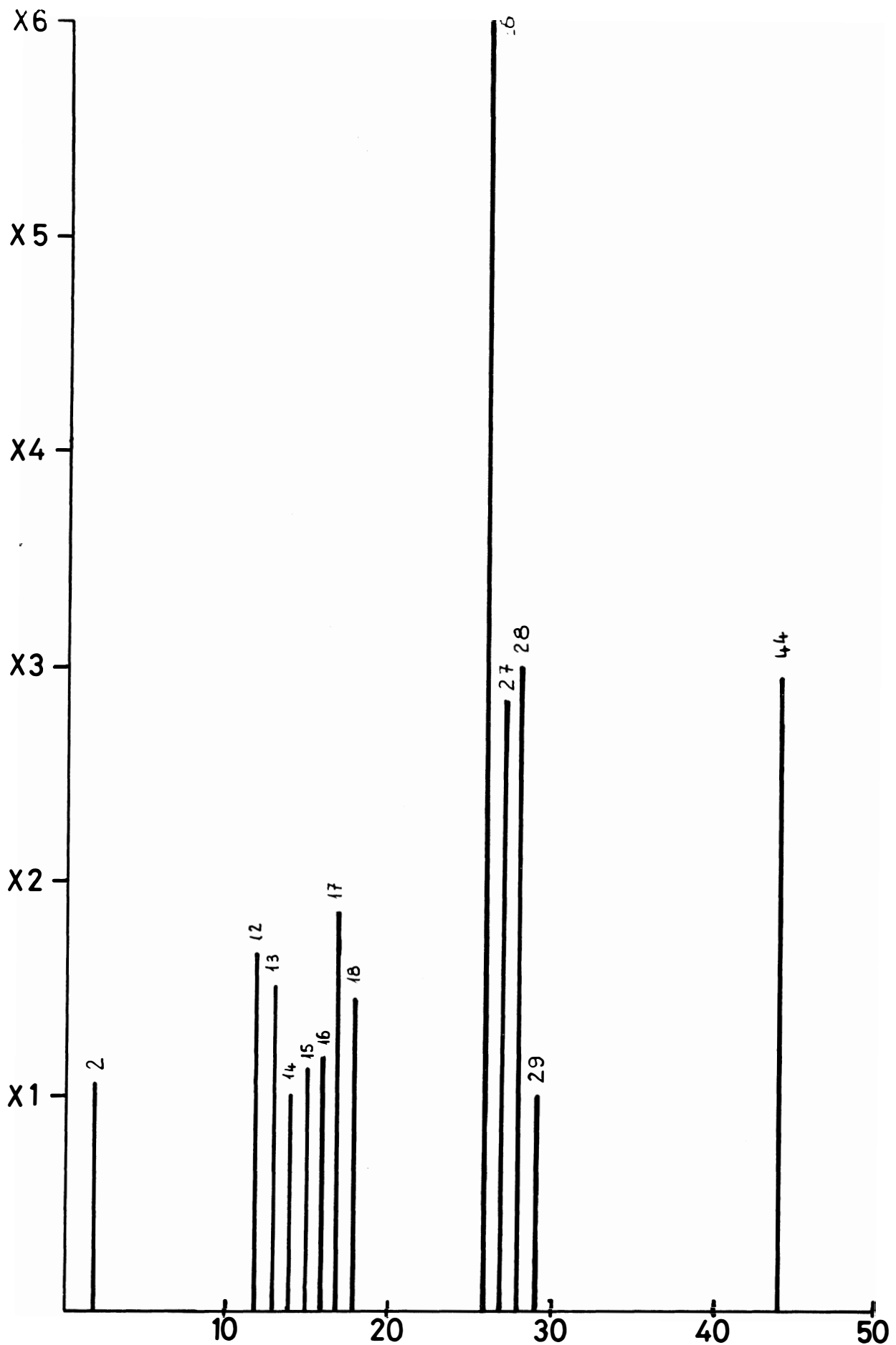


Fig.6. Illustration of increase in gas phase components as a result of ion-bombardment.(Stainless steel sample.) e.g. mass 2 increased by a factor 1.04 and mass 26 by a factor of 6.