NASA Technical Memorandum 81484

(NASA-TM-81484) PRACTICAL APPLICATIONS OF SURFACE ANALYTIC TOOLS IN TRIBOLOGY (NASA) 45 p HC A03/MF A01 CSCL 20K
N80-23430
Unclas
G3/26 20117

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Prepared for the
International Lubrication Conference
cosponsored by the American Society for Mechanical
Engineers and the American Society of Lubrication Engineers
San Francisco, California, August 18-21, 1980

E-422

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ABSTRACT

Many tools are currently available for surface analysis. Some give topographical information and others give elemental and/or chemical analysis. In this review a brief description of many of the currently, widely used tools is presented. Of this list, those which have the highest applicability for giving elemental and/or compound analysis for problems of interest in tribology along with being truly surface sensitive (that is less than 10 atomic layers) are presented. The latter group is critiqued in detail in terms of strengths and weaknesses. Emphasis is placed on post facto analysis of experiments performed under "real" conditions (e.g. in air with lubricants). It is further indicated that such equipment could be used for screening and quality control.

INTRODUCTION

In the past 10 years a number of surface analytical techniques have developed to a point where they can be regarded as standard laboratory analytic equipment. This has not been fully realized outside of groups that have used this equipment to perform fundamental studies in tribology, e.g. Buckley's group (1, 2). As a result, there have been few attempts (3-17) to apply modern surface analysis to problems in lubrication, although much of this equipment has been available for years.

A problem facing engineers and scientists in evaluating these tools is the plethora of acronyms, AES, XPS, ESCA, SEM, SAM, EDX, SIMS, ISS, UPS, etc. It is difficult for a researcher new to the area to sort out what it is, let alone what the analysis will do. A principal goal of this review is to overcome this obstacle and to assist the tribologist in selecting those techniques which can help him learn more about tribological surfaces. In fact, if certain important criteria are selected for limiting their application, the list narrows rapidly. Often in the field of lubrication one must deal with specific applied problems and there is little time for equipment development. Therefore, interest centers on analytical tools that are commercially available. Also, since the experiments are often on engineering materials, the choice must not be material limited, e.g. studies of single crystals may be of fundamental importance but are of limited immediate practical value. Finally, the tool must provide chemical and structural information which can be acquired and interpreted with some degree of confidence in the results.

This paper, therefore, will attempt to give a physical description of the best developed tools then categorize them as fundamental or practical. The purpose is to identify systems that can be used for post facto spectroscopic analysis in practical situations and are commercially available. Following this, a more detailed physical discussion of the narrowed more practical techniques will be given, along with examples and suggestions for their applications to practical problems in lubrication. Some analytical tools such as infrared spectroscopy will not be treated since these have been traditionally used by workers in lubrication and are discussed in more detail elsewhere (18).

BACKGROUND

Although spectroscopy is a term that evokes certain specific connotations if we are willing to broaden our perspective a number of analytic techniques can fall into this category. A process diagram can be set up that represents a general description of the analytic tools (1).

Excitation (Interaction)
↓
Dispersion
↓
Detection
↓
Spectrogram

The first step, excitation or interaction, represents the production of the particles to be analyzed, for instance, in light or photon emission spectroscopy a spark might produce photons. In another case the particle analyzed could be an atom or cluster of atoms obtained by sputtering. The dispersion stage could be thought of as a filtering process where the selected information or particle is allowed to pass and other information is rejected. In light spectroscopy this would correspond to the use of a grating or prism, for an ion or electron it might be an electrostatic analyzer. Next, is detection of the particle which could be a photographic plate for light or an electron multiplier for ions or electrons. And finally, the spectrogram tells what materials are present and hopefully how much is there.

An excellent survey of surface analytic tools was done by Murday (19). The results of the Murday's survey were republished by Powell in a more accessible publication (20), along with an evaluation of the current state of surface analysis. In this paper a narrower set of analytical tools than presented by Murday or Powell will be selected which either have a greater promise for application in tribology or are more familiar to scientists working in tribology. We will now proceed to describe and evaluate this narrowed list in terms of considerations already mentioned.

In order to help the reader appreciate their usage, the tools are grouped into five categories: Elemental and chemical analysis by

(1) Electron levels; (2) Mass; (3) Vibrational state and structural analysis by; (4) Macroscopic and (5) Microscopic features.

Elemental and Chemical Analysis by Electron Levels

AES-SAM (Auger Electron Spectroscopy - Scanning Auger Microscopy). - A surface is bombarded with electrons and the emitted secondary electrons are detected and energy analyzed. AES is a surface sensitive tool that gives elemental analysis. It can provide chemical information in some cases and is semiquantitative. The SAM feature rasters the electron beam over the surface and thus gives elemental composition maps. The equipment is commercially available. The technique can be used for basic research and practical studies.

ESCA - XPS - Electron Spectroscopy for Chemical Analysis or its new name, X-Ray Photoelectron Spectroscopy. - A surface is bombarded with X-rays and the photo-emitted core and valence electrons are detected. It gives elemental and chemical information, is surface sensitive and is semiquantitative. The equipment is commercially available. The technique is both a research tool and can be applied to practical studies.

UPS - Ultraviolet Photoelectron Spectroscopy. - Ultraviolet light is directed at a surface and the emitted photoelectrons are detected. The energy distribution of the photo-emitted electrons is determined. UPS gives information on the bonding states of adsorbates on surfaces and can give structural information using angle resolved photoemission. The technique is surface sensitive but is a basic research tools. It is commercially available.

APS - Appearance Potential Spectroscopy. - A surface is bombarded with electrons and the emitted soft X-rays (photons) are detected. APS is surface sensitive and will give elemental analysis, however, it has low sensitivity for certain elements. The surface of interest is flooded with electrons, therefore, APS has limited spatial resolution. The energy of the incident electrons is varied through the energy threshold for creating a core hole in an atom after which the total X-ray yield of the excited surface is measured. This technique is extremely simple to construct but is not commercially available.

EM - Electron Microprobe. - This is not really surface sensitive in the sense of other techniques such as AES which samples a few atomic layers. In this technique, electrons are fired into a sample and characteristic X-rays are detected. Actually, a number of spectroscopies fall into this category such as energy dispersive X-ray analysis (EDX) and wavelength dispersive X-ray analysis. Both give elemental analysis and are quantitative. The former is simpler and is included with scanning electron microscopes. A variation of this technique called X-alpha which uses radioactively supplied alpha particles is also good for thin film analysis. The latter has a higher resolution and can detect lighter elements. All are commercially available and of practical value in thin film analysis.

XF-X-Ray Flourescence. - A sample is irradiated with X-rays and the emitted characteristic X-rays are detected which enables quantitative elemental analysis. It is not a surface tool but is useful in analysis of thin films. The equipment is commercially available.

Chemical and Elemental Analysis by Mass

ISS - Ion Scattering Spectroscopy. - A beam of ions is aimed at a surface at 45° to the surface normal and detected at 90° to the incident direction. The scattered ions are then energy analyzed which gives the mass of surface atoms. The technique is surface sensitive and gives elemental and quantitative information. It is commercially available, and can be used for basic and practical studies.

RBS - Rutherford Back Scattering. - This technique is quite similar to ISS but uses higher energy incident ions. RBS is good for thin film analysis and is not really a surface tool. It is limited because of the need for high energy, 1 Mev, ions. It is commercially available.

SIMS - Secondary Ion Mass Spectroscopy. - A beam of ions is directed at a surface and the sputtered charged particles are mass analyzed. The technique is surface sensitive and will do elemental and compound analysis. The equipment is commercially available and can be used for basic and practical studies.

IMP - Ion Microprobe Analysis. - An ion beam is directed at a surface and the sputtered atoms are mass analyzed. It is also possible to look at characteristic X-rays. This is basically not a surface technique because of the high ion current density. IMP gives elemental and quantitative information and is commercially available. It is a valuable tool for analysis of thin films.

Elemental and Chemical Analysis by Vibrational State

ELS - Energy Loss Spectroscopy. - Very low energy electrons are scattered off surfaces with adsorbates. Inelastic losses of the electrons are observed in order to obtain structural information about absorbed molecules. It gives information similar to infrared spectroscopy. Commercial equipment is available. This is basically a research tool limited to single crystal surfaces.

Structural Analysis, Macroscopic Features

SEM - Scanning Electron Microscope. - In the SEM a highly focused electron beam is rastered over a surface and the secondary electrons emitted by the surface are detected. The detection system is an electron microscope optics. The resulting image is displayed on a cathode ray tube in which the number of emitted electrons modulates the intensity of the image. Thus, SEM gives a high magnification, high resolution image of a surface. SEM is not an analytic tool, i.e. does not give elemental and compound surface analysis. If equipped with energy dispersive X-Ray analysis, bulk elemental analysis can be performed since it is not a surface analytic tool, it will not be treated in more detail in this review. The equipment is commercially available.

ELL - Ellipsometry. - An optical technique for obtaining the thickness and refractive index of thin films, both solid and liquid. The equipment is commercially available and is surface sensitive but its value is limited in lubrication applications since the substrate surfaces must have an excellent surface finish and the information given is of limited value.

Structural Analysis Microscopic

EXAFS - SEXAFS - Extended X-Ray Absorption Fine Structure. - Surface EXAFS - The fine structure in the X-ray absorption coefficient of a particular atom in a material is examined to obtain local i.e. nearest neighbor, structural information. Surface effects can be obtained by monitering photoelectrons emitted by the process. Excitation can also be done with an electron source which makes the technique more accessible. This is at present a research tool, but is quite promising for future use.

