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Report on techniques and methods for surface characterization of glasses and ceramics

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Mellerud, augusti 1980

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REPORT ON TECHNIQUES AND METHODS FOR SURFACE CHARACTERIZATION OF GLASSES AND CERAMICS

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REPORT ON TECHNIQUES AND METHODS FOR SURFACE CHARACTERIZATION OF GLASSES AND CERAMICS

by

Bengt Kasemo

SUMMARY

This report is intended to serve as a basis for experimental studies of corrosion phenomena on surfaces of glasses and ceramics. An introductory orientation is given about the problems connected with quantitative surface analysis and about the related surface physics questions. The main part of the report is a description and evaluation of the existing surface sensitive methods. Conclusions are drawn about suitable combinations of methods for characterization of surfaces of glasses/ceramics. Alternative solutions with respect to capability and cost are given. A rather detailed list of references is supplied covering the relevant literature about the mentioned methods and phenomena. Finally, the report contains names of laboratories where surface analytical investigations are performed (adress, contact persons, methods used and the cost per hour or day).

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1. INTRODUCTION

The avalanche in development of the surface sensitive spectroscopies throughout the past 20 years has tremendously improved the possibilities of studying the chemical composition on thin surface layers at an atomic level. Using the most modern instruments at least a qualitative picture of a composition can be achieved at a lateral and depth resolution of down to 50 nm and 1 nm, respectively, for elements at an abundance of approximately 1% or more. This also applies to materials with a complex composition. In advantageous cases considerably lower concentrations can be registered.

All the surface sensitive spectroscopies are built on the principle that a beam of particles (photons, electrons, ions, atoms, molecules...) is shot against the specimen. The system responds to this perturbation by sending out one or several kinds of the particles mentioned above. The energy distribution of the emitted particles is a function of the energies of the incoming particles, which can be controlled, and of the surface atoms in the material, e g the chemical composition of the surface. Since different particles interact at different strengths with a specimen, different surface sensitivities are achieved for different particles. As an example, photons have a relatively large depth of penetration while low-energy electrons and especially slow ions are extremely surface sensitive probes. An important consequence of this is that a combination of several methods of measurement is often necessary if a reasonably complete picture of the chemical composition of an unknown surface system should be achieved.

The report is concentrated on a description and evaluation of the surface sensitive spectroscopies. First, a brief orientation on problems in connection with analysis of surface layers is given. The intimate coupling between the methods here described and the subjects surface-physics/surface-chemistry motivate a brief description of this together with the most important elementary processes at surfaces. Thereafter the surface sensitive methods are described. Special problems that may influence the reliability of the analysis are treated in a separate section together with an evaluation of the drawbacks and benefits of the different methods. A brief and

far from exhaustive evaluation of the use of indirect methods and methods for the studies of dynamics is also given. Finally, an inventory is made of laboratories where surface analyses can be performed.

2. ORIENTATION ON PROBLEMS

The development of surface sensitive spectroscopies has been primarily dictated by the needs of basic science to as exactly as possible characterize specimens in ultra-high vacuum regarding chemical composition, purity, crystal structure etc. A very important factor has also been the needs within material sciences, leading to a development of the methods into commercially available instruments. The dominating amount of experience of the practical use of the methods and of material analyses are to be found within the area metallic materials, specially iron and steel. Typical problems have been the enrichment or depletion of alloy elements in the surface region (the outermost atomic layers), in oxides on the surface, enrichment in impurity elements on surfaces or in grain boundaries and on surfaces of fracture etc. Other common problems have been concerning elements present on a surface after the material has undergone a special process or been subjected to a special chemical environment.

The empirical knowledge on more complex materials, to which glasses/ceramics must be counted, is considerably lower. An exception is metallic oxides which belong to the simpler ceramic materials from the composition point of view. The reason for this exception is in part the basic science interests for these materials, and in part that oxides in air are formed spontaneously on all metallic materials. The experiences from studies of metal oxides M_nO_m (M=metal, O=oxygen) should be of great value in the studies of more complex glasses and ceramics.

Below a brief schematic picture is given of some analytical steps which may be necessary in order to map the surface layer of a given glass specimen and to elucidate why it has achieved it. The bulk properties i e composition and structure far from the surface are supposed to be well-known. Even if a specimen has not been subjected to any other outer influences than the creation of a surface (e g through a fracture), the surface composition may be different than the bulk composition, due to optimization of surface energy etc. A mapping of concentration profiles in the surface layer of the unperturbed specimen may be of vital importance in order to understand e g how the material later reacts by different

chemical attacks.

In a systematic investigation the next step may be to expose identical specimens to a series of relevant outer perturbations such as temperature, pressure, chemical environments etc. and to thereby analyze accompanying changes in the surface layer. These analyses possibly demand both a high lateral resolution (in order to reveal e g point attacks) and depth resolution. In the latter case it is necessary to with a quantitative control peel off atomic layer after atomic layer from the surface in order to achieve a depth profile. Most often the whole analysis is made as a part of a model construction for the studied system and the analysis may be made to support or refute a hypothesis. Thereby it may be particularly desirable to analyze one or a few critical components for which the process of measurement is optimized regarding sensitivity and consumption of time.

A quantitative analysis is, as is described below, associated with considerable difficulties. An important part may therefore be to produce and measure on systems with a known composition in order to achieve points of calibrations.

