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THE EFFECT OF METAL OVERLAYERS ON THERMIONIC DISPENSER CATHODES

Final Technical Report

by

Richard A. Tuck
Heather B. Skinner

March 1985

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ABSTRACT

This study has been undertaken to further the understanding of the physics and chemistry of thermionic dispenser cathodes and to test a model for the mechanism of operation of these devices. The surface structure and work function of cathodes coated with a variety of metals has been investigated using surface analytical techniques, including Auger Electron Spectroscopy. The theoretical implications of the results are discussed.

Key words: Thermionic cathodes, dispenser cathodes, surface structure, metal overlayers, angle resolved Auger electron spectroscopy.

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U.S. ARMY CONTRACT
THE EFFECT OF METAL OVERLAYERS ON THERMIONIC DISPENSER CATHODES
EMISSION EVALUATION AND SURFACE ANALYTICAL STUDY OVER A
WIDE RANGE OF METALS

1. INTRODUCTION

The fundamental object of this work has been to further the understanding of the physics and chemistry of thermionic dispenser cathodes as used in microwave devices.

With the continuing need for high power, high frequency devices, cathodes suitable for higher current densities are desirable. Also, for long life applications (e.g. spacework) the cathode is required to operate at a modest current density but at lower temperature in order to minimise depletion of the active impregnant material.

For both these conditions a highly efficient cathode of low work function is required.

The specific work undertaken in this contract was designed to test a model for the mechanism of operation of dispenser cathodes. The model was proposed by THORN EMI VARIAN Limited in a previous publication (Reference 1).

This model suggests that the barium oxygen adsorbate exists on the cathode surface in a highly ordered arrangement which depends on the chemical interaction between the substrate and the adsorbate.

2. RANGE OF STUDY AND TECHNIQUES EMPLOYED

The following metal coatings were investigated:

Titanium (Ti)
Nickel (Ni)
Copper (Cu)
Palladium (Pd)
Tantalum (Ta)
Osmium (Os)
Iridium (Ir)
Platinum (Pt)
Gold (Au)

The experimental work was divided into two sections;

- a) Emission tests and general surface analysis.
- b) Angle Resolved Auger Spectroscopy - this technique was applied to only a selection of the metals referred to. This was intended to provide information regarding the vertical ordering of atoms on the cathode surface.

2.1. Emission tests/general analysis

The cathodes used for these experiments were based on standard TEV production items.

These were dispenser cathodes consisting of a 20% porous tungsten matrix impregnated with $6BaO : CaO : 2Al_2O_3$. They were flat, 9 mm in diameter

and contained an integral heater constructed from W/Re wire (3% Re) coated with alumina.

All the cathodes were analysed in the CASSOCK Multi-technique Analytical System (Reference 2). This is a UHV system fitted with various surface analytical facilities together with a planar anode system for emission testing; the anode can be heated to approx. $950^{\circ}C_B$ for cleaning.

Before coating with the appropriate metal, the basic B-type cathodes were heated overnight in CASSOCK and emission tested; only cathodes with zero field emission values of greater than $3.5 A cm^{-2}$ at 1340 K were accepted. They were then allowed to cool, removed from the system and coated with 1 micron of the chosen metal.

All coatings were applied by magnetron or r.f. sputtering except for Ni, Cu and Au which were applied by evaporation.

The magnetron sputtering was carried out in the THORN EMI Central Research Laboratories using targets of 8 cm diameter. Originally we had intended to use our in-house fine beam micro-sputterer, however the deposition rate was found to be very low, with the undesirable result that the films incorporated a high proportion of residual gases.

The cathodes were then returned to CASSOCK and heated to an appropriate temperature (see following section). Emission testing and surface analyses were carried out at various stages of activation.

These analyses consisted mainly of Normal Resolution Auger Electron Spectroscopy and also some X-ray Photo-electron Spectroscopy (XPS).

The Normal Resolution AES in these experiments employed a 0.25 mm diameter electron beam at 3 keV energy directed at the sample. The resultant secondary electrons were energy analysed using a lens-accessed hemispherical analyser. The precise positioning of the Auger peaks in the secondary electron spectrum indicated the elemental composition of the first few atomic layers.

XPS was carried out using Mg $K\alpha$ radiation; the bombardment conditions were 10 kV/20 mA. Unlike AES, this technique produces an average elemental analysis over the whole cathode surface but provides more specific information on chemical state.

2.2 Angle Resolved Auger Spectroscopy

For these experiments, special cathodes were constructed with a cylindrically-shaped emitting area (fig. 1a). In order to minimise surface roughness effects they were polished down to 1 micron with diamond paste before impregnation. All other processing was the same as that for the flat samples.

Because of the unusual shape, emission testing was not possible. However, this information was provided by the flat counterparts coated with the same metal.

Fig. 1b gives a more detailed illustration of the geometry.

By raising or lowering the sample with respect to the electron beam and energy analyser, changes occur for both the exit angle of secondary electrons (θ) and for the incident electron angle (ϕ) with respect to the surface plane.

Position 1 represents the cathode close to the lowest analysis position.

Position 5 is almost the highest analysis position beyond which the electron beam would miss the sample.

From positions 1 to 5 it can be seen that both θ and ϕ increase to 90 and then decrease. The changes are not completely in phase since θ reaches a maximum at 3 and ϕ at 4. The effect will, however, be enhanced for the lower energy secondary electrons and therefore changes in ϕ will strongly predominate. Overall, the surface sensitivity will decrease to a minimum around position 4 and then begin to increase again.

It was considered that this technique had the potential to provide information about the vertical ordering of molecules on the cathode surface. Some interesting results have been obtained and these will be reported on in a later section.

3. RESULTS

3.1. Emission Tests and General Analyses (AES and XPS)

The physical/chemical characteristics and emission performance of a B-type cathode (uncoated) and an M-type cathode (Os coated; 1 micron) will be described first.

The two types of cathode are standard production items, the M-type producing three times the emission current density of the B-type at the same temperature.

3.1.1. B-Type Fig.2 is an Auger spectrum 50 - 1050 eV of a standard B-type cathode after two days heating at 1070 °C_B.

Peaks are observed from oxygen, barium and the W substrate.

Important factors to consider are the ratio of the O to Ba signals and the ratio of both to the tungsten substrate. In this case

$$O/Ba = 4.38 \quad O/W = 0.67 \quad Ba/W = 0.15$$

The emission current density vs temperature is shown in Fig.3. This represents an effective work function of 2.01 eV.

Temperature measured with a spectral pyrometer at 0.65 μm are abbreviated °C_B. No correction is made for emissivity.

3.1.2. M-Type. Fig.4a shows the corresponding spectrum for an Os coated cathode after two days at 1070 °C_B. Fig.4b is an expanded spectrum from 150 - 200 eV. Information from previous calibrations (Reference 3) indicates that the shape of the peak results from a 60% : 40% osmium/tungsten mixture. This implies that cracking of the osmium film or alloying between Os and W has occurred early in the cathode life.

Confirmation of this is given by another spectrum from 1000 - 2000 eV, Fig.4c, where the Os and W MNN signals are well separated. In this case the proportions are calculated to be 68% Os, 32% W, i.e., a slightly higher Os proportion than measured from the 160 eV peak.

At the lower electron energy the analysis depth in the sample is less (approx. 4 monolayers at 160 eV rather than 10 monolayers at 1800 eV). See Reference 4.

These results imply that the Os concentration decreases towards the surface. This is consistent with the formation of an Os/W alloy with tungsten predominant in the first few atomic layers.

It can be seen from Fig.4c that the O/Ba ratio is 2.9; less than that for a B-type. The O : Substrate ratio is 0.5 and the Ba : Substrate ratio 0.19, compared with 0.67 and 0.15 respectively for a B-type. (These calculations were made using the appropriate correction factor for the difference between the Os and W Auger sensitivities; see Reference 5).

It therefore appears that the oxygen concentration relative to the substrate is less for an M-type than for a B-type cathode, whereas the barium concentration remains fairly constant. This will be discussed in a later section.

The emission current density vs temperature is shown in Fig.5. The effective work function is 1.9 eV.

We, as others, observe that the emission of M-type cathodes improves during life, accompanied by further Os/W alloying and a drop in the Os concentration. At some optimum stage the emission reaches a peak. The reasons for this will be discussed in Section 3.

4. OTHER METAL COATINGS

4.1 Nickel

Fig. 6a is the Auger spectrum from 50 - 1050 eV, of the coated cathode after 15 minutes heating at 1000 °C_B. The Ni is clearly visible together with sulphur, a common impurity in nickel. There is also a small signal from the tungsten substrate.

Barium and oxygen also appear, in the ratio 2:1 O:Ba. This ratio is low compared with that for a standard B-type (approx. 4:1).

Fig. 6b is another 50 - 1050 eV spectrum taken after 8 hours heating. The sulphur peak is smaller, probably due to depletion of bulk sulphur in the film, and the W peak larger, implying diffusion of nickel into the matrix or cracking of the film. There is otherwise little change.

At this stage the emission was measured. Fig. 7a is a sample of zero field current density/temperature and shows the emission performance to be poor compared with a B-type. This graph indicates an effective work function of 2.2 eV.

The cathode temperature was then raised to 1050 °C_B and left overnight.

Fig. 6c is the Auger spectrum taken at this time. The substrate W peak is now predominant and the Ni and S peaks are undetectable. The O:Ba ratio is now approx. 3:1, closer to that of a B-type.

The emission was measured at this stage and was found to have improved significantly to a value slightly higher than that of a B-type (fig. 7b).

This represents an effective work function of 2.0 eV.

Clearly, the nickel had disappeared overnight from the surface, but it was not immediately apparent where it had gone. This was eventually investigated more thoroughly and the results are reported in a later section (7.1).

The fact that slight emission enhancement is observed implies that the nickel is still present and is, perhaps, influencing the chemistry within the matrix.

4.2 Copper

In view of the low melting point of copper, this cathode was heated initially to only 875 °C_B.

Fig.8a is the Auger spectrum (50-1050 eV) taken after 30 minutes heating. The predominant elements are copper, sulphur, oxygen and barium in the ratio 1.3:1 ; much lower than for a standard B-type.

The W substrate and carbon are also observed. Fig.8b is the same spectrum taken after 3 hrs heating at 875 °C_B. The copper is now almost undetectable and the predominant elements are tungsten and oxygen and barium in the ratio 3:1.

The disappearance of copper at this stage could be due to evaporation and/or diffusion into the matrix. See Section 7.1.

The emission at this point was immeasurably small, possibly due to the effect of copper within the matrix, or simply the low temperature of the cathode which allowed the adsorption of carbon onto the surface.

The cathode was then left to run overnight at 1050 °C_B. Fig.8c is the spectrum taken after this time and the only obvious elements are tungsten, oxygen and barium (O/Ba = 3.9).

The emission performance was equivalent to that of a standard B-type. Fig.9 is the graph of zero field emission vs. temperature. It is probable that most of the copper has evaporated, leaving a standard B-type cathode in an unpoisoned state.

4.3. Gold

Due to the low melting point of gold, this cathode was heated initially to only 960 °C_B.

Fig.10a is the Auger spectrum from 50-1050 eV taken after 30 minutes. The only signal other than gold is from barium; this is in contrast with the copper sample, where barium and oxygen appeared together.

Fig.10b is the same spectrum taken after 60 minutes and shows oxygen beginning to appear. At this stage the emission was immeasurably small. After overnight heating at 980 °C_B, the gold signal had disappeared (Fig.10c); the predominant element is now tungsten, together with oxygen and barium in the ratio 4:1. This value is close to that for a standard B-type, however the emission at this stage was such lower. Fig.11 shows the zero field emission vs. temperature; this represents a work function of 2.18 eV.

4.4. Palladium

Fig.12a is an Auger spectrum from 50-1050 eV after 1 hour at 1030 °C_B. The palladium signal predominates. Also visible are tungsten, sulphur (probably an impurity in Pd) and barium. As in the case of the copper and gold coated cathodes, barium appears on the surface before oxygen. At this stage the emission was immeasurably small.

Fig.12b is the spectrum taken after overnight heating at 1070 °C_B. The palladium has now disappeared and the tungsten substrate peak is clearly visible. Oxygen is present on the surface and the O/Ba ratio is 4.25:1, similar to that for a B-type.

Fig.13 is the zero field current density vs. temperature. This corresponds to a work function of approx. 2.02 eV, similar to that for a standard B-type cathode.

4.5. Platinum

Fig.14a is an Auger spectrum from 50 - 1050 eV after 3 hours at 1050 °C_B. The predominant signals are platinum and barium. No oxygen is observed at this stage.

Fig.15a shows the zero field current density vs. temperature; this is much less than for a standard B-type and represents a work function of 2.24 eV.

After 3 days heating at 1050 °C_B the emission had increased slightly (Fig.15b).

The Auger spectrum now shows oxygen as well as barium, although the O:Ba ratio is only 1.58, considerably less than for a B-type (fig.14b). The Pt and W NNN signals at 160 eV are partially superimposed; however, for Pt and W the appropriate calibration data to determine the Pt/W composition was not available as it was for Os and W.

Fig.16 shows the spectrum between 1000 and 2000 eV where the MNN transitions are clearly separated. This indicates a high proportion of tungsten, the Pt/W composition being calculated as 70% Pt, 30% W (Reference 5).

4.6 Iridium

This cathode showed very similar characteristics to those of a standard M-type (Os coated) cathode.

Fig. 17a is an Auger spectrum (50 - 1050 eV) measured after two days heating at 1050 °C_B. The O:Ba ratio is 2.75, slightly less than for an M-type.

Fig. 17b is a high energy Auger spectrum (1000 - 2000 eV) showing the Ir and W MNN transitions. The high proportion of tungsten is indicative of W/Ir alloying or film cracking. The composition was calculated to be 48% Ir, 52% W.

The emission was somewhat less than M-type at this stage.

Fig. 18 is a graph of zero field emission vs. temperature. This represents an effective work function of 1.98 eV.

4.7 Tantalum

Fig. 19a is an Auger spectrum from 50 - 1050 eV after 4 hours heating at 1050 °C_B. An obvious difference from the previous cathodes is the very high O:Ba ratio.

In the high energy spectrum (1000 - 2000 eV) no tungsten is observed (fig. 19b). At this stage the emission was very low, corresponding to an effective work function of 2.6 eV.

After a further 8 days heating at 1070 °C_B, the emission had improved ($\phi_{\text{EFF}} = 2.36$ eV) and the O:Ba ratio had dropped to 8:1 (fig. 19c). This is still very high in relation to a B-type.

The high energy spectrum (1000 - 2000 eV) still shows no evidence of tungsten.

4.8 Titanium

Fig. 20a is an Auger spectrum from 50 - 1050 eV after 30 minutes heating at 1000 °C_B.

Titanium, tungsten and oxygen are observed, but no barium. The O:W ratio is very high compared with a B-type; 3.7 compared with approx. 0.6.

The emission from this cathode was immeasurably small.

After a further 3 days heating at 1030°C_B , the spectrum and the emission were unchanged (Fig.20b).

5. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Due to instrumentation problems this technique was used on only two samples; the M-type (Os coated) and the Ta coated cathodes.

In both cases Mg K α radiation was used (energy 1257 eV) to study the 4f electron shell of the metal overlayer. This includes the valence electrons most closely associated with bonding, where any changes in chemical environment are likely to influence the shape of the photoelectron peaks.

Fig. 21a is a spectrum from 1150 - 1250 eV of the Os cathode which shows the two 4f 7/2, 5/2 doublets, one for Os and one for W.

Fig. 21b is the same spectrum for the tantalum cathode. In the case of the Ta 4f "doublet" the peaks are not resolvable and appear as one. This indicates that a mixture of chemical states is present. The effect of a change in chemical environment is to alter the binding strength of the 4f electrons which will produce an energy shift in the spectrum. The result of two or more doublets superimposed with slightly different energies will be a broad, unresolvable peak, as observed.

By contrast, the Os doublet on the M-type cathode is fairly well resolved, suggesting less chemical interaction. The fact that the tungsten doublet is slightly less resolved may indicate that tungsten is more "chemically altered" than osmium on the M-type cathode surface.

These effects will be discussed further in a later Section.

6. ANGLE RESOLVED AUGER SPECTROSCOPY

Results were obtained for three different cathode types; osmium (M-type), tantalum and platinum coated.

The coatings were applied to the semi-cylindrical cathodes by r.f. or magnetron sputtering, the thickness being approx. 1 micron.

Each sample was then placed in CASSOCK in approximately the usual Auger analysis position for flat samples. It was then lowered until the electron beam could be seen hitting the top of the cathode area.

Before any measurements were taken the cathode was activated by heating at 1050 °C_B for 12 hours.

It was then raised in increments of 1 mm and an Auger spectrum taken at each point (120-620 eV, 3 KeV beam). This range includes the overlayer metal NNN; the oxygen KLL and the Ba MNN transitions (at 160, 510 and 580 eV respectively).

After 8 mm of movement a cut off was reached after which the electron beam failed to intercept the sample.

Graphs were then plotted of O:Ba O:Substrate and Ba:Substrate ratios vs. vertical distance (in mm) of the sample from its starting position. ("Substrate" refers to the metal overlayer or a mixture between this and the underlying tungsten depending on what is observed in the spectrum). Each graph represents an average of at least 2 experimental runs - error bars are shown.

The ratios include no correction for elemental sensitivity. This is unnecessary for direct comparison of O:Ba ratio on different cathode surfaces but would be more desirable for the O:Substrate and Ba:Substrate measurements in order to obtain precise values of coverage.

However, mixing of the metal overlayer with the tungsten substrate to varying extents confuses the Auger NNN signals and makes quantitative measurements difficult.

6.1. Osmium Coated Sample

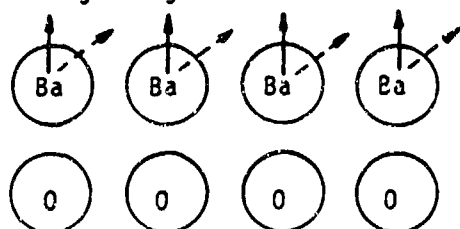
Fig.22 is a graph of O:Substrate, Ba:Substrate and O:Ba real height ratios vs. vertical distance of sample from starting position.

O:Substrate and Ba:Substrate decrease slightly and then increase moving from glancing to normal to glancing electron exit angle. This implies, as expected, that the Barium and Oxygen are both lying above the substrate.

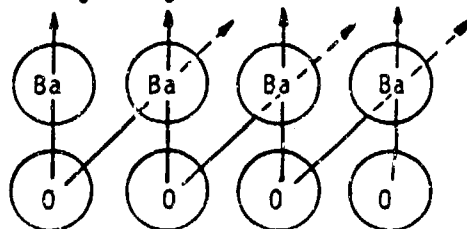
In this case the substrate is a mixture of Osmium and tungsten as determined from high energy Auger measurements (MNN transitions) and previous work on osmium coated cathodes (Ref 3).

The O:Ba ratio shows an obvious increase and then a small decrease from glancing to normal to glancing electron exit angle. This implies either that BaO is lying above oxygen or is significantly larger in size. The following diagrams illustrate how these two situations would produce the same effect. This will be further discussed in Section 3.

a) Ba:O sandwich
Auger signal from Ba



Auger signal from O

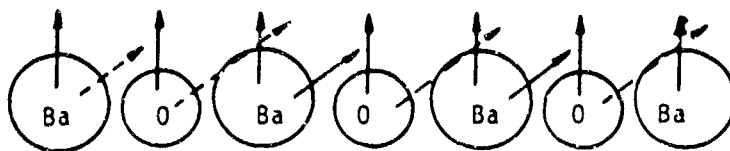


————— normal electron exit angle to surface
----- glancing electron exit angle to surface

For the Ba secondary electrons there is little change in the path length to the surface between glancing and normal electron exit angle.

Electrons from oxygen, however, have a longer path length to the surface for glancing exit angle. This will tend to suppress the oxygen signal relative to barium under these conditions.

b) Ba larger than O but co-planar



————— normal electron exit angle to surface
----- glancing electron exit angle to surface

As before, the oxygen Auger electrons have a longer path length to the surface at glancing exit angle and so the oxygen signal in relation to barium will be suppressed.

Returning to fig. 22, the ratios at the "cut off" position do not return to these at the start. This is due to the geometry of the system, which causes the cut off to occur before complete glancing exit angle is achieved at the bottom of the cathode.

6.2 Platinum coated cathode

This cathode was initially examined after only two hours activation at 1040°C_B .

Consistent with the flat counterpart, no oxygen was observed at this stage, only Pt, Ba, S and some W.

Fig. 23 is a plot of S:Ba, S:Pt and Ba:Pt against distance from start position.

In all cases there is a decrease in the ratio followed by a small increase. This may suggest that S is lying above Ba and both are above the Pt substrate. The cathode was then heated for 12 hours and re-examined. By this time oxygen had appeared at the surface and sulphur had almost disappeared.

Fig. 24 is a plot of O:Ba, O:(Pt+W) and B:(Pt+W) vs. distance from start position. Superficially, the curves are similar to those for the osmium coated cathodes, implying that Ba and O are above the substrate and that either barium is above oxygen or they are co-planar, with the barium significantly larger.

Some differences are to be observed between this and the osmium coated cathode. The maximum O/Ba ratio observed at normal incidence is less for the Pt than for the Os coated cathode (2.7 vs. 3.2). This appears to result more from a decrease in oxygen relative to the substrate than an increase in barium, as the Ba:substrate ratios are similar for the two cathodes.

Comparison of the two flat cathodes produced the same conclusions.

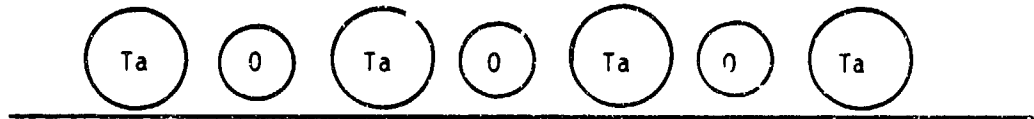
6.3 Tantalum coated cathode

This cathode was examined after 12 hours heating at 1040°C_B . A very large O:Ba ratio and a much reduced Ba:substrate ratio is observed compared with the M-Type (Os coated). High energy Auger results reveal no tungsten. Again, these observations are consistent with the flat sample.

Fig. 25 shows curves of O:Ba, Ba:Ta and O:Ta vs. vertical distance from start position. Here, very different results are obtained from those of previous cathodes.

Ba:Ta decreases from glancing to normal incidence, suggesting that Ba is lying above tantalum. However, O:Ta very obviously decreases; this implies that oxygen is lying below a surface layer of tantalum or that they are co-planar with tantalum significantly larger.

This is consistent with the high stability of tantalum oxide causing oxygen to be absorbed into the structure of the tantalum film.



7. DISCUSSION AND FURTHER EXPERIMENTS

7.1 General observations

From these preliminary results, the flat cathodes studied can be divided into two groups;

- i) Those in which the metal coating caused a permanent change in the characteristics of the B-type cathode even after heating for tens of hours at above standard operating temperature ($\sim 1000^{\circ}\text{C}_B$).
- ii) Those cathodes whose characteristics reverted to B-type after heating at above 1000°C_B .

Group (i) includes tantalum, titanium and platinum which caused degradation in emission, and osmium and iridium which produced enhancement.

For all these cathodes, the metal overlayer was seen by Auger analysis to remain on the surface, although in all cases except Ta the W substrate was also visible (for this cathode no tungsten was ever observed by Auger analysis even after prolonged heating at 1070°C_B).

Group (ii) includes the gold, copper, palladium and nickel coated cathodes.

Common to all these was the apparent disappearance of the metal overlayer after prolonged heating. This can be accounted for by evaporation and diffusion into the matrix as will be explained later in this Section. From these results a general statement may be made that

"A metal coating applied to the surface of a B-type cathode will permanently influence the emission performance only if it remains stable at the surface during normal operation (i.e. between 1000 and 1050°C_B).

This, however, does not allow for situations where a metal (e.g. gold) may be continuously evaporating from an external source or diffusing from a much larger reservoir. In this case cathode poisoning would be permanent.

There is also one exception to the general statement. The nickel cathode did appear to show some emission enhancement even when no nickel was observed in Auger analysis. This implies that the nickel may be influencing the cathode chemistry within the matrix.

As an additional experiment, the nickel and palladium cathodes were removed from CASSOCK (after all the Pd and Ni had apparently vanished from the surface) and each coated with 1 micron of osmium.

On reactivation it was found that the Pd+Os cathode performed as a standard M-type, whereas the emission from the Ni+Os cathode was slightly less than M-type. The emission vs. temperature results are shown in fig. 26. This again indicates that Ni is continuing to have an influence on the cathode performance.

This sample was eventually subjected to bulk analysis by atomic absorption spectroscopy. This was carried out by Mr. D.N.Nicholas of Fulmer Research Laboratories.

3.5×10^{-5} g of Ni were detected in the sample. The original quantity in the evaporated film was estimated at 2.8×10^{-4} g. According to vapour pressure calculations (Ref. 5) this quantity should have completely evaporated during the 24 hours that the cathode was at the final operating temperature (1050°C_B).

This suggests that, at the initial lower operating temperature, nickel diffused into the matrix and limited the subsequent evaporation.

The copper coated cathode was then analysed in a similar manner.

5.4×10^{-5} g was detected after approx. 12 hours heating at 1050°C_B . However, the vapour pressure calculations indicate that the 2.8×10^{-4} g originally applied would have completely evaporated at that temperature in 5 minutes. This implies, therefore, that diffusion of copper into the matrix at the lower initial temperature (950°C_B) limited evaporation, as was the case for nickel.

7.2 Chemical interaction between metal coatings and barium and oxygen-periodic trends

The transition metals found to have a permanent effect on cathodes Ta, Os, Ir, Pt and Ti all have reasonably high melting points which ensures that they remain on the surface at normal operating temperature.

Those elements at the centre of the transition block (Os and Ir) tend to enhance emission whereas those at the left hand side (Ta and Ti) and the right hand side (Pt) suppress emission.

From the Auger analysis of the flat cathodes it appears that Ti and Ta combine with oxygen at the surface far more readily than with barium. This results in a very high O:Ba ratio.

The angle resolved experiments for Ta suggest that the oxygen is incorporated within the structure of the film. This is consistent with strong reducing properties (i.e. ability to supply electrons) which are associated with elements at the left hand side of the transition

block. This arises from electronic structure and atomic size effects and produces a tendency to form stable oxides.

Moving towards the right hand side of the transition block, elements tend to become more oxidising (i.e. electron accepting) and form less stable oxides.

