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COLOPHON

The attached paper has no connection with my current research in Computer Science and Digital Documents. It is yet another in a series of experiments to see how long it takes me to re-build electronic versions of my published early papers as properly re-typeset 'PDF Normal' rather than just as a bitmap scan.

This particular paper was co-authored with my PhD colleague, Mike Cross and my Ph.D supervisor, Andrew Robertson, together with two colleagues from industry who were also working in the area of sharp-edge field-ionization mass spectrometry. The paper appeared in the International Journal of Mass Spectrometry and Ion Physics (Elsevier) in 1968. This, of course, was well before the era of desktop publishing and all I had was a pre-print of the original paper. The raw text was scanned from the pre-print using an HP Scanjet 8250 and HP's own ReadIris Pro software. The quality of the OCR recognition was surprisingly good and the copy-editing was straightforward because I already had a set of well-tested set of *troff* macros available for this particular journal, as a result of re-typesetting a slightly earlier publication¹.

Hence, UNIX *troff* was used to set up the correct typeface (Times) and to get the line and page breaks as accurate as possible. Specialist material within the paper was re-set with the *refer*, *tbl*, *pic*, *eqn*, and *psfig* pre-processors for *troff*.

As expected it was the 21 Figures in this paper (5 line diagrams and 16 photographs) that posed the greatest challenge. All were scanned in from the double-sided pre-print and all needed considerable cleaning up, in Adobe Photoshop, not least because of high levels of 'print through' from the non-scanned side of each sheet. The five graphs, after being cleaned up in Photoshop, were then vectorized using Adobe Streamline. The lettering on these graphs was re-set in Adobe Illustrator using Monotype's Arial Rounded Bold before exporting each diagram to version 3.0 of Illustrator's Encapsulated PostScript (but with no TIFF preview). For the 16 photographs, extensive cleanup of 'print through' noise was needed, followed by export of the grayscale images as bitmap Photoshoped EPS (again, with no preview)

All of the Encapsulated PostScript files were then incorporated into the paper using *psfig*.

This form of "rescue" of an early paper can produce a pleasing result but the time taken to do it (15 hours in this case) makes it prohibitively expensive for any publisher to undertake as a general procedure, especially given that there needs to be total familiarity with something like *troff*/*eqn*, or L^AT_EX before one can even begin.

The International Journal of Mass Spectrometry and Ion Physics is now very simply the "International Journal of Mass Spectrometry". The earlier incarnation of this journal has its home page at:

<http://www.sciencedirect.com/science/journal/00207381>

PDF versions of the papers in that journal are available (to subscribers) from volume 1 onwards though the early PDFs are, of course, just bitmap scans of pages. Indeed, a PDF bitmap version of this very paper is available via the above Web page (but, again, one needs to be a subscriber to the journal).

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EXPERIMENTAL INVESTIGATION OF THE USE OF SHARP EDGES FOR THE PRODUCTION OF POSITIVE IONS IN FIELD-IONIZATION MASS SPECTROMETRY

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The edges of razor blades and etched metal foils are sharp enough to act as field-ionization sources for mass spectrometry. In a previous paper¹, the calculation of electric field strengths at a sharp edge was discussed. In this paper the actual use of sharp edges in field ionization mass spectrometry is considered.

EFFICIENCY OF BLADES AND FOILS FOR FIELD IONIZATION

The efficiency was estimated by measurements of total current, as before^{2,3}. The blade or foil was suspended perpendicular to a flat plate, the edge to plate distance being kept as nearly as possible equal to 0.25 mm. The length of edge was usually 1.3 cm (except where mentioned later). The test gas flowed continuously through the system from a reservoir separated from the test vessel by a sintered-glass plug. The edge was positively charged; and the total current between edge and plate was measured. The test gases were ethylene (standard National Physical Laboratory sample of 99.92% purity), oxygen (cylinder) and nitrogen (cylinder). These gases were selected because their ionization energies cover a useful range, and the efficiency of a sharp edge for field ionization depends strongly on the ionization energy of the molecule ionized⁴. The gas pressure was measured with a McLeod gauge. The vessel containing the electrode system was immersed in liquid air to reduce residual gas pressures. Results are thus comparable with those already reported^{2,3,5}.

