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Light Filaments of Incandescent Lamps Studied by Auger Electron Spectroscopy

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ABSTRACT: The use of Auger electron spectroscopy as a method in forensic science investigations of fractured incandescent lamps is described. Special emphasis is given to the oxidation of the tungsten filament. The method makes possible an identification of filaments that have been fractured under various conditions.

KEY WORDS: criminalistics, spectroscopic analysis, incandescent lamps

In the forensic science examination of an incandescent lamp one is often looking for physical evidence of whether the lamp was lit or not in an accident case. The light filament is usually examined by optical methods. These range from a simple inspection of the filament with the naked eye, through the optical light microscope [1], to the scanning electron microscope (SEM) [2,3]. A filament broken under hot conditions may exhibit discoloration, distortion, or molten glass fragments on the tungsten surface [4].

The SEM has come into use for filament investigations during recent years because of its increased depth of field and the larger magnification possible. Another advantage with the SEM is that a detector system that allows an energy dispersive X-ray analysis of the elemental composition of different materials can be fitted to it. This can simplify an identification of glass fragments that have been welded onto the filament during an impact.

It is, however, desirable to detect the amount of oxide that is normally formed on the tungsten surface upon fracture of the lamp. The thickness of the oxide layer might give a hint as to the condition of the lamp when it was fractured. Such an analysis is not possible with the SEM because of the low fluorescence yield for the lighter elements. Sodium is normally considered to be the lightest element detectable by X-ray analysis.

The X-ray emission process used in the SEM is illustrated in Fig. 1a. In addition, there is a second competing mechanism called the Auger process (Fig. 1b). The primary event is, in both cases, the creation of an inner shell vacancy (for example, in the K shell) by electron impact or X-ray radiation. The core hole that is created can then relax by two different physical mechanisms, either by emission of X-rays (Fig. 1a) or by a radiationless transition where an electron from a higher lying core level fills the primary vacancy

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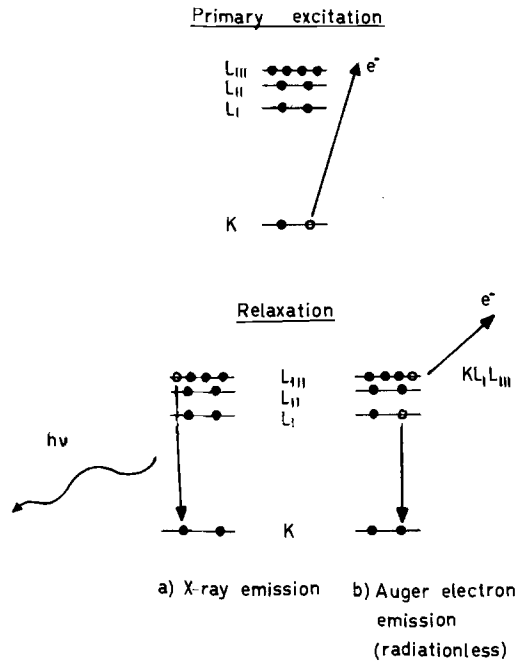


FIG. 1—Illustration of the difference between the X-ray emission and Auger electron emission processes.

(Fig. 1b). This takes place simultaneously with the emission of a third electron called the Auger electron.

The Auger process is much more probable than X-ray emission for lower transition energies (for example, transitions to the K shell for the lighter elements). Thus, Auger electron spectroscopy has a much higher sensitivity for oxygen and is therefore a more suitable method for studies of filament oxidation. A second important difference concerns surface sensitivity. The X-rays detected in the SEM originate from the bulk material down to a depth on the order of a micrometre, whereas the detected Auger electrons emanate from the first one or two atomic monolayers. Oxidation is a surface phenomenon and the Auger technique should therefore be a suitable method for examining it.

The present paper describes the application of Auger electron spectroscopy to an investigation of the history of different filaments from incandescent lamps by considering the oxidation effects. The purpose of this work was to find out if Auger electron spectroscopy is a suitable tool in forensic science investigations of filaments as a complement to the optical light microscope and the SEM.

Experimental Details

The filaments studied in this investigation originated from incandescent lamps (Philips Research Laboratories) with a power of 60 W and a voltage of 220 V. This power was chosen since it is very common and corresponds fairly well to the power used in vehicle headlights.

The lamps that are of interest to forensic scientists have normally been fractured or damaged in some way, giving rise to a characteristic condition of the tungsten filament. To evaluate the usefulness of Auger electron spectroscopy to filament investigations we divided the filaments into seven different groups as shown in Table 1. The mechanical

TABLE 1—*The different groups of filaments investigated in the present work.*

Group	Lamp Condition
A—new lamp	filament intact and never illuminated
B—new lamp	lamp with hot filament broken as a result of mechanical shock
C—new lamp	lamp with cold filament (never illuminated) broken as a result of mechanical shock; lamp switched on after fracture
D—used lamp	filament intact
E—used lamp	filament burnt out because of age
F—used lamp	lamp with hot filament broken as a result of mechanical shock
G—used lamp	lamp with cold filament broken as a result of mechanical shock; lamp switched on after fracture

shock, which was used to simulate an impact between two vehicles, was created by firing an airgun. It was chosen in order to have the fractures created under conditions as similar as possible. When fracturing took place while the filament was hot, the filament was allowed to be illuminated about 1 min before the shot was fired. Four filaments in each group were prepared and investigated. Reference samples of single crystalline tungsten carbide and polycrystalline tungsten trioxide were also studied.

The experiments were performed in a commercial Auger spectrometer from Varian Associates (Varian 981–2001). The experimental setup of the system is illustrated by the block diagram in Fig. 2. The system consists of an ion-pumped ultra-high vacuum chamber, the main parts of which are the sample holder, the electron gun, the analyzer, and the ion gun. The electron gun is situated in the center of the analyzer, which is of a cylindrical mirror type. An AC-modulated retardation voltage is supplied between the inner and outer cylinders.

Sputtering and data accumulation were performed in an atmosphere of argon at a pressure of 6.6 mPa (5×10^{-5} torr). The sputtering was provided by the ion gun operating at an energy of 3 keV. The ion beam was scanned over a large area to achieve a fairly uniform sputtering over the investigated surface (about $40 \mu\text{m}^2$). The sputtering rate at this energy is on the order of 10 nm/min. A beam probe, based on the Faraday cup principle, was used to center the ion beam around the electron beam.

The electron gun was also operated with an energy of 3 keV. The differentiated Auger

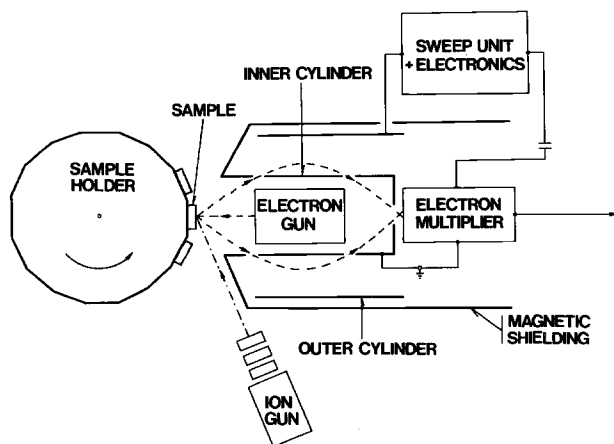


FIG. 2—A block diagram showing the principal parts of an Auger electron spectrometer.

spectra were recorded with a modulation voltage over the cylindrical mirror analyzer of 1 V peak-to-peak. The 500 eV wide spectra were recorded with a sweep rate of about 5 eV/s, whereas a slower sweep rate of about 0.5 eV/s was used to record the detailed spectra of tungsten, oxygen, and carbon.

By operating the ion gun and the electron gun alternately, it was possible to construct depth profile diagrams from the differentiated Auger spectra. These diagrams give a semi-quantitative picture of the atomic composition from the exposed surface as a function of the sputtering time. The negative peak amplitudes of the Auger spectra were measured and approximately corrected for the elemental sensitivity by using the data given by Davis et al [5]. The depth profile data were normalized by assigning a value of 100 to the added, corrected signal strengths from the major Auger peaks of tungsten, carbon, and oxygen.

Results and Discussion

Comparisons Between Different Filaments

Typical differentiated Auger spectra of a new, unused tungsten filament are shown in Fig. 3. These were recorded from a filament (Group A) before argon sputtering and after 2 min of sputtering. One interesting feature in the spectrum of the untreated filament is a large peak at 120 eV energy assigned to phosphorus. This peak decreases below the detection limit after a sputtering time of about 2 min. Its presence was not observed in any of the other groups of filaments. This indicates that it has been liberated from the surface during heating of the filament. The phosphorus probably originates as a contaminant during the production of the filament. Traces of carbon and oxygen can also be seen in the Auger spectrum (Fig. 3).

Figure 4 also clearly demonstrates the disappearance of phosphorus as a function of sputtering time. Further, it shows a fairly uniform concentration of carbon and oxygen amounting to a few percent.

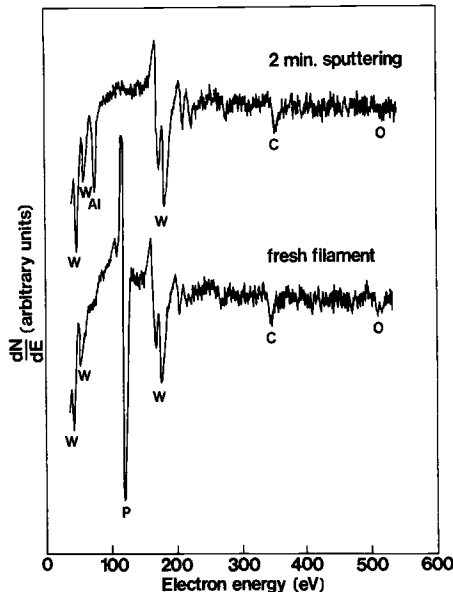


FIG. 3—Auger spectra of a tungsten filament of Group A. The spectra were recorded before sputtering and after 2 min of sputtering.

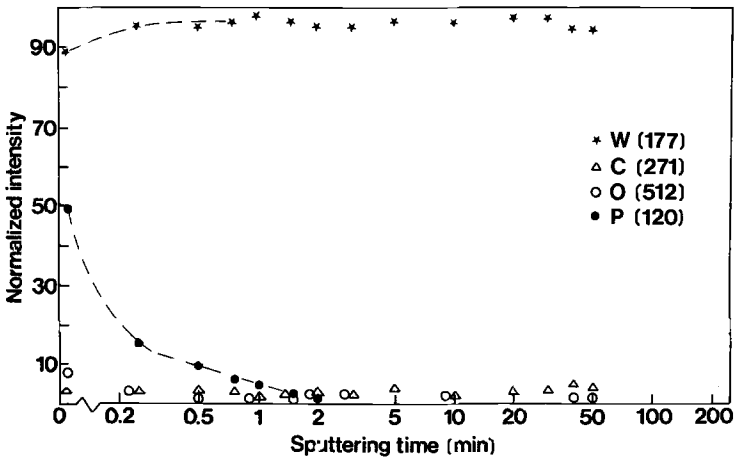


FIG. 4—A depth profile diagram constructed for a filament of Group A. The added corrected signal strengths of the tungsten, carbon, and oxygen peaks have been normalized to a value of 100. Each set of points represents the average values obtained from four independently investigated filaments.

Auger spectra and depth profiles of filaments of Groups D and E are similar to those presented in Figs. 3 and 4. The concentrations of carbon and oxygen are higher, almost by a factor of two as compared to the filaments of Group A. It is most probable that carbide and oxides were formed when the filaments were heated to a high temperature. The usage times of these filaments are not exactly known, but are probably on the order of several hundred hours each.

Of a greater forensic science interest are those lamps that have been damaged in some way. In Fig. 5 we present a depth profile for a used filament that was hot when the bulb was fractured (Group F). This filament has been heavily oxidized, as shown in the value of the points representing the oxygen concentration. The oxygen intensity decreases as a function of sputtering time in a characteristic manner. Straight lines can be fitted to the points representing oxygen concentration and the break points between crossing lines can

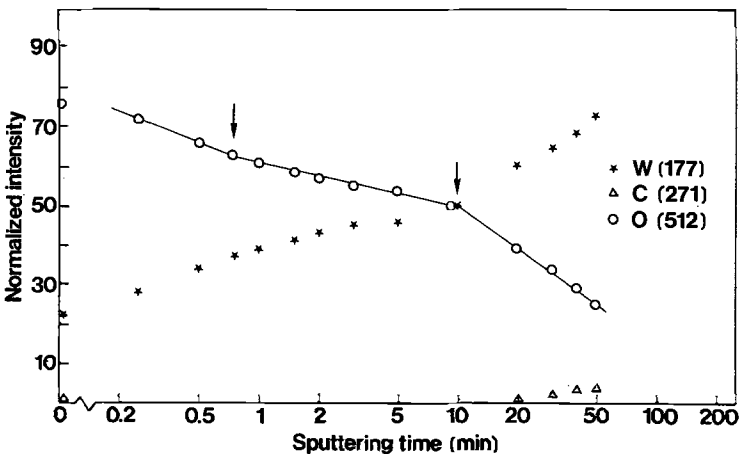


FIG. 5—A depth profile diagram constructed for a filament of Group F. Each arrow indicates the break point between two straight lines fitted to the curve representing the oxygen concentration.

be identified. Break points appear after around 45 s and 10 min of sputtering time. The depth profile of filaments of Group B also reproduced the break points after the same sputtering times as in the depth profile of filaments of Group F.

During an oxygen adsorption process the oxidation rate depends on a variety of factors such as the sticking coefficient of the adsorbate on the clean substrate, the substrate temperature, the surface purity of the substrate, and the amount of oxygen already adsorbed. Furthermore, the oxide is most probably not uniform throughout. It is more likely that it consists of regions with combinations of different oxide phases or oxide/physically adsorbed phases. A physically adsorbed phase is more easily sputtered away from the surface because of weak bonding. This results in a more rapid decrease of the oxygen signal strength during sputtering, as indicated by the larger slope of the fitted line after a short sputtering time (Fig. 5).

The depth profile of a used filament, which was cold during the fracture of the bulb but illuminated in air afterwards (Group G), is presented in Fig. 6. The oxygen concentration as a function of sputtering time shows the same trend as that of Filament F (Fig. 5). However, there are several quantitative differences. One of these is that the oxygen concentration on the surface (O s sputtering) is significantly lower than that in Filaments B and F (Fig. 7). The oxide layer is also thinner. After 20 min of sputtering, it is almost penetrated in contrast to the results of Filaments B and F. The corresponding break points between the fitted straight lines also appear after shorter sputtering times for Filament G. These are indicated by arrows in Fig. 6 at about 20 s and 2 min.

The results in the case of Filament C resemble those of Filament G, with a few minor differences. The break points between the lines of oxygen concentration in Filament C appear after about 30 s and 5 min of sputtering. As a consequence of this, the oxygen concentration after 50 min of sputtering is about 8%, compared to 1 to 2% for Filament G, but still far less than for Filaments B and F, which have a concentration of around 25%. Thus Filament C has a slightly thicker oxide layer than Filament G. This might be associated with the higher concentration of carbon and oxygen in the used filaments. (See the previous discussion about the difference between Filaments A and D.)

One simple conclusion to be drawn from this is that a filament that has been heated from room temperature in air (Groups C and G) produces a thinner oxide layer than a hot filament that has been suddenly exposed to air (Groups B and F). Thus, both the temperature and the carbon concentration affect the growth rate of the oxide.

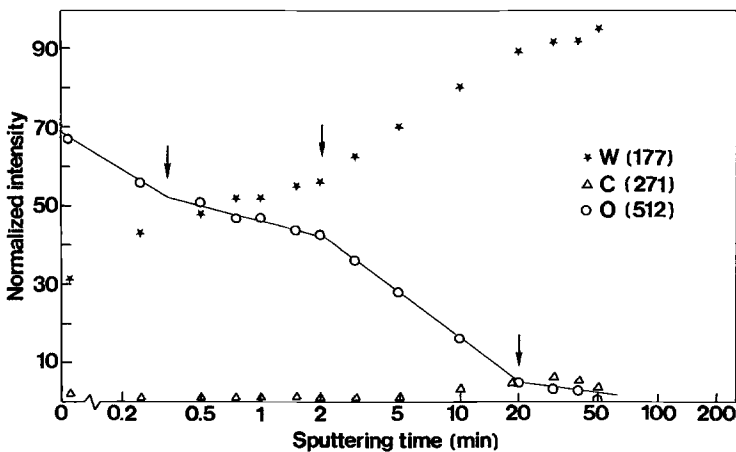


FIG. 6—A depth profile diagram constructed for a filament of Group G.

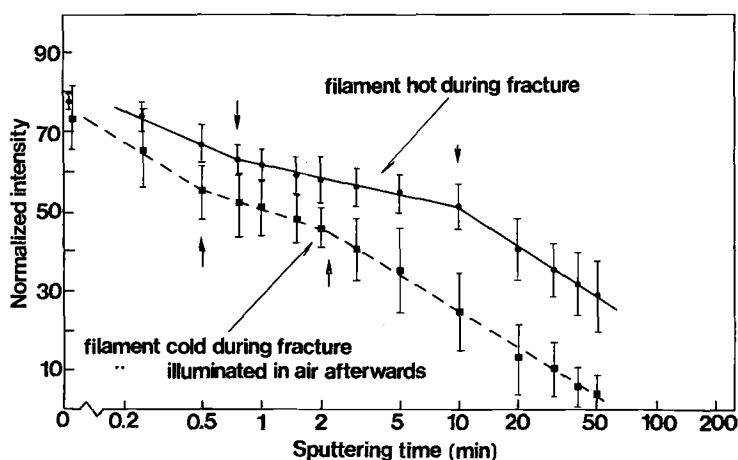


FIG. 7—A depth profile diagram showing the differences in oxygen concentration for Filaments B and F on one hand (solid circles) and Filaments C and G on the other (solid squares). Each point represents an average value obtained from eight independently investigated filaments. A bar around the average value, representing the standard deviation, is included to show the scattering of data.

The oxygen/tungsten system is one of those most intensively studied in surface physics. Most of the chemical adsorption experiments have been carried out at room temperature. Bas and Bänninger [6], however, studied the adsorption of oxygen on tungsten at elevated temperatures up to 3000 K and observed a strong influence of carbon on the oxidation rate. An initially carbon-contaminated surface had an oxygen peak with a strength of only about 10 to 15% of that from a clean tungsten surface after an oxygen exposure at 1650 K. They also reported that decarbonization was achieved by heating at a high temperature (2500 K) in a dry oxygen atmosphere (about $13 \mu\text{Pa}$ [1×10^{-7} torr]) for a few minutes.

It has also been reported [2] that the rise time of the filament temperature from room temperature to operation temperature when a motor vehicle headlight is switched on is on the order of 50 ms.

Considering this information, we can draw the following conclusions regarding the oxidation of Filaments B, C, F, and G. Filaments C and G have an oxide layer thinner than that of Filaments B and F since the former are heated from room temperature during exposure to air. The curves representing oxygen concentration in the depth profiles of Filaments B and F (hot during fracture) are indistinguishable from each other, independent of the carbon contamination. This must be due to the violent oxide reaction at this high temperature. Decarbonization must be a less important factor affecting the oxidation process with this combination of filament temperature and oxygen pressure.

The picture is slightly different for Filaments C and G, however. Filament G (with the higher carbon content) was not effectively decarbonized before fracture (within a few seconds after switch-on) since this filament was initially heated from room temperature. Thus the carbon contamination acts in this case as a passivator so that a lower oxidation rate is achieved.

At this point it should be stressed that the differences between the results of Filaments C and G are much smaller than the differences between the results of Filaments B and F on one hand and Filaments C and G on the other. This is nicely illustrated in Fig. 7, which shows the depth profile of the oxygen concentration for these two groups of filaments irrespective of age.

These results illustrate that Auger electron spectroscopy is a technique capable of discriminating between tungsten filaments that have been damaged in different ways.

Chemical Effects

So far we have only discussed the variations between the different filaments according to the concentrations of oxygen and carbon on the tungsten surface. By using Auger electron spectroscopy [7,8] it is also possible to detect chemical effects such as changes of peak shape and chemical shifts (energy shift of peak positions resulting from different atomic environment).

Chemical effects in Auger spectra of oxygen have recently been investigated by Chesters et al [9]. They did not observe any sensitivity of the Auger peak shape to the chemical environment of the adsorbate. They reported an oxygen KLL Auger spectrum similar to that presented in the lower lefthand corner of Fig. 8.

Figure 8 illustrates the differences in the Auger spectra of the oxygen KLL transitions observed between Filaments B and F on one hand and Filaments C and G on the other. The lower spectra were recorded prior to sputtering (0 s). The right spectrum (Group G) is very asymmetric compared to the left (Group F) and to previous reports. We believe that this difference is associated with the passivation effect of carbon. The oxygen KLL spectra obtained after sputtering are shown in the upper part of Fig. 8 and exhibit even larger differences. These spectra were recorded after different sputtering times, but they represent roughly equal oxygen KLL/tungsten MNN ratios (Filament F has a thicker oxide layer than Filament G). A new peak at 506 eV energy grows to a strength comparable with the 512 eV peak as a function of sputtering time for Filament F (upper lefthand part of Fig. 8), whereas the 506 eV peak appears only as a small structure through the entire oxide layer in Filament G (upper righthand corner of Fig. 8).

The 512 eV peak was used for all types of filaments as a semiquantitative measure of the relative oxygen concentration. Had the added strengths of the 506 eV and 512 eV peaks been used instead, a much larger value for the oxygen concentration in Filaments B and F should have been obtained, resulting in an even larger separation between the two curves in Fig. 7.

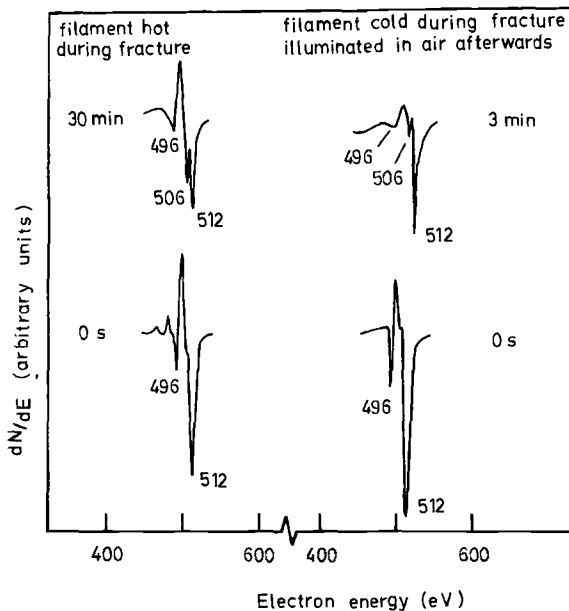


FIG. 8—The oxygen KLL spectrum for Filament F (left) and Filament G (right) after different times of sputtering.

Effects on the Filament Holder

We also investigated a few nickel wires that hold the tungsten filament in the correct position inside the bulb. Wide energy scan Auger spectra of two such wires are presented in Fig. 9. The upper spectrum is from a nickel wire of an incandescent lamp that had been in use for a long time without being damaged (nickel wire to Filament D). Besides Auger transitions from nickel at 52 eV, 715 eV, 774 eV, and 848 eV, and from the common contaminants of carbon, nitrogen, and oxygen, phosphorus was found in large concentrations. It had probably been condensed on the nickel wire after evaporation from the tungsten filament, as was discussed in connection with the tungsten Filament A (Figs. 3 and 4). Sulfur is a common impurity of transition metals such as nickel [10]. The tungsten peaks that were observed must represent atoms evaporated from the filament onto the nickel holder during the normal use of the lamp.

A comparison with a nickel wire from the holder for Filament F shows several interesting features. Starting at the low energy end we observe the appearance of a peak at 91 eV. It is due to silicon and its origin is assigned to a small glass fragment from the bulb that became stuck to the nickel wire during the fracture. The phosphorus impurity has been lost during the violent reaction following fracture. The sulfur impurity has grown, possibly because of segregation to the surface. A strong increase of the oxygen peak is also observed as expected.

Summary

Auger electron spectroscopy has been discussed as a method in forensic science investigations of tungsten filaments of incandescent lamps. The unique advantage of this method is its ability to identify and quantify an oxide formed on the tungsten filament during fracture of the bulb. The present investigation has also demonstrated the possibility

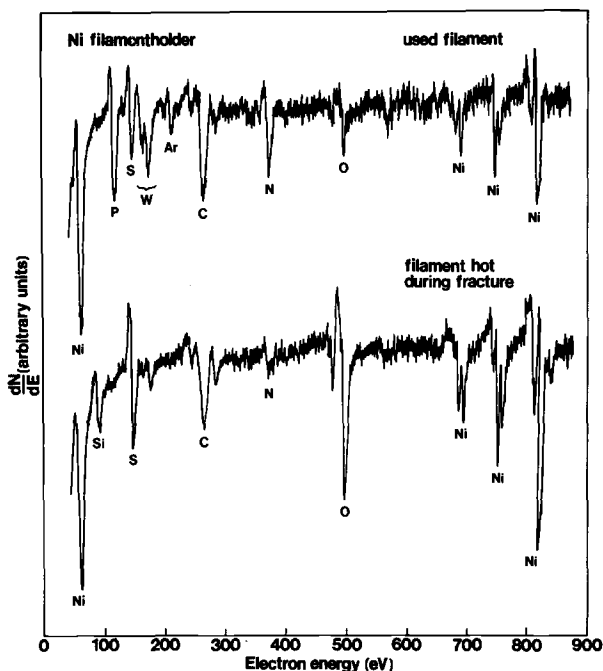


FIG. 9—A wide-scan Auger spectrum of the nickel filament holder for Filament D (top) and Filament F (bottom).

of discriminating between filaments with different histories, such as a filament that is fractured while illuminated and a filament that is fractured when the switch is in the off position but is later illuminated in air. These two groups of filaments can normally not be discriminated, except when molten glass fragments can be identified.

The oxidation that takes place on the tungsten surface is a well-defined process. Understanding and experimentally describing it are important for a forensic scientist to be able to determine the history of a given filament. Auger electron spectroscopy is such a suitable tool to complement the optical light microscope and the SEM in forensic science investigations of light filaments.

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