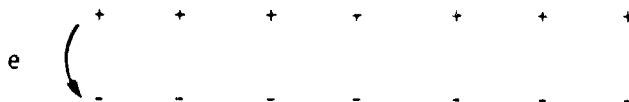
The extreme cases are platinum and palladium. For these cathodes no oxygen was observed by Auger analysis during the first few hours of heating; only barium and sulphur (this was observed temporarily for the gold coated cathodes for which similar chemistry might be expected to apply).

Fig. 27 is a graph of the first ionisation potential, I.P.1, of the metals of interest as a function of O:Ba ratio on the appropriate cathode.

I.P.1 is a measure of the energy required to remove the first outer electron from the atom. The points fall into two groups, each corresponding with a row of the transition series. Both show a strong negative relationship with O:Ba ratio on the cathode. This implies, as expected, that reducing (electron donating) elements with low I.P.s, i.e. Ti and La, tend to have high O:Ba ratios, combining more readily with O than Ba.

How do these factors influence cathode emission? In order to explain the effects it is necessary to discuss first the operating mechanism of a standard B-type cathode.

It is generally accepted that this depends on the presence of a favourable surface dipole set up as shown below:

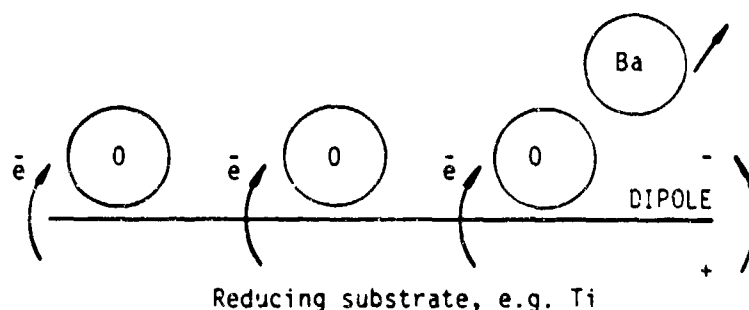


The precise nature of the surface layer which would give rise to this is a matter of some controversy. It is suggested here that the cathode surface consists of a monolayer of barium oxide orientated with barium at the surface.

As well as electron transfer of $\text{Ba} \rightarrow \text{O}$, there will also transfer from $\text{W} \rightarrow \text{O}$. This will result in a weakened Ba/O bond with respect to bulk barium oxide. In order to preserve the favourable $\text{Ba} \rightarrow \text{O}$ dipole, the electron transfer from $\text{O} \rightarrow \text{W}$ is required to be less intense and directional than that from $\text{Ba} \rightarrow \text{O}$.

On this basis a simple explanation can be developed for the influence of the poisoning metal overlayer.

For the reducing (electron donating) metals such as titanium and tantalum, the metal/oxygen interaction is very strong to the extent that the $\text{Ba} \rightarrow \text{O}$ bond becomes unfavourable and most of the Ba is desorbed. The result is an unfavourable surface dipole and a high work function (see below).



The XPS results are significant in this context. The poor resolution of the Ta 4f doublet is indicative of a mixture of chemical states, i.e. Ta and Ta^{2+} .

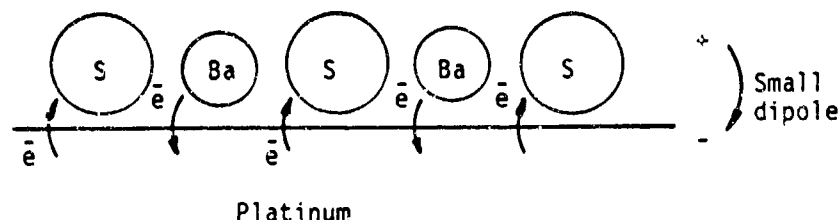
The corresponding W and Os doublets as measured on an M-type cathode are more clearly resolved, although this is not complete. W appears slightly less well resolved than Os. Therefore, although the large energy shifts associated with oxide formation are not apparent, more subtle changes in chemical state may be indicated.

Moving towards the more oxidising (electron seeking) elements at the righthand side of the transition block (Pt, Pd, etc.), the metal/oxygen interaction is highly unfavourable with the result that only barium and sulphur are initially observed on the surface.

The angle resolved experiments suggest that either S is situated above barium or they are coplanar, with sulphur considerably larger than barium.

The presence of sulphur may be related directly to the absence of oxygen as there is considerable evidence to suggest that they are in competition for sites on this cathode surface (unpublished in-house work). However, platinum would be more likely to form a stable bond with sulphur than oxygen due to the less oxidising (electron seeking) character of sulphur.

A possible arrangement for the Pt cathode surface early in life is shown below;



Ba $\rightarrow$ Pt is the only interaction likely to produce a favourable surface dipole, but this is likely to be very weak and is also offset by the S $\rightarrow$ Pt reverse dipole. The overall result would be a high work function surface and low emission, as is observed.

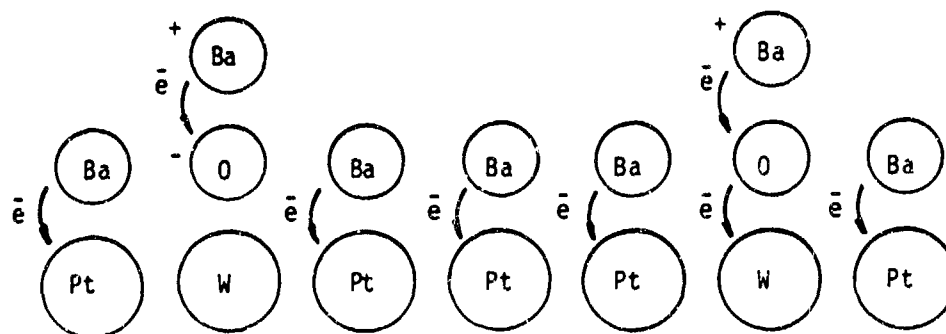
After overnight heating, the surface characteristics of the Pt cathode changed completely. Oxygen appeared and sulphur disappeared in the Auger spectrum. A possible reason for these changes could be the increased alloying of Pt with, or exposure of, the tungsten substrate. At this stage the proportion of W in the substrate was calculated as 30% (70% Pt). Tungsten was always observed in the 50 - 1050 eV spectrum even early on in the life of the cathode. It is likely, however, that tungsten has a significant influence on the cathode properties only if it is present in the first few atomic layers of the substrate.

To obtain this information, Auger transitions below 100 eV must be examined. Fig. 28 shows an Auger spectrum from 10 - 100 eV for the Pt cathode after a) 4 hours and b) 6 days at 1050 °C. There is a

noticeable decrease in the 60 eV Pt peak relative to those around 25 and 40 eV which are made up of Pt and W contributions. This implies that there has been a change in the composition of the first few atomic layers resulting in an increased proportion of W, although, based on the high energy Auger, this is unlikely to be more than 30% of the substrate.

On this basis a model can be prepared for the surface structure of the Pt coated cathode later in life.

Where tungsten is present at the surface, sites are available for the adsorption of an oriented BaO "molecule" as for a B-type. A proportion of the surface will therefore have a favourable surface dipole. The remainder, however, will consist of Ba loosely bound to Pt, which results in only a weak dipole.



This model is consistent with several other observations;

- i) The initial emission obtained from the Pt coated cathode was greater than that for Ta or Ti, consistent with the presence of a favourable $\text{Ba}^+ \text{Pt}^-$ dipole as opposed to an unfavourable $\text{O}^- \text{Ta}^+$ dipole.
- ii) The emission of the Pt cathode improved after overnight heating, consistent with the increased exposure of W at the surface and the associated B-type character.
- iii) The angle resolved study shows an increase in the Ba:O ratio at glancing electron exit angle consistent with Ba lying above oxygen.
- iv) The O:Ba ratio on a Pt coated cathode is considerably less than for a B-type. This would be the case if a significant proportion of the surface sites contained Ba but no O.

If this model is valid another important question is raised.

For the Ti coated cathode, W was always visible in the 50 - 1050 eV Auger spectrum, but without any barium or B-type character appearing in the Auger spectrum or in the emission performance.

It appears that the answer again lies in the low energy Auger spectrum 10 - 110 eV. Fig. 29 shows this spectrum for the Ti cathode after 4 days at 1050 °C_B. A very broad peak is observed between 20 and 30 eV which probably represents a mixture between titanium and titanium dioxide.

No peaks are observed at 38 and 48 eV for W.

It appears, therefore, that the first few atomic layers of the Ti cathode are titanium alone, i.e. Ti is strongly segregated to the

surface of the cathode. This would account for the persistent low emission and lack of barium observed throughout the life of the cathode.

This tendency is even more evident for Ta where no W is apparent even in the high energy spectrum (analysis depth ~ 10 monolayers).

For Pt there is some tendency towards surface segregation of W, resulting in the mixed character of the cathode.

So far, this discussion has produced a fairly simple explanation for the action of those metal overlayers which suppress cathode emission. This is based on simple chemical effects and fits most of the observations.

A more difficult task is to produce a model for the emission enhancing overlayers.

7.3 Emission enhancing overlayers

The emission enhancing metals examined were osmium and iridium. These elements lie in the centre of the transition block, whereas the emission suppressing elements, lie at each end.

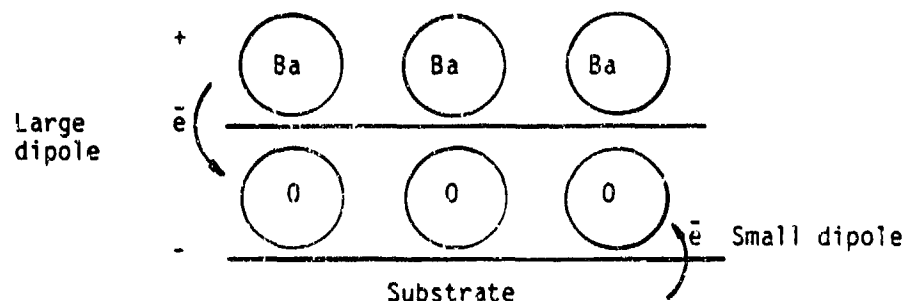
It has been suggested that the reducing metals at the left-hand side interacted so strongly with oxygen that the O-Ba bond was weakened to the extent that barium was desorbed.

By contrast, at the right-hand side, the metal/oxygen interaction was so unstable that oxygen was desorbed and only barium was to be observed on the surface.

Both these conditions lead to an unfavourable surface dipole and poor emission.

It seems reasonable to suggest that osmium and iridium represent an intermediate situation, i.e. where the interaction of the substrate with oxygen is just strong enough to allow adsorption of a BaO molecule on the surface with minimum weakening of the Ba-O bond.

Ideally, this would result in a surface consisting of orientated BaO molecules, with barium at the surface, in which the Ba $\rightarrow$ O dipole is stronger than the substrate $\rightarrow$ O dipole.



This situation is believed to exist for a B-type cathode; how is it improved upon by the addition of osmium or iridium?

The angle resolved plots for the Os cathode indicate that the O/Ba ratio increases and then decreases, going from glancing to normal to glancing electron exit angle. This implies that either barium is lying above oxygen or that barium has a larger atomic radius. Which is more likely?

If significant electron transfer from barium to oxygen has occurred, then the Ba atom is likely to be smaller than O.

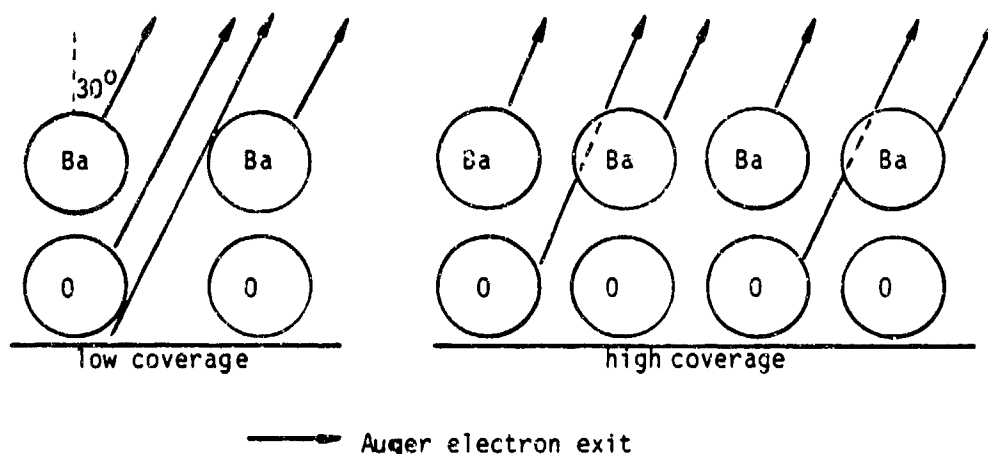
Barium lying above oxygen is possibly, therefore, a more likely explanation for the angle resolved results.

The Auger analysis of the flat B-type and Os coated cathode indicates a decrease in the oxygen concentration in the latter compared with the B-type.

What changes in the cathode surface would produce this effect? There are two possibilities:

a) If the overall surface concentration of orientated BaO molecules was higher on the M-type.

For flat samples the Auger electron exit angle is approx. 30° to surface normal. In this situation, a higher coverage of molecules would tend to produce a decrease in the O signal relative to barium as indicated in the diagram below. However, it would also tend to enhance both the Ba and O signals relative to the substrate and this is not observed in these cathodes. Ba/substrate remains fairly constant and O/substrate decreases for the Os coated cathode.



b) Another, more likely, explanation could result from the mixed character of the Os and Ir cathodes. It has been observed for many examples of these cathodes that W becomes visible at the surface very early in life and continues to increase in concentration with time.

There is a corresponding improvement in emission which reaches maximum at a certain Os/W (Ir/W) concentration. This implies that it is the Os/W or Ir/W mixture which is really responsible for the emission enhancement and not the metal overlayer itself.

Early in life the surface of an M-type cathode is likely to consist of "patches" of (Os+W) and pure osmium. It is possible that the pure osmium areas have little affinity for O and tend to absorb Ba alone, leaving the orientated Ba-O molecules associated with the (Os+W) areas. This would account for the apparent decrease in O on the M-type cathode surface, as some sites would contain barium but no oxygen.

Later in the life of the cathode, when alloying has progressed further, the oxygen concentration relative to the substrate and to barium would be expected to rise; this has been observed in-house for many samples.

Thus so far the situation described is very similar to that devised for the Pt coated cathode, but with very different results with respect to work function. The nature of the Pt/W "alloy" must therefore be different from that of Os/W or Ir/W.

It is observed from the binary phase diagrams for Os, Ir and Pt that definite phases are produced for W/Os and W/Ir. These phases represent intimate atomic mixing, resulting in intermetallic compounds of a definite and different structure from either of the original metals. This is not observed in the platinum-tungsten system.

It is possible that it is the new structures and electronic effects resulting from the Os/W and Ir/W alloys which produce the ideal cathode surface.

We suggest that surface sites are produced which combine with BaO in such a way that the weakening of the BaO bond is minimised.

The XPS results indicate that Os and W are not significantly oxidised, i.e. there is little transfer of electrons from Os & W $\rightarrow$ O compared, for instance, with Ta.

A further piece of evidence comes from the low energy barium transitions which, in the case of Os and W cathodes, are free from interfering peaks.

Fig. 30 a,b and c shows the low energy Auger transitions from 40 - 90 eV for a B-type, an M-type and a cathode coated with a mixture of Os and W (this last cathode had the best emission performance).

The peak at 72 eV arises from the Ba 2s valence electrons. It is largest for the B-type and smallest for the Os/W cathode, indicating that the latter has fewest Ba 2s electrons and the B-type has most, i.e. there has been the most electron transfer from barium to oxygen for the Os/W cathode. This would result in the largest δ^{+Ba}_{-O} dipole and the lowest work function.

This method of analysis was suggested by Haas, et. al. (Ref. 6), studying monolayer BaO films on mixed W and Ir substrates; slightly different conclusions were drawn, however.

8. CONCLUSIONS

8.1 In general, a metal overlayer on a dispenser cathode appears to have a permanent effect on emission performance only if it remains at the surface. Those cathodes for which the metal overlayer evaporated from, or diffused into, the matrix, reverted to B-type.

One exception to this was found to be the nickel cathode for which an emission improvement was observed even after the surface nickel concentration had become undetectable in AES. This effect is unexplained at present.

In a situation of continuous evaporation from an external source (a technique which was not used in this work), the effect on the emission performance for metals in this category would be expected to be extended.

8.2 Reducing (electron donating) metals at the extreme left of the transition series (Ti and Ta) decompose BaO to free Ba, which is desorbed, and O which remains on the surface. This sets up an unfavourable surface dipole, resulting in a high work function.

8.3 Oxidising (electron seeking) metals at the extreme right of the series (Pt, Pd, Au) react more favourably with barium than with oxygen, with the result that oxygen is desorbed and only barium is observed on the surface. This sets up a small favourable dipole which results in a higher work function than S-type but lower than for the reducing metals.

Later in cathode life, Pt was the only metal from this group which remained visible with Auger spectroscopy and this cathode was the only one to maintain a high work function. Tungsten was also visible, which contributed to some B-type character.

8.4 The emission-enhancing metals studied (Os and Ir) occur at the centre of the transition series. They were always visible at the surface, but were extensively alloyed with the tungsten substrate.

Other important observations of the emission-enhanced cathodes were;

8.4.1 Angle resolved Auger spectroscopy indicates that barium is lying above oxygen.

8.4.2 These cathodes appear to have less oxygen relative to the substrate than B-type.

8.4.3 The oxygen concentration increases with life, corresponding with increased alloying with the substrate and improved emission.

8.4.4 XPS results indicate Os and W are not strongly oxidised, i.e. there is little significant electron transfer from Os $\rightarrow$ W and W $\rightarrow$ O.

8.4.5 Low energy Auger results indicate an increase in electron transfer from Ba for Os and Os/W cathodes relative to B-type.

8.5 These observations are thought to be consistent with the following model;

8.5.1 Early in life the Os (or Ir) cathode consists of patches of Os and patches of Os/W alloy.

8.5.2 The pure Os areas are combined only with Ba and produce only a small favourable dipole.

8.5.3 The Os/W areas are combined with orientated BaO molecules with barium oxide at the surface and in such a way that the $O \rightarrow Ba$ dipole is stronger than is the case on a B-type cathode, i.e. more electron transfer from $Ba \rightarrow O$.

8.5.4 This is possibly achieved by the special electronic and structural properties of the Os/W and Ir/W alloys which enable BaO to be adsorbed on the surface with minimal electron transfer from substrate to oxygen and therefore minimal weakening of the $O - Ba$ dipole.

8.5.5 During the life of the cathodes, increased alloying produces an increase in the oxygen concentration, more electron transfer from $Ba - O$ and an improvement in emission.

While this model appears to correspond with the observations from these experiments, the authors would be willing to agree that other explanations may be possible.

It appears fairly certain that the formation of an Os/W or Ir/W alloy is the critical factor in the emission enhancement of these cathodes. However, the precise electronic interactions between Os+W, Ba and O are difficult to determine and any model should be regarded as speculative until more evidence can be obtained.

9. SUGGESTED FUTURE WORK

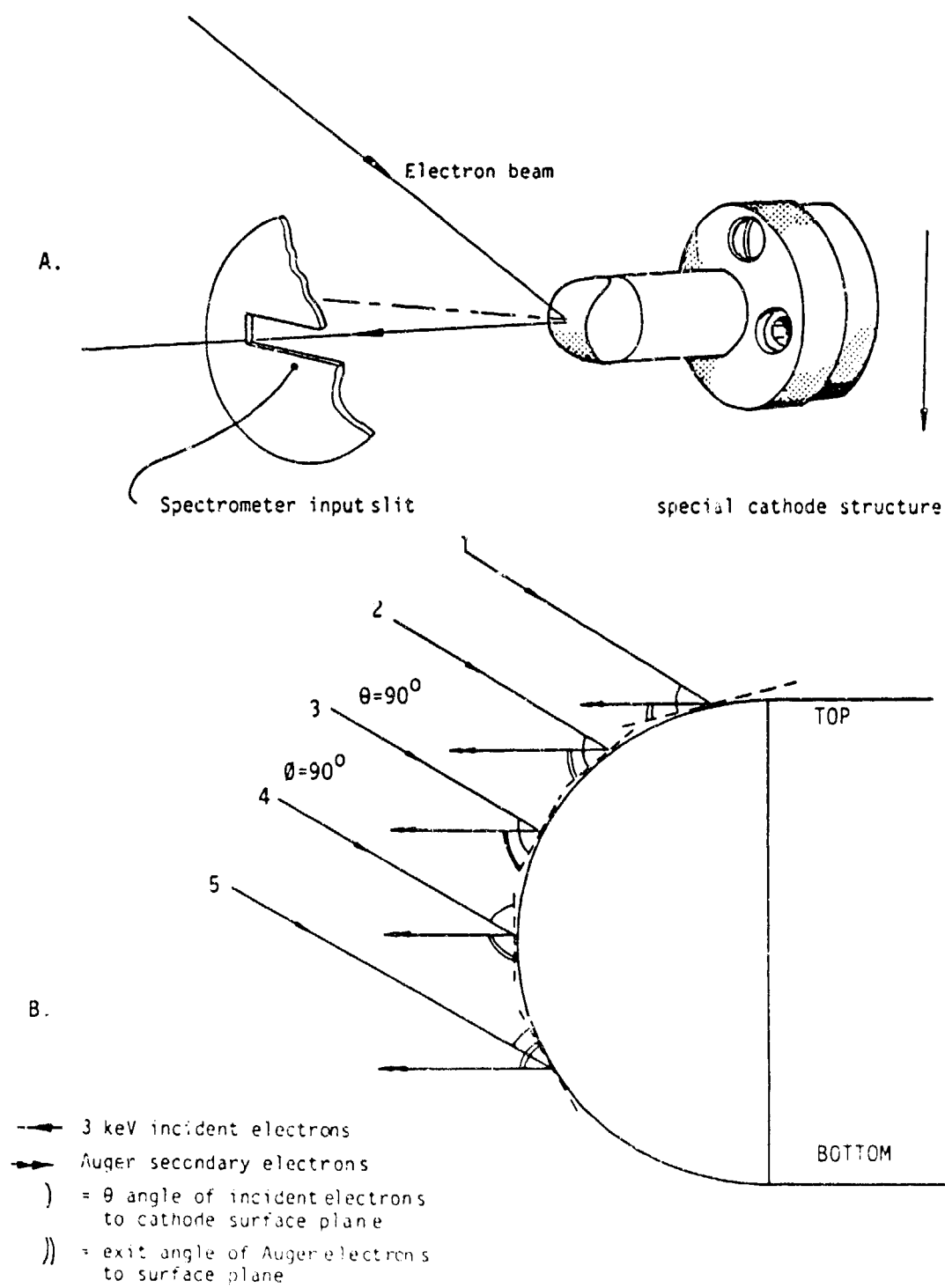
Further cathode improvements are most likely to be made by studying binary and ternary alloys of the heavy transition metals towards the centre of the periodic table.

Other possibilities to be investigated are multi layer film structures of varying composition. To obtain more precise information on the alloy structure and positions of Ba and O on the surface more sophisticated surface analytical techniques will need to be investigated.

10. REFERENCES

1. H.B.Skinner, R.A.Tuck, P.J.Dobson: J.Phys.D.Appl. Phys.15 (1982)
1519 - 1529.
2. Contract to AFOSR No. F49620-79-C-0026.
3. R.A.Tuck; Vacuum 33 10-12 715 (1983).
4. M.P.Seah, W.A.Dench; Surface and Interface Analysis, Vol. 1,
No. 1, 1979.
5. Scientific Foundations of Vacuum Technique; Dushman, Lafferty,
publ. Wiley, Chapter 10.
6. G.A.Haas, A.Shih, C.R.K.Marrian; Naval Research Lab. Report
(pre-publication).

Fig. 1. Angle resolved AES



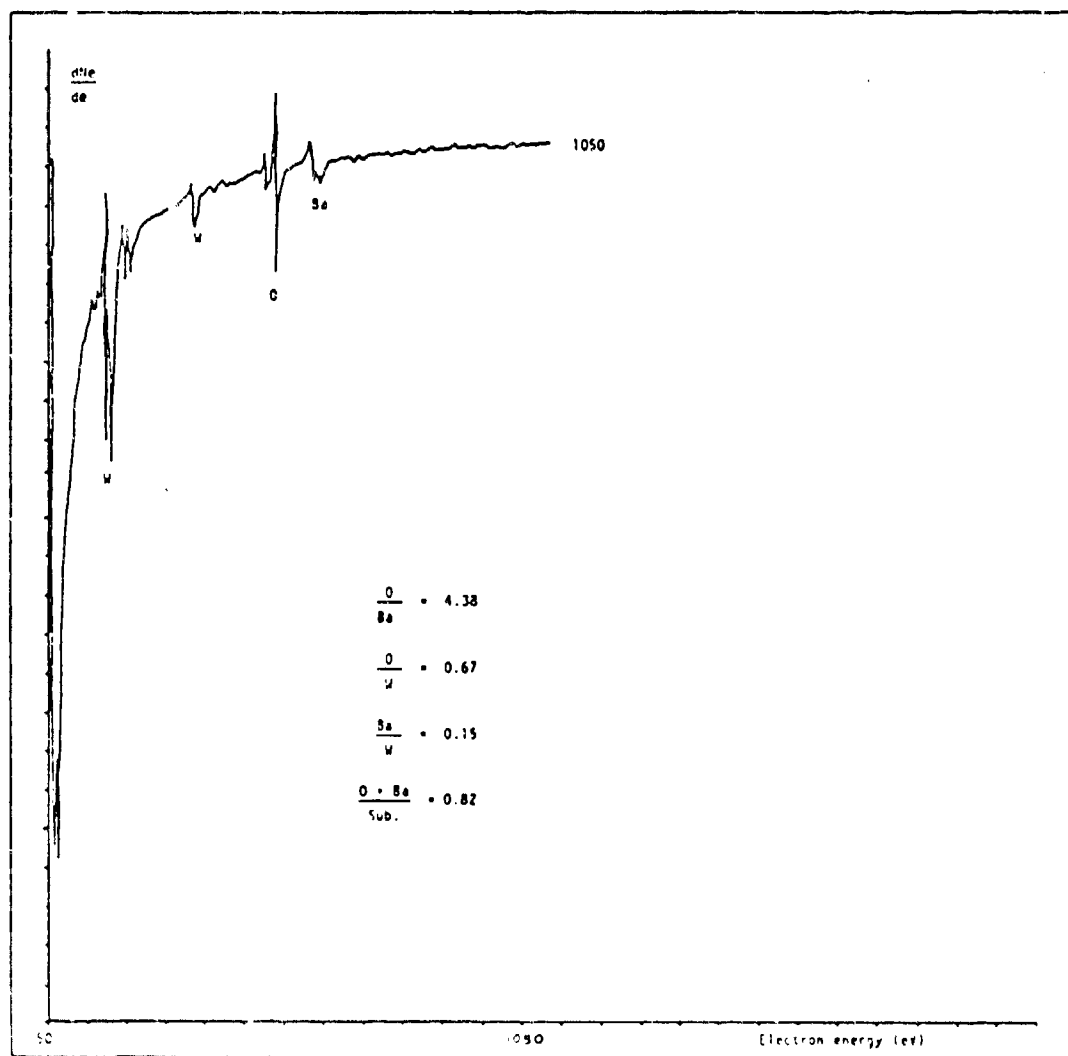


Fig.2. Auger spectrum of an activated B-type Cathode.

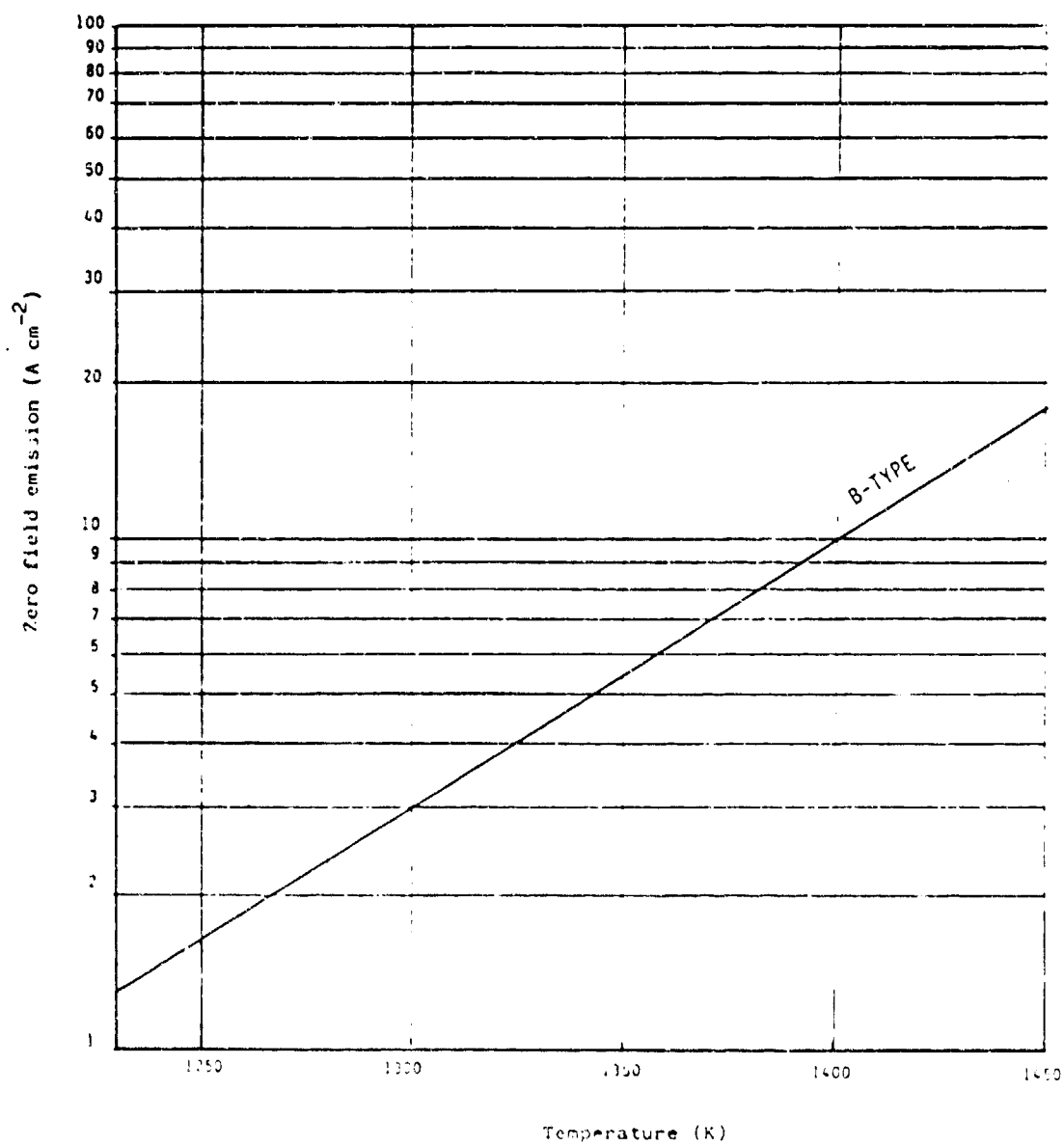
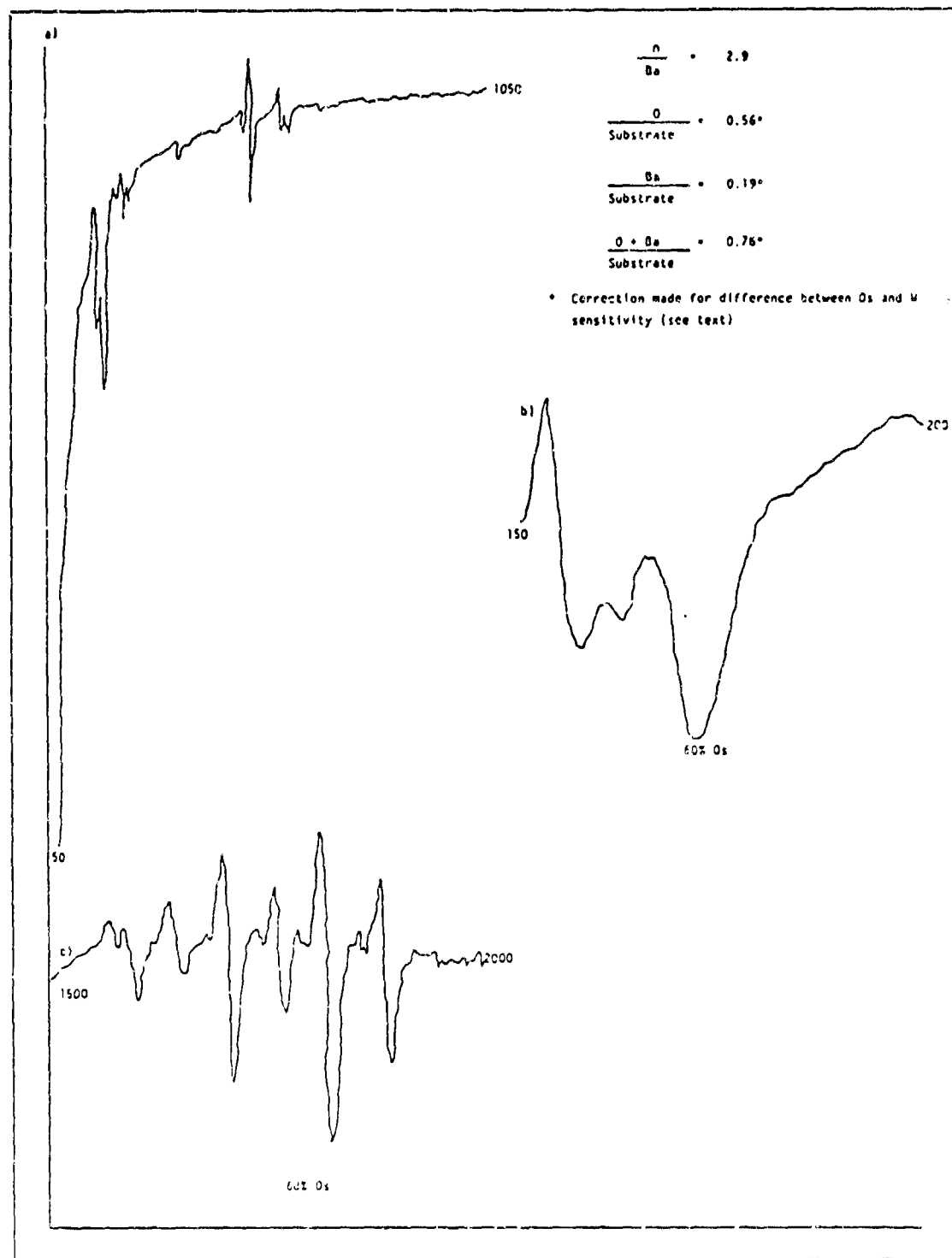


Fig.3. Emission performance of an activated B-type cathode



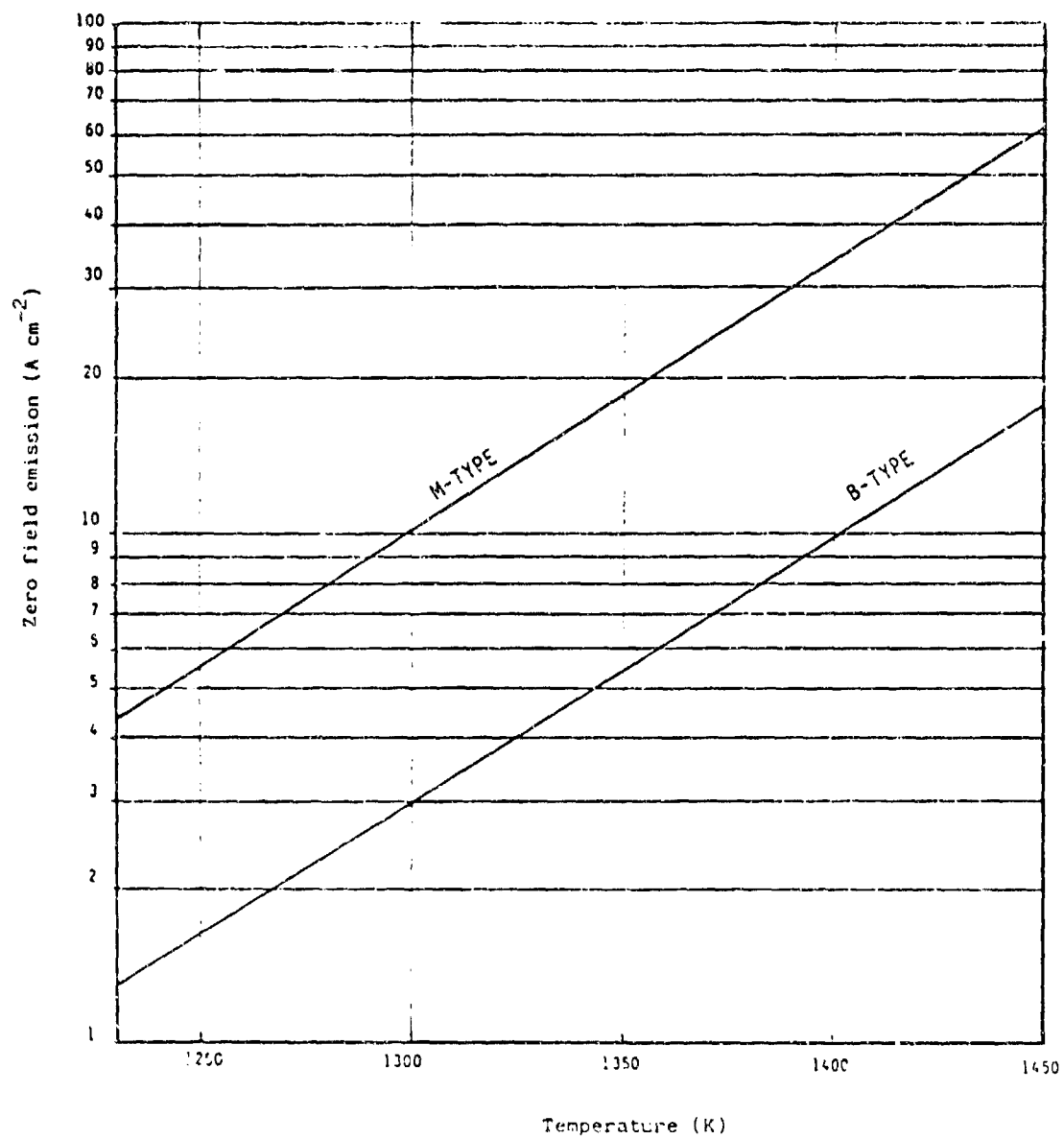


Fig.5. Emission performance of an activated M-type cathode.

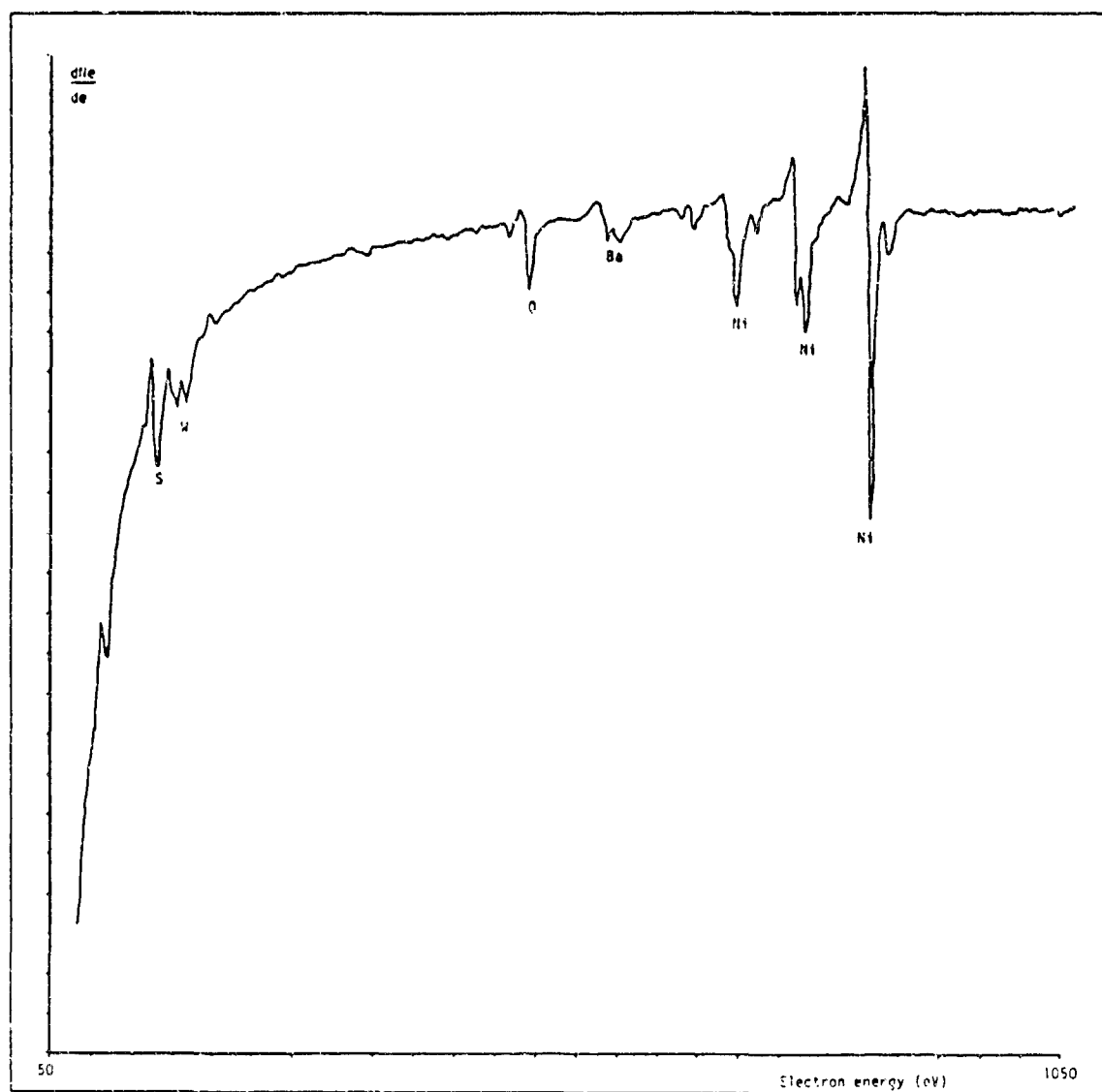


Fig.6a Ni coated cathode after 15 mins at 1110°C_B

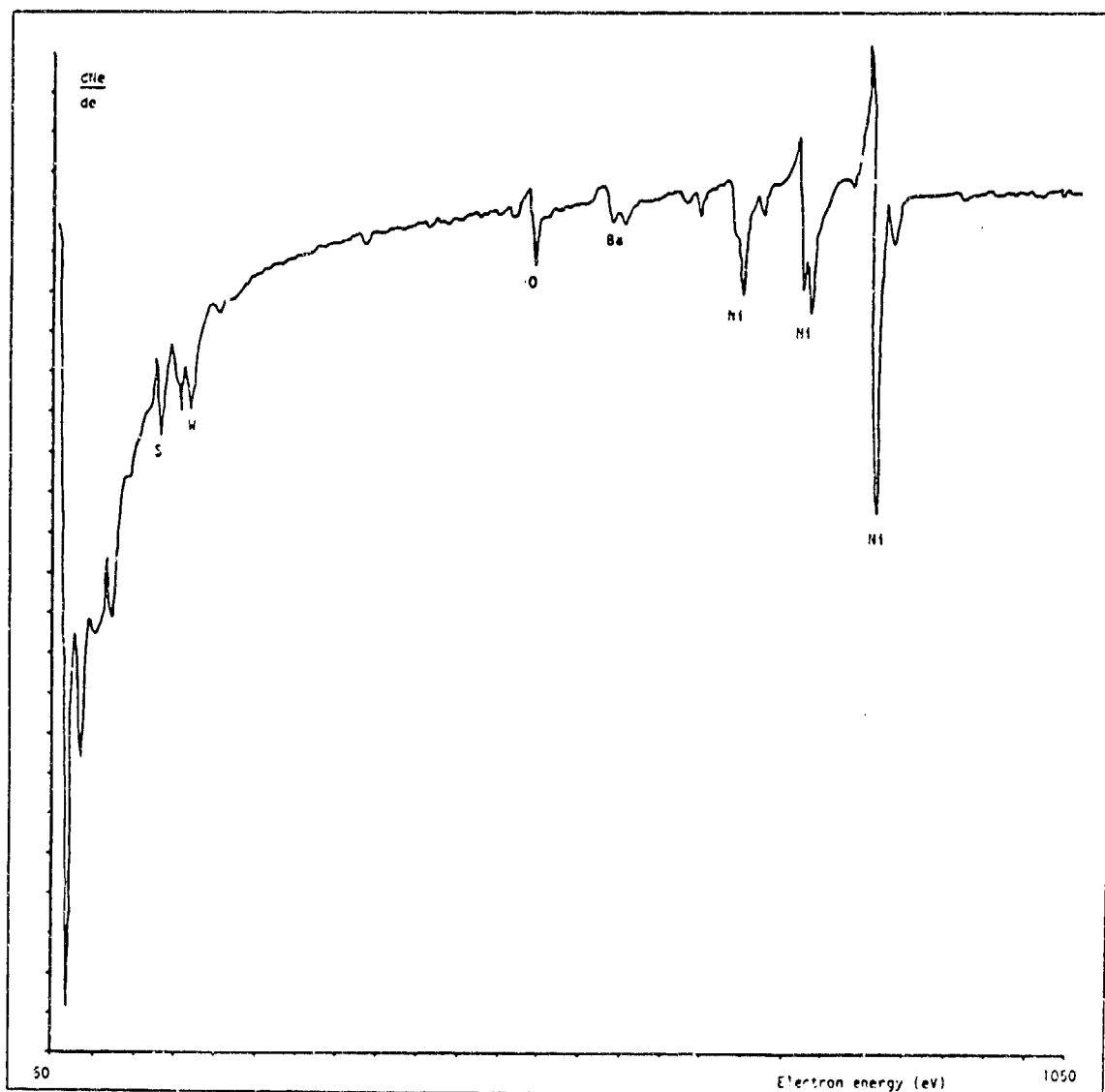


Fig.6b. Auger spectrum of Ni coated cathode after 8 hours at 1000 °C_B

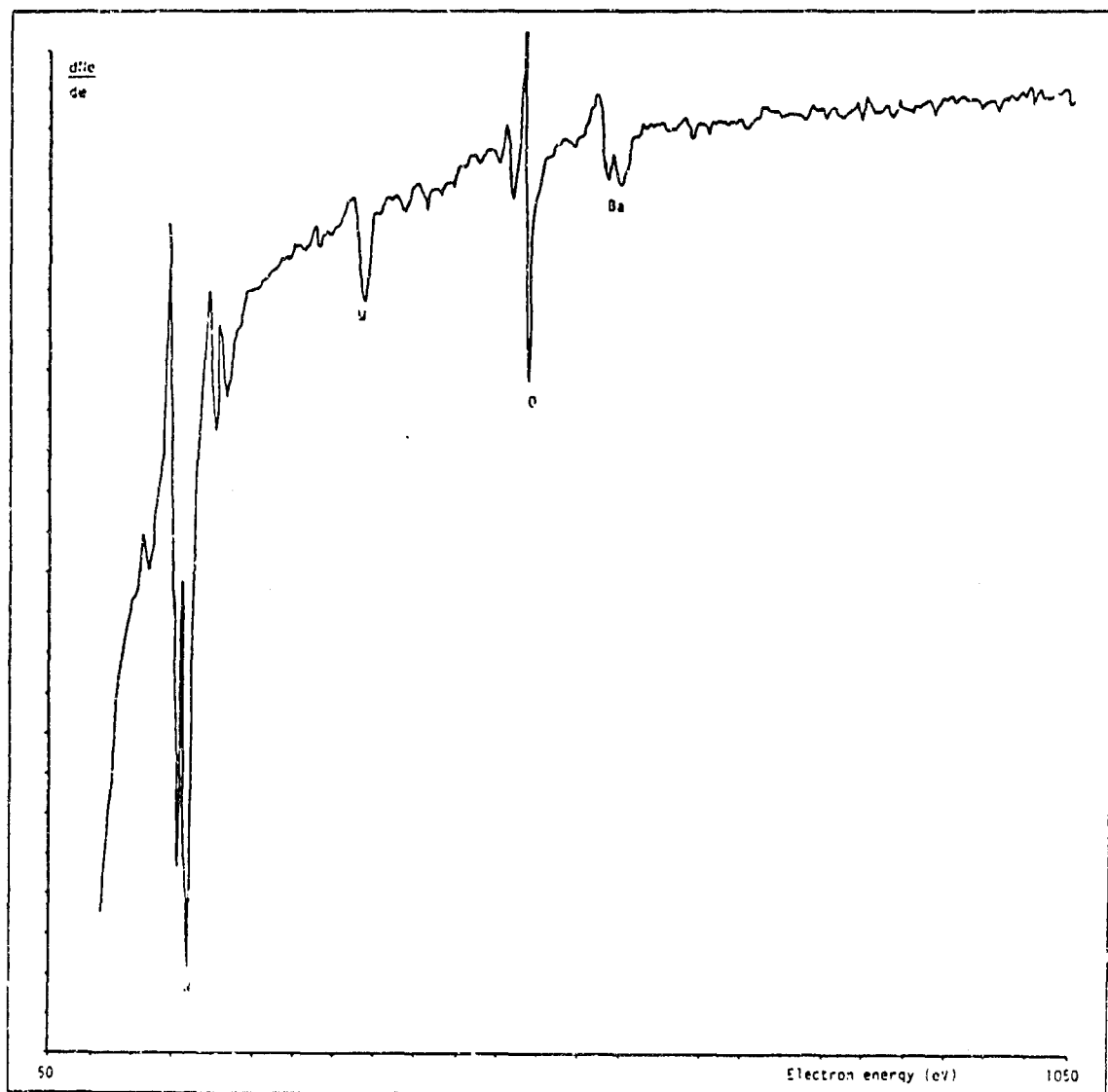


Fig.6c. Auger spectrum of Ni coated cathode after 12 hours at 1050 °C_B

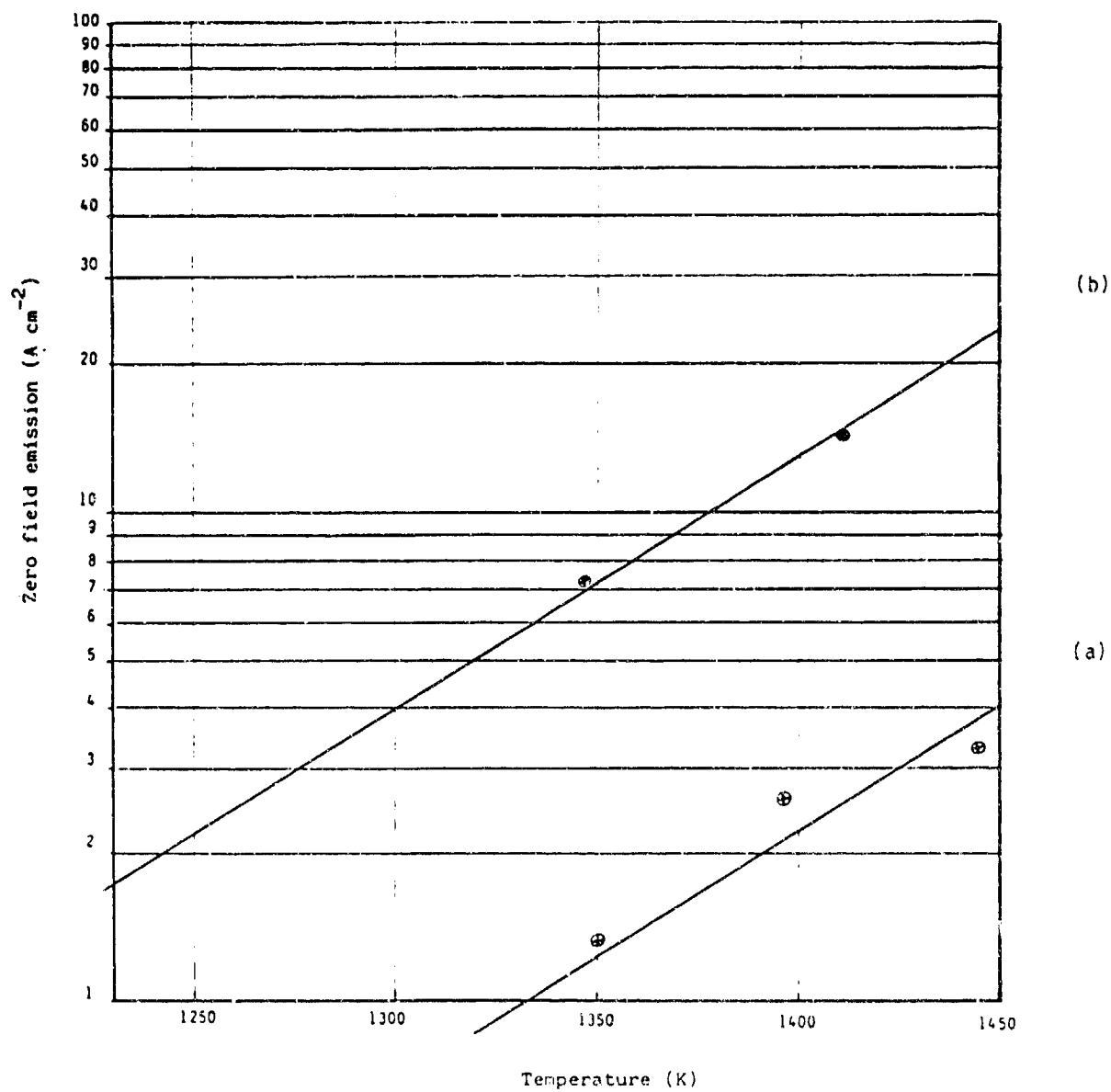


Fig.7. Emission performance of Ni coated cathode.

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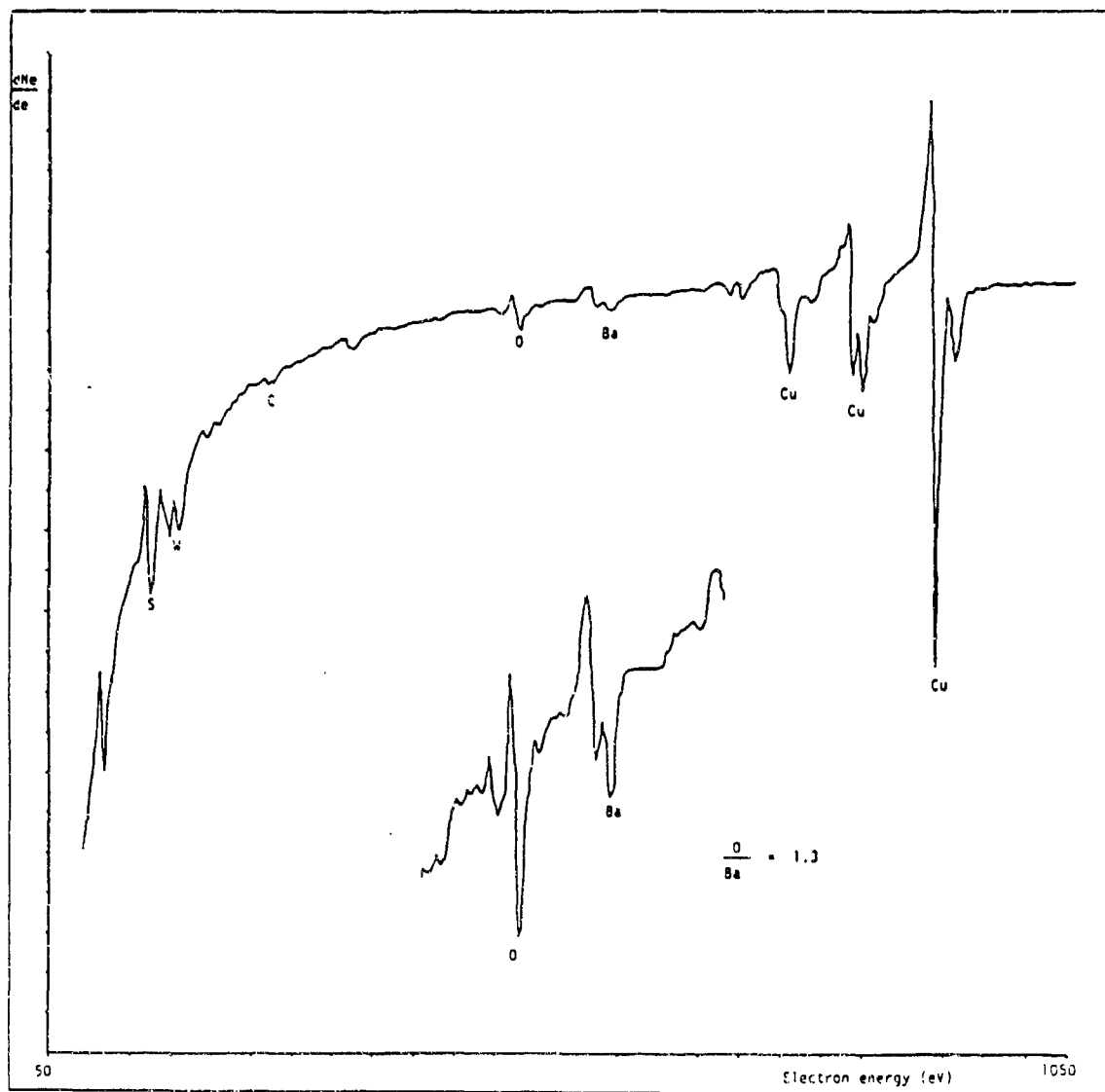


Fig.8a. Auger spectrum of Cu coated cathode after 30 mins at 875 °C_g

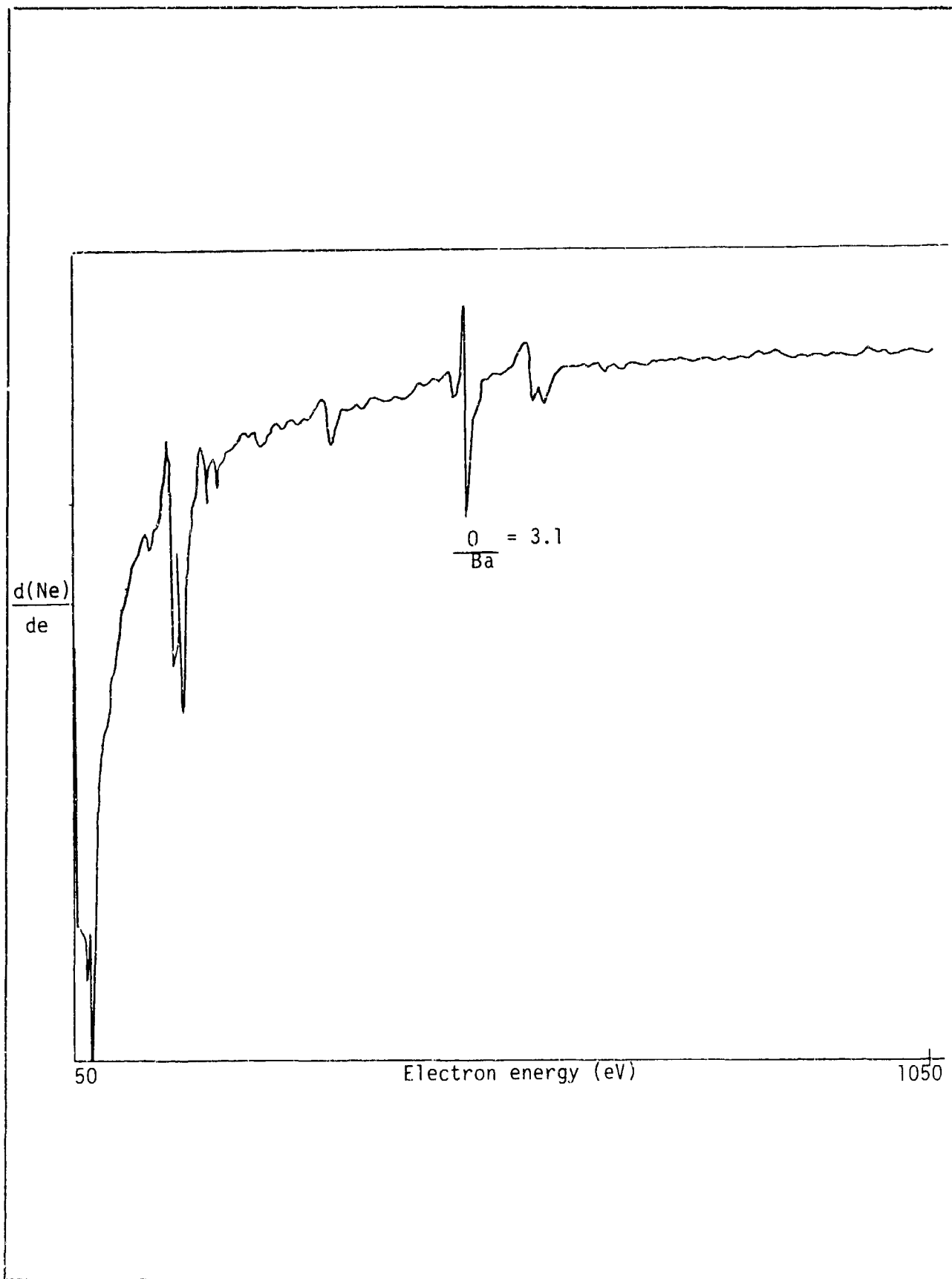


Fig.8.b. Auger Spectrum of Cu Coated cathode after
3 hrs at 875 C_B

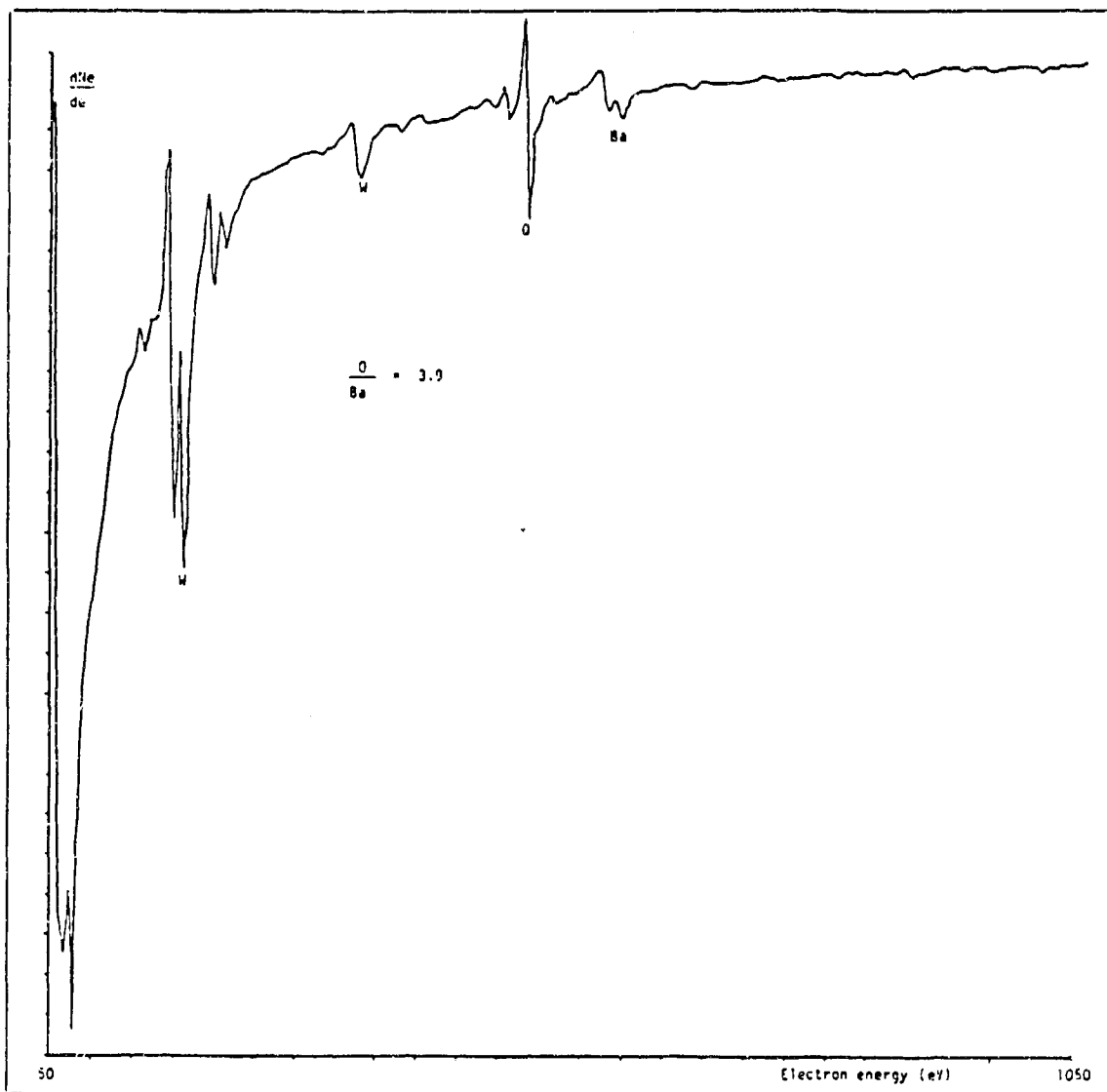


Fig.8c. Auger spectrum of Cu coated cathode after 12 hours at 1070 °C_B

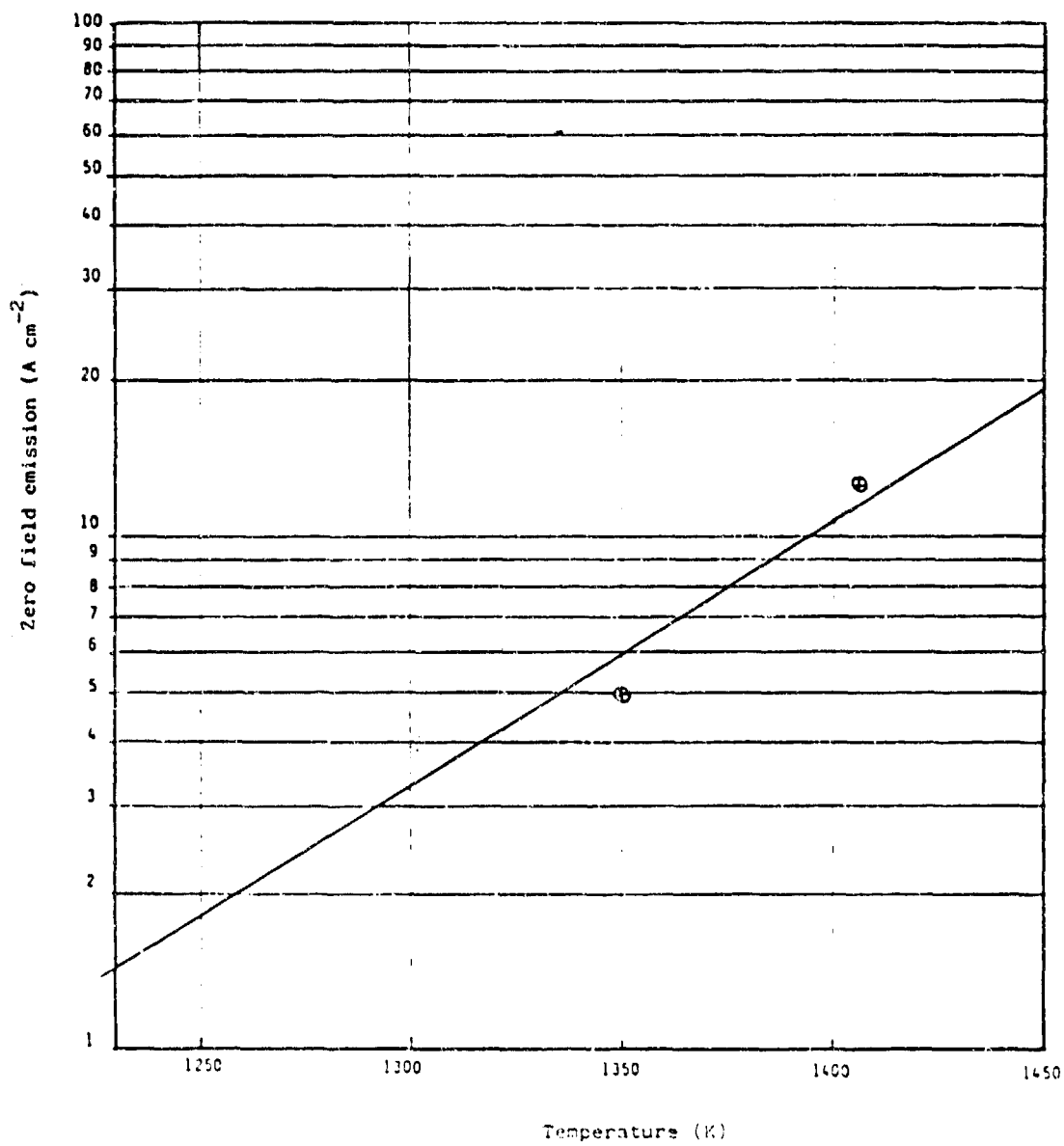
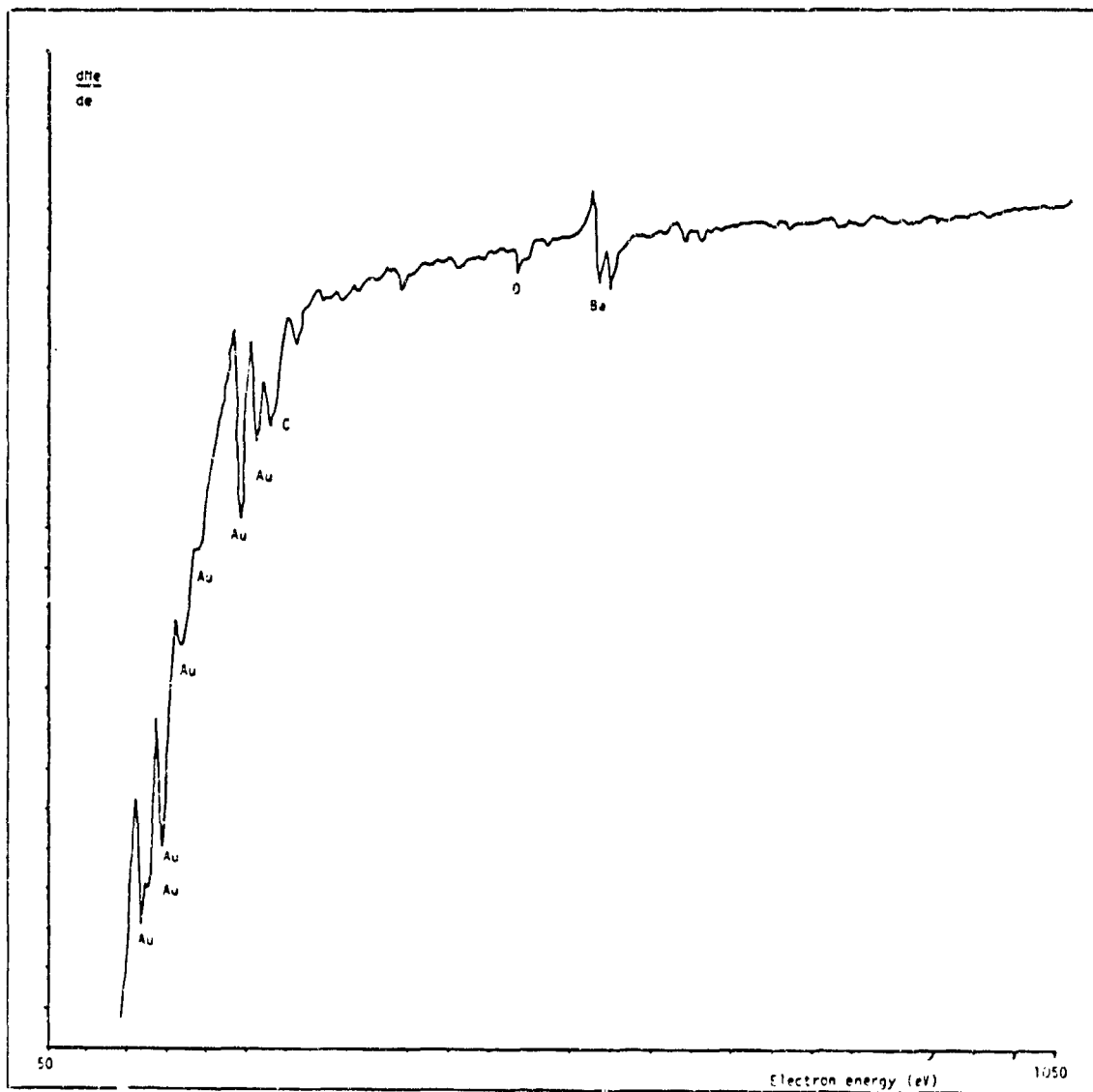


Fig.9. Emission performance of Cu coated cathode after 12 hours at 1070 °C_B.



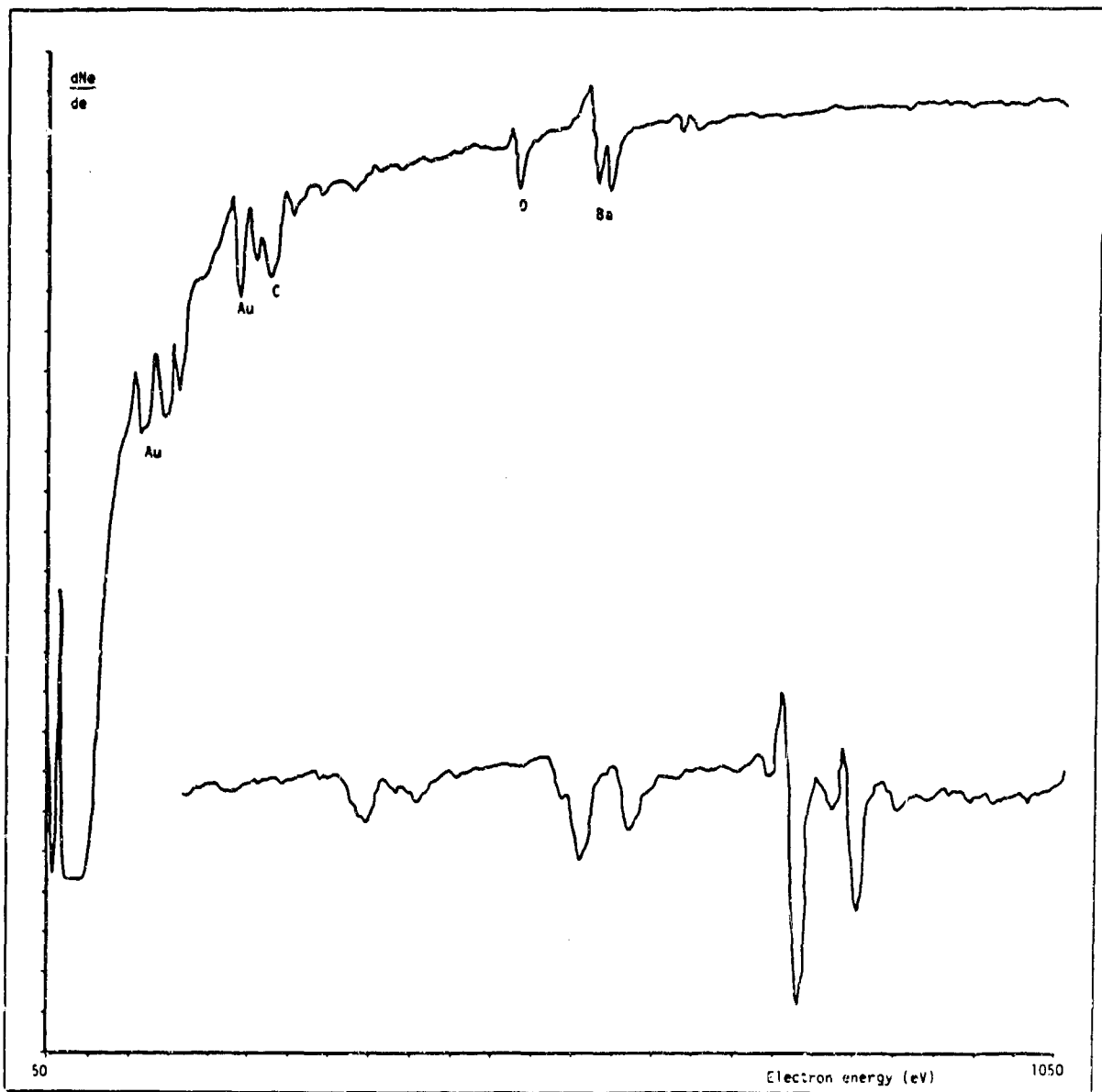


Fig.10b. Auger spectrum of Au coated cathode after 900 °C_B

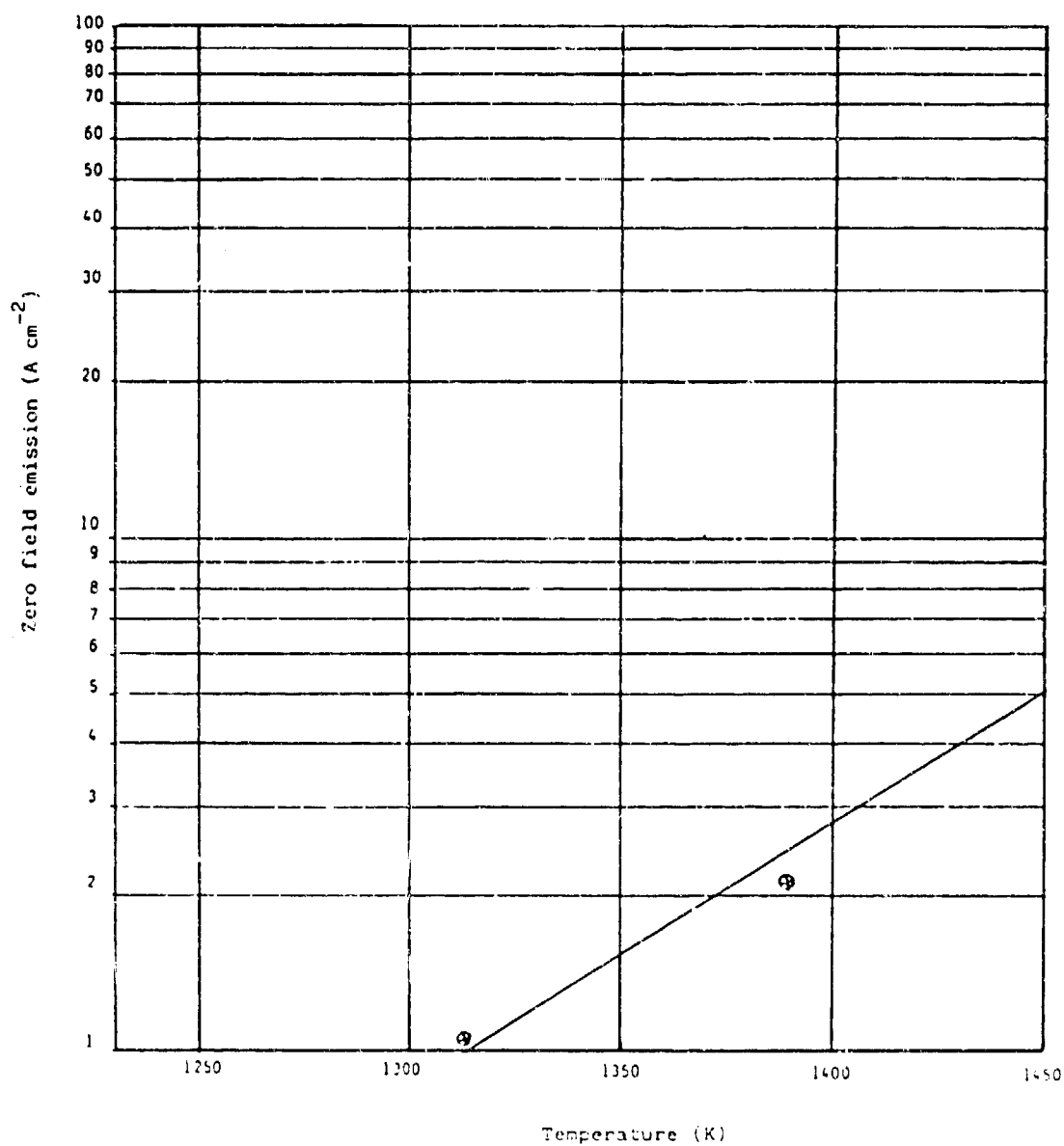


Fig.11. Emission performance of Au coated cathode after 12 hours
at 980 °C_B

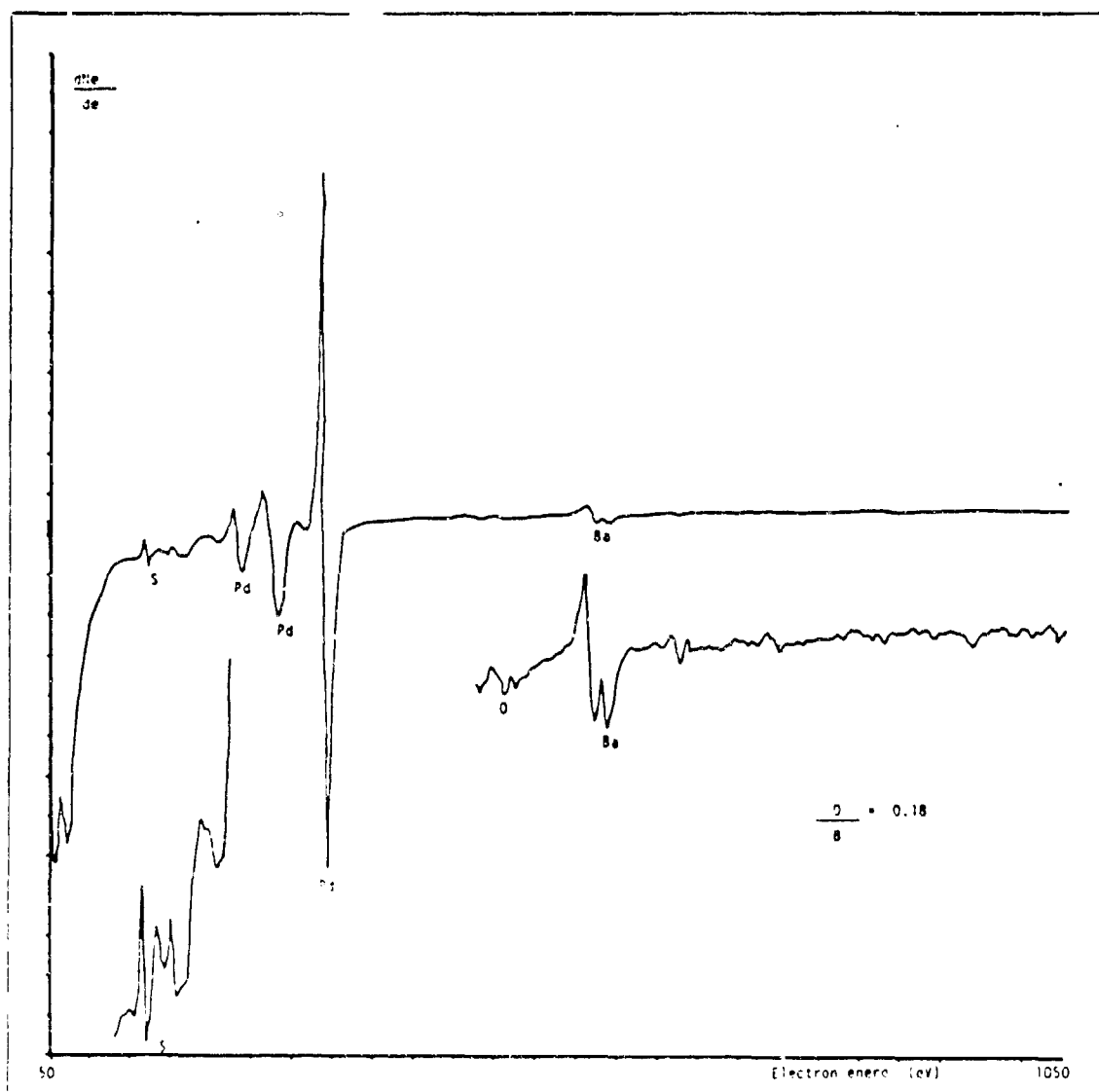


Fig.12a Auger spectrum of Pd coated cathode after 1 hour at 1000 °C_B

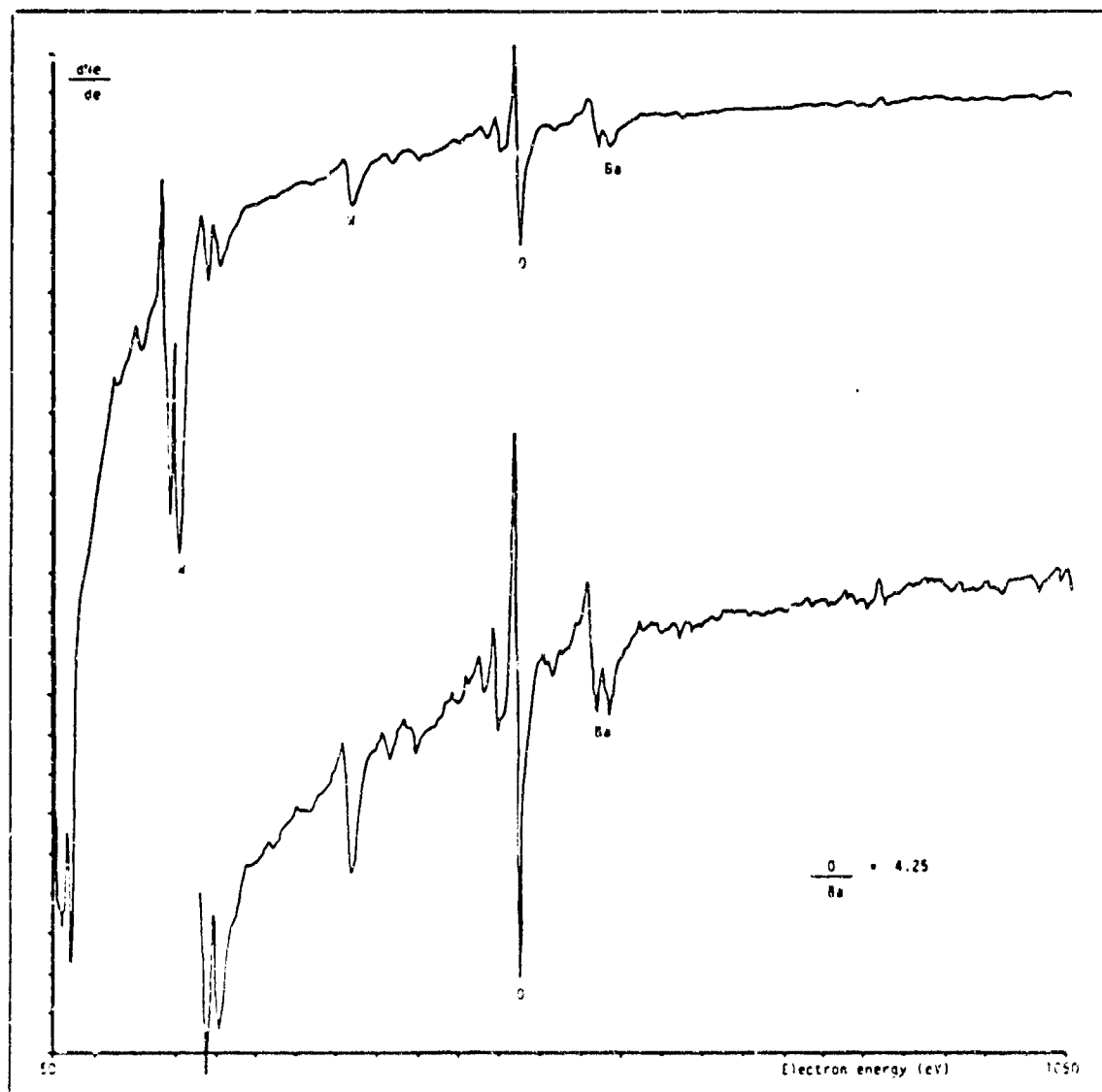


Fig.12b. Auger spectrum of Pd coated cathode after 12 hours at 1070 °C_B

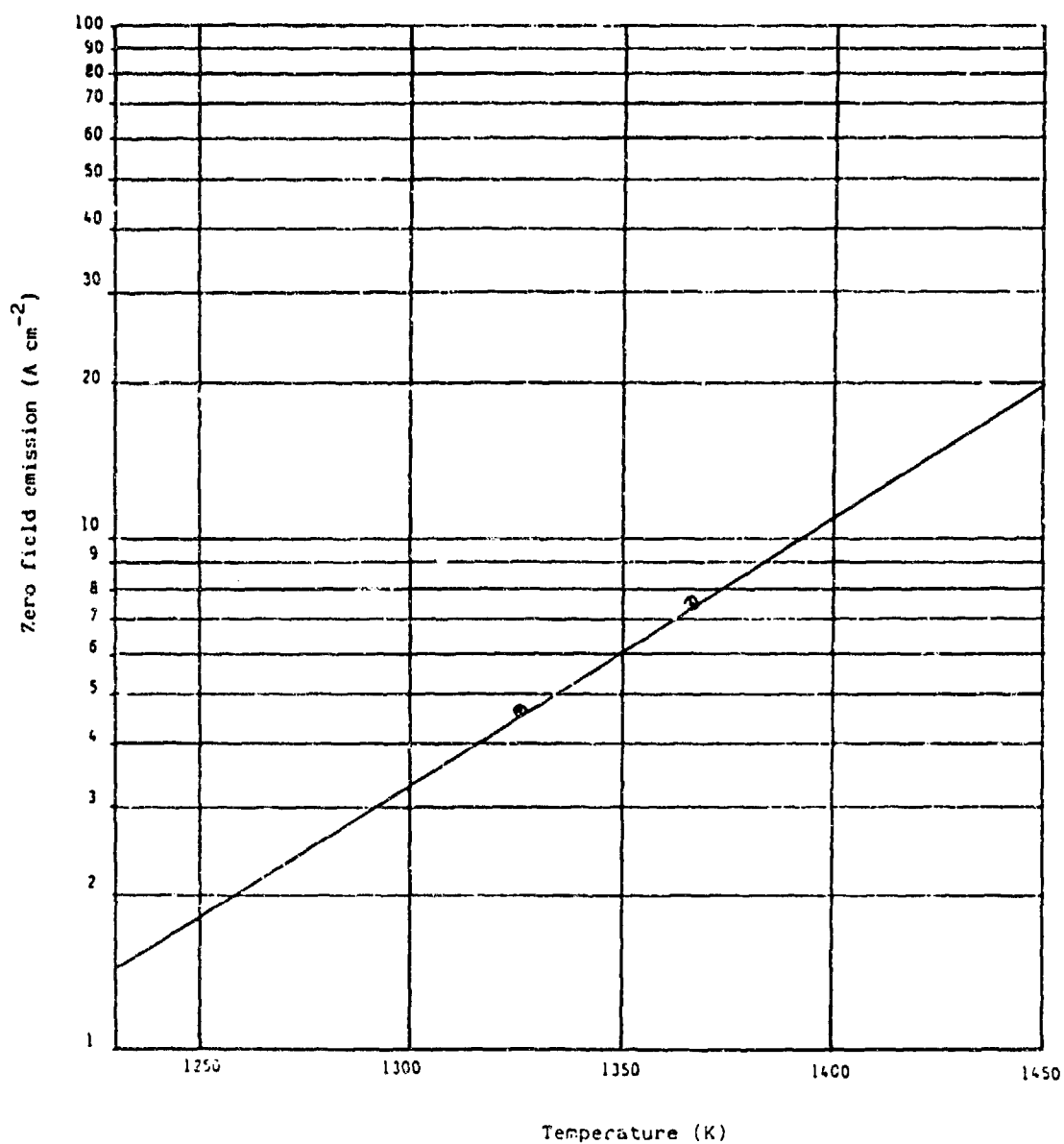


Fig.13 Emission performance of Pd coated cathode after
12 hours at 1070 °C_B

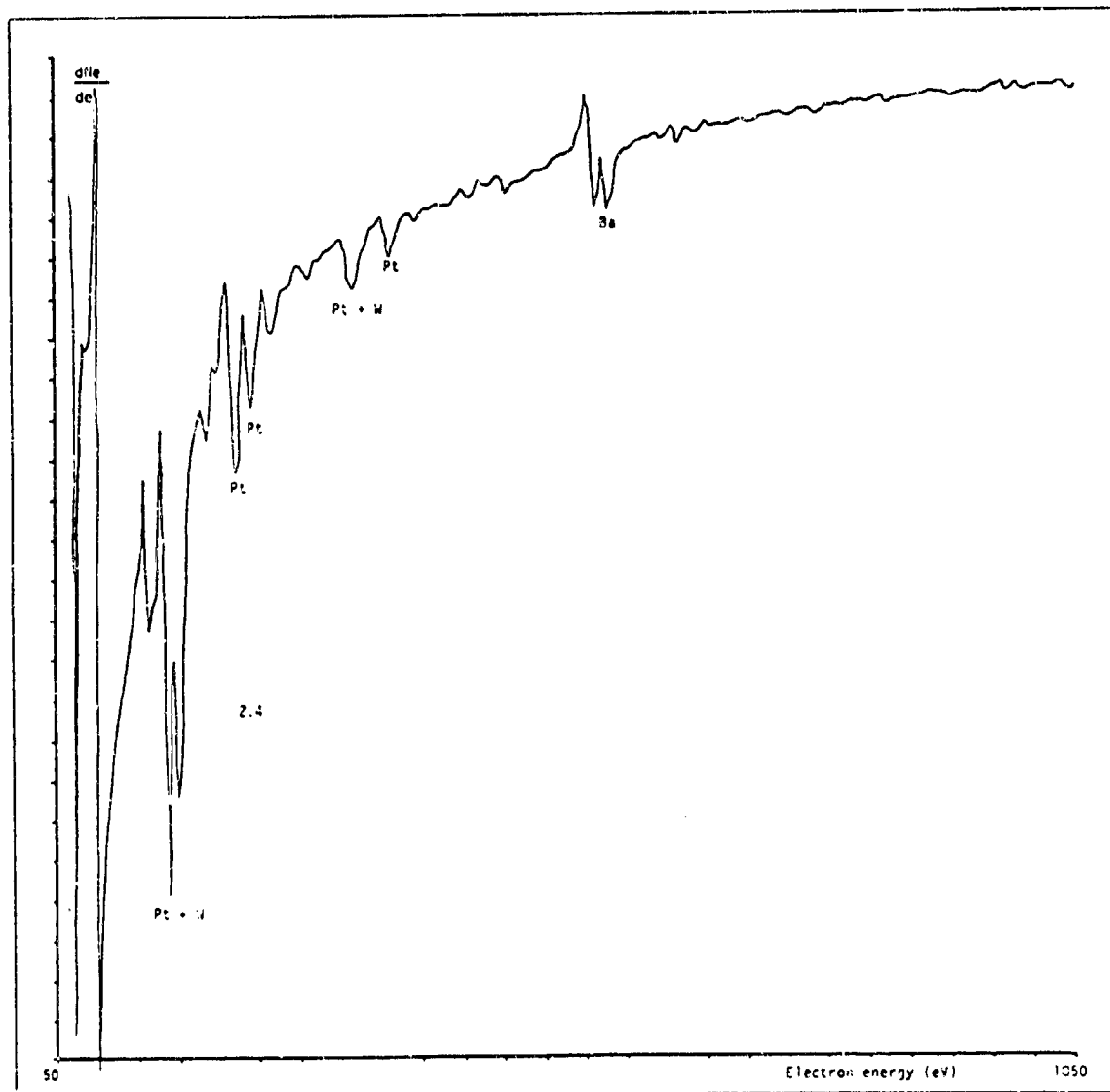


Fig.14a Auger spectrum of Pt coated cathode after 4 hours at 1020 °C_B

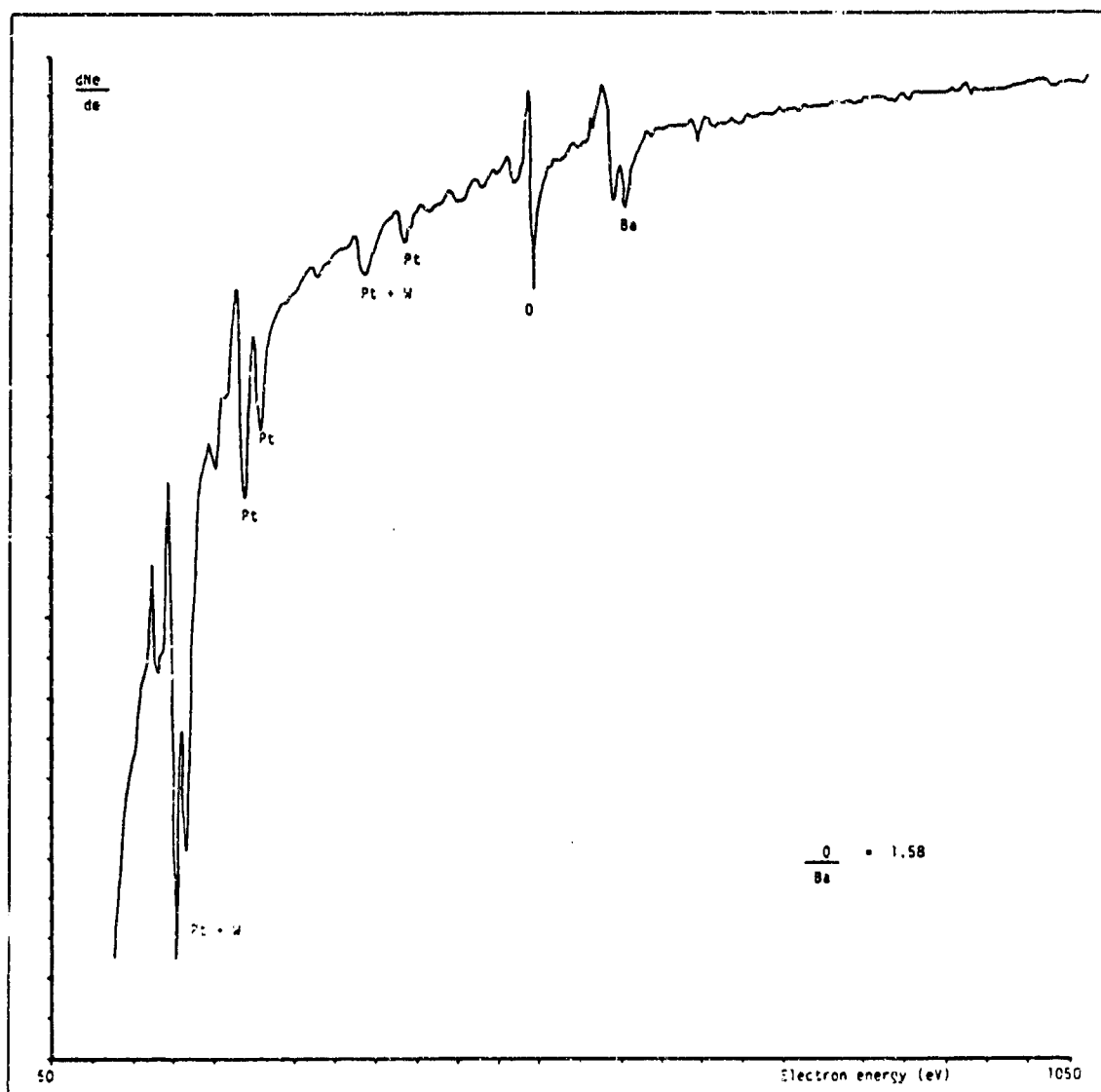


Fig.14b Auger spectrum of Pt coated cathode after 3 days at 1050 °C_B

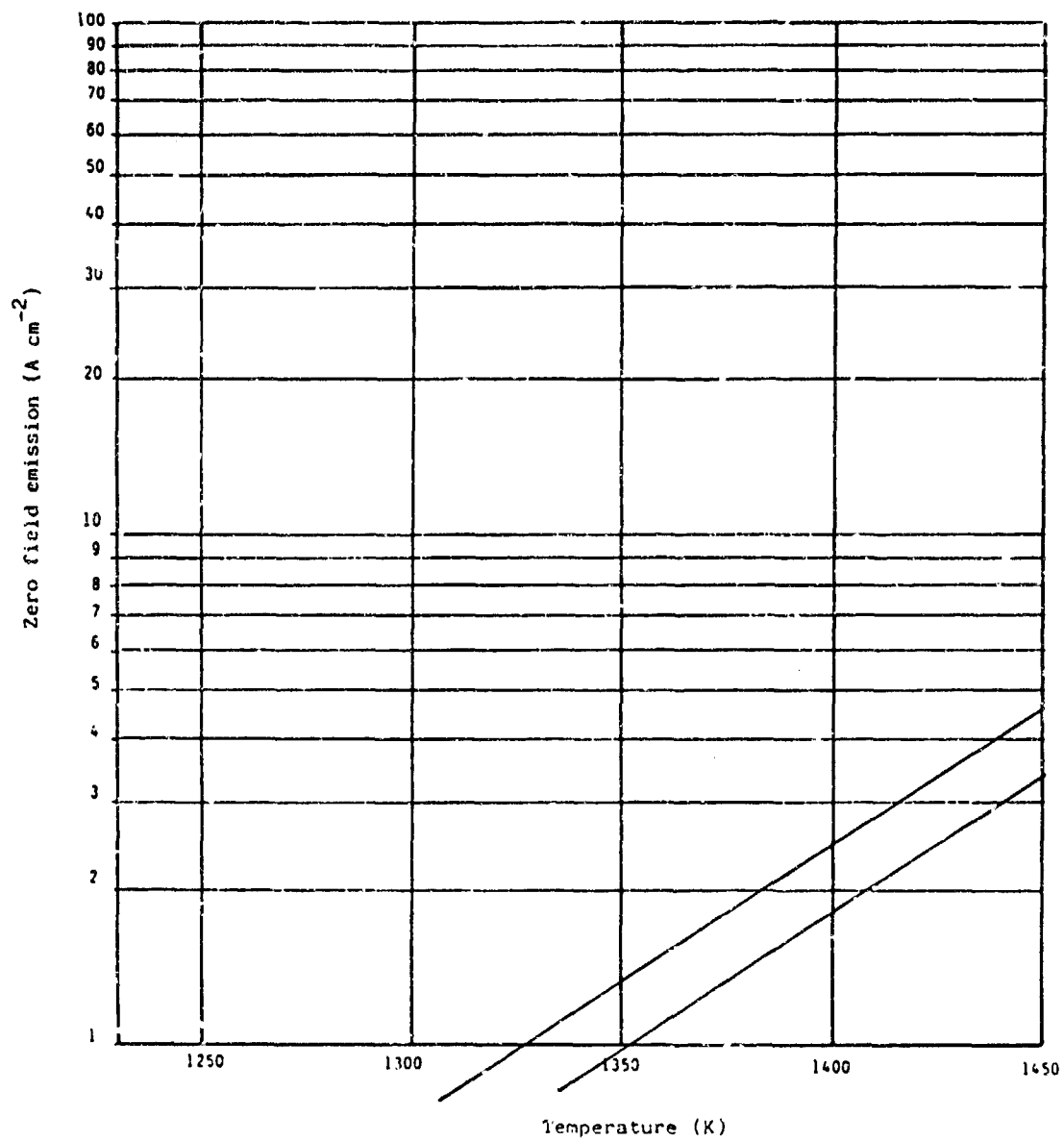


Fig.15 Emission performance of Pt coated cathode after
 (a) 4 hrs at $1050^{\circ}C_B$ (b) a further 3 days at $1050^{\circ}C_B$

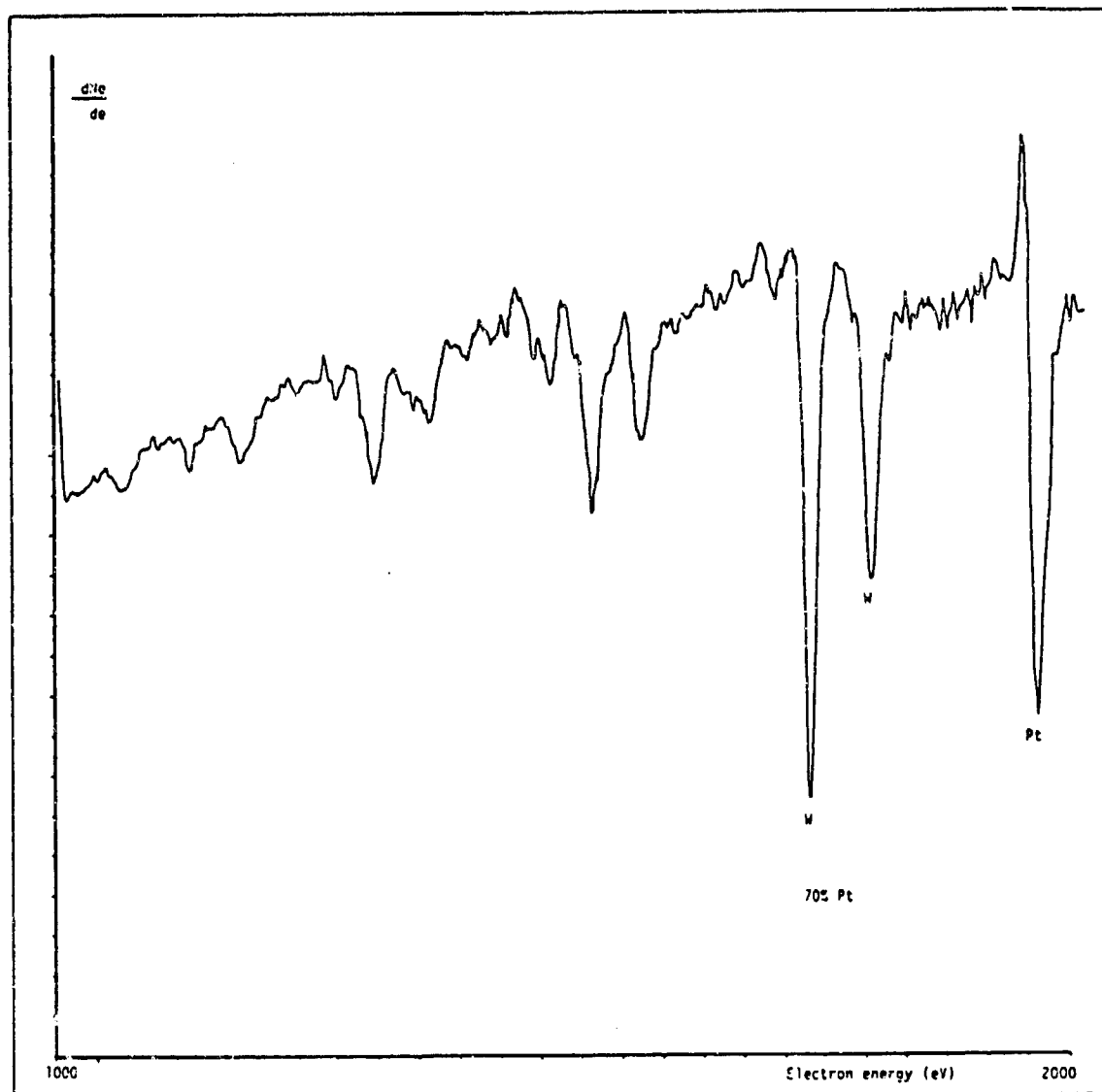


Fig.15. High energy Auger spectrum of Pt coated cathode after 3 days
at 1050°C_B

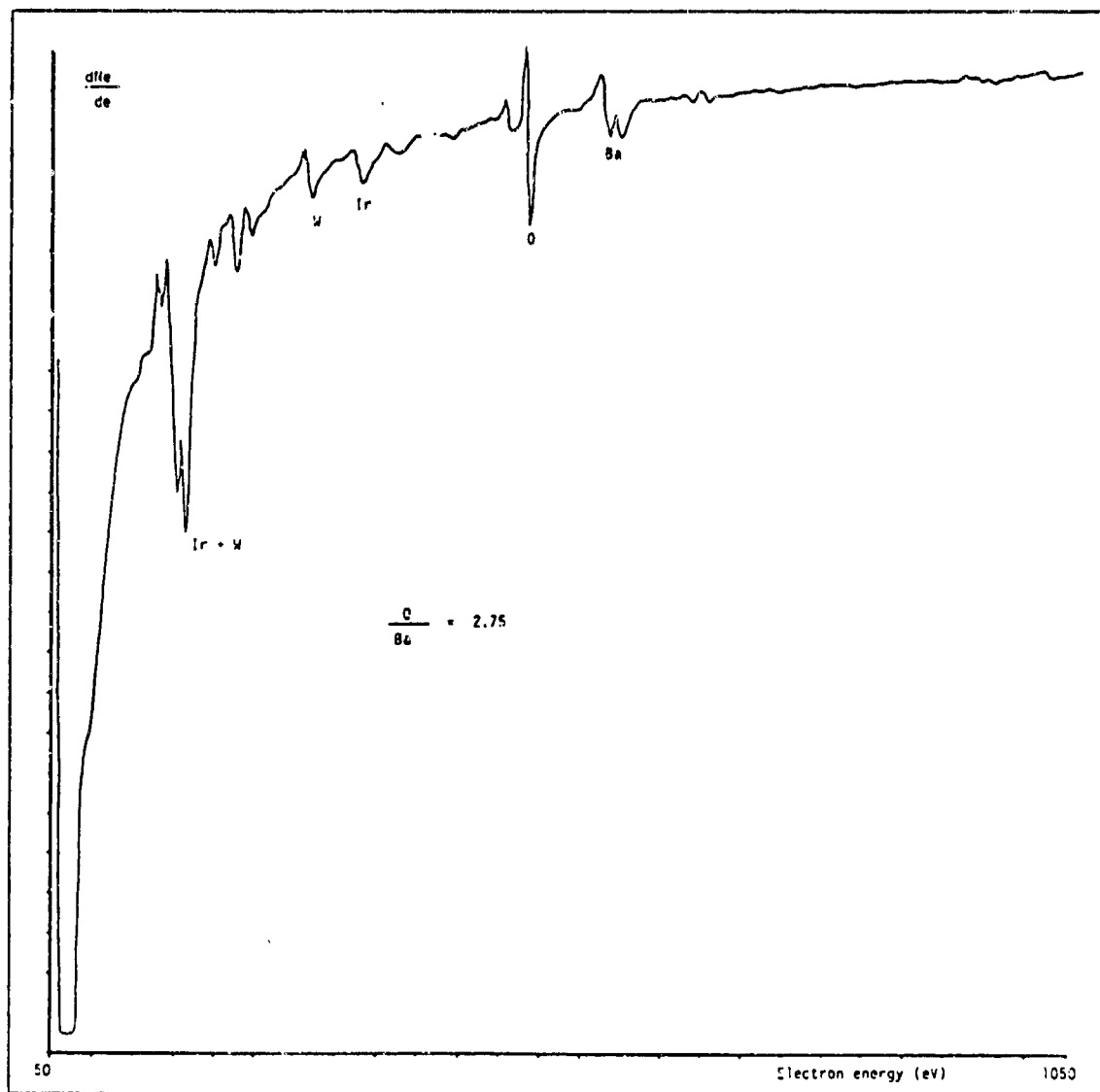


Fig.17a Ir coated cathode after 2 days at 1050°C_B

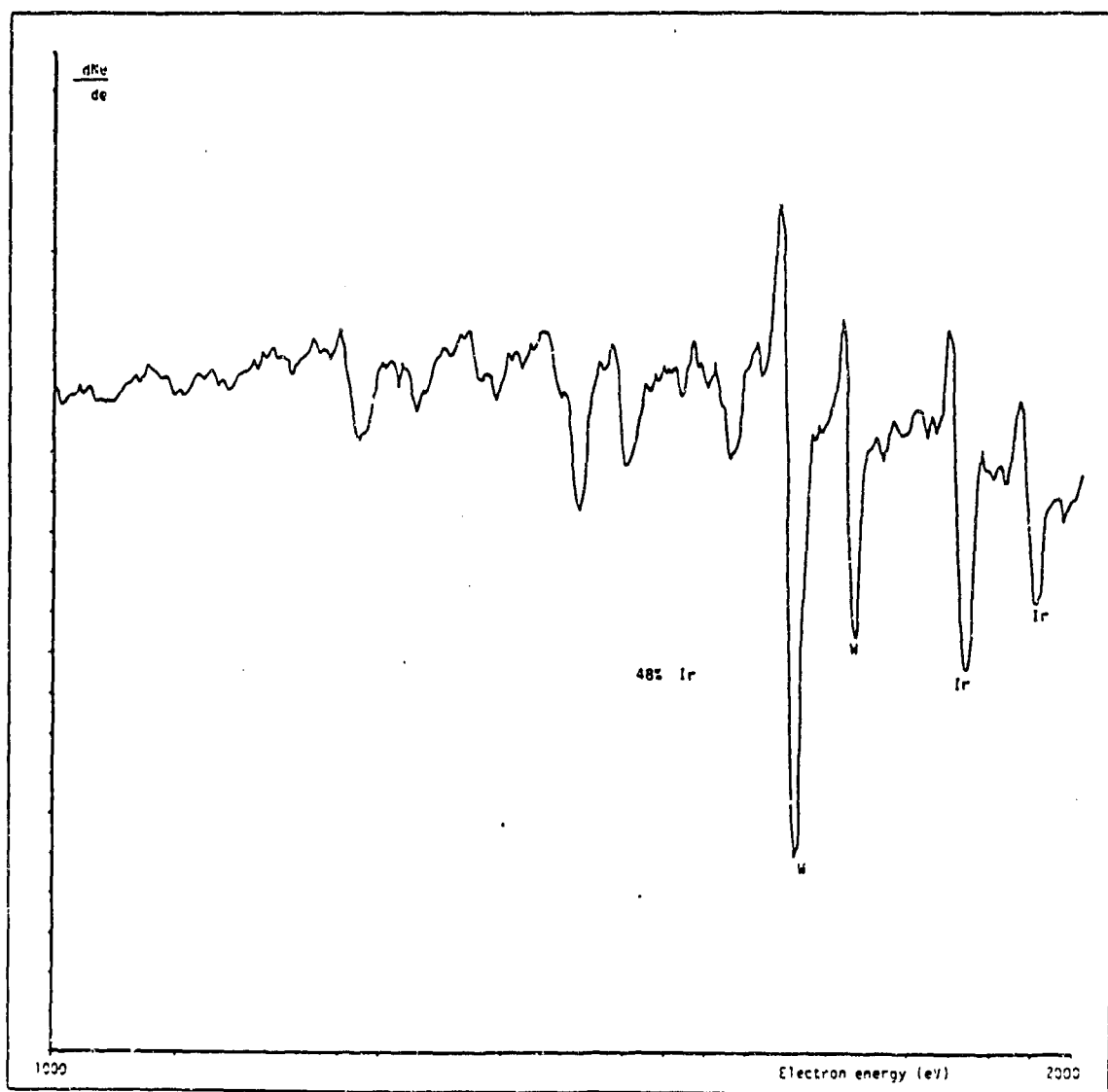


Fig.17b High energy Auger spectrum of Ir coated cathode after 2 days
at 1050 °C_B

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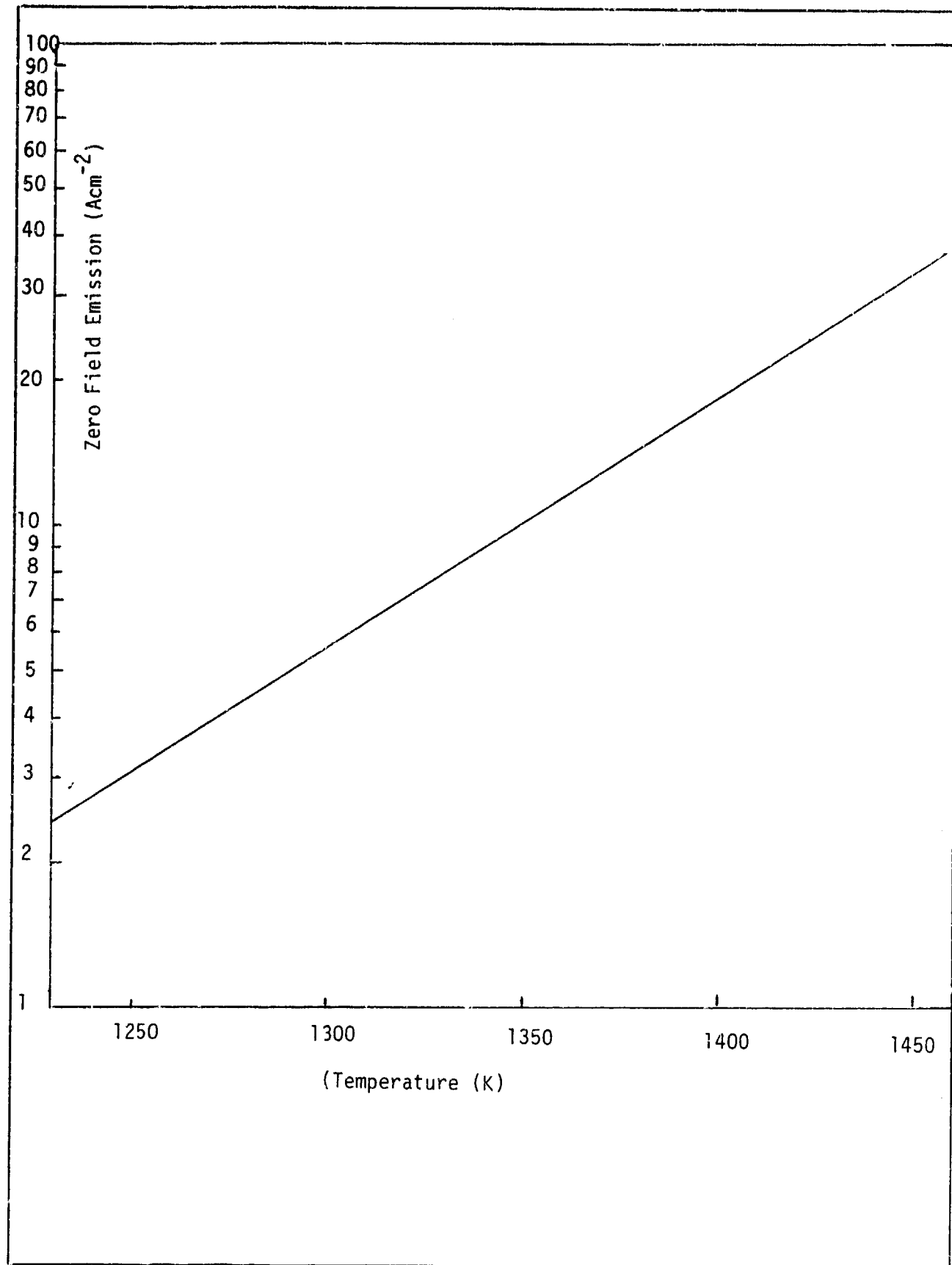


Fig.18. Emission performance of an Ir coated cathode after 2 days at 1050 C_B

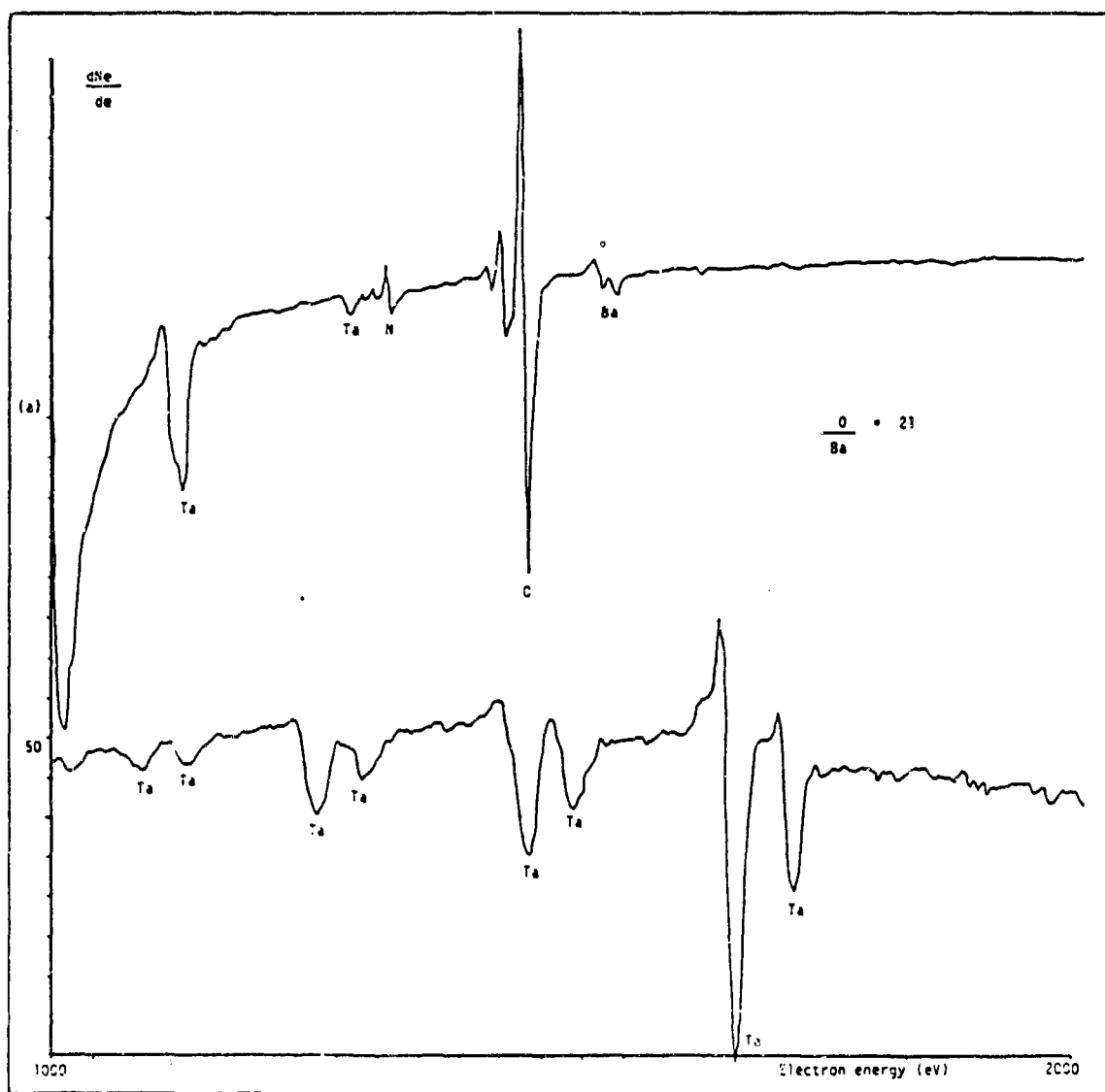


Fig.19a Auger spectrum of Ta coated cathode after 4 hours at 1050°C_B

Fig.19b High energy spectrum after 4 hours at 1050°C_B

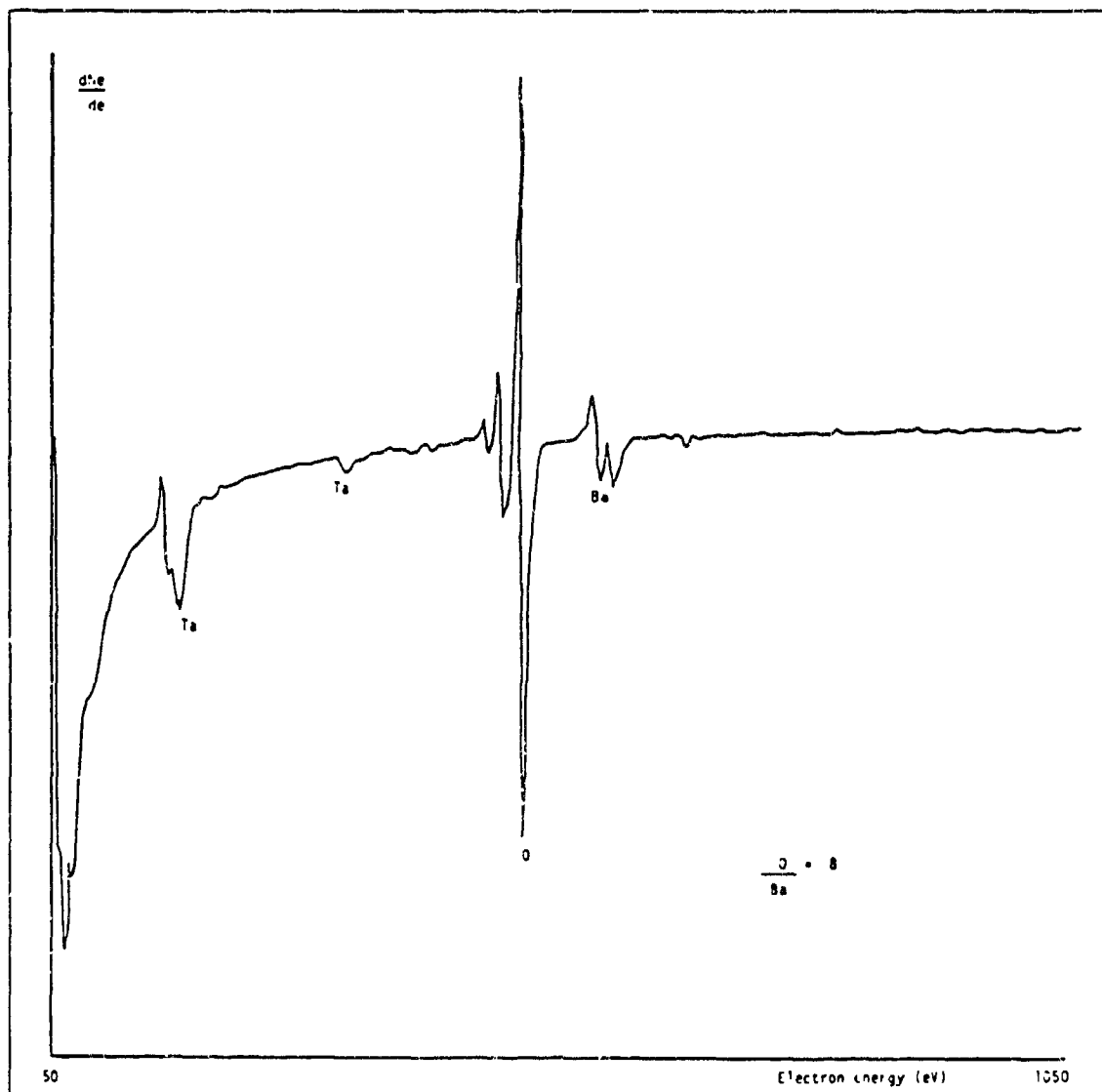


Fig.19c Auger spectrum of Ta coated cathode after 8 days at 1050 °C_B

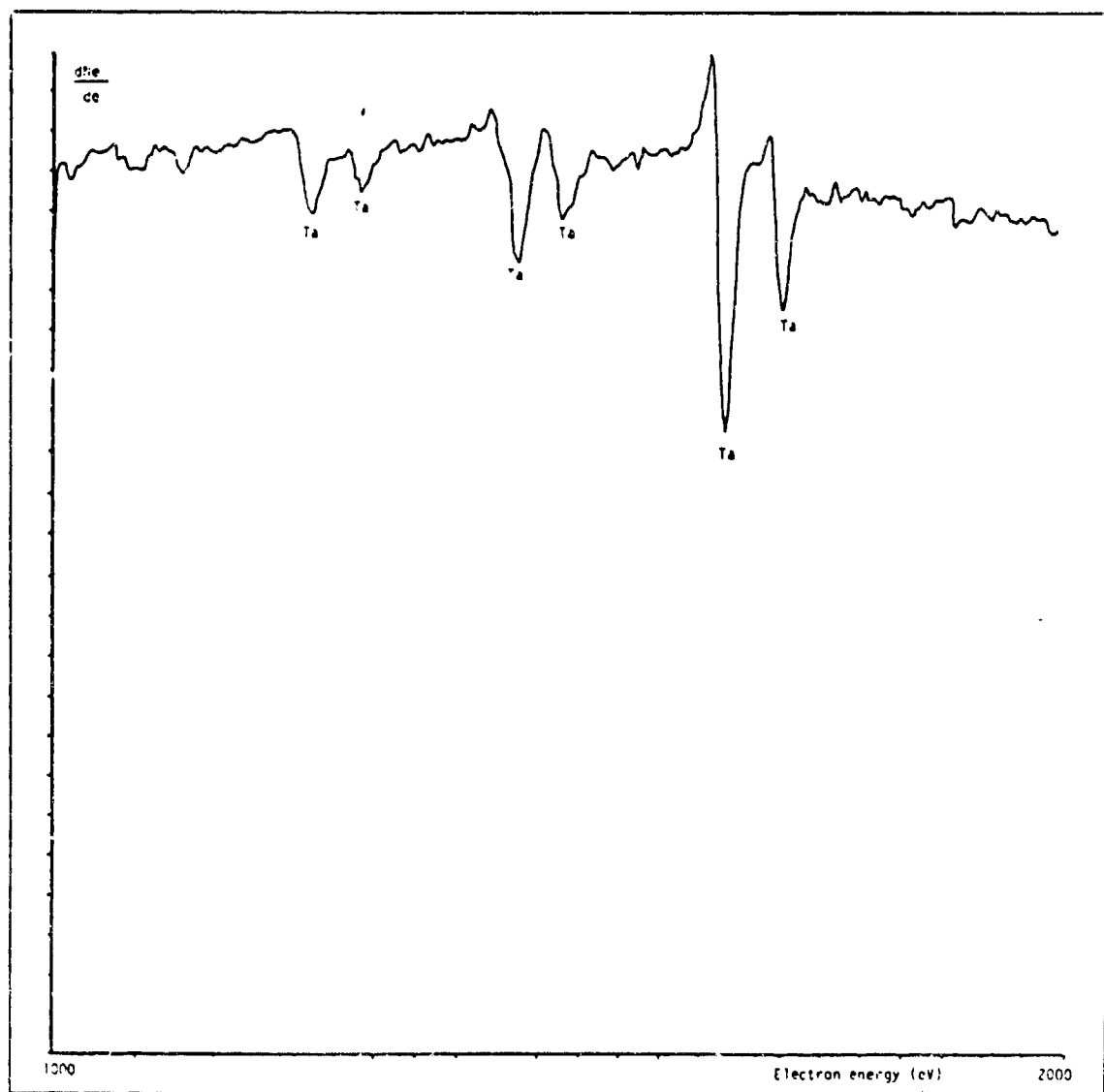


Fig.19d High energy spectrum of ta coated cathode after 8 days
at 1050°C_B

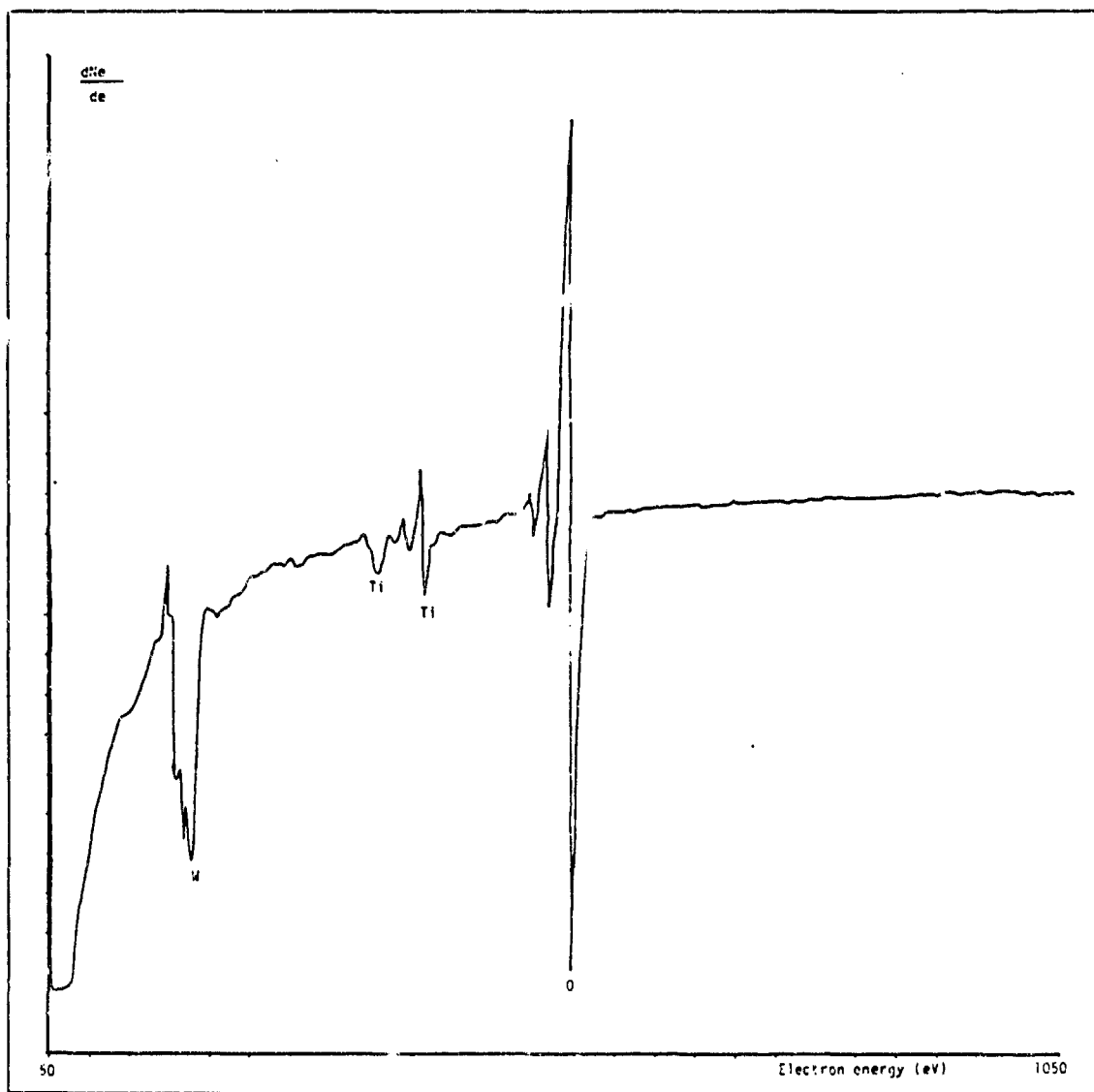


Fig.20a Auger spectrum of Ti coated cathode after 30 mins at 1000°C_B

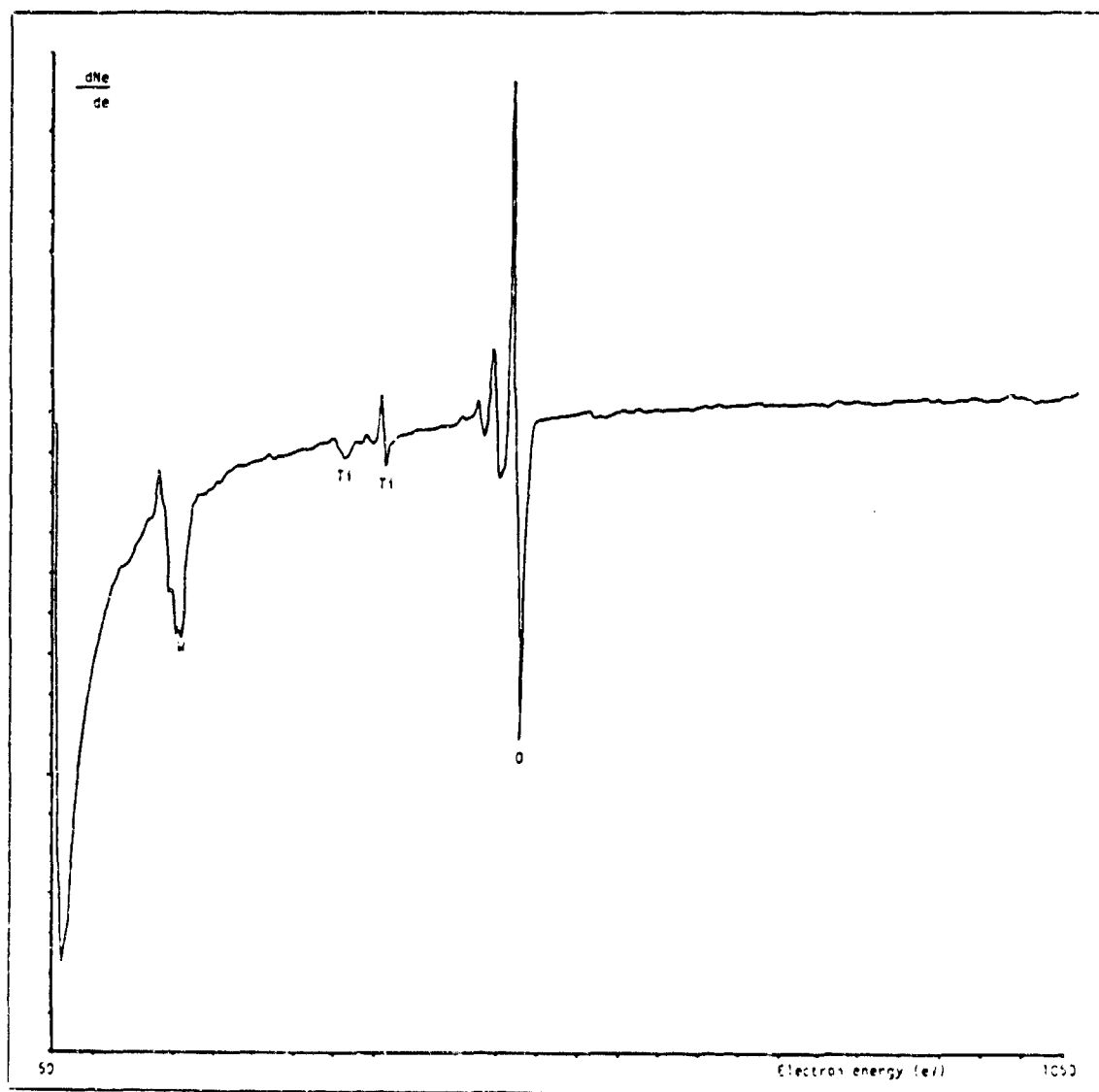


Fig.20b. Auger spectrum of Ti coated cathode after 3 days at 1030 °C₃

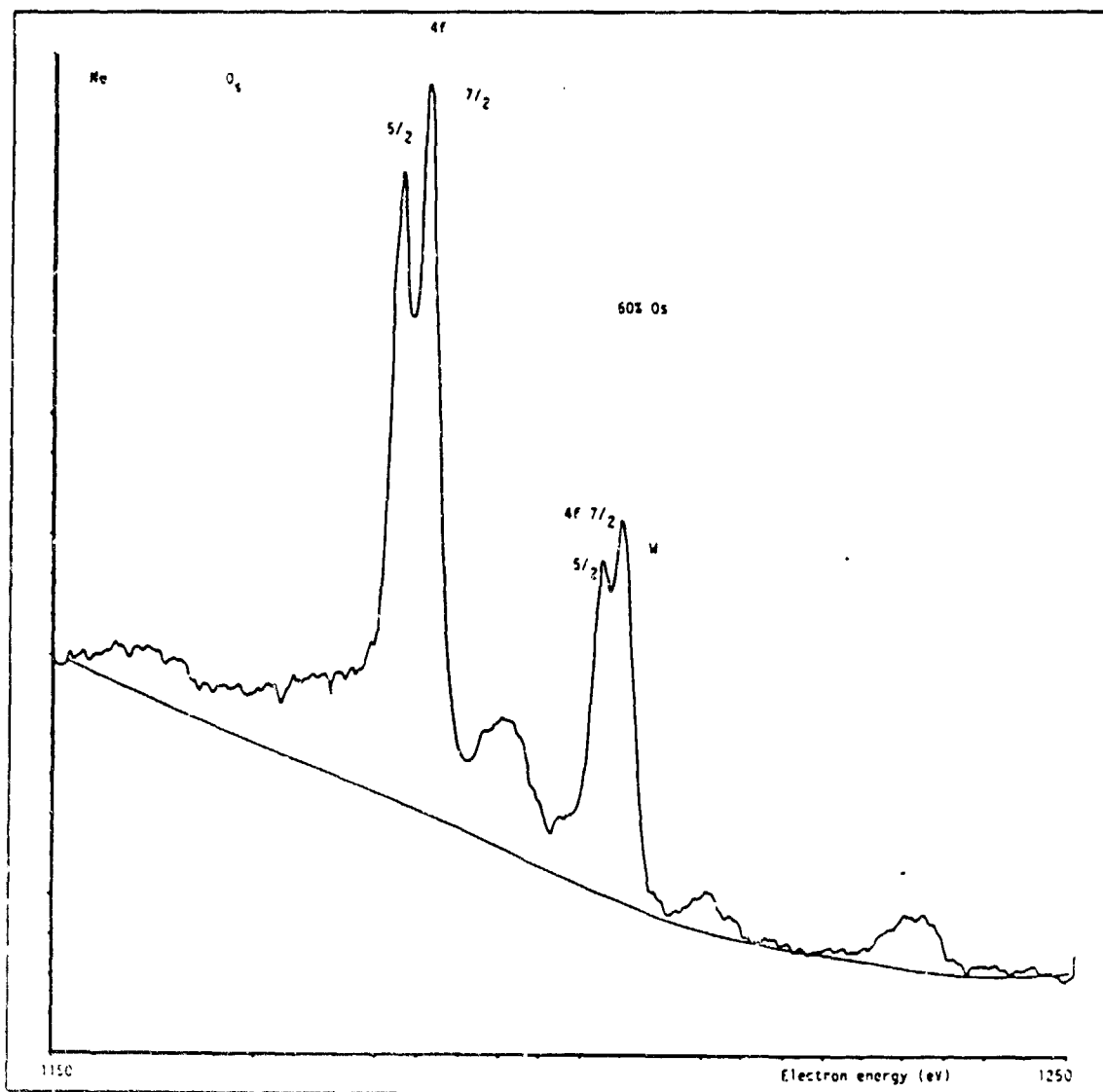


Fig.21a XPS spectrum of M-type cathode after several days at 1050 °C_B
showing Os and W 4f peaks

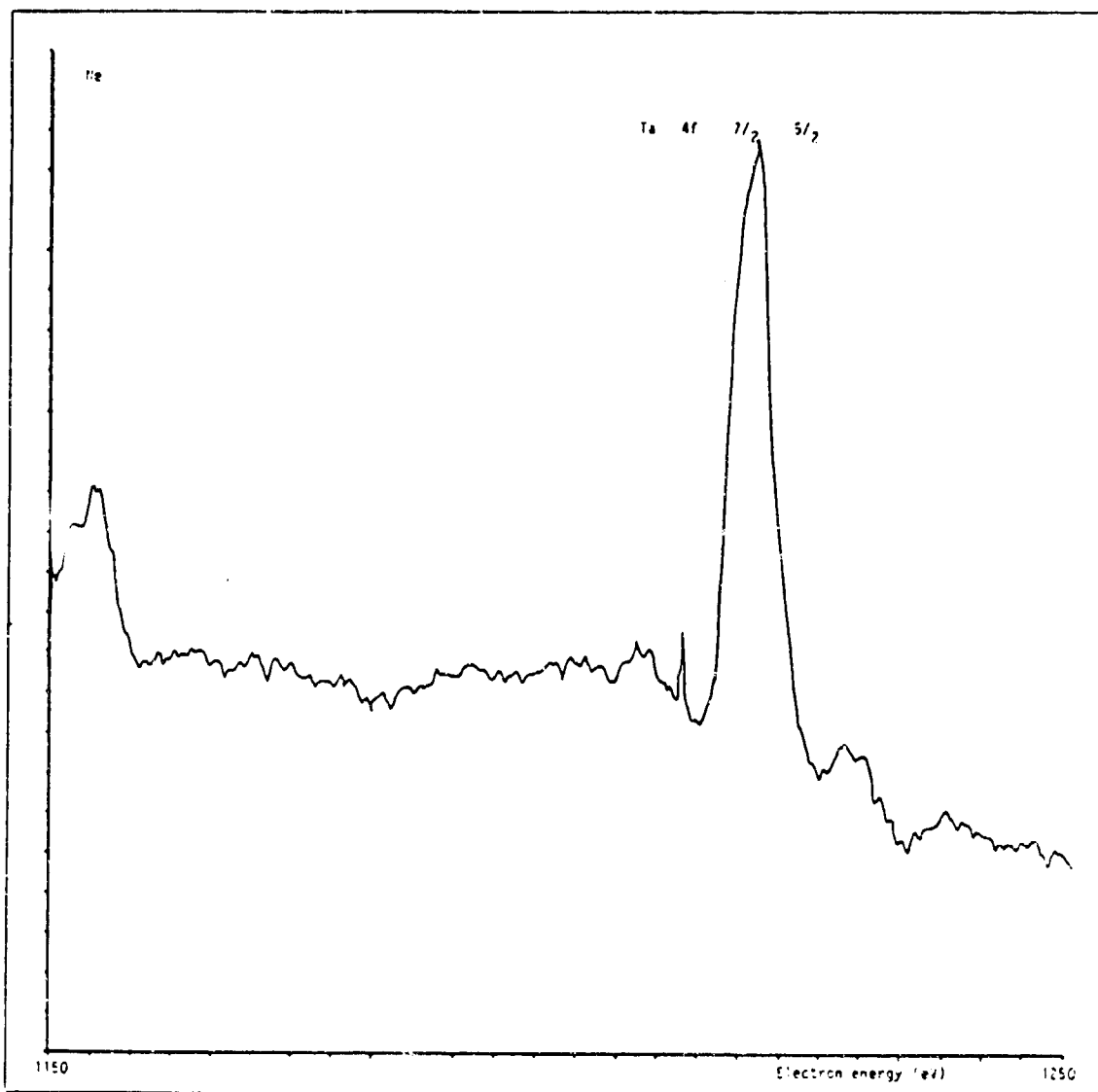


Fig.21b XPS spectrum of Ta coated cathode after several days at 1050 °C₃
 showing 4f peak

Fig.22 Angle resolved Auger plot for active M-type cathode at 1050 °C_B

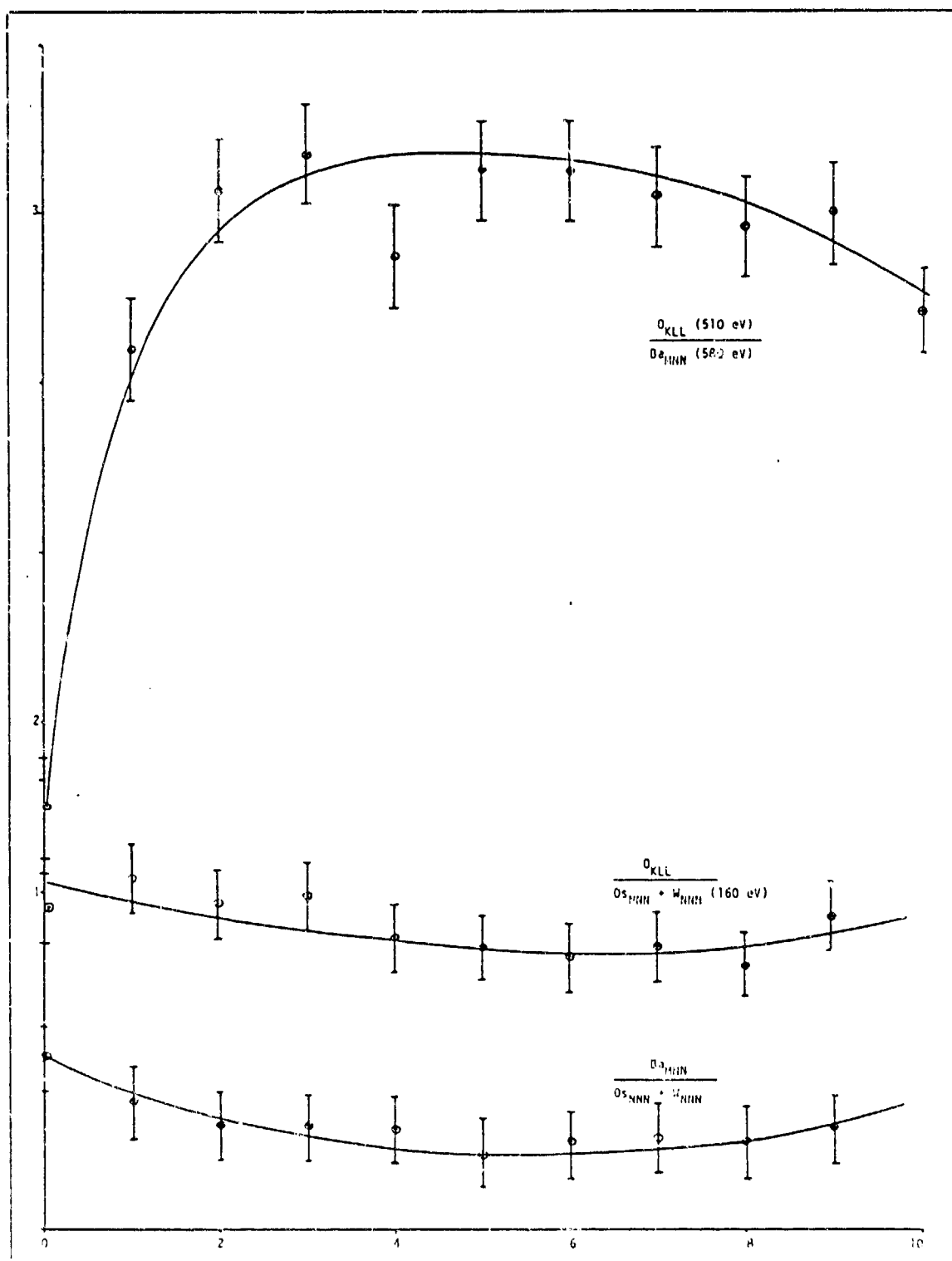


Fig.23 Angle resolved plot for Pt coated cathode after 2 hours
at 1040 °C_B

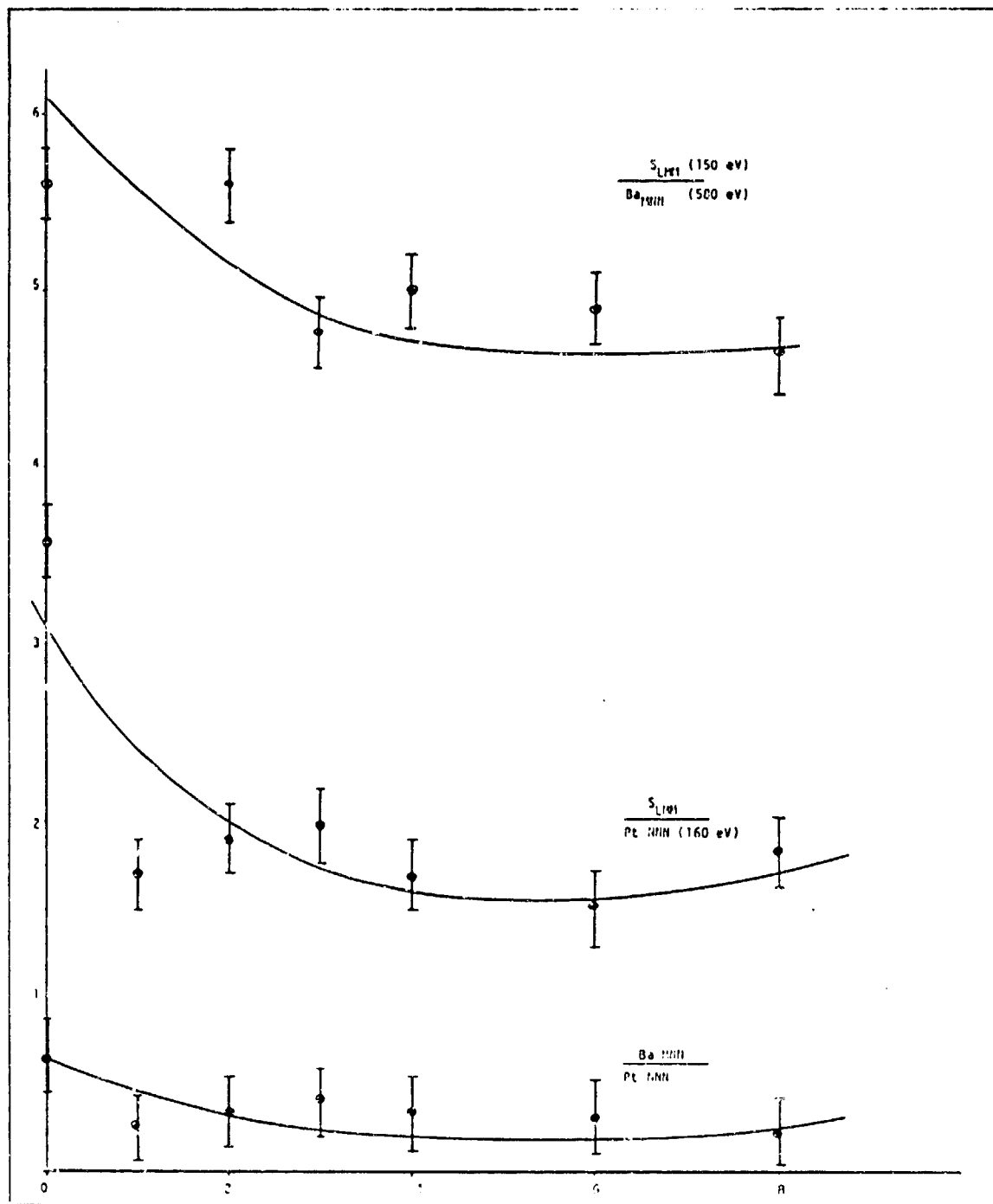


Fig.24 Angle resolved plot for Pt coated cathode after 12 hours
at 1040 °C_B

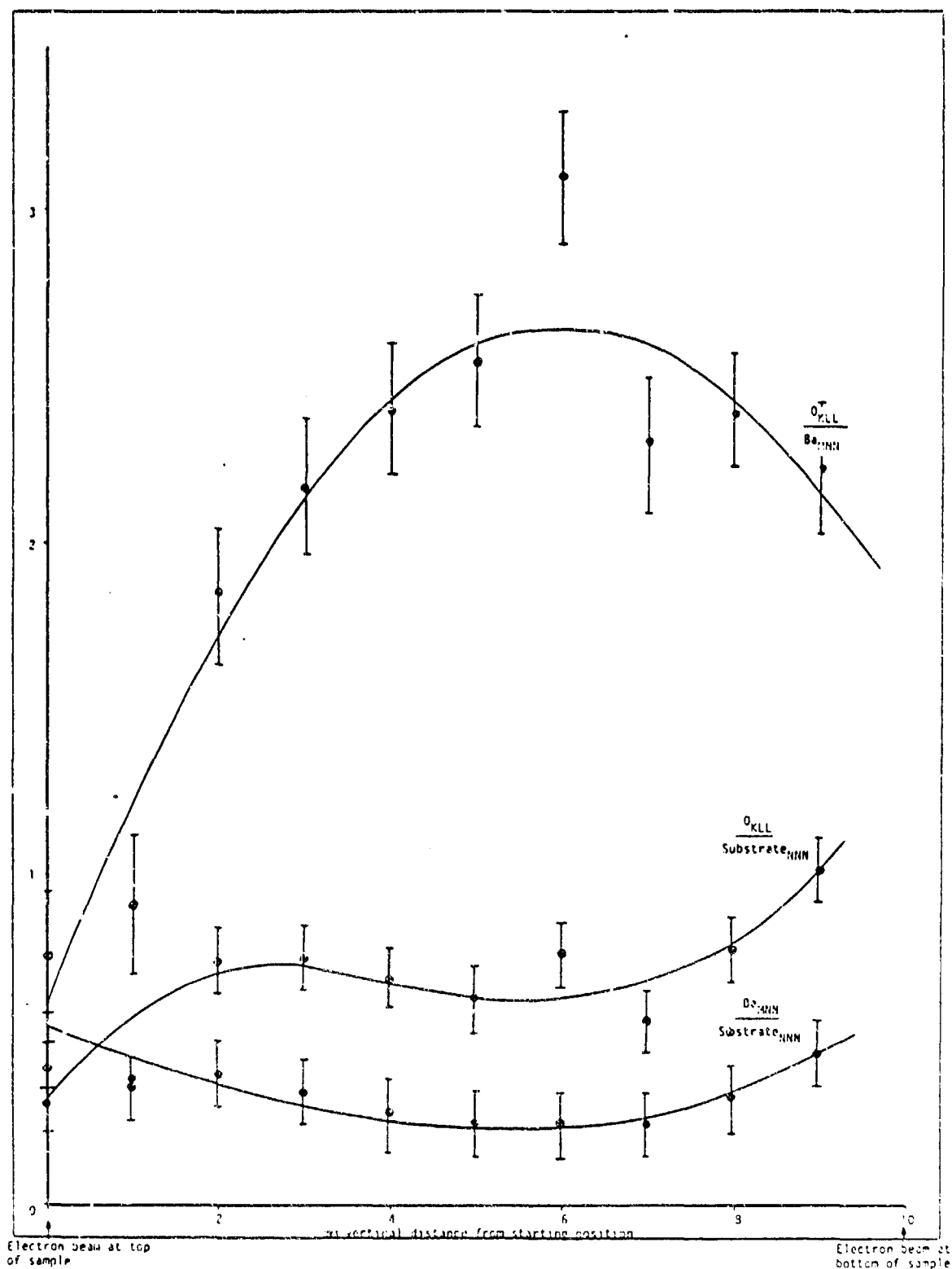
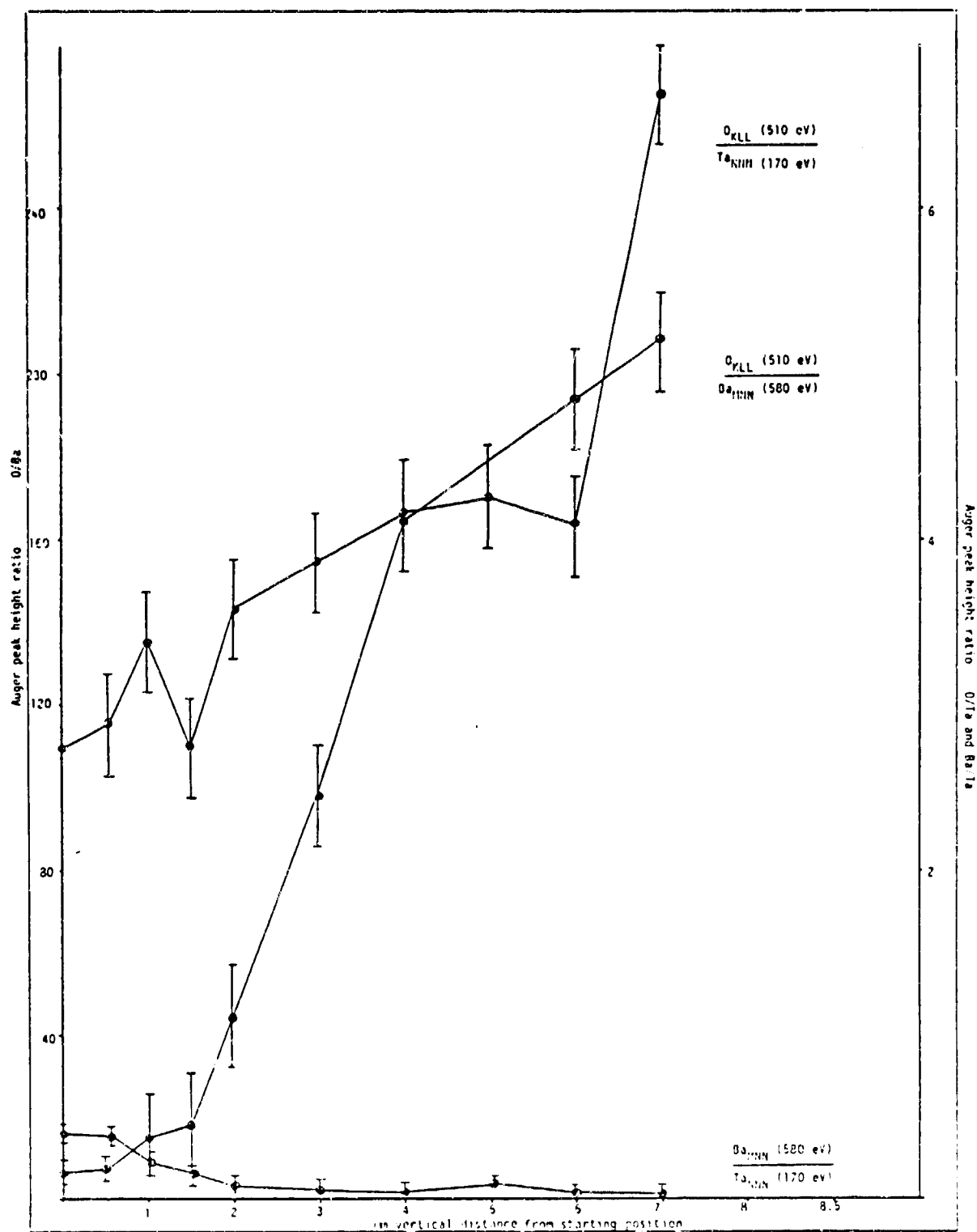


Fig.25 Angle resolved plots for Ta coated cathode after 12 hours at 1040 °C_B



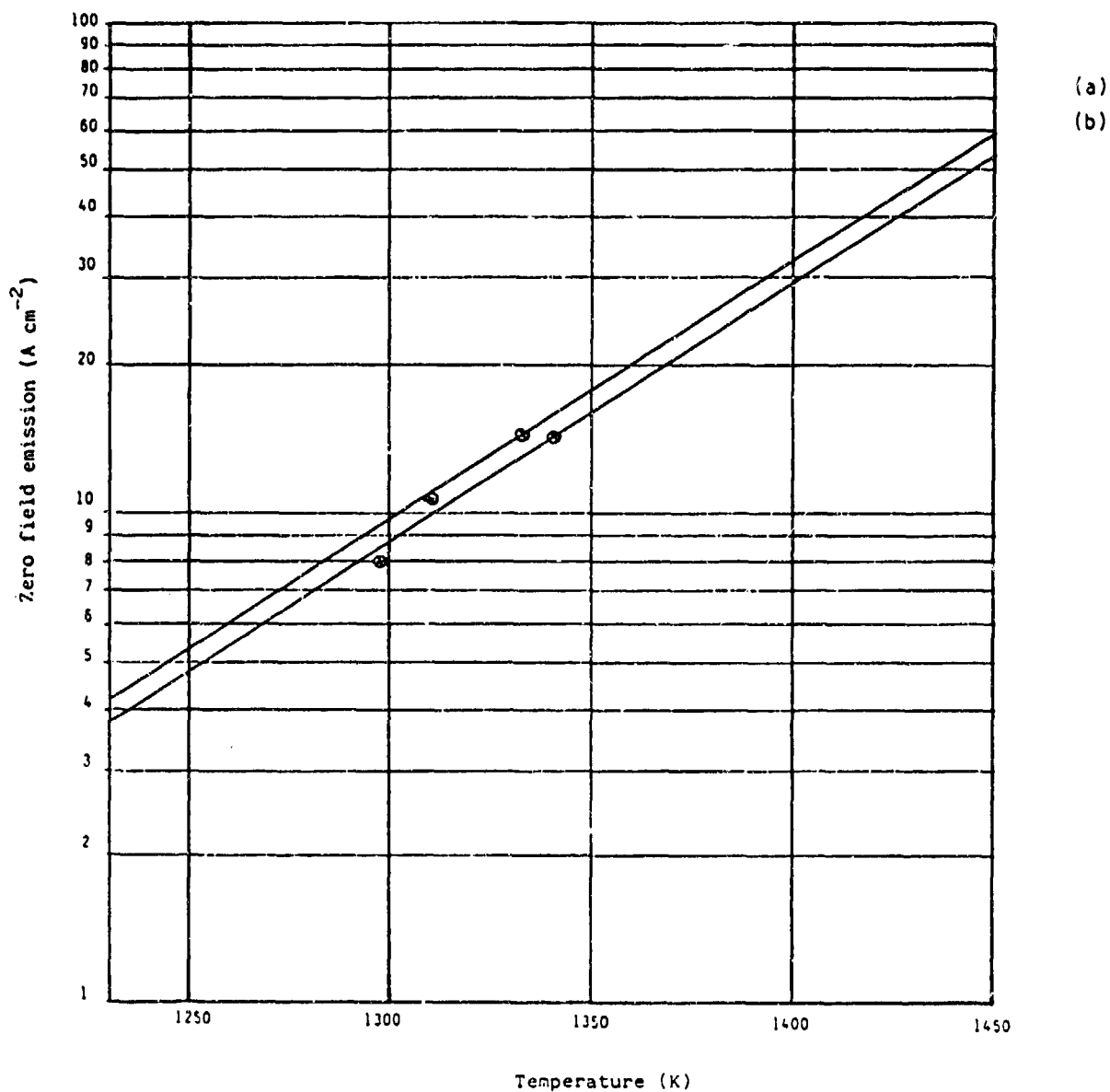
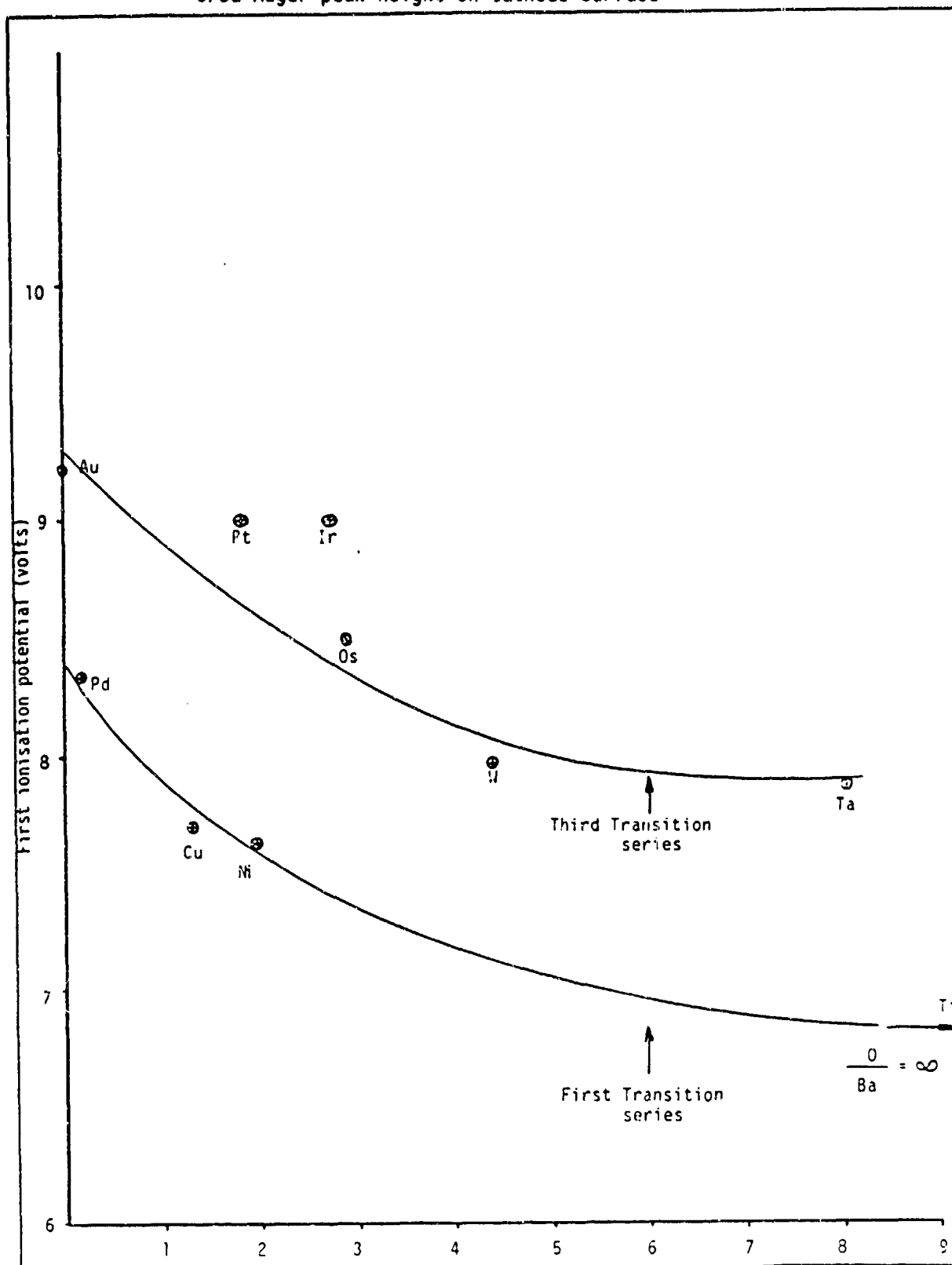


Fig.26 a) Pd coated cathode + 1 micro Os
b) Ni coated cathode + 1 micro Os

Fig.27 Graph of 1st ionisation potential of metal overlayers vs. O/Ba Auger peak height on cathode surface



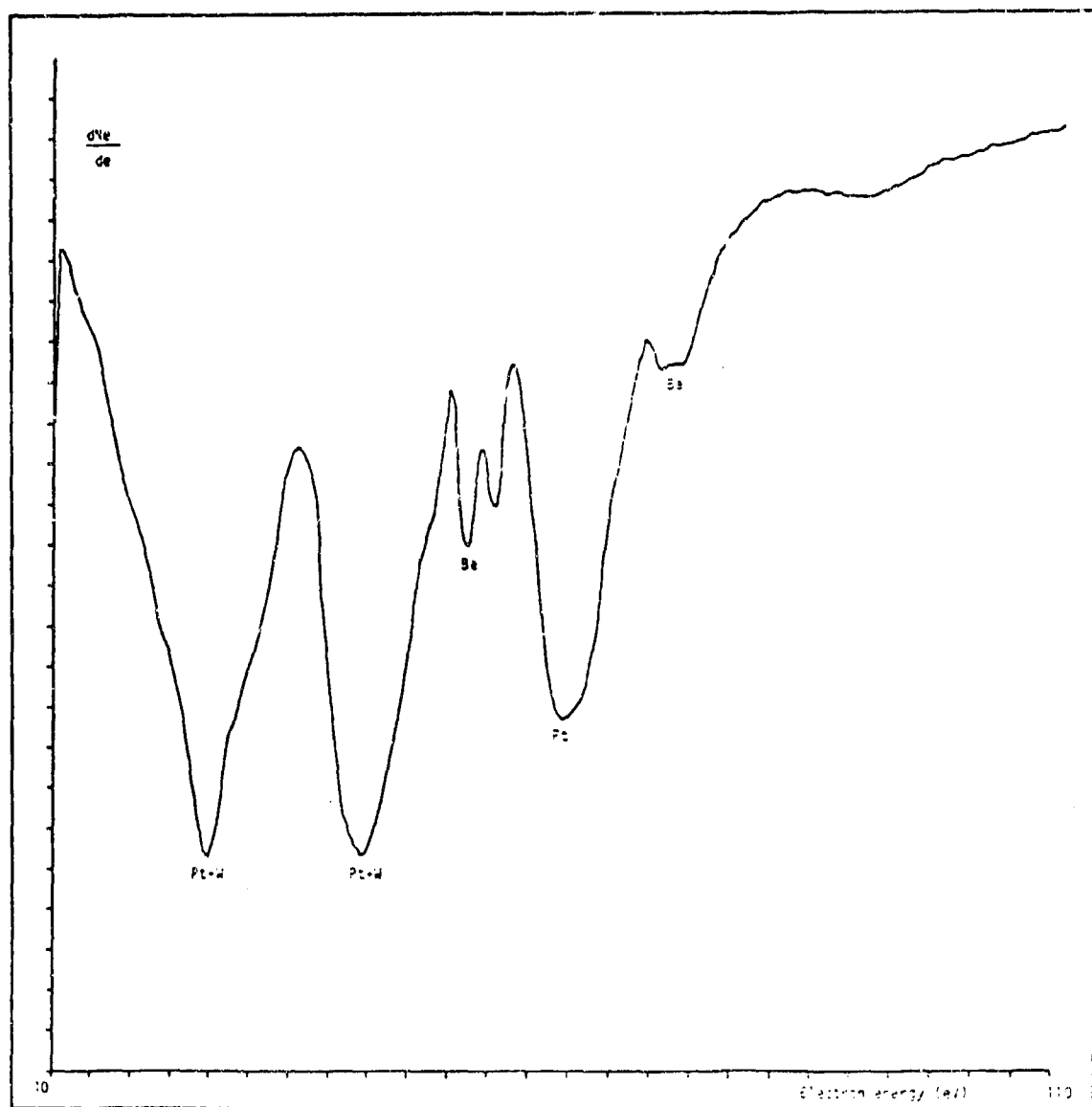


Fig. 28a Low energy spectrum of Pt coated cathode after 1 hr at 1050 °C_B

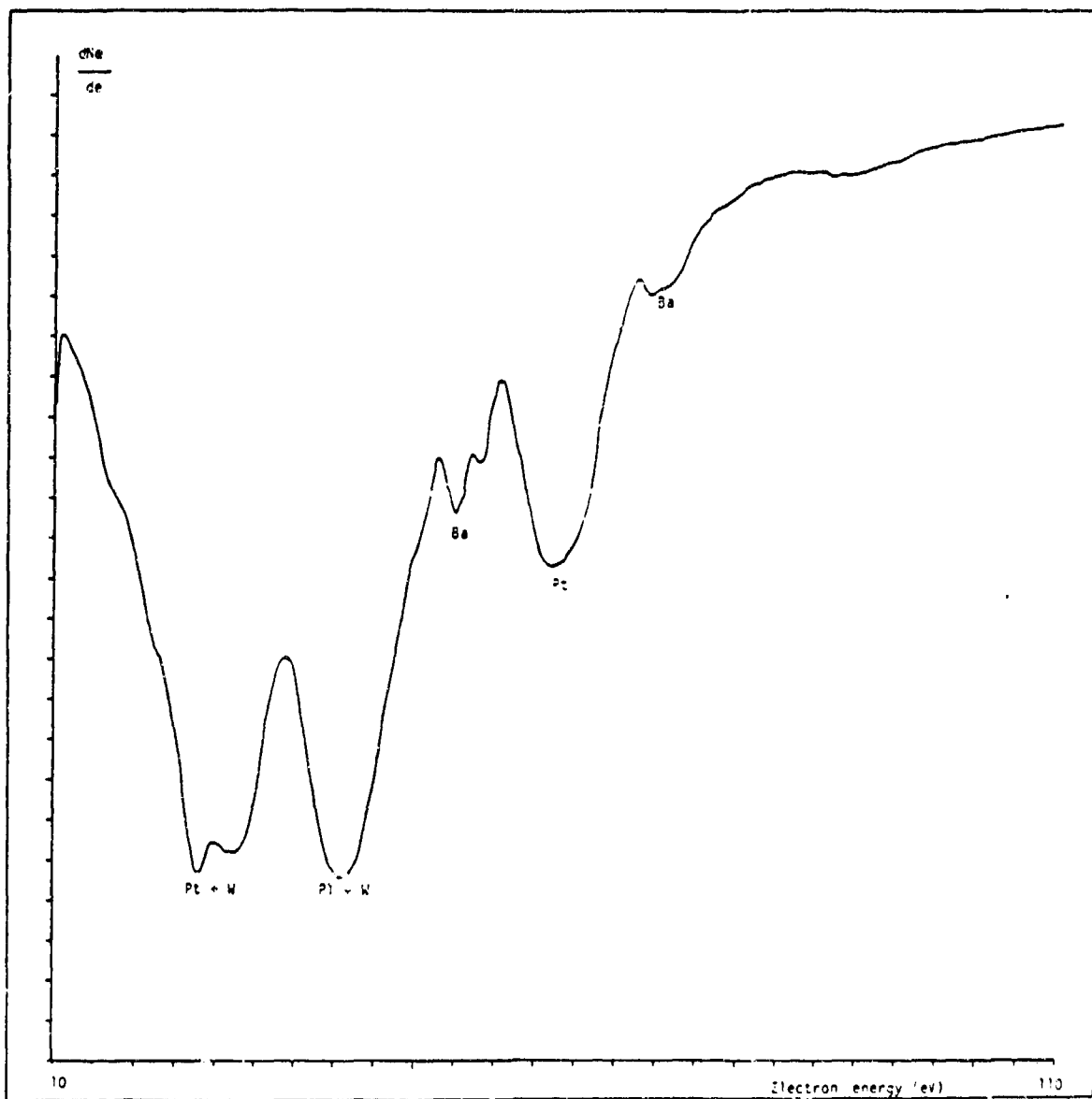


Fig. 28b Low energy spectrum of Pt coated cathode after 6 days at 1050 °C_B

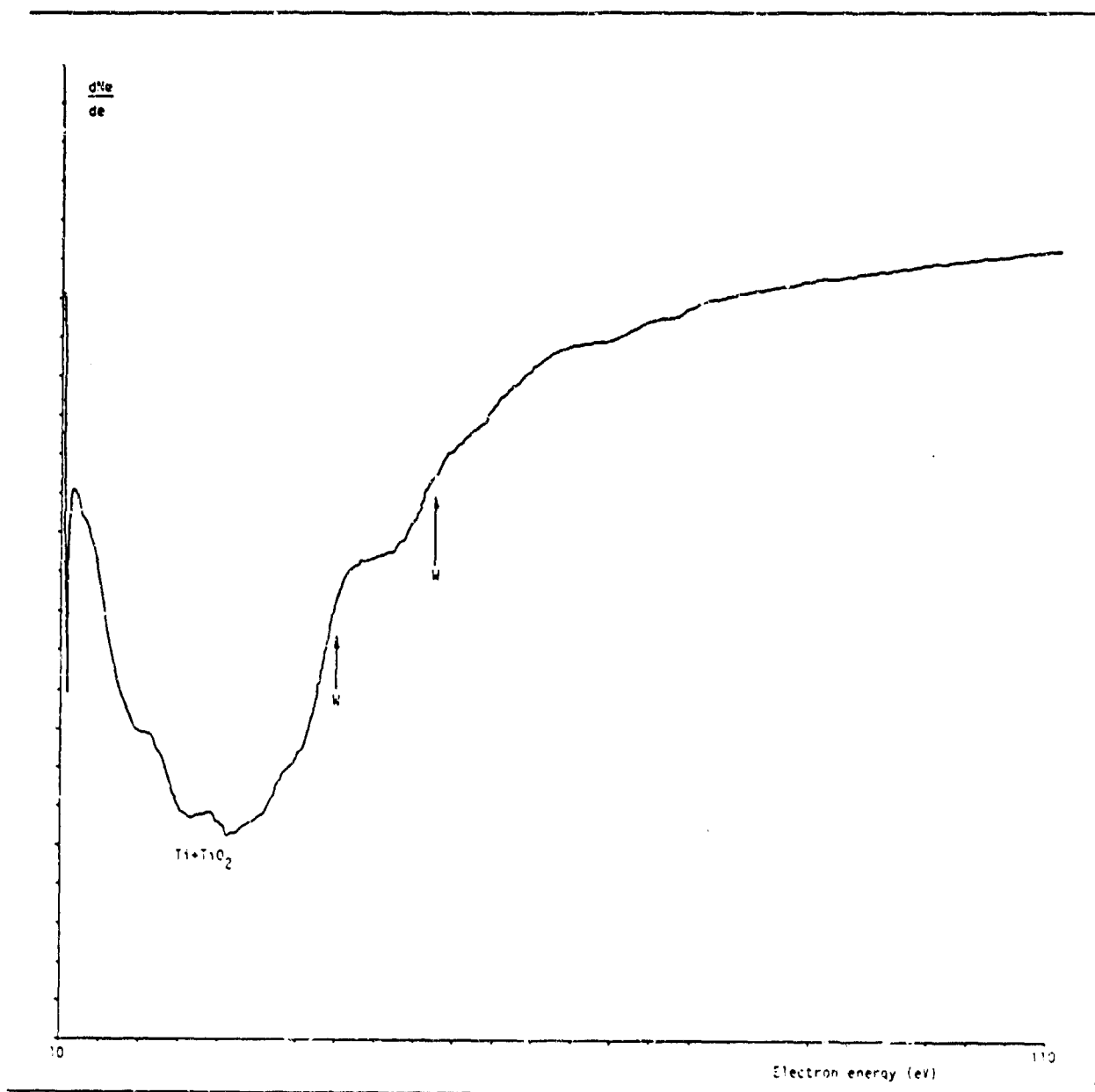


Fig. 25 Low energy spectrum of Ti coated cathode after 3 days at 1050 °C₃

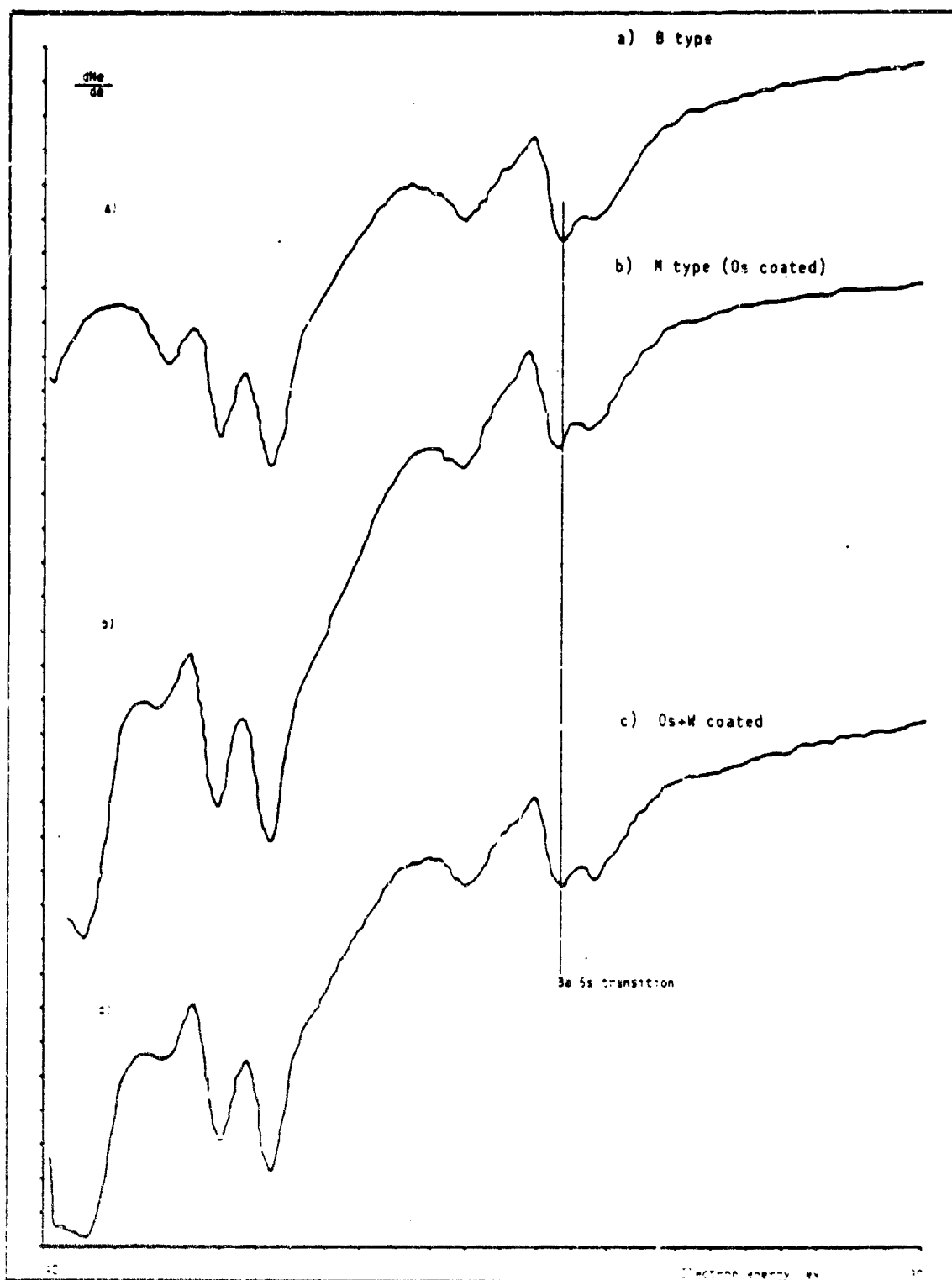


Fig.30. Low Energy Auger Spectrum (40-90 eV) of 3 Cathodes.