LEED - Low Energy Electron Diffraction. - Low energy electrons are scattered from single crystal surfaces giving a diffraction pattern that reveals surface structures with some mathematical effort. It is commercially available but is a basic research tool.

FIM - Field Ion Microscopy - Helium atoms are ionized at a single crystal tip ~1000 A^o in diameter which are then accelerated to give structural information about locations of atoms on different crystalline planes. The FIM has been combined with the atom probe which is a time of flight mass spectrometer which gives qualitative analysis of particles on the tip. FIM has been applied in contact studies by Brainard and Buckley (2), but is a tool for fundamental studies. It is commercially available.

We summarize the results of this presentation in the following table:

	Surface Sensitive	Commercially Available	Analysis of Practical Systems	Elemental Analysis	Compound Analysis	Analysis Quantitative
1. Elemental and chemical results by electron levels						
AES	Yes	Yes	Yes	Yes	To a degree	To a degree
ESCA-XPS	Yes	Yes	Yes	Yes	Yes	To a degree
UPS	Yes	Yes	No	No	No	No
APS	Yes	No	Yes	Yes	No	To a degree
EM	No	Yes	Yes	Yes	No	Yes
XF	No	Yes	Yes	Yes	No	Yes
2. Chemical and elemental analysis by mass						
ISS	Yes	Yes	Yes	Yes	No	To a degree
RBS	No	Yes	Yes	Yes	No	Yes
SIMS	Yes	Yes	Yes	Yes	To a degree	To a degree
IMP	No	Yes	Yes	Yes	No	Yes
3. Elemental analysis by vibrational state						
ELS	Yes	Yes	No	No	No	No
4. Structural analysis, macroscopic features						
SEM	Yes	Yes	Yes	Yes with EDX	No	No
ELL	Yes	Yes	Yes	No	No	No
5. Structural analysis microscopic						
EXAFS	Yes	No	Yes	No	No	No
LEED	Yes	Yes	No	No	No	No
FIM	Yes	Yes	No	Yes, with an atom probe	To a degree	No

As can be seen, if we are to apply the criteria of surface sensitivity of a few atomic layers, qualitative and quantitative analysis and possibly compound analysis, commercial availability, and applicability to practical systems four techniques stand out: AES, XPS, ISS and SIMS. Since none of the structural techniques except the well known SEM is very practical the rest of this review, therefore, will be devoted to giving a more complete description of these techniques and giving examples of where they have been applied to tribology for post facto elemental and chemical analysis.

The purpose of this paper is to emphasize post-experimental studies. Therefore, examples will be limited to experiments done in "dirty" real systems, i.e. in air and on lubricated surfaces. The examples may be considered fundamental in the sense that what happens in controlled experiments can be examined or could fit into the category of pre or post screening in real systems.

I. AUGER ELECTRON SPECTROSCOPY

The physics of the Auger Process is shown in Fig. 1. An electron causes the ionization of an inner level of an atom (i.e. an electron is knocked out). In the relaxation that follows an electron falls into the hole from a higher level and the energy released is absorbed by another electron. If the energy released is sufficient, the final electron will escape from the atom. Therefore, the final electron's energy will have a simple relationship to energy levels in the atom. The technique won't detect hydrogen, helium, and atomic lithium simply because there aren't enough occupied energy levels. AES is surface sensitive because the energies of the escaping characteristic electrons are low enough so that they can't originate from very deep within the solid without suffering any inelastic losses. Surprisingly there is little enough overlap in the energies of the final electrons detected from different elements to make the identification of most elements of interest unequivocal. The equipment is schematically shown in Fig. 2. The details of the equipment can be found elsewhere (1, 21). There are two types of analyzers most frequently used, the Cylindrical Mirror Analyzer (CMA) and the Retarding Field Analyzer, (RFA). In addition, other types of electrostatic analyzers such as hemispherical or sector analyzers are used. Although the details of operations of these analyzers differ somewhat, the net result is the same. A typical spectrum from a wear scar on a pure iron bullet run in dibutyl adipate with 1 w/o (ZDP) zinc-di-alkyl-dithiophosphate after sputtering a short time is shown in Fig. 3. The wear test was run in air and then analyzed after the test. The AES peaks shown can be regarded as spectral lines whose positions on the energy axis identify the elements. The peak-to-peak heights correspond roughly to the amount of a given element present. The relative peak heights (from element to element) have to be corrected for relative sensitivities, chemical effects and matrix effects to make quantitative comparisons between elements (22).

It is interesting to note that the peaks have different shapes, and these shape differences can indicate the chemical state of an element. In addition, the energy of the AES peak may shift on compound formation, i.e. the energy levels of the atoms change when in a compound, consequently the energy of the Auger peak changes. Often these energy shifts are small and aren't used much because most experimenters don't have high resolution spectrometers. An example, of peak shape changes in compound formation (Fig. 4) is shown in some elegant work performed by Shafrin and Murday (8). In Fig. 4 we see the low energy iron and phosphorous AES peaks after various stages of presoaking 52100 steel in TCP (tricresyl phosphate) along with the same spectra taken from iron phosphide and iron phosphate. The three day presoaks were somewhat uncertain as to the chemical states present, probably because the reaction proceeds slowly, but after 21 days the features clearly approach those of the phosphate (Fig. 4(b)). These studies show a great deal of promise for extending the usefulness of AES and indeed Ramaker, Murday, and Turner (23, 24) is using molecular orbital theory to calculate Auger peak shapes of elements in compounds to enable the extraction of more chemical information from Auger spectra.

A. DEPTH PROFILING

Depth profiling is actually a technique that can be used in conjunction with any of the analytical methods, i.e. AES, XPS, SIMS and ISS. In fact, it can't be avoided with the last two. It is simply combining analysis with an ion bombardment which gradually strips away layers from the surface and thus gives the concentration of an element with time, (therefore depth). It is the surface analog of metallurgical sectioning. Figure 5 shows two depth profiles of a wear scar on an iron pin worn against M2 steel with a dibutyl sebacate base stock and 1 w/o ZDP as an additive. Figure 5(a) shows the results for a pin run in pure nitrogen and Fig. 5(b) shows it run in dry air. We can see that there are substantial differences between the two films. In nitrogen, the principle elements are iron and sulfur with some phosphorous present whereas with dry air it was oxygen, sulfur, iron and a negligible amount of phosphorous. It can be hoped that such information along with wear tests will produce information for understanding the effects of additives on wear.

Difficulties are involved in depth profiling. One such difficulty is shown in Fig. 6. This figure shows the ratio of the sulfur to molybdenum peak heights versus sputtering time for pure molybdenite, and two sputter deposited films.

Figure 6 indicates that the amount of sulfur is decreasing with time. Obviously with the Molybdenite this can't be the case and thus we are seeing a difference in sputtering rates between molybdenum and sulfur. Further, because of the penetration of knock-on particles, one may have an alteration of the subsurface composition. Another problem is that the actual thickness of a film is difficult to measure accurately. Normally sputtering rates are obtained for films of known thickness for a material other than the surface to be analyzed. Another acute problem for wear surfaces is surface roughness (15), when the surface isn't smooth, shadowing (Fig. 7(a)) of the ion beam can occur. Since sputtering and analysis are not normally done at normal incidence, false impressions of the actual elemental distributions can occur. Debies and Johnston (15) tried to solve this problem by using two ion guns. In addition, since the examining electron beam is small, usually 25 microns or less, the observer may be obtaining only local compositions, i.e. only the area under the beam (or in the analyzing region for the othe techniques, Fig. 7(b)). Consequently, a local analysis may be representative of lubricant trapped in a pit or a high point. On the other hand, if the surface roughness is small compared to the beam diameter, one may be observing averages as discussed below scanning Auger is a convenient way to avoid this problem. In spite of these limitations, depth profiling gives information that would be difficult to obtain in any other way. An advantage with AES is that commercial equipment called a multiplexer is available which automates and accelerates data taking.

B. SAM - SCANNING AUGER MICROSCOPY

The difficulties mentioned in studying rough surfaces with AES and depth profiling (i.e. surface homogeneity) can be overcome in part by using Scanning Auger Microscopy. What SAM does is raster over a region of a surface as in a scanning electron microscope; it gives a composition map ($20A^o$ sampling depth) similar to but much more surface sensitive than maps obtained from X-ray energy dispersive analysis (EDX) (~1 micron sampling depth) which is often attached to SEM's (Fig. 8). The composition maps can be directly correlated to topographical maps at the same region. Murday and Shafrin (8) were the first to apply SAM to bearings run in lubricated wear tests. Debies and Johnston (15) also applied it to surface obtained in wear tests. Defocusing the electron beam can be used to give an average over a larger region of the surface but this still would not necessarily be representative and would degrade resolution.

SAM is very desirable to have in performing wear studies. The high cost of the equipment is offset by the information obtained from it. That is, the uncertainties involved in analyzing inhomogeneous wear surfaces require equipment which displays the surface distribution of elements.

C. QUANTITATIVE ANALYSIS

A review of quantitative analysis in AES and XPS is presented by Powell (25). There are several routes to follow in performing quantitative analysis: (a) direct comparison to standards, (b) determing elemental sensitivity factors or (c) first principle model calculations. All these routes are under development by Auger spectroscopists. Until recently, the great bulk of quantitative studies have been made using the peak-to-peak heights in the derivative "dN/dE" mode of operation (i.e. what you work with is the derivative of the line shape rather than the peak itself). The peak-to-peak heights are scaled by published relative sensitivities (26). This is at best, semiquantitative, but gives estimates which are useful. Some of the difficulties involved with this are that peak shapes can have complicated structures and that the line shapes must change due to chemical differences and processing. Also, the background can cause peak distortions in some parts of the spectrum and there can be damage caused by the electron beam which changes the peak shape and the chemical state as can be seen in Fig. 9. Recently, AES spectra have been treated by numerical or instrumental methods to improve the quantitativeness, e.g., integration of the "dN/dE" peaks along with background stripping and with deconvolution of instrumental broadening. Murday et al, (24), have tried to treat matrix effects and chemical changes in peak shapes by comparing analytically and experimentally derived peaks and superimposing the analytic peaks to determine how much of each material contributes to the final experimental peak structure. With the effort currently devoted to quantitative studies, substantial improvements should be available in the near future.

D. APPLICATIONS OF AES TO TRIBOLOGY

An excellent review of the application of AES and XPS to tribology is given by Singer and Murday (11). The limited number of references and the fact that many are recent indicates that the application of these techniques to tribology for examining materials run under real conditions is in its infancy. In this section we would like to summarize the results of experiments already obtained and point out the implications of these experiments to future applications.

Phillips (3) et al performed wear tests on a modified 4-ball tester with ZDP as an additive and used AES - depth profiling for analysis. Although wear results were not reported, the interaction of the additive with the metal was clearly demonstrated by controlled experiments with and without the additive present. McCarroll et al (7) used AES and depth profiling to examine sulfur and chlorine containing additives. They found thicker surface films formed with the sulfur than with chlorine containing additives and also that greater wear occurred with chlorine containing additives. In addition, sulfur concentration and penetration increased with load. Debies and Johnston (15) performed SAM and depth profiling studies on a steel ring rotated against a steel block with ZDP, DBS (dibenzyl disulfide) and Hexadecyl diethyldithiocarbamate (HDDC). With DBS they found that scarred regions had low sulfur, high oxygen and high iron concentrations whereas sulfur was more abundant in smooth regions. For HDDC (which failed the wear tests) sulfur was distributed over the entire surface. It had a low sulfur and high oxide concentration in scarred regions. Similarly, ZDP produced the lowest scarring in sulfur rich regions. Brainard and Ferrante (16) performed pin on disk wear studies on a number of diester lubricants with ZDP as an additive with AES depth profiling for analysis. The wear results are shown in Fig. 10. They found that ZDP reduced the wear rate in all cases with the exceptions of dibutyl oxalate and dibutyl sebacate. Depth profiling of surfaces run in dibutyl oxalate revealed thin surface films and visual inspection indicated wear debris strongly suggesting corrosion. With the sebacate there was evidence of interaction of the surface film with ambient oxygen (Fig. 5). The same test run in dry nitrogen showed reduction of wear along with a surface film composed largely of sulfur and oxygen. The test run in nitrogen, having no additive, had the highest wear rate indicating that the oxide produced by the ambient oxygen reduced wear.

Shafrin and Murday (9, 10) performed studies examining preconditioning of bearing surfaces by various cleaning techniques along with presoaking in tricresyl phosphate (TCP). AES depth profiling and SAM were used for the first time in lubrication studies. In this study, various pretreatments were evaluated in terms of compounds formed which are needed to optimize bearing lifetime. A SAM examination of the inner race of a bearing which failed revealed that there was lubricant breakdown in the wear scar which was mainly iron oxide whereas outside the wear scar the presence of ZDP was evident. Bernett et al (12) used AES and XPS to examine solvent cleaning methods on instrument bearings and found that the least contamination was obtained with freon vapor degreasing.

In summary, AES, depth profiling, and SAM have been used to evaluate the effects of additives on wear and the composition of bearing surfaces. The wear studies were performed on lubricated systems run in air rather than vacuum systems. AES was used to perform post facto analysis of the surfaces. The results of the wear studies, although preliminary, indicate that use of AES will aid in understanding the effect of additives.

There is another perspective in the use of AES as indicated in the work of Shafrin and Murday. AES can be used for screening. Once the characteristics of a particular preparation are established and tabulated, AES can be used for quality control by sampling bearings and other components for proper pretreatment prior to use. Finally, as SAM studies have shown, AES can be used for failure analysis in real systems (e.g. a failed machine part or engine component).

II. X-RAY PHOTOELECTRON SPECTROSCOPY OR ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

The physical processes involved in XPS are shown in Fig. 11. As can be seen, XPS is a much simpler process than is AES which involves a folding together of several interactions. A monochromatic beam of X-rays is directed at an atom and an inner level of the atom is ionized. The emitted electron is detected and its kinetic energy is the difference between the X-ray energy and the binding energy of the electron in the atom. A schematic diagram of the equipment is shown in Fig. 12. A typical "line spectrum" for XPS is shown in Fig. 13. The analyzers used are similar to those used in AES details of which are reported elsewhere (21, 27). Unlike AES, the peaks shown in the spectrum are not derivative peaks, thus the peak height is more representative of the amount of material; further in XPS it is easier to strip the background and obtain the area under a peak. Note also that the AES peaks are contained in the XPS spectrum.

In Fig. 14 we show the chemical shifts characteristic of compound formation with XPS for a wear scar on 440C steel run in mineral oil containing DBS. As can be seen, the different peak positions identify the reaction films present on the surface. In addition, we can see a mild sputtering reveals a different surface composition. This may be a real feature of a wear scar or may indicate that the, as is, surface layer was changed by transporting and cleaning after the wear test. In general, many of these chemical shifts which enable compound identification are available in the literature (20).

In general, XPS has much lower spatial resolution than AES, because the analyzed area is much smaller with AES (~2 mm compared to 0.2 - 2.5 microns). Thus, you are averaging over a much larger area with XPS which limits the size of the wear scars analyzable without masking. It is also used in a different manner. AES is typically used as a fast surface probe giving elemental analysis. XPS is often used mainly for compound identification. Because of the inability to raster the X-ray beam and the difficulty in rastering the sample something equivalent to SAM is not possible with XPS. Even if rastering the beam were possible, the large spot size would limit its effectiveness. Consequently, rough, inhomogeneous surfaces present problems in interpretation since you are averaging over a large area. In general, more time is devoted to obtaining and XPS spectrum but more information is obtained. An important advantage of XPS, however, is that it is non-destructive whereas, as has already been shown (Fig. 9) an electron beam can be destructive.

Depth profiling can also be performed with XPS and in general the same limitations mentioned with AES are applicable here. There are some limitations with XPS, however, that make depth profiling more difficult. The large XPS spot size make it necessary to raster the ion beam over large areas in order to get a uniform sputtering crater. This increases the sputtering time for a given film thickness thus making analysis more time consuming. Furthermore, in order to simultaneously sputter and analyze it is necessary to use a differentially pumped ion gun due to limitations in the X-ray source. AES with multiplexing enables rapid automated acquisition of elemental profiles.

A. QUANTITATIVE ANALYSIS

XPS has a number of great advantages in performing quantitative analysis. First, since you are dealing with the peaks instead of the derivatives of the peaks, manipulation of the data to obtain areas under peaks is considerably simpler. Next, the narrowness of the peaks, no major loss corrections and a simple background contribute to the simplicity. At present the newer XPS systems have dedicated microprocessors for background stripping deconvoluting and integrating of areas under peaks. XPS has another advantage in that relative sensitivities of elements are much better known than with AES, (20) and are tabulated. XPS has an extra advantage because its chemical sensitivity gives more specific quantitative information than AES (i.e. amount at a given compound present). The relative sensitivities for elements can also be used with compounds. The electrons analyzed originate from core levels and thus elemental sensititivites and aren't affected greatly by chemical shifts. A disadvantage with XPS is that it samples a relatively large area and thus for a heterogeneous surface the results represent an average over the area sampled. There are also disadvantages in using XPS in conjunction with depth profiling as mentioned earlier. Since the time required to acquire spectra is longer, the quantity (i.e. number of elements analyzed in a given time) of information is limited.

B. APPLICATION TO TRIBOLOGY

There have been limited applications of XPS to tribology to date. An excellent summary of these applications is presented by Singer and Murday (11). Here we will just summarize the main results of these studies (4, 5, 6, 11, 13 and 14) and also present the results of applications of XPS to this film deposition by Brainard and Wheeler (28, 29) which are of interest to tribologists.

Baldwin (3, 4 and 5) used XPS to examine surface composition following wear studies in a falex tester where the lubricants had a number of sulfur containing additives. He concluded that wear was inversely related to sulfide content in the film and that amines inhibited the wear effectiveness of the sulfur. Bird and Galvin (6) also used XPS to examine surface composition following wear studies performed by rubbing a flat on a cylinder. Their work emphasized the difference between static immersion and wear generated films and again found that sulfides were a major component in the wear scar. Wheeler (13, 14) performed wear studies using a modified shaper with a pin on disc configuration generating large wear scars on the disc. The disc surface was examined with XPS for a lubricant containing dibenzyl disulphide (DBDS) as an antiwear additive. Wheeler found that in the mild wear region, the surface layer converted to sulfide at the expense of oxide. Wheeler, (14) also performed an interesting study in air and in nitrogen using a pin and a flat iron button on a disc. He examined both the wear surface and wear debris with XPS. In this work DBDS was added to hexacane, Wheeler found that the oxide had the lowest wear rate. The highest wear rate occurred with both air and DBDS present. The surface film was mainly sulfide with a nitrogen ambient and the wear debris showed the presence of an organic sulfide. The wear debris also showed a sulfate for DBDS in air indicating possibly that corrosive wear occurred. Bernett et al (12) used XPS among other analytical methods to effectively evaluate bearing, cleaning and packaging procedures in a direct practical application.

Brainard and Wheeler (29, 30) used XPS to examine the relationship of the composition of hard refractory films and their adherence to the condition for sputter deposition. A number of interesting conclusions were drawn from these studies among the most interesting of which was that the adherence of certain coatings be improved by introducing seed gases into the plasma. For example, the adherence of TiC to Rene 41 (a nickel based alloy) could be improved by the introduction of a small amount of acetylene to the sputtering plasma.

Again, we see that XPS has been used to understand the results from a wide variety of experiments performed in air and other ambient conditions rather than vacuum. These results ranged from the effects of sulfur containing additives on wear to improving packaging of bearings to improving the adherence of hard faced coatings.

III. SECONDARY ION MASS SPECTROMETRY (SIMS)

An excellent discussion of SIMS is presented in (31). Both SIMS and ISS will be given less space in this review since they are somewhat less versatile than AES and XPS and there is only one study that has been done to date (17) applying them to tribology. In SIMS a solid surface is bombarded by any of a number of ions having energies from a fraction to many keV. A diagram of the process is shown in Fig. 15. From the wide range of particles emitted from a surface e.g. electrons, photons, ions, neutral, atoms, etc. SIMS looks at only the sputtered charged particles. A schematic diagram of the equipment is shown in Fig. 16. Since SIMS looks only at charged sputtered particles, the mass spectra are obtained by filtering the particles through a mass spectrometer, typically a quadruple mass spectrometer and then are detected by a standard means such as an electron multiplier. The detected particles can range from elemental ions to charged molecules to charged clusters of atoms. SIMS is fundamentally different from AES or XPS in the sense that there is more ambiguity in the identification of the materials present since there is more spectral interference in a mass spectrum due to polyatomic particles and the possibility of multiple charging. Therefore, more information may be required about what materials may be present initially. Chemical information from SIMS is obtained from clusters of atoms sputtered from surface, e.g. Fe_2O_3. Therefore, by examining the masses of sputtered clusters, it is possible to come to conclusions about compounds present on the surface. A sample SIMS spectrum is shown in Fig. 17. In general, the physics of the sputtering process is not as well known as the physics of AES and XPS. Surface roughness creates problems similar to those in depth profiling with other techniques. SIMS can be used to study organic adsorbates or deposits on metals (31, 32) and thus has application to systems of interest in tribology.

A. QUANTITATIVE SIMS

In order to perform SIMS quantitatively, (33), a number of quantities must be known, the most important of which is the differential sputtering yield (i.e., the number of sputtered ions of a specific type per incident ion). This quantity can be determined either experimentally or analytically. However, there are questions as to how well the yields will translate for complicated combinations of materials, such as wear surfaces where matrix effects may substantially alter the yields. Depth profiling is obviously possible with SIMS since you are sputtering as you analyze. Depth profiling suffers from the same limitations with SIMS as AES or XPS. It would be conceivable to obtain surface maps similar to SAM with SIMS.

Again, SIMS can be used for post facto analysis of experiments performed, or equipment used, outside of vacuum systems. Since there is only one reference using SIMS and ISS applied to tribology the discussion of applications will be deferred until after discussing ISS.

IV. ION SCATTERING SPECTROSCOPY (ISS)

ISS in many respects is the simplest of the surface analysis techniques. A schematic of the apparatus is presented in Fig. 16. A beam of ions is directed at a surface and this beam is energy analyzed after being scattered by the surface. The physics of the process is quite elementary, and is based on the fact that some of the incident ions surprisingly undergo elastic collisions with surface atoms, even though the incident particle is charged and the surface particles are bound. The kinematics of the two body collision can be simply worked out for a 90° angle between the directions of incident and scattered particles resulting in

$$\frac{E_1}{E_o} = \frac{M_a - M_i}{M_a + M_i}$$

where E_o is the incident energy, E_1 is the energy of the scattered particle M_i is the ion mass and M_a is the surface atom mass. Thus peaks appear in the scattered ion energy spectrum (Fig. 18) corresponding to an element of mass, M_a. We can infer the element from the energy E_1 which determines M_a. The primary problems with ISS is that it has relatively low resolution, i.e., it is hard to separate peaks as M_a increases, furthermore, the sputtering process produces large backgrounds of low energy ions in some cases. The incident ion can be changed in some cases to alleviate the resolution problem. Some of these difficulties can also be alleviated by digitizing the data and using background stripping, peak resolving, etc., techniques.

Again, ISS suffers from the same types of problems encountered in depth profiling, e.g., shadowing from rough surfaces. Depth profiling can be performed with ISS. Something akin to SAM is possible but with difficulty. ISS is probably the most surface sensitive of the techniques discussed. An important advantage of SIMS and ISS is that they can be easily incorporated into vacuum systems with equipment normally available in surface analysis laboratories.

A. QUANTITATIVE ANALYSIS

Performing quantitative analysis with ISS is similar to the other techniques described in that the relative sensitivities are based again on elemental standards. The important difference between elements is the cross-section for elastic scattering between incident and target particles at a given incident energy. Other effects such as surface roughness, or selective sputtering are important to the results, a detailed discussion of these effects is given by Baun (34). Baun raises serious questions about the quantitativeness of ISS and stresses the necessity of having uniform standards reproducible from laboratory to laboratory. In spite of the difficulties, ISS probably is as accurate as XPS and AES in giving quantitative results and its principal strength is true monolayer sensitivity.

B. APPLICATIONS OF SIMS AND ISS TO TRIBOLOGY

The only paper in the literature at present applying SIMS and ISS to tribology is by Oppelt, Muller, and Bartz, (17). In this paper, a block on cylinder apparatus is used to study step loading wear for mineral oil with ZDP and MoS_2 as additives on a 90Fe-10MnCrV alloy. The remarkable result of this paper is that there is no agreement with any of the results obtained by others who used AES and XPS as analytical tools. With these other studies, sulfur was the main ingredient in the surface films formed in wear scars from the additive. In this study, zinc, phosphorous and oxygen were prominent. No sulfur was found. Unfortunately, it is difficult to evaluate whether these differences relate to the analytical tools used or some details of the experiment. The materials in the block are not clearly defined and, in fact, the only depth profile in the paper seems to show Fe as the prime ingredient, whereas none of the other ingredients in the alloy were detected. In addition, no details of cleaning procedures were given. In the AES-XPS studies, the wear surfaces were rinsed in a solvent before being placed in a vacuum system, but no such procedure was specified in (17). This could be an important difference in that materials removed from the surface by rinsing could be important in the wear process. The presence of more than one additive could also have been relevant. Unfortunately, since necessary details have been omitted from the paper, it is impossible to evaluate the results with regard to information obtained from ISS and SIMS.

V. CONCLUDING REMARKS

In this presentation, we present a description of a number of surface analytical tools and narrow the number to be discussed in more detail to those which are felt to have the most application to applied research and general analysis in tribology. A summary of the main features of these analytic tools are presented in Table 1. The conclusion is that of the truly surface sensitive tools AES, XPS, SIMS and ISS would be most useful. This conclusion was based on the ability to analyze engineering materials, availability as commercial apparatus, and the direct applicability of the information obtained to tribology. The main thrust of this paper is that these techniques can be used for standard chemical analysis and can be applied to experiments done in a real system for post facto analysis. Examples have been given from studies that range from applied research to studies that could be considered quality control, such as evaluations of contamination from packaging and cleaning procedures.

In general, AES and XPS are probably the most useful techniques. In order to study wear on rough wear surfaces, a scanning Auger microscope would be highly desirable, and almost necessary. In general, it is desirable to use as many techniques available as possible to interpret results both qualitatively and quantitatively. In fact, there are commercial systems available that include SEM and EDX with the surface tools. The ability to observe topography and perform bulk and surface analysis in situ would be highly desirable in tribology.

The tone of this review may have seemed negative because of extensive discussions of problems and limitations. It must be pointed out that there are no other analytic tools available which offer such detailed information. Consequently, it is the obligation of the users to creatively overcome the difficulties in the application of these tools to tribology.

ACKNOWLEDGEMENTS

The author would like to thank Dr. James Murday for making preprints available and for helpful discussions and Dr. Donald R. Wheeler for helpful discussions.

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TABLE 1. - COMPARISON OF FEATURES OF SURFACE ANALYTIC TECHNIQUES (2)

	AUGER	ESCA	ISS	SIMS
Spatial resolution imaging	3 m Elemental maps	2 mm No scanning	100 m Scanning	Large area to 100 m ION microprobe 5 m
Depth resolution profiling	20 A continuous profiles	20 A step profiles	1 Atom layer continuous profiles	1 Atom layer continuous profile necessarily
Chemical information	Possible not well understood yet	Yes	No losses elemental discrimination at high mass number	Yes but interpretation is unclear
Quantitative	Semi-quantitative in some systems	Semi	Semi	Difficult and unreliable
Sensitivity	0.1% Bulk 0.01 monolayer	0.1% Bulk 0.1 monolayer	0.01 monolayer	ppm
Sample Consideration	Intense electron beam, modifies chemistry of surface	X-Ray beam has little effect on sample	Less damage than auger. sputter rate can be very low	Analysis not much altered by damage polymers and biological specimens possible
Speed and simplicity	Fastest elemental data easy quantitative and chemical Data harder	Slowest data easily interpreted	Can be as fast as auger. easy to interpret for light elements	Intermediate speed relatively most difficult to interpret

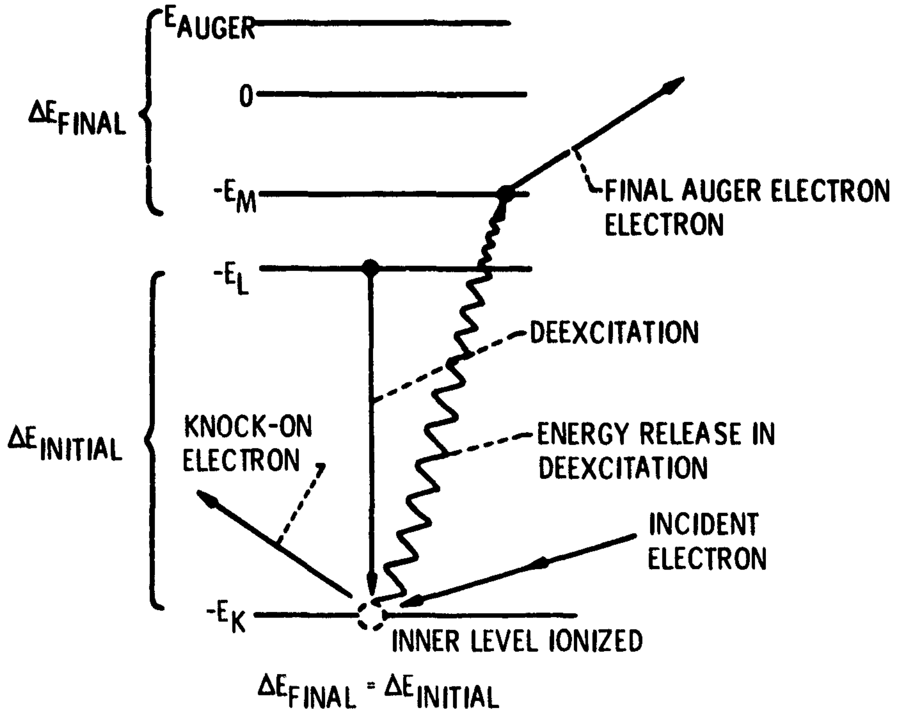


Figure 1. - Auger transition diagram for an atom (ref. 1).

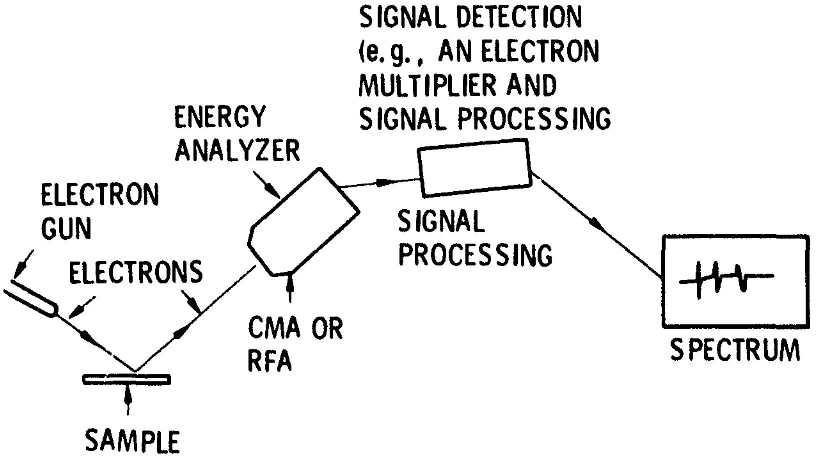


Figure 2. - Schematic diagram of AES apparatus.

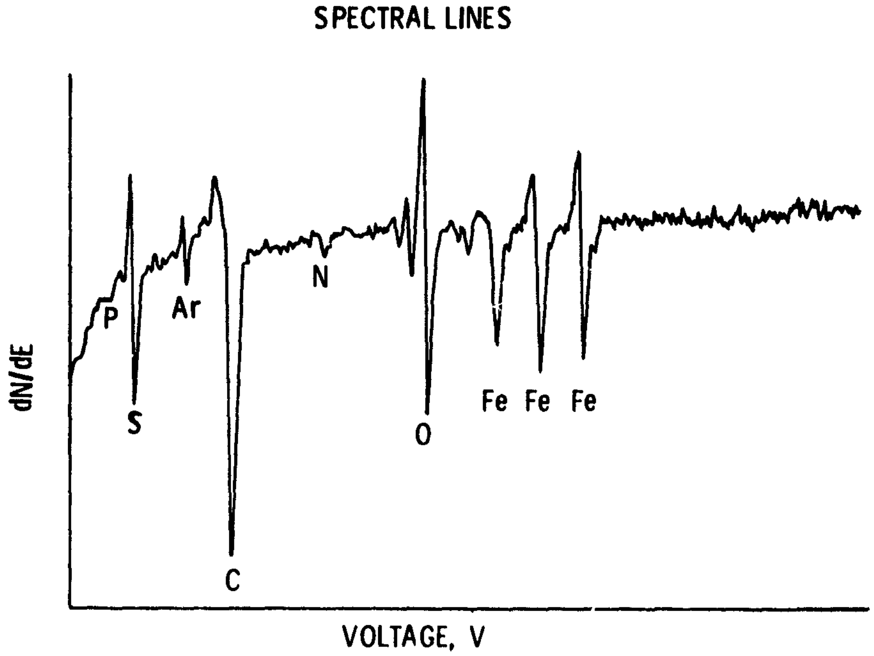
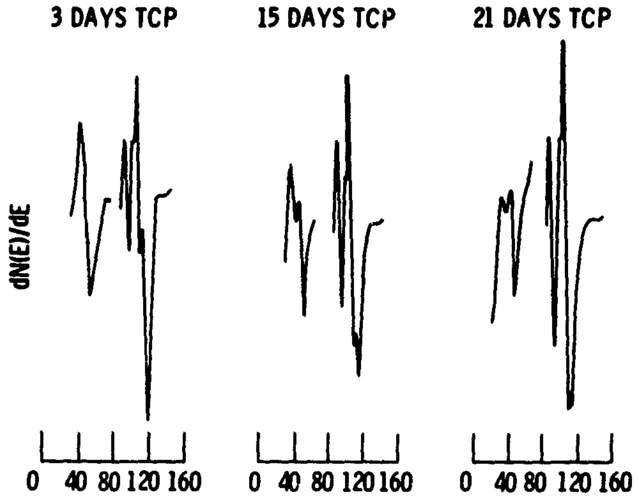
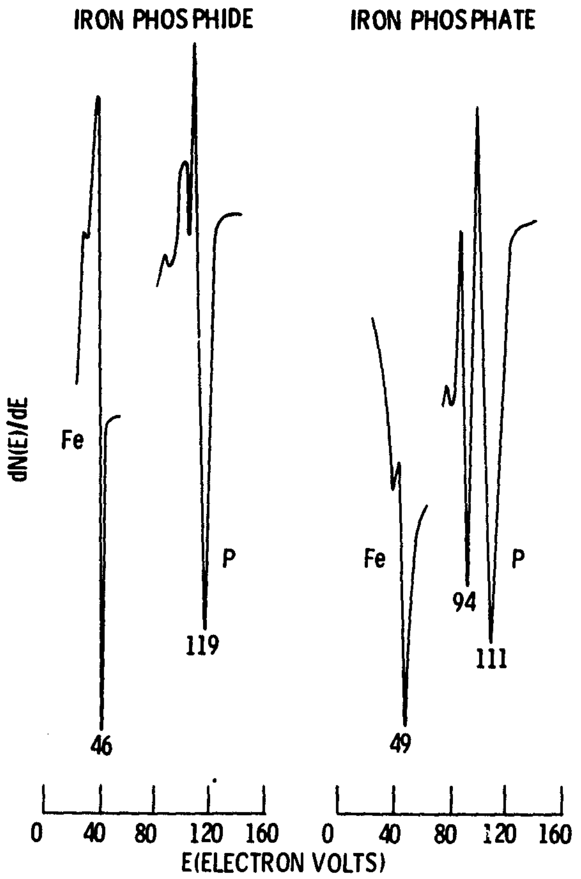


Figure 3. - Auger spectrum of wear scar on pure iron pin run against M-2 tool steel disk in dibutyl adipate containing 1-wt% ZDP. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air.(ref. 16).

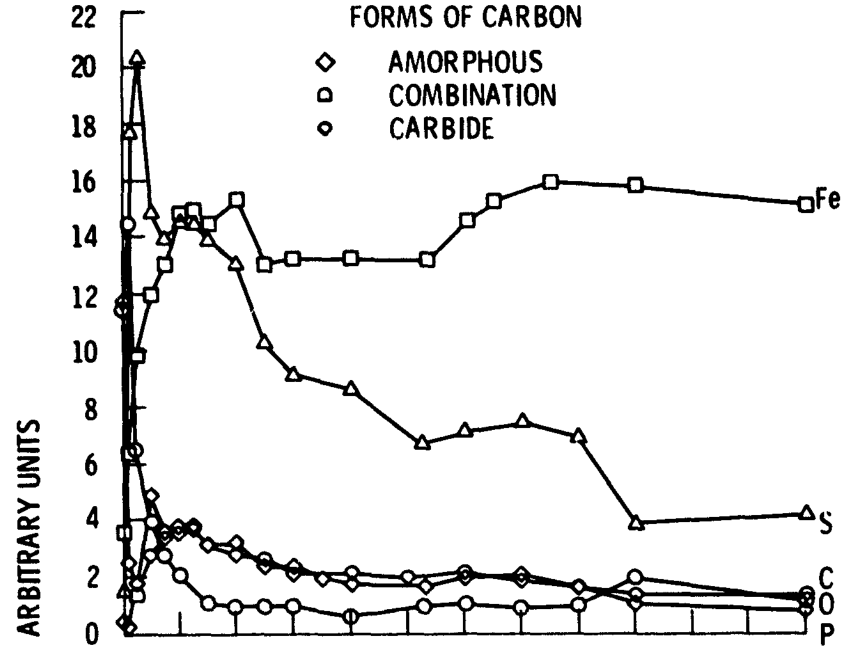


(a) THE Fe_{MMM} AND P_{LMM} AUGER ELECTRON LINE SHAPES OF 52100 STEEL EXPOSED TO TCP AT 110° C FOR 3, 5 AND 21 DAYS, RESPECTIVELY.

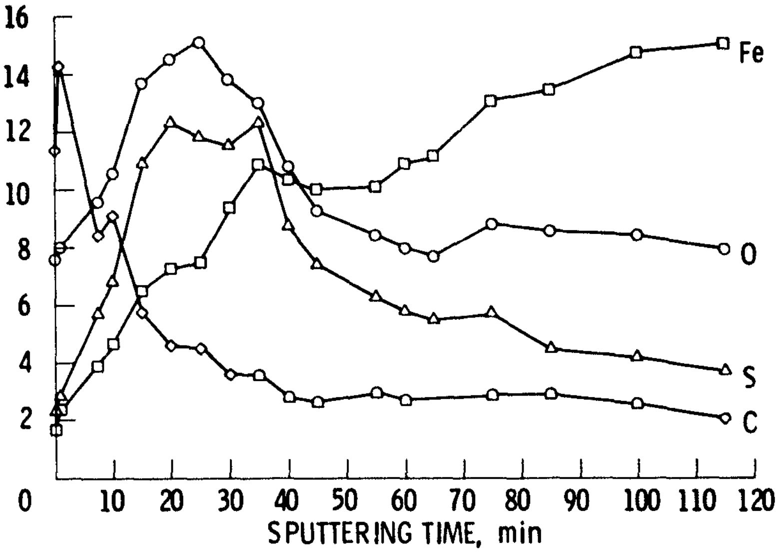


(b) THE Fe_{MMM} AND P_{LMM} AUGER ELECTRON LINE SHAPES FOR POWDERED IRON PHOSPHIDE AND IRON PHOSPHATE (REF. 8).

Figure 4. - Auger electron line shapes of reacted steel surfaces and of corresponding metal compounds.



(a) ATMOSPHERE, DRY AIR.



(b) ATMOSPHERE, DRY NITROGEN.

Figure 5. - Elemental depth profile of a wear scar on an iron pin run in dibutyl sebacate plus 1 percent ZDP. Sliding speed 2.5 cm/sec, load 4.9 N.

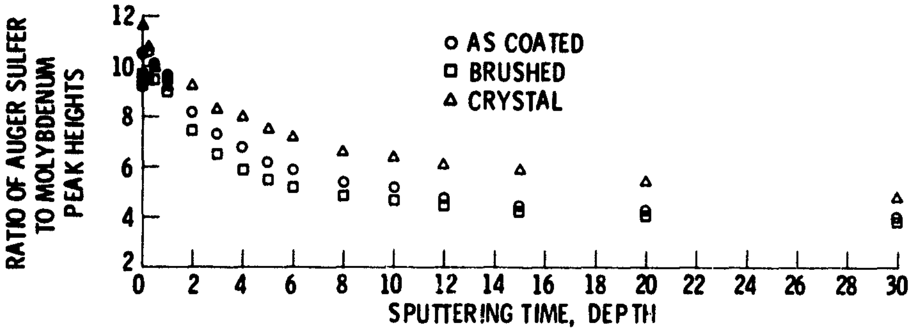
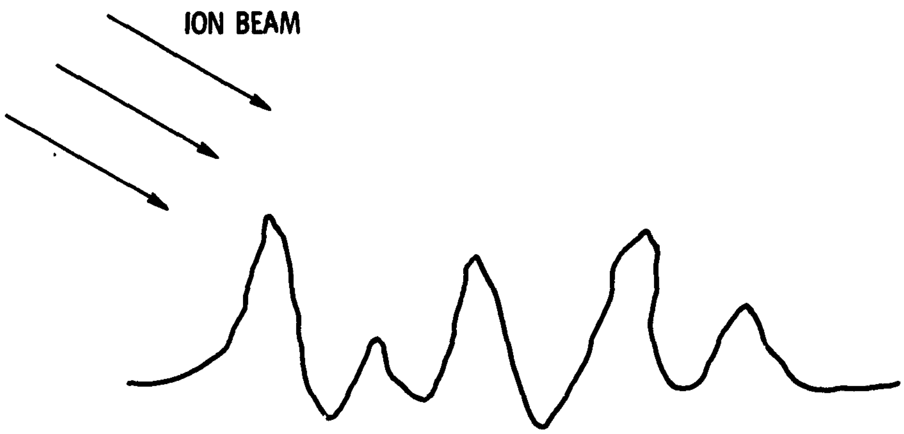
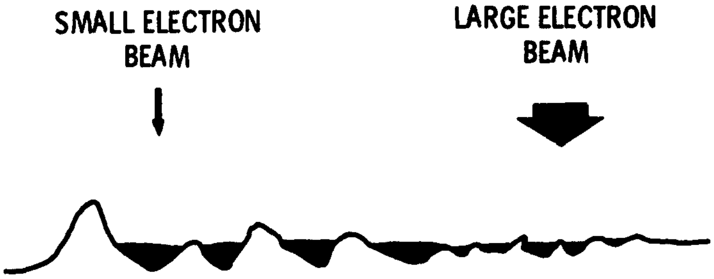


Figure 6. - An AES depth profile of different MoS_2 coatings showing different sputtering yields for Mo and S.

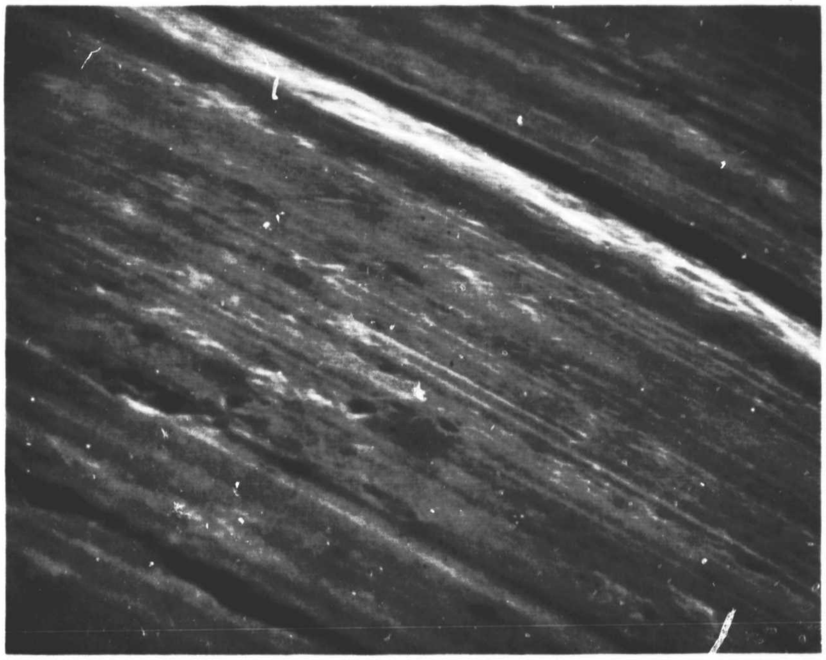


(a) SHADOWING OF AN ION BEAM BY A ROUGH SURFACE.

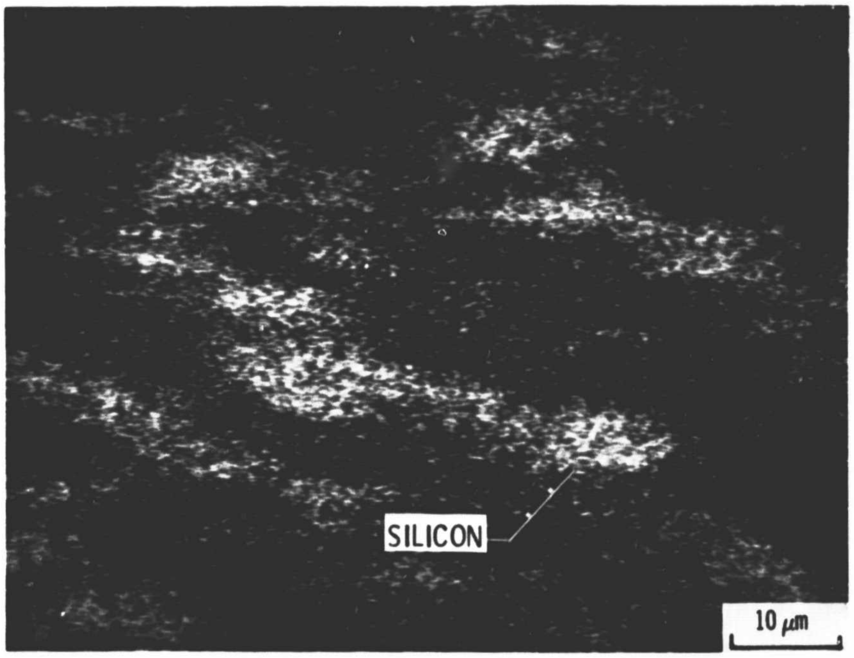


(b) LOCAL EXAMINATION AND AVERAGING BY A SMALL AND LARGE ELECTRON BEAM.

Figure 7. - Topographical problems in depth profiling and analysis.



(a) SEM TOPOGRAPH.



(b) XDA IMAGE.

Figure 8. - An SEM and X-ray dispersive analysis of a wear scar on an Al-8 w/o Si bullet.

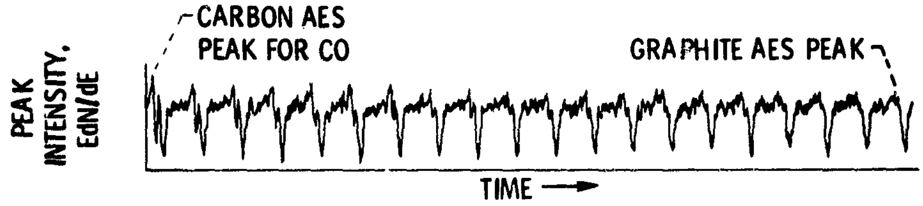


Figure 9. - Electron beam damage to CO adsorbed on Ni (111), beam energy, 2000 eV, beam current, 50 nA, beam spot size, 25 µ.

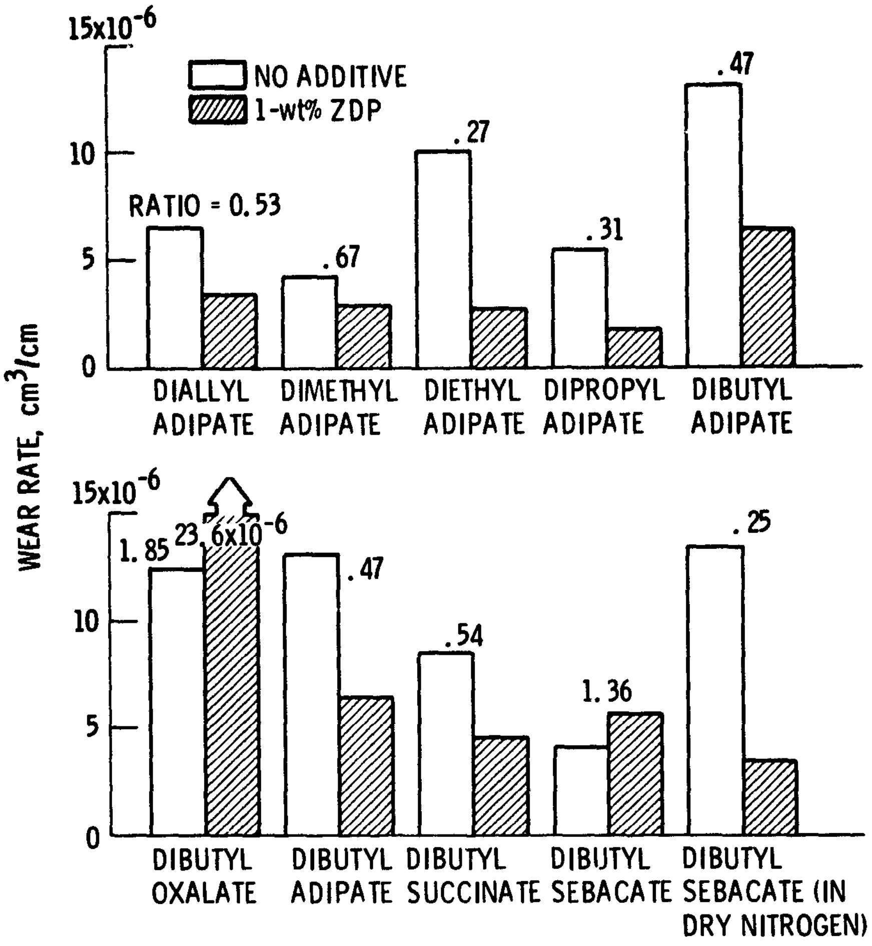
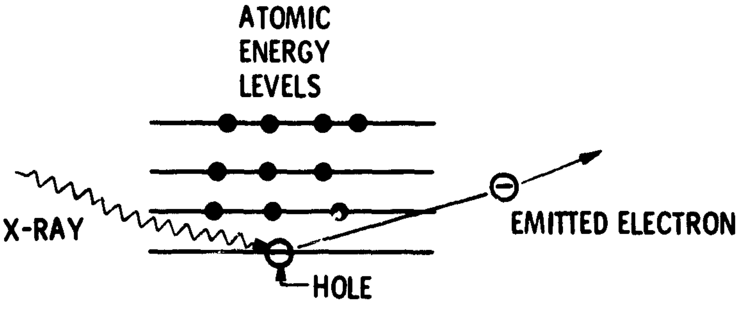


Figure 10. - Wear rates of pure iron sliding on M-2 tool steel in various diesters with and without ZDP antiwear additive. Sliding speed, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air except where noted as dry nitrogen (ref. 16).



$E_{\text{KINETIC ENERGY}} = E_{\text{X-RAY}} - E_{\text{BINDING ENERGY}}$

Figure 11. - Physical process in XPS.

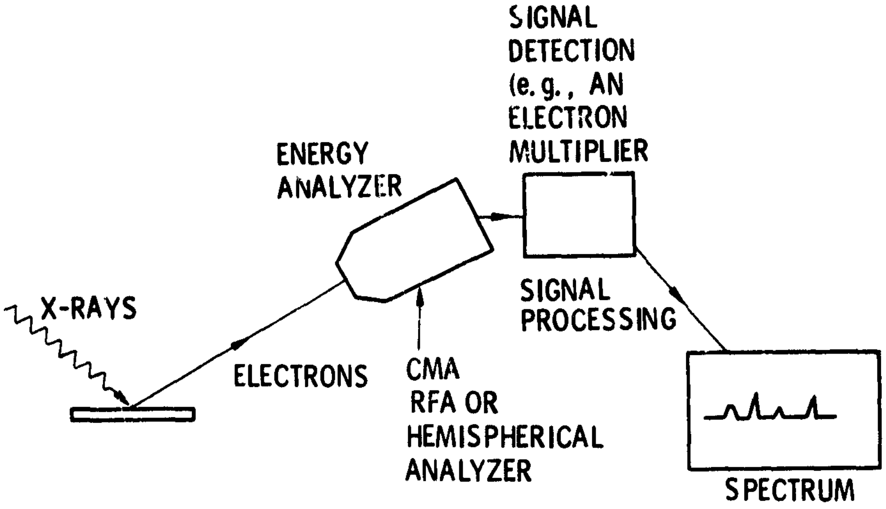


Figure 12. - Schematic diagram of XPS apparatus.

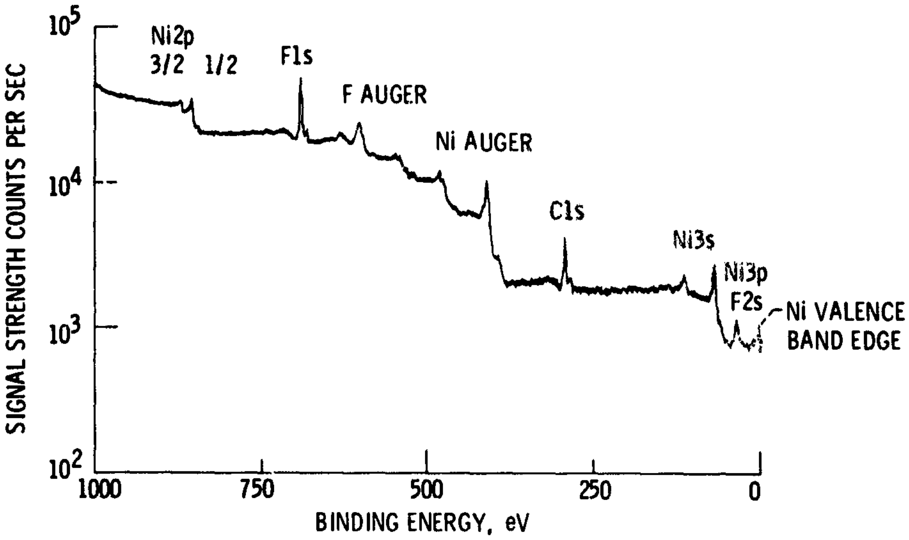
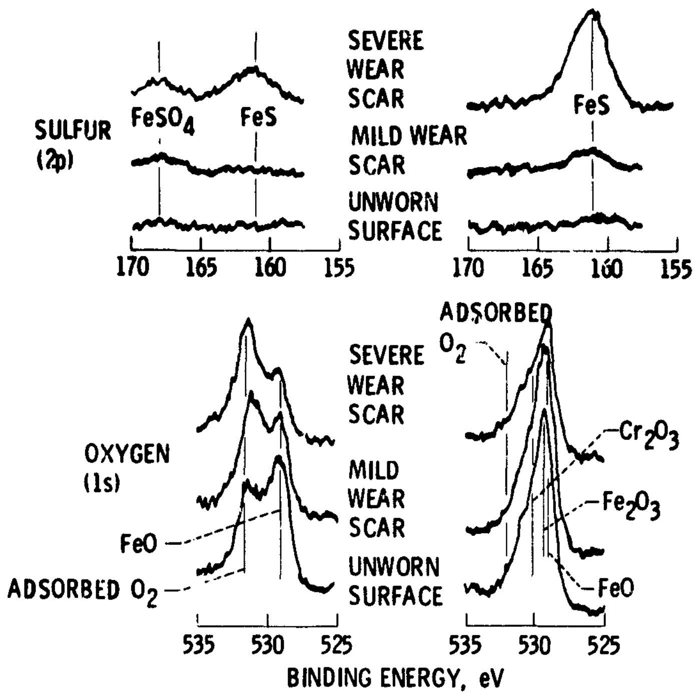
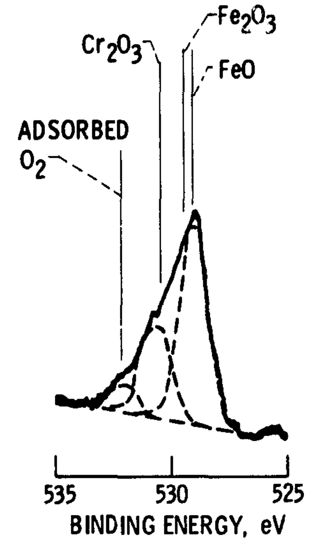


Figure 13. - AES line spectrum.



(a) BEFORE SPUTTERING.

(b) AFTER 30 seconds OF SPUTTERING.



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(c) OXYGEN (1s) SPECTRAL LINE FROM WEAR TEST SPECIMEN SHOWING BINDING ENERGIES OF 1s ELECTRON IN SEVERAL COMPOUNDS AND RESOLUTION OF PEAK OBTAINED WITH ANALOG CURVE RESOLVER.

Figure 14. - Sulfur (2p) and oxygen (1s) XPS peaks from unworn iron surfaces and wear scars run in mineral oil with 1 w/o DBDS (ref. 13).

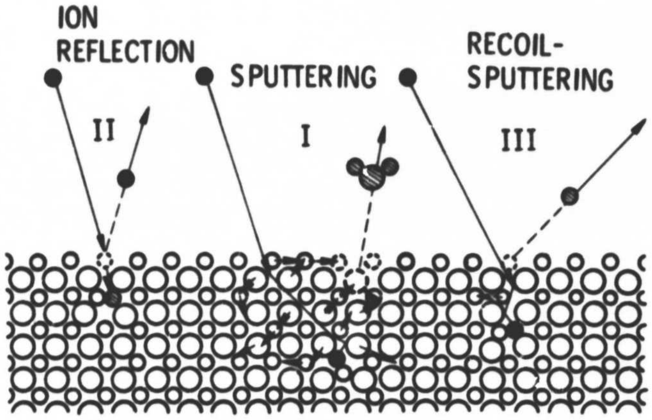

Figure 15. - Interaction processes of an ion with a solid surface resulting in the emission of heavy particles (ref. 29).

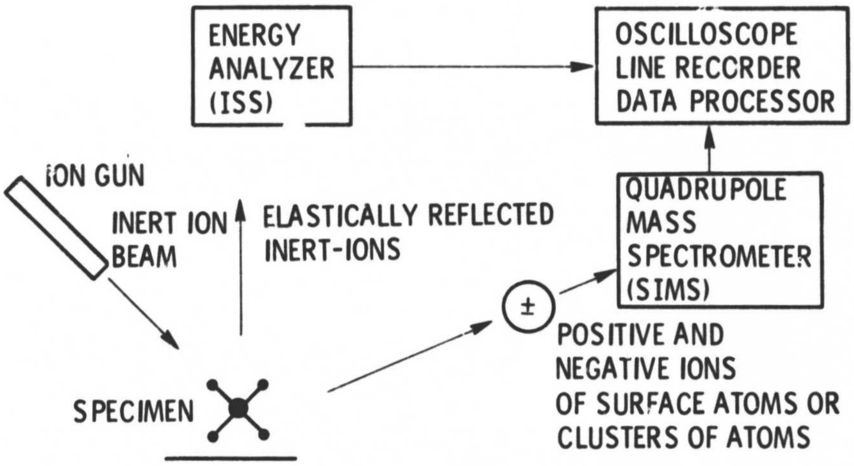

Figure 16. - Outline of the ISS/SIMS surface analyzing system (ref. 17).

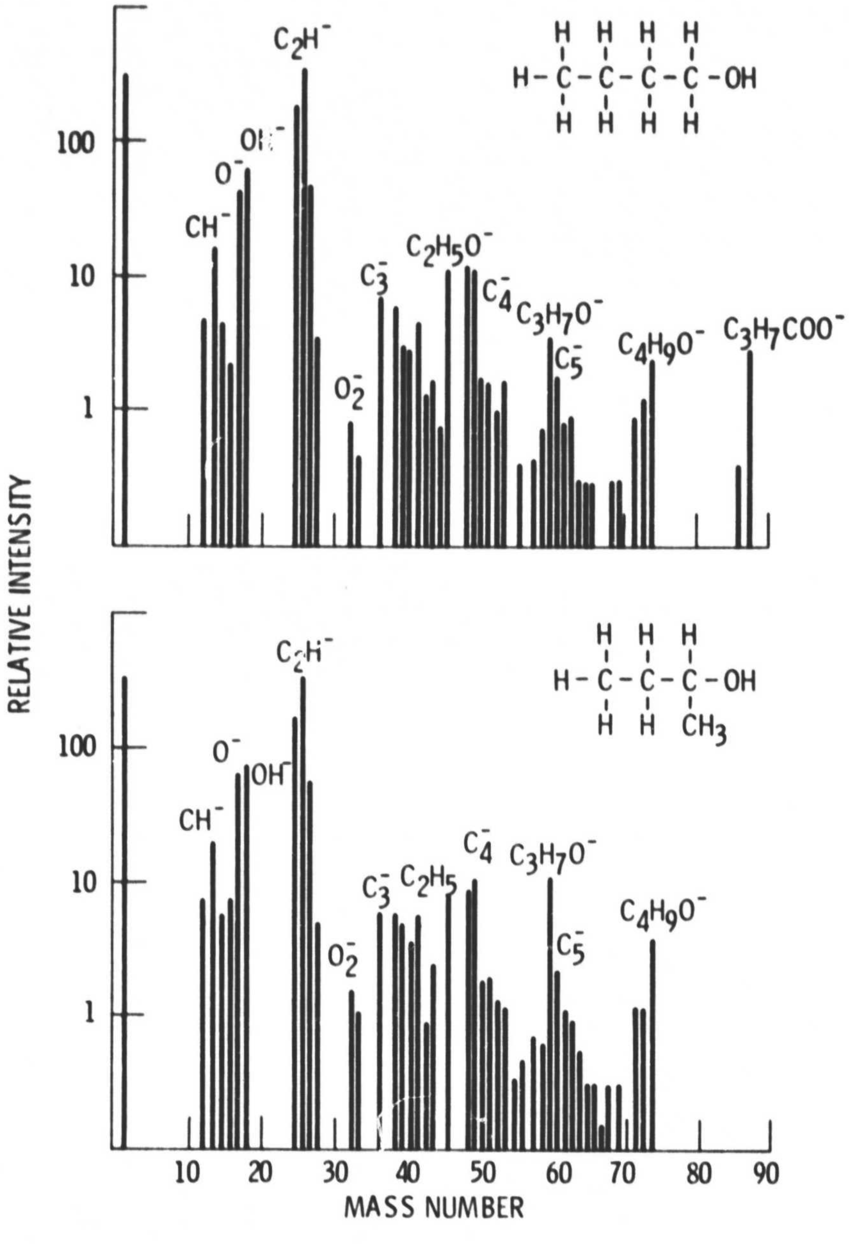

Figure 17. - Secondary ion spectrum of adsorbed molecules: 1- and 2-butanol on molybdenum (ref. 29).

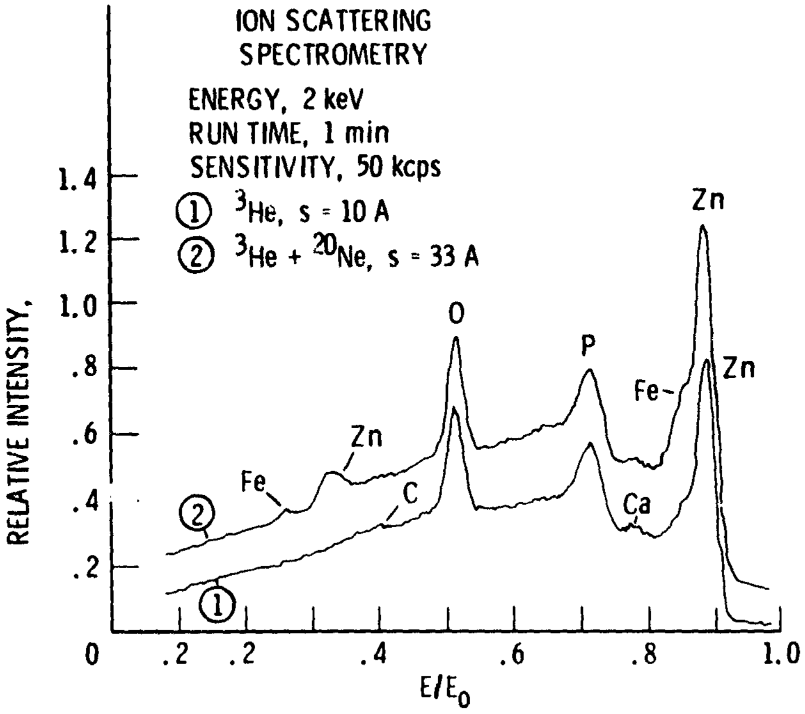

Figure 18. - ISS-Spectra of block wear scar with a mixture of mineral oil, 1 percent n-C_8ZnDDP and 1 percent MoS_2, I (ref. 17).