Razor blades

Five types of blade tested were: (1) standard stainless-steel blades without

a polytetrafluoroethylene coating; (2) similar stainless blades, specially selected to be probably sharper than normal, on the basis of electron-microscopic observations; (3) similar stainless blades definitely sharper than normal; (4) standard carbon-steel blades; (5) standard carbon-steel blades which had been given an extra sharpening process.

TABLE 1

TOTAL CURRENTS OBSERVED WITH OXYGEN PRESENT AT 1.8 mtorr PRESSURE

Blade type	1	2	3	4	5
Current (nA)	<1	10	5.9	6.4	7.2

Oxygen was not appreciably field-ionized under normal conditions by the charged razor blades previously examined². Table 1 shows total currents observed in this work with oxygen present and 10 kV between blade and plate. This voltage was about the highest usable without trouble from discharges.

Blades of types 2–5 are more efficient for ionizing oxygen than the blades tested by Cross and Robertson². However, the smallness of the currents with oxygen present and the closeness of the conditions to those giving discharge, made this method of comparing razor blades unsatisfactory. A better method seemed to be the use of ethylene at different pressures as test gas.

Different blades of the various types tested with ethylene gave the results shown in Fig. 1. Plotting ion current against pressure of ethylene sometimes gave linear plots passing through the origin (as with thin wires³) but in other cases

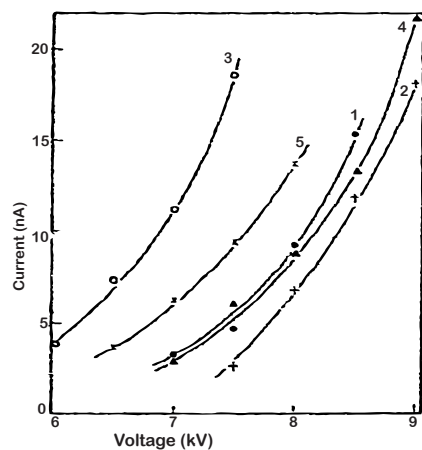


Fig. 1. Curves of total current against voltage with razor blades of types 1-5. Ethylene was present at a pressure of 0.96 mtorr.

non-linear plots were found which seemed to arise from irreversible changes of the blade edge. From the linear plots found with a voltage of 8 kV, gradients were found by the method of least squares and are shown in Table 2. These gradients seem to give a good indication of the efficiency of a razor blade for field ionization.

TABLE 2

ION CURRENTS WITH ETHYLENE AS A FUNCTION OF GAS PRESSURE

Blade type	1	2	3	4	5*
Gradient (nA/mtorr)	8.0	8.4	31.7	7.6	11.5

* The blade of type 5 did not have the usual length of 1.3 cm, since a portion had been removed for electron microscopy; the results were scaled linearly to correspond to 1.3 cm length.

These results show that although normal razor blades are not convenient for ionization of substances of ionization energy greater than about 12 eV⁴, a marked improvement results from further sharpening of a normal blade.

Etched Foils

Platinum foils were etched as before². However, their mechanical weakness was a disadvantage, so the etching of tungsten sheet initially 100 μ m thick was investigated. Various foils were prepared as follows.

Type A. Electropolished. Prior to electropolishing a layer of non-conducting lacquer was applied to the edges of a 1.5 \times 3 cm section of the 100 μ m thick tungsten sheet, its purpose being to eliminate preferential polishing at the edge of the sheet. This lacquering left an unprotected region of about 1.25 \times 2.75 cm at the centre of the tungsten sheet, on both sides. Electropolishing was carried out using a 3% sodium hydroxide solution at room temperature and an operating potential of 8V d.c. A pair of sheet electrodes was aligned with their edges adjacent to the faces of the specimen. Specimens were electropolished until a suitable length of straight edge had formed.

Type B. Electropolished and chemically etched. Specimens were electropolished as for type A, and then immersed for 10 sec in a solution containing 10% potassium ferricyanide and 10% sodium hydroxide.

Type C. Electro-etched. The method of preparation was similar to that described under type A, the only difference being that an operating potential of 3V d.c. was used.

Type D. Electropolished and electro-etched. Initial specimen preparation was that described under type A, and was followed by the application of a potential of 3V d.c. for about 10 sec.

Type E. Electro-etched. The thin sheet was etched in 25% (w/w) aqueous

potassium hydroxide solution at 10V a.c. with a current density of 3 A cm^{-2} for 20–25 min.

The foils were tested with ethylene and oxygen in the same way as the razor blades. Electron micrographs of foils A-D were taken before and after these tests, and of foil E after test. If the foil did not have the standard length of 1.3 cm, results of current measurement were linearly scaled to this length.

When high voltage was first applied to all the foils sudden bursts of current were noted, even in the absence of test gases, presumably due to lumps of tungsten, or even whole layers, field evaporated as ions. Indeed, after these bursts a deposit was observed on the cathode plate immediately below the foil edge.

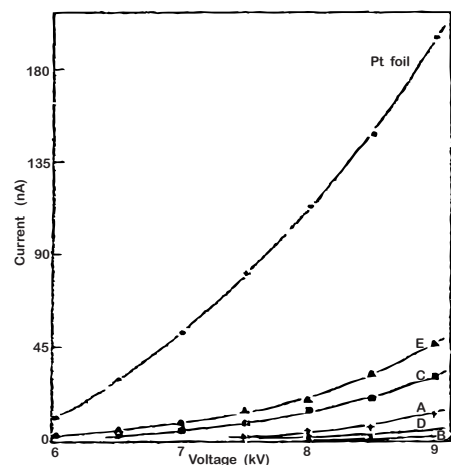


Fig. 2. Curves of total current against voltage with tungsten foils of types A-E, and with a platinum foil. Oxygen was present at a pressure of 0.45 mtorr.

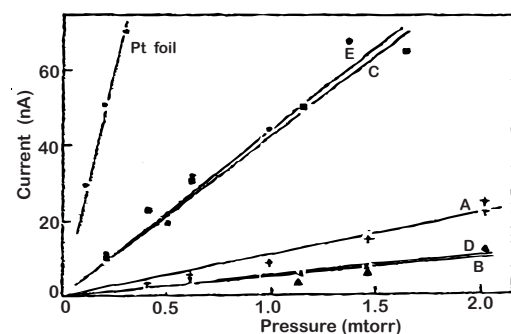


Fig. 3. Total current against pressure of oxygen with tungsten foils of types A-E, and with a platinum foil. The voltage was 8 kV.

Graphs of total current against voltage at a constant pressure, and of total current against pressure at constant voltage, are shown in Figs. 2 and 3, for oxygen present.

In Table 3 the gradients of the linear portions of the lines in Fig. 3 are given with a rough indication of the amount of material which was at first field evaporated. Results with ethylene present were similar, but the gradients of the current-pressure graphs were 2–3 times greater.

Ionization of nitrogen

Both platinum and tungsten foils could ionize nitrogen. Graphs of total current against voltage and against gas pressure are shown in Figs. 4 and 5. The

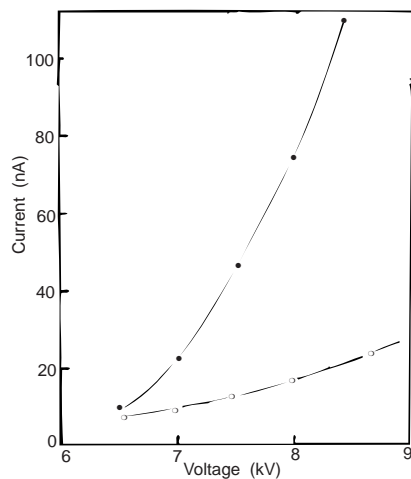


Fig. 4. Total current against voltage with (○) tungsten and (●) platinum foils. Nitrogen was present at a pressure of 0.46 mtorr.

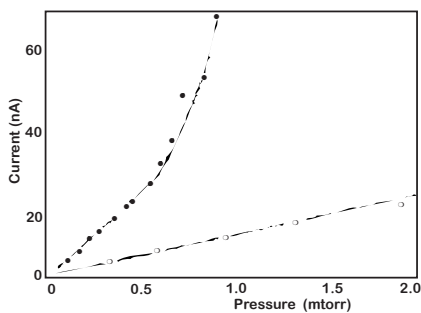


Fig. 5. Total current against nitrogen pressure with (○) tungsten and (●) platinum foils. The voltage was 7 kV.

TABLE 3
EFFICIENCY OF VARIOUS FOILS FOR FIELD IONIZATION OF OXYGEN

<i>Type of foil</i>	<i>Gradient (nA/mtorr)</i>	<i>Amount of field evaporation</i>
A	11.4	small
B	5.4	large
C	42.8	moderate
D	5.7	small
E	48.5	large
Platinum	243.3	large

platinum foil was prepared by the method of Cross and Robertson² and the tungsten foil was of type E. The non-linear current-pressure curve obtained with the platinum foil may arise from field evaporation of platinum from the edge. The measurements were made starting at the highest pressure, and the foil may have been somewhat blunted, or have lost some protrusions, during these first measurements. The graph is linear for later measurements.

Removal of material from edges

Material is removed from the tungsten edges soon after the high voltage is applied. With newly-prepared foils of types A, B and D the total current with oxygen present at 1.2 mtorr pressure was measured with 6.5 kV. The voltage was next raised to 9 kV for 2 min and then reduced to 6.5 kV, when another total current reading was made. The consequent reduction in current is shown in Table 4. Further studies of removal of material were made by electron microscopy.

TABLE 4
TESTS ON REMOVAL OF MATERIAL FROM EDGES

<i>Type of foil</i>	<i>Current before 9kV applied (nA)</i>	<i>Current after 9 kV had been applied (nA)</i>	<i>Ratio of currents</i>
A	4.5	0.9	0.2
B	16.4	10.5	0.64
D	54.5	37.7	0.69

ELECTRON MICROSCOPY

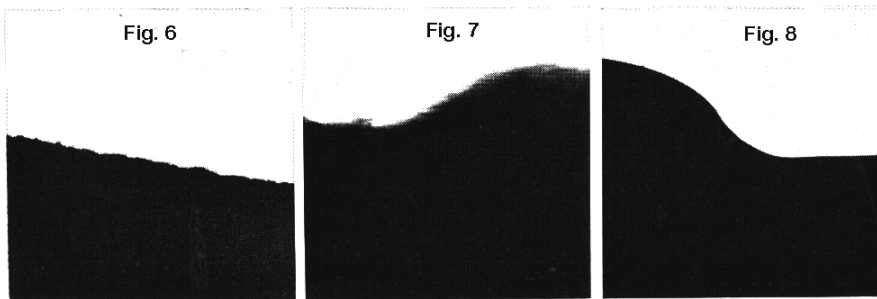
Experimental

Specimens were sectioned using a scalpel and pair of scissors and were examined, by transmission electron microscopy, in an A.E.I. E.M.6 instrument operating at a potential of 100 kV.

Examination of edges

1. Razor blades

Edges of a number of commercially-produced razor blades were examined in the electron microscope. Fig. 6 shows the degree of roughness along the edge of one such razor blade. Further examination at a higher magnification showed the extent of electron transmission associated with the edge; electron transmission only occurred in regions of thickness less than about 2000 \AA . In Fig. 7 electron transmission is restricted to a narrow strip of varying width. The radius of curvature of the edge can be inferred from the width of the transparent region and would appear to be as low as 300 \AA in some regions, but was on average about 700 \AA .



Figs. 6–8. Edge of razor blade. (6), $\times 1500^*$; (7), $\times 40,000$; (8), $\times 40,000$ after test.

* The magnifications given are those of the original photographs, which have been reduced for reproduction by a linear factor of 1.88.

When razor blade edges were examined after field ionization work a severe modification had occurred. The edge, which had largely been destroyed under high field conditions, was very rough at low magnifications and the electron transparent region had disappeared (Fig. 8).

2. Foil edges

(a) *Platinum foil.* An electrochemically-etched platinum foil was examined and found to have an extremely ragged edge, though with an electron transmission band, and hence an area of thickness less than $\sim 2000 \text{ \AA}$, which extended $4 \mu\text{m}$ into the specimen (Fig. 9). The radius of curvature of the edge was clearly very small and variable and was estimated to be less than 100 \AA .

(b) *Tungsten foils.* Tungsten foils were examined before use, after ionization tests, and after removal-of-material tests, with the results summarized in Table 5.

TABLE 5
TUNGSTEN FOILS

<i>Before test</i>	<i>After ionization tests</i>	<i>After removal of material tests</i>
<p><i>Type A. Electropolished.</i> Electropolishing produced a straight uniformly thinned edge. In the electron microscope electron transmission was observed to a depth of 5μm in from the edge (Fig. 10). Calculations based on the presence of "Bragg contours"⁶ in the thin regions (i.e. contours that result from interference of the direct and diffracted electron beams and which occur at regular thickness intervals) showed that the radius of curvature of the edge was ~100 Å and that it was fairly uniform along its length. (Figure 10)</p>	<p><i>Type A.</i> This was unaffected by the test. (Figure 14)</p>	<p><i>Type A.</i> Excessive wear had taken place during the test. Little electron transmission was observed in the electron microscope. (Figure 19)</p>
<p><i>Type B. Electropolished and chemically etched.</i> A high degree of electron transmission was associated with the edge; however, it was ragged along its length and contained a number of holes in the thin regions. (Figure 11)</p>	<p><i>Type B.</i> As shown in Fig. 15 there was little electron transmission, and most of the thin regions had been destroyed. The edge was also very rough along its length. (Figure 15)</p>	<p><i>Type B.</i> As can be seen from the extent of electron transmission in Fig. 20 most of the thin regions of the edge had been removed by the test. (Figure 20)</p>
<p><i>Type C. Electro-etched</i> The edge was ragged along its length and a number of holes was associated with the edge region. The extent of electron transmission was much less than either of the two previous samples. (Figure 12)</p>	<p><i>Type C.</i> This was unaffected by the test. (Figure 16)</p>	
<p><i>Type D. Electropolished and electro-etched.</i> The edge was very ragged along its length and there were numerous holes in the region adjacent to the edge. Electron transmission was low and variable. (Figure 13)</p>	<p><i>Type D.</i> Excessive wear of the edge had taken place and the extent of electron transmission was now very low (Fig. 17). There were also pronounced undulations along the length of the edge. (Figure 17)</p>	<p><i>Type D.</i> Some of the very thin areas of the edge had been destroyed in the test, but the overall appearance was similar to that before test. (Figure 21)</p>
	<p><i>Type E. Electro-etched.</i> The edge was very ragged and contained many holes and small protrusions. Electron transmission was observed in small patches. (Figure 18)</p>	

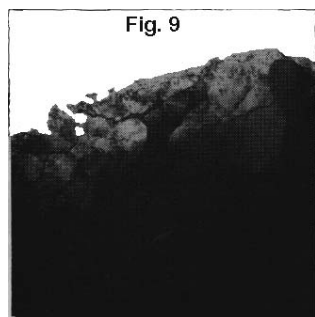


Fig. 9. Platinum edge (x 10.000)

MASS SPECTROMETRY

The simple ion source (without a focusing electrode) of Robertson and Viney⁵, was used in a single-focusing instrument, with a platinum foil replacing the razor blade. Mass spectra were essentially similar to those found by Robertson and Viney^{4,5}, with the molecular ion usually predominant. With neopentane the $C(CH_3)_3^+$ ion was predominant, and the fragmentation increased with ionizing field strength, in agreement with the considerations of Beckey⁷. Appreciable formation of the molecular ion of neopentane was found with the lower ionizing fields. With substances of high proton affinity the formation of a protonated molecular ion was observed. To obtain reasonable mass assignments from the accelerating

TABLE 6

FIELD-IONIZATION MASS SPECTRA OF ACETYLENE WITH A RAZOR BLADE AND AN ETCHED PLATINUM FOIL

<i>Edge used</i>	<i>Gas pressure (mtorr)</i>	<i>Ion current for most prominent ion (10^{-15} A)</i>	<i>Voltage used (kV)</i>	<i>Mass of ion</i>	<i>R.I.</i>	<i>Probable formula or formulae of ion</i>
Razor blade	0.1	100	5.5	31	6	CH_3O^+ , $C_2H_7^+$
				29	30	$C_2H_5^+$, HCO^+
				27	100	$C_2H_3^+$
				26	67	$C_2H_2^+$
				Any other ion	< 1	
Etched platinum	0.1	61	3.5	43	14	$C_3H_7^+$, CH_3CO^+
				29	70	$C_2H_5^+$, HCO^+
				27	100	$C_2H_3^+$
				26	60	$C_2H_2^+$
				Any other ion	< 1	

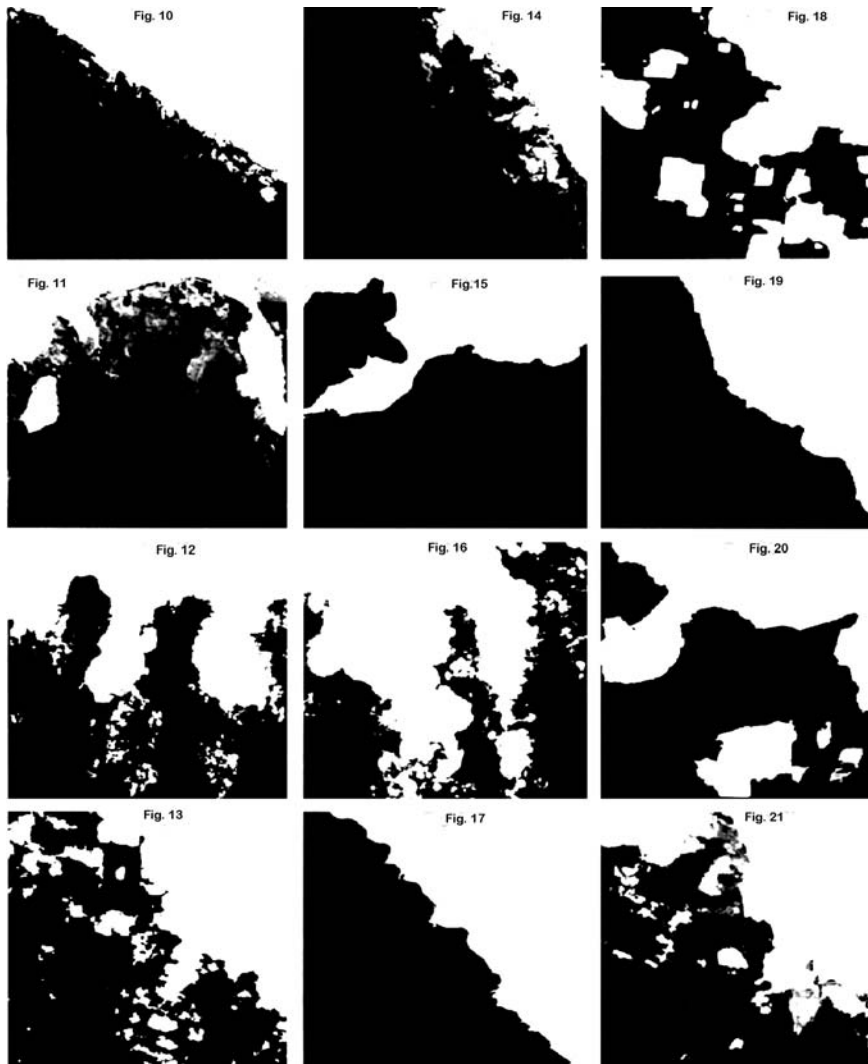


Fig. 10. Electropolished tungsten edge type A ($\times 10,000$).

Fig. 11. Electropolished and chemically etched tungsten edge type B ($\times 16,000$).

Fig. 12. Electro-etched tungsten edge type C ($\times 10,000$).

Fig. 13. Electropolished and electro-etched tungsten edge type D ($\times 10,000$).

Figs. 14–18. Tungsten edges after ionization test, $\times 10,000$. (14), type A; (15), type B; (16), type C; (17), type D; (18), type E.

Figs. 19–21. After removal-of-material test, $\times 10,000$; (19), type A; (20), type B; (21), type D.

voltage used this needed a small correction (10–20V) as with razor blades^{4,5} . and again this correction decreased as the ionizing field increased.

An example of comparative mass spectra obtained with acetylene with a razor blade and a platinum foil is given in Table 6, presented as before⁴. In both cases the principal ions are $C_2H_2^+$ and $C_2H_3^+$; the differences observed with masses 43 and 31 are explicable by the previous suggestion⁴. that these fragments are formed by reactions of carbon or hydrocarbon fragments with adsorbed water. These reactions may be subject to catalytic and residual gas effects.

However, the results with the foil did not show a great improvement of resolved ion current as compared with that produced with a razor blade, although nitrogen and oxygen could be ionized readily with the foil, but not adequately with the blade. The foil gave a mass spectrum of air, but with resolved currents of only 7.7 fA for O_2^+ and 4.6 fA for N_2^+ . The transmission of the mass spectrometer with the foils was never greater than 10^{-5} although 10^{-3} was attained with a razor blade source. This low transmission seemed to arise because the foil was pulled towards one or the other side of the slit. An investigation of this effect was made with an auxiliary electrode arrangement outside the magnetic field, so that the movement of the foil could be directly observed. An ion beam from a foil passed through three slits and was then measured on a collector. The foil was 0.3 mm above a first slit of width 0.5 mm. Even when the ions experienced only accelerating fields, a maximum of only 1.6% of the total current reached the collector. The foil was observed to bend suddenly to one side of the slit of the first electrode when the potential difference between the foil and this electrode reached about 4.5 kV. However, unobservable bending may have occurred at lower voltages, and this might explain the difference of 100 times between the mass spectrometer transmissions observed with razor blades and foils.

Mass spectra were also obtained using the A.E.I. MS. 7 double-focusing mass spectrometer, modified for field ionization use as described previously⁸. As before the cathode slit was at earth potential and voltages up to 20 kV were applied to the edge; the edge-cathode distance was constant at 0.75 mm.

The spectra obtained from a variety of compounds showed no gross differences attributable to the varied nature of the ionizing edges. Thus associated ion species were detected in the spectra of many simple aromatic compounds⁹. and the familiar low abundance of fragment ions was observed as before⁸. Spectra were recorded on a photographic plate so that subtle differences in relative ion abundance would not have been detected.

From the point of view of ionization efficiency, measured at the ion current monitor of the spectrometer, tungsten edges in general were superior to the commercial razor blades hitherto employed on this instrument, but as observed on the single-focusing mass spectrometer. etched platinum foils were not satisfactory due presumably to their bending out of line of the cathode slit under the influence of the field.

Field emission microscope observations with foils

Two tungsten foils, of types A and B, were examined in a simple projection microscope. The foil was suspended with its edge along the axis of a glass cylinder 5 cm in diam. The inside surface of the glass had a conducting coating of tin oxide and was coated additionally with zinc sulphide. This screen was earthed, and an increasing negative voltage was applied to the foil, when, at first, brief but intense flashes of light filled the whole screen opposite the edge. This was presumably due to material removed from the edge. The foil was then kept at -12 kV when (with both foils) a pattern of about a dozen electron-emitting centres was noted, consisting of isolated bright spots. However, as Metzinger and Beckey¹⁰ point out, centres of most importance in field emission are not necessarily of greatest importance for field ionization.

DISCUSSION

Razor blade edges

Although no field evaporation was noticed during tests of blades by measurements of total current, deterioration was noticed after several months of use in a mass spectrometer. The electron micrographs of razor blade edges show that the hyperbolic approximation used before¹ is reasonable.

Metal foil edges

The electropolished tungsten edge is remarkably straight and quite thin along its edge, and probably corresponds quite well to the hyperbola approximation. The other foils, both tungsten and platinum, show pronounced roughness at the edge on both a large and a small scale, leading to pronounced field intensification. The platinum foil is extremely thin at the edge and moreover remains very thin for some distance behind the edge. The honeycomb-like structure of the edge will increase the field at the edge since no field lines can terminate at a hole. However, in view of the evidence for field evaporation of material from the edge it seems likely that this structure will not persist under high fields. In fact several of the electron micrographs show a field-produced smoothing. The amount of field evaporation shown in Table 3 is well correlated with the corresponding photographs.

The electropolished tungsten foil shows little removal of material after extensive use (see Figs. 10 and 14). However, foil of type B (Figs. 11 and 15) had lost most of its thin part after extensive use. This corresponds with the large amount of field evaporation and the poor performance observed. Foil of type C

(Figs. 12 and 16) is apparently unaffected by extensive use, and this again correlates with its use for field ionization. Foil of type D (Figs. 13 and 17) shows considerable wear, and did in fact give a poor performance in field ionization. Fig. 18 shows the appearance of foil of type E after extensive use. The degree of electron penetration is low and most of the edge has a thickness exceeding 2000 Å. However, the edge is still ragged with much honeycomb-like structure, and this may explain the good field ionization performance. The extremely good performance of the platinum foil is consistent with Fig. 9 which shows an extremely thin edge before use. Thus material can be stripped off in the high field and a sharp edge is still left.

Photographs of edges before and after they had been treated by the procedure summarised in Table 4 are shown in Figs. 19, 20, 21, which should be compared with Figs. 10, 11, 13. Foil of type A shows pronounced wear, whereas types B and D show less wear. This correlates with the current ratios in Table 4. Even though the duration of the exposure to high fields suffered by these three foils is much less than that for the foils used in the extensive ionization tests, nevertheless all three foils show noticeable wear.

It seems (Table 4, Type D) that foils which have been both electro-polished and electro-etched show promise. The largest ion currents with the best foils correspond fairly well to every molecule striking the edge being ionized, if the edge is considered to be half a cylinder with a radius of 100 Å and the collision rate is calculated directly from kinetic theory with no correction for enhancement from polarisation effects, so for these foils the limit of performance has probably been reached.

We thank the Institute of Petroleum and the Gas Council for support to D.F.B. and C.M.C respectively, and Messrs. Gillette Industries for razor blades and information on them.

SUMMARY

Various commercial razor blades have been tested for field ionization performance and compared with edges prepared electrochemically from platinum and tungsten foils. The results are correlated with data obtained from electron micrographs of the various edges. It is concluded that tungsten edges offer the best compromise between field ionization efficiency and durability of the edge.

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