3. ORIENTATION ON SURFACE PHYSICS

Surface physics was characterized from the beginning of the 1960'ies till about 1975 by an avalanche in development of new experimental methods and a far advanced so called ultra high vacuum technique. The objective was to create conditions for preparation and studies of really clean surfaces and by using different physical methods of measurement characterize the surfaces as detailed as possible. When this objective was beginning to be realized more complicated systems than clean single-element surfaces were investigated, and the properties of adsorbed atomic and molecular layers gained a central position. This is the situation today and the subject can regarding experimental methods, concepts and theoretical models be regarded as established. The frontier of research is characterized by:

- combining different developed methods of measurement into one single instrument in order to achieve an as facetted picture as possible of a given surface system within the framework of one single investigation.

- a theoretical description of e g the properties of adsorbed molecules and adsorbed layers, that is already advanced and rapidly improving. This also applies to the theoretical background of the different spectroscopic methods.

- studying systems with increasing complexity, e g adsorbtion of polyatomic molecules and biomolecules, and more complex substrates such as alloys, ceramics, polymers etc.

- combining the investigations at low pressures (10^{-10} - 10^{-5} Torr) with studies performed at high pressures (~1 atm) in the same instrument

- studying dynamics. There is a rapidly growing interest in the dynamics of various surface reactions. Within this problem area (which cannot be regarded as established) a rapid development of experimental and theoretical methods will take place throughout the coming years.

4. SURFACE REACTIONS

4.1 Elementary steps of reaction

The most fundamental process in a solid phase - gas phase surface reaction is the adsorption of a molecule. This implies that a molecule from the gas phase becomes bound to the atoms on the surface of the solid; the molecule is adsorbed. Fig. 1a-c shows schematically this sequence. Stage b-c implies that the molecule dissociates i.e. is broken into fragments. This sometimes happens but not always. The sequence in the figure illustrates also several other processes:

- desorption implying that an adsorbed molecule returns to the gas phase (b→a)

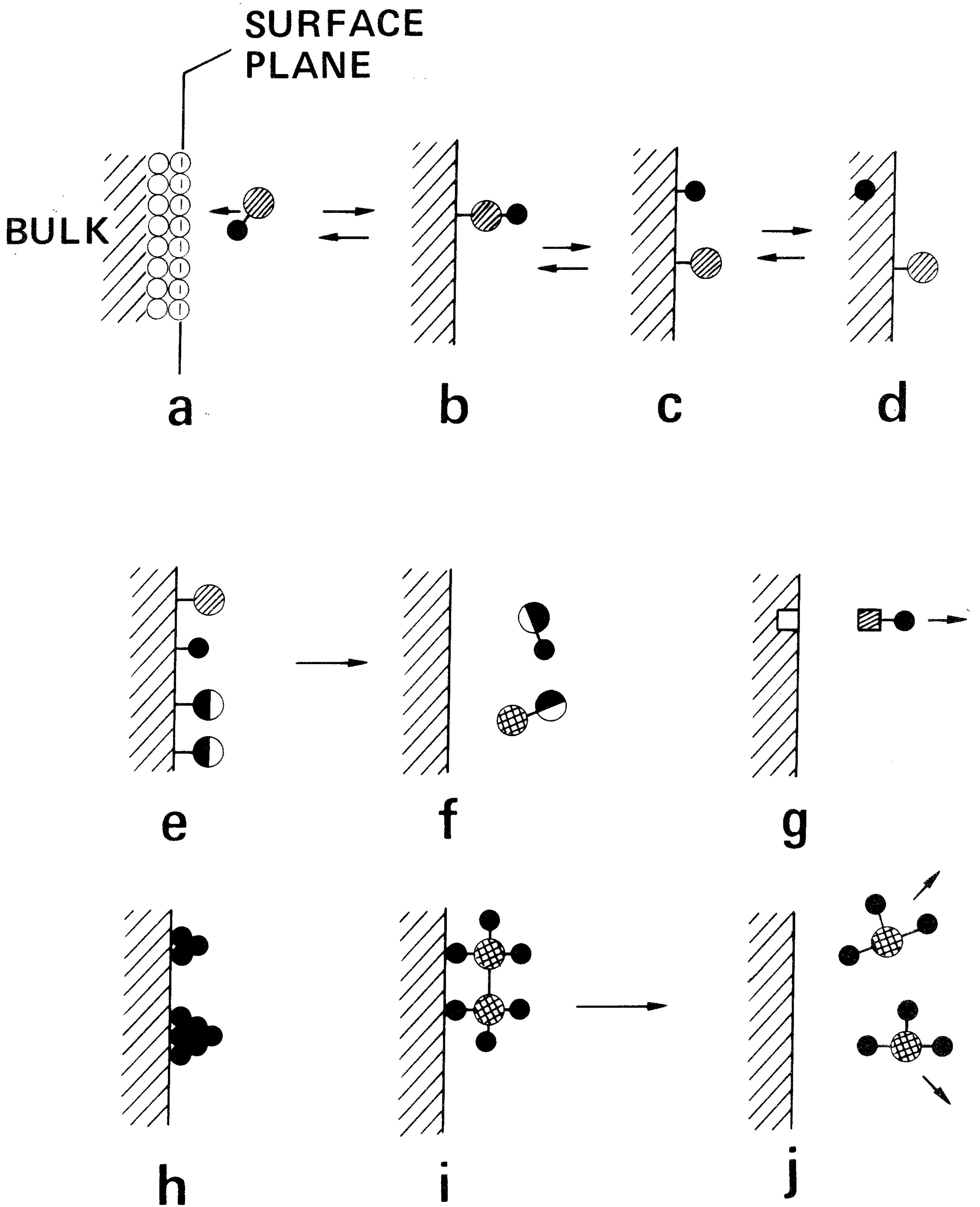
- absorption implying that an atomic dissociation fragment diffuses from the surface into the solid (see c→d). This is an important stage in e g oxidation and corrosion

- segregation implying that an atom dissolved in the solid material is deposited on the surface (d→c)

- heterogenous catalysis; e illustrates the situation when two molecules AB and C_2, originally gas molecules, are adsorbed dissociatively onto the surface. e→f shows how A reacts with C to a product molecule AC which is desorbed from the surface. In the same way B reacts with C to BC. This sequence describes a heterogenous catalytic reaction with the sum formula $AB + C_2 \rightarrow$ $\rightarrow AC + BC$

- g illustrates a case which is particularly important at high temperatures, namely reactions between fragments of an adsorbed molecule and surface atoms of the solid material itself. An example is metals reacting with oxygen under the formation of volatile oxides. The process may be called chemical etching or reactive sublimation.

- h shows how atoms or atomic fragments of molecules are enriched to one particle (clustering, nucleation). This is the initial


SURFACE
PLANE
BULK
a
b
c
d
e
f
g
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j

stage to a formation of particles that may eventually join other particles into a covering layer. For this and most other processes described here surface diffusion (i e the thermally activated movements of the atoms over the surface) is important.

- cracking is a term used for several processes. Here a special form of dissociation is meant, namely when a molecule is adsorbed and broken up into two or several fragments that thereafter return to the gas phase (are desorbed) sometimes as radicals (Fig. 1i→1j).

4.2 Special types of reactions and processes

The most important of these is the corrosion process. By corrosion several of the above-mentioned elementary reaction steps are taking place, e g adsorption, absorption, nucleation and diffusion, whether in liquids or gases. The particular additional processes that take place in liquid solutions or electrolytes are not dealt with here.

A great number of other surface processes have an indirect but large importance in different connections. Most of them are closely related to the subject of materials science e g: crack formation, fracture mechanisms, fatigue, embrittlement, abrasion and wearing, and friction. The combination of a chemically reactive atmosphere and the presence of a solid surface can lead to a rapid break-down of the material e g through depletion of an important constituent in the material surface through a direct chemical attack. The process may then eventually cause crack formation, fractural impression and/or enhanced corrosion. In the same way the surface layer may be enriched in components which are material destructive (as e g by hydrogen embrittlement).

5. SURFACE SENSITIVE SPECTROSCOPIES

We will here briefly describe the most important surface sensitive spectroscopies. A grouping of the methods has been made with regard to which quantities are studied or which information is desirable (see table 1). This naturally implies that the same method may be discussed in several contexts. Most of the spectroscopic methods require high vacuum or ultra-high vacuum to function, e g LEED, XPS, AES, EELS, UPS or SIMS, which is a limitation. Infra red reflection spectroscopy can in principle be used even with high pressure. A short characterization of the different methods of measurement follows below. For a more exhaustive description references are made to literature.

5.1 X-ray photoemission spectroscopy (XPS or ESCA)

The principle of the method is that X-rays of well-defined energy (approx. 1 keV) is incident on the specimen (Fig 2). When a photon is absorbed by an electron the electron gains a kinetic energy high enough to leave the specimen. By analyzing with respect to energy the

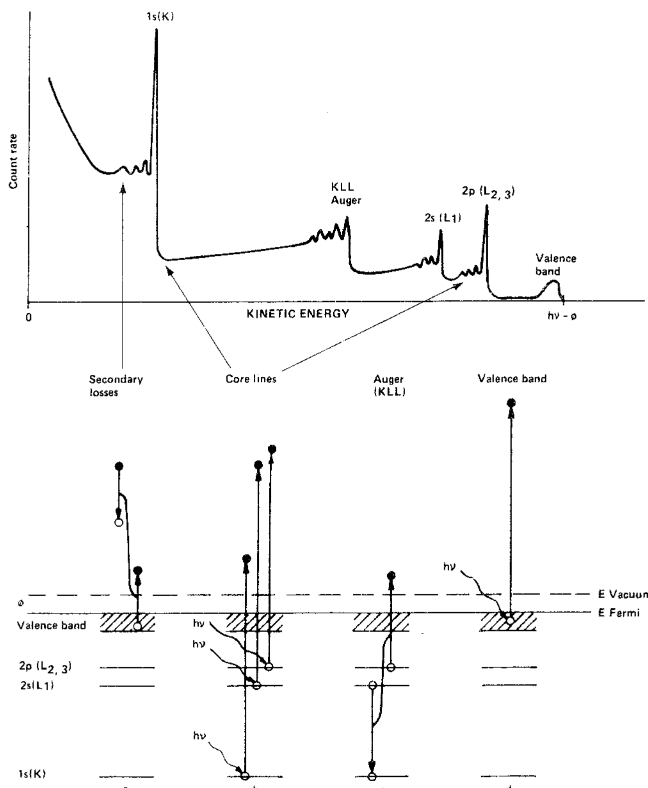


Figure 2. The basic processes contributing to an XPS (ESCA) spectrum
a) direct optical excitation of core electrons
b) direct optical excitation of valence electrons
c) vacancy de-excitation via an Auger process
d) inelastic losses giving rise to secondary electrons

TABLE 1

Properties	Methods of measurements
Chemical composition	XPS = X-ray photoemission spectroscopy (also called ESCA = electron spectroscopy for chemical analysis) AES= Auger electron spectroscopy SIMS = Secondary ion mass spectroscopy ISS = ion scattering spectroscopy
Electronic structure	XPS, AES UPS = ultra-violet photoemission spectroscopy EELS = electron energy loss spectroscopy
Vibrations of adsorbed molecules	HREELS = high-resolution EELS IRS = infrared reflection spectroscopy
Crystal structure	LEED = low energy electron diffraction ARUPS = angularly resolved UPS
Reaction kinetics	AES; XPS, HREELS, IRS MS = Mass spectrometry GC = Gas chromatography Microbalance methods Volumetric methods

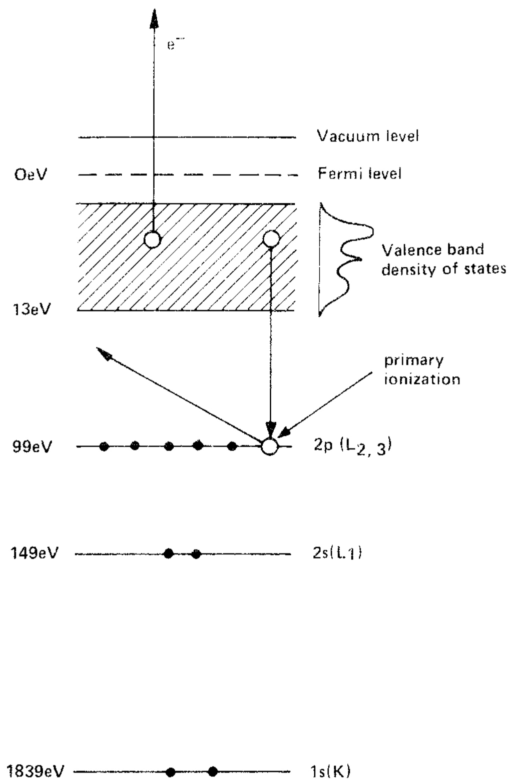


Figure 3. Auger process (involving the valence band) in silicon.

electrons coming out from the specimen one can determine their original energy in the specimen before the photon absorption. Since the inner atomic levels are specific to the element the method is very useful for the analysis of chemical composition. Additionally, chemical information is achieved from observed shifts in the inner energy levels (cfr free atoms). An XPS spectrum also contains a "picture" of the energy distribution of the valence electrons which depict the electronic structure of the studied specimen. In the latter case XPS is an analogue to UPS. XPS is like UPS, AES and other electron spectroscopies very surface sensitive due to the short electron mean free path (approx. 1 nm) at the electron energies in question. XPS demands a rather sophisticated X-ray source (and by optimal resolution an X-ray monochromator) and an electron spectrometer for the analysis of the kinetic energy of the photo electrons.

5.2 Auger electron spectroscopy (AES)

In AES an electron beam is shot onto the specimen, Fig 3. An electron may ionize a surface atom by knocking out one of its inner electrons.

When one of the higher lying electrons falls down into this now vacant electronic level the released energy may be absorbed by a second electron (in an inner level or in the valence band) which then leaves the specimen. In the same way as in XPS one analyzes the outgoing electron energies which are specific to the element. The Auger process is more complex than the photo emission process and the interpretation of the spectra is therefore much more difficult if a detailed electron structure information is needed. However, for the analysis of chemical composition the method is extremely useful. The sensitivity is about the same as for XPS; approx. 0.1 - 1% of a contaminant or of an adsorbed monolayer on the surface can be detected. An Auger electron spectrometer is more simple (no X-ray source is needed) and more compact and considerably cheaper than an XPS equipment. In more sophisticated designs "Scanning Auger" is used, where the exciting electron beam (diameter 0.05-10 μm) is swept over the surface so that lateral variations in surface composition can be studied. Further, depth distributions of different elements can be studied using a so called "Sputtering Auger", where atomic layer after atomic layer is peeled off from the surface (using an ion beam) under a continous Auger analysis. This type of analysis gives information which is analogous to but more easy to interpret than SIMS-information (see below).

5.3 Secondary ion mass spectroscopy (SIMS)

In SIMS atomic layer after atomic layer is peeled off from the surface using an ion beam as in "Sputtering Auger" but the information on the surface composition is achieved through mass spectrometric analysis of the charged fragments (atoms, molecules) leaving the surface as a result of the ion bombardment. Lateral and depth resolution can in advantageous cases be as good as approximately 1 μm and 1-10 nm respectively. The sensitivity can by far exceed "Sputtering Auger" (sensitivity $< 10^{-4}$) but due to the complexity of the ion emission process, data for a given system is difficult to interpret if not a vast empirical background knowledge is at hand, i e extensive calibrations may be necessary. Coinciding mass numbers can often be embarrassing, i e two entirely different fragments may have the same mass number so that they cannot be separated. An advantage with SIMS (compared

to XPS, AES and others) is that hydrogen can be detected and different isotopes can be registered separately.

5.4 Ion scattering spectroscopy (ISS)

Ion scattering spectroscopy has throughout the past years achieved a steadily increasing interest for both basic science analyses and technological analyses. The principle is very simple and can be understood from classical mechanics. If ions with well-defined energy and mass m_j are shot against a specimen with atoms M the ions loose at the collision a certain amount of kinetic energy. The energy loss depends on the ratio $\frac{m_j}{M}$. By analyzing the velocity of the scattered ions the chemical composition of a specimen can thus be analyzed. The method is extremely surface sensitive. Using ions of approx. 1 keV energy, practically only the outermost atomic layer is analyzed. Depth profiling is achieved in the same way as in AES and SIMS, i e by sputtering away atomic layer after atomic layer, successively. The sensitivity for quantitative analysis varies very much between different instruments but seems most often to be better than 1% and often 0.1-0.01%. Both high- (100 keV - 1 MeV) and low-energetic (1-10 keV) ions are used. The scattering process is simpler for higher energies (Rutherford scattering) while surface sensitivity, particularly for light elements, is higher using low-energy ions. The method stands out as a very interesting complement (and in certain cases alternative) to the regularly used XPS, AES and SIMS.

Ion scattering is also useful for structure studies, since the angular distribution of the scattered ions (and its dependence on the angle of incidence of the primary beam) reflects the crystal structure of the surface.

5.5 Ultraviolet photoemission spectroscopy (UPS, ARUPS)

UPS is completely analogous to XPS but operates with considerably lower photon energies than the latter. The most common light source is a helium lamp giving discrete photon energies at about 20 and 40 eV (cfr XPS approx. 1000 eV). UPS is an electron spectroscopy for the valence band and has given large amounts of valuable information both on bulk materials (band structure) and the electronic

structure of adsorbed layers. By studying the angular distribution of the emitted electrons an especially detailed information is achieved on electronic structure and to a certain extent on atomic geometry. For applied materials analysis the applicability of the method is rather limited.

5.6 Electron energy loss spectroscopy (EELS)

In EELS the specimen is bombarded with an electron beam of well defined energy (by electronic structure studies ± 0.1 eV). In the specimen the electrons undergo energy losses which are characteristic for the studied system. By studying the energy distribution of electrons leaving the specimen information is achieved on the electronic structure of the system. The method is reasonably easy to handle but the excitation process and thereby the interpretation of data is more complicated than in UPS. The applicability of the method is about the same as for UPS.

5.7 Vibrational spectroscopies (HREELS and IRS)

The function for HREELS is the same as for EELS but the energy spread of the electron beam is much more narrow (0.005-0.05 eV) since the method is intended for studies of molecular vibrations and phonons. The method has developed rapidly during the past few years and has had a great success. The reason for this is that data is easy to interpret and give much information on adsorbed molecules. Commercially available instruments are just appearing.

IRS is used with the same intent as HREELS i e to study molecular vibrations. In IRS a monochromatic beam of infrared light is incident on the specimen and the reflected intensity is measured. By continously sweeping the wave-length of the light, variations in light absorptions of the specimen surface is revealed. When the wave length coincides the vibrational transition in an adsorbed molecule an increased absorption is observed. The method has a higher resolution than HREELS and is in principle independent of vacuum. However, HREELS covers a wider wave length span than IRS.

5.8 Low energy electron diffraction (LEED)

LEED is a diffraction method. A monochromatic electron beam hits the surface of a single-crystal specimen, possibly with an adsorbed surface layer. The electrons are diffracted by the atomic lattice and the diffracted electrons leave the specimen with an intensity and direction determined by the crystal structure of the surface. The intensities of the diffracted beams are measured as a function of electron energy and possibly as a function of angle of incidence. For structural analysis the measured intensities are compared with calculated intensities. The calculations demand exhaustive computer capacity.

If the objective is restricted to study the symmetry of the adsorbed layer it is sufficient to observe (photograph) the diffraction pattern on a fluorescence screen. The method is limited to single-crystal materials.

5.9 Mass spectrometry (MS)

This method is a method for gas analysis rather than a surface physics method, but is of importance for the analysis of reaction products from surface reactions, and for control of residual gas composition in vacuum systems. Only one application of MS will be touched upon here, namely thermal desorption spectroscopy. Using this method adsorption energies can, among other things, be determined and the different binding states can be revealed. Briefly, the method consists of heating a specimen in such a way that a known linear increase in temperature with time is achieved. The mass spectrometer measures continously the pressure in the vacuum chamber for the desorption product to be studied. The analyses of these data can apart from binding energies also give information on adsorption- and desorption kinetics.

6 SOME LESS SURFACE SENSITIVE SPECTROSCOPIES

6.1 X-ray fluorescence spectroscopy

When a sample is irradiated with X-rays, electrons are excited from filled inner levels to empty states above the Fermi level. Upon deexcitation, electrons (XPS, AES) or X-rays (X-ray fluorescence) with energies characteristic for the elements are emitted. Due to the weak damping of X-rays, this spectroscopy is not particularly surface sensitive. By using grazing incidence or special sample preparation a resolution on the 1 μm-scale can be achieved.

6.2 Electron microsond

The principle is the same as for X-ray fluorescence spectroscopy but the excitation is achieved by using electrons (energy 10^4-10^5 eV) instead of X-rays. The method has a higher surface sensitivity due to the stronger damping of the exciting electrons in the specimen. Depending on sample thickness, electron energy and angle of incidence, the lateral and depth resolution may vary. Typical values are 1 μm for both depth- and lateral resolution for bulk specimens. The use of grazing incidence can, when this is possible, enhance the depth resolution. Concentrations down to 0.1% can in certain cases be detected. More typically the concentration limit is one or a few per cent.

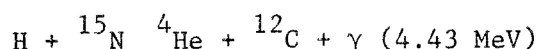
The method has been widely spread, thanks to a relatively simple X-ray detection attachment which can be combined with a sweep electron microscope (where the exciting electron beam is already present). In commercial instruments X-ray detection is most often made by using a semi-conductor detector. Discrimination of different X-ray quantum energies (which is a condition for elemental analysis) can be achieved since different energies give rise to different pulse heights in the detector. The method is called "energy dispersive analysis" to be separated from the so called "wave-length dispersive" analysis which takes place in conventional X-ray spectrometers. The latter are necessary in order to detect lighter elements (typically in the interval B-Na).

6.3 Electron microscopies

These are not within the scope of this report. However, it is justified to mention sweep electron microscopy (SEM) as an easily accessible instrument for the determination of the topography of surfaces. Since most SEM also can be equipped with an energy-dispersive X-ray analysis unit a more or less quantitative picture of the chemical composition of the specimen can be achieved (limitations concerning lighter elements and resolution as mentioned above should be kept in mind). Further information is available in the rich special literature on electron microscopies.

7 OTHER SURFACE SENSITIVE METHODS

The above-given list of methods is by no means exhaustive but contains the most important and most commonly used methods together with some less common methods. A great many other methods from nuclear, atomic, molecular and solidstate physics can, under certain circumstances, offer enough sensitivity for surface studies, e g Mossbauer spectroscopy, Raman scattering, neutron diffraction, optical fluorescence. Of special interest in this connection are nuclear reactions used for hydrogen detection. The most commonly used nuclear reaction is:



$$H + {}^{15}N \quad {}^{4}He + {}^{12}C + \gamma \ (4.43 \ MeV)$$

The ^{15}N hydrogen profiling method makes use of a narrow, isolated resonance in the reaction to measure hydrogen concentration vs depth in solids. When a sample is bombarded with ^{15}N at the resonance energy of 6.385 MeV, the yield of γ-rays at 4.43 MeV energy is proportional to the hydrogen concentration on the surface. Above the resonance the cross-section for the reactions is three orders of magnitude smaller than the resonance cross-section. As the ^{15}N, with energy > 6.385 MeV, slows down passing through the solid, it reaches the resonance energy at some depth and a nuclear reaction with any present hydrogen can take place. Hence, to determine the hydrogen concentration vs depth, the yield of characteristic γ-rays is measured vs ^{15}N energy. In order to get an absolute depth scale the energy loss of the ^{15}N particles per unit length in the sample must be known. The method is currently used e g for determining the depth of the hydrated layer in glasses and ceramics, and has a sensitivity of 0.1%, typically. An advantage of the method is that no ion or other etching techniques have to be used. The major drawback is that several different nuclear reactions must be used if elements other than hydrogen also should be detected. Furthermore, the method demands costly instruments, i e particle accelerators.

8. METHODS FOR STUDYING KINETICS AND DYNAMICS

All the above mentioned methods can, of course, be used and are used to a great extent in order to follow dynamic processes e g by recording a series of spectra taken in a sequence from a system which is changing with time. Here are mentioned some methods which have been directly developed for such studies (such as reaction kinetics) and which are sometimes used in combination with the surface sensitive spectroscopies.

When surface reactions give rise to gaseous reaction products, information on reaction kinetics can be achieved through analysis of the reaction products. For this purpose mass spectrometry and/or gas chromatography can be used. When reaction products are formed on the solids the weight of the specimen increases. In a number of sensitive weighing methods, the so called microbalance methods, this is used in order to follow reaction kinetics, e g in oxidation and corrosion phenomena. An alternative way to follow the reaction is to measure the decreasing pressure caused by gas consumption. This is the principle for the volumetric methods.

9. INDIRECT METHODS

Of these are the traditional wet chemical methods of certain interest. However, the time-consuming (costly) procedure of analysis seems to, in most cases, lead to the use of surface sensitive spectroscopies. Activation of the surface layer by means of nuclear physical methods (irradiation) or doping with radioactive isotopes can be useful especially in following transport phenomena in the surface layer. The use of these and many other methods giving indirect information on the properties of the surface layer is, however, very scarce when quantitative information on the depth scale <100 nm is desired.

10. EVALUATION AND CHOICE OF METHODS. COSTS

Of the above-mentioned techniques XPS, AES and SIMS and to some extent ISS are to be put in a separate group as general surface sensitive methods where the development of commercial instruments is far advanced (ISS is an exception from this but a rapid development is most probable). The vibrational spectroscopies HREELS and IRS are methods which are analytically very useful, especially for the studies of adsorbed molecules on surfaces. For XPS, AES, HREELS and IRS the principles and functions are simple and well understood and described in great detail. A vast amount of data is already accumulated. The principle for ISS is also simple but there is considerable lack of understanding regarding ion-neutralization and other effects.

Concerning SIMS the case is different. The emission of ionised fragments (ions, molecular ions) as a result of an ion impact on the surface, is a complicated process, and the interpretation of SIMS-spectra must at present, to a higher degree, be based on empirical knowledge (calibrations). For all spectroscopies applies that the most safe method for quantitative analysis is to compare measured spectra with spectra from known systems which are used as calibration standards. However, such are often missing. An alternative method is then to use the estimated cross sections for different elements for the different processes in AES, XPS and SIMS evaluated from existing literature data. This method gives qualitatively acceptable results and can be used quantitatively if the so called matrix effects can be controlled. (The matrix effects imply that the cross section for a given process depends on the chemical environment.)

There is no doubt that the experimental basis for a major investigation of the surface related properties of glasses and ceramics should be performed on a combination instrument using XPS, AES and SIMS possibly with ISS and/or vibration spectroscopy as a complement. The priorities at a lower level of ambition or if some investigations are performed as separate tasks by consultants, are more difficult. If the aim is to partly perform analyses and partly to improve ones own knowledge on the surfaces of glasses and ceramics XPS is probably the best alternative. The advantage

compared with AES is, among other things, spectra more rich in details, more easily accessible valence band information and more chemical information. Further, the decomposition problem is considerably lower using XPS. The advantages with AES are the good lateral resolution, the shorter time of measurement and the lower cost. The choice between AES and XPS could be made keeping these differences in mind.

The combination XPS and/or AES and SIMS is a powerful instrument. Here the great advantage of having a combination instrument instead of using two or three separate instruments should also be taken into consideration. Systematical errors can more easily be controlled and calibration of e g SIMS can be made in situ. Further, the need of a skilful and knowledgeable operator must be strongly emphasized. Without an experienced operator the results may be useless or even misleading.

10.1 Conclusion

The combination XPS, AES and SIMS and possibly completed with ISS or one vibration spectroscopy is a suitable and powerful combination. The use of other methods could at least primarily be made through consultants giving a basis for a possible later purchase of additional instrumentation.

10.2 Costs

Only approximate prices can be given since the prices to a high degree depend on the design of specimen chamber, vacuum system, irradiation sources, analyzer and data collection and data handling equipment. The cost of a well composed but not too sophisticated XPS or AES (with lateral and depth profile analyses) or SIMS instrument is in the range 0.5 - 1.5 million Swedish Kronor. The price in US Dollars is obtained by dividing by ~4.2. Prices valid for 1980. In a combination instrument with XPS, AES and SIMS the large costs for vacuum system, sample handling and preparation, electronics and data collection etc are reduced and the costs for a combination instrument fall in the range 1.5 - 3 Swedish Kronor, depending on the degree of sophistication. The most advanced AES-instrument with the highest lateral resolution includes SEM

facility, energy dispersive X-ray emission analysis, depth profiling and computer control of data collection and analysis. The cost for such a system is about 3 million Swedish Kronor. The absolutely cheapest complete alternative, based on surface sensitive spectroscopy, and with some possibility of doing the desired surface characterization, is probably an AES unit with poor lateral resolution and no scanning or depth profiling facility (costs approx. 300.000,- Swedish Kronor).

11. SPECIAL PROBLEMS AND RISKS FOR FALSE INFORMATION

Here are identified some of the problems, in connection with quantitative analyses, which are not associated with the instrumentation (instable sources of radiation and/or detectors, varying transmission factors etc).

11.1 Specimen contamination

Specimen contamination is always a problem. If the specimen is prepared in the ambient outside the chamber of analysis, the surface of the specimen is nearly always contaminated. Even by an "in situ" preparation residual gas in the chamber of analysis can cause contamination and false results. Proper specimen cleaning and preparation procedures are very important.

11.2 Charging effects

Charging effects are frequent and especially serious when studying insulators. Two standard methods are used to minimize the problem:

- The charging is eliminated through a/ spraying the specimen with particles (electrons or rare gas ions) with a suitable charge and intensity and by b/ minimizing the intensity of the exciting radiation and c/ optimizing its angle of incidence and energy (see further reference literature according to reference list below).
- Atoms with known spectral lines (most often gold but also inplanted rare gas atoms) are mixed into the specimen.

The mentioned spectral lines then serve as calibration points for the energy scale (by AES and XPS). If three of several well-separated lines are available it can be controlled if the magnitude of the effect varies along the energy scale.

11.3 Decomposition effects

This paragraph only refers to AES and XPS and other electron spectroscopies which are in principle non-destructive, to be separated from SIMS which is inherently destructive. Especially using AES

but sometimes also using XPS the incident radiation may cause surface alterations which are reflected in the spectra. The incoming electrons may knock out ions (giving rise to a depletion), dissociate surface molecules (e g CO → C+O) or cause structural changes. The electron beam can also stimulate the diffusion of individual components to or from the surface. When using sputtering for depth analysis the ion radiation can cause different types of structure and composition changes in the surface (see literature listed below).

11.4 Influence of radioactive elements

Influence of radioactive elements on the measurement is of particular relevance for this report. No reference literature seems to be at hand. However, the disturbances should to a high degree be eliminated by using a suitable screening of the detector (which in most cases is an electron multiplier).

12. REFERENCE LITERATURE

For the most common spectroscopies there is a number of excellent survey articles and books. In "Methods of Surface Analysis", AW Czanderna Ed., /1/ there are several articles where important information for this report has been collected. The book contains among others the following articles:

- The aspects of Sputtering in Surface Analysis Methods by G.K Wehner
- A Comparison of the Methods of Surface Analysis and their Applications by D. Lichtman
- Low Energy Ion Scattering Spectrometry by T.M. Buck
- Surface Analysis by XPS by A. Joshi, L.E. Davis and P.W. Palmberg
- Secondary Ion Mass Spectrometry (SIMS) by J.A. McHugh

Other books with similar contents are: "Characterization of Solid Surfaces", by P.R. Kane and G.B. Larrabee, eds., /2/ and references /3/ and /4/. Recently published survey articles with excellent reference material are the references /5/ and /8/ where quantitative surface analysis with XPS, AES, SIMS and ISS is discussed. In /6/ an introduction is given and the different spectroscopies are discussed.

More specialized literature for the different techniques are:

- AES: /1/ pp. 160, /7/, /8/ (which also give an excellent list of references to previous AES-work), /9/ chap. 2, /10/, /11/
- XPS: /1/ pp. 103, /6b/, /9/ chap. 4, /10/, /11/
- SIMS: /1/ pp. 223
- ISS: /1/ pp. 75, /3/ pp. 175
- HREELS: /11/
- IRS: /3/ pp. 281
- ^{15}N: /21/

Literature concerning the structure and properties of surfaces and surface reactions and other surface properties are to be found in the references /9/, /11/ and /12/ - /18/.

Charging effects and how to control them in XPS and AES are treated

in /8/ pp 149, /2/ pp 549, /19/ and /20/ and in the references in these works.

Decomposition effects and other problems in AES and XPS are treated in /8/, /2/ pp 549 and in references in these articles and to some extent also in other specialized literature.

Problems in connection with SIMS are excellently treated in /1/ chap. 6, and problems in connection with ion sputtering in /1/ chap. 1.

Two very recent papers treat the particular problem of corrosion of glass surfaces. The first one /22/ gives a nice short review of the limitations of traditional methods to study glass corrosion and of the virtues of modern spectroscopic techniques for such studies. The second paper /23/ reports on a SIMS study of aqueous leaching of a borosilicate glass.

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14. LIST OVER LABORATORIES WHERE SURFACE ANALYSES ARE PERFORMED

The information in this part has been collected by talking to representatives for the different laboratories. The list is considering Sweden virtually exhaustive. Of the sites outside Scandinavia only the two most attractive (concerning capacity and equipment) sites have been included. With the term "Shorter works" is meant one day or less and with "longer works" is meant several weeks. The prices quoted below refer to shorter work and were valid by June 1980. Reduction in price for longer work is possible.

1. Dept of Engineering Metals. Chalmers University of Technology, Gothenburg.

   Person to contact: I. Olefjord, telephone 031-81 01 00

   Equipment: XPS and Scanning AES
   "Fracture device"
   Electrochemical cell (wet chemistry)
   Oxidation-reduction oven
   2 ion guns for sputtering
   Evaporation sources
   "Floodgun" for compensating charging effects
   Depth profiling through "Sputter profiling"
   Lateral resolution in AES 3μ

   Waiting time: Shorter work: approx. 1 week
   Longer work: several months

   Price: Analysis 350 SEK/h
   Personnel 150 SEK/h
   Report writing 200 SEK/h

2. Dept of Physics and Measurement Technology, The University of Linköping.

   Person to contact: S.E. Karlsson, telephone 013-11 17 00

   Equipment: Scanning AES + some possibilities to UPS and XPS

Lateral resolution 5 µ
Depth profiling through sputtering
Flood gun

Waiting time: Shorter work: < 1 month
Longer work: upon agreement

Price: 350 SEK/h

3. Dept of Physical Chemistry, The Royal Institute of Technology, Stockholm.

Persons to contact: J.C. Eriksson, G. Hultqvist, telephone 08 - 787 70 00

Equipment: Scanning AES
Lateral resolution 5 µ
Depth profiling through sputtering

Waiting time: max. two weeks

Price: 2000 SEK/day for instrument + operator

Comment: At the Institute of physical chemistry, the Institute of physics and others at KTH a new XPS+AES-equipment will be available from January 1981.

4. Dept of Physics, Chalmers University of Technology, Gothenburg.

Persons to contact: A. Lodding, telephone 031-81 01 00
H. Odelius

Concerning SIMS for possible investigation of glasses and ceramics of interest to KBS: A. Lodding

A. Benefit

Chemical analysis of surface layers; sensitivity high enough to detect very diluted (sub-ppm) impurities; in principle, the majority

of elements in the periodic table (incl. hydrogen and other light elements) can easily be analyzed on any given point on the specimen. The analysis can as a rule be made quantitatively.

The analysis can be performed continously in depth (depth profiles) from approx. 5 nm to approx. 2 µm. The depth resolution in amorphous materials can be better than approx. 5 nm.

The pictures of the surface distribution of different elements can be achieved at a resolution of the order of 1 µm. Different phases can be identified and referred to topographical details. If the particle size exceeds approx. 5 µm chemical composition of the grain boundaries can be studied at different depths. If the particles are larger than approx. 10 µm the phases can be analyzed quantitatively separately.

SIMS is thus in principle a very suitable technique for the study of micro leakage as well as corrosion.

B. Limitations

The focussing of the distribution pictures, expecially at greater depth, is limited by surface charges on the insulators. Detection of certain elements can possibly be complicated and hampered by a spectral overlay of molecular ions based principally on Si and Al.

Quantification may in some cases call for an external standard (such are available at e g NBS).

When depth profiling into heterogenous material the depth resolution is gradually deteriorating by increasing depth.

C. Preferred sample conditions

1) The sample surface should be plain, preferably optically reflectant; however, also moderately rugged surfaces can be investigated. We wash the sample in an ultra-sonic bath and cover the surface with a thin metallic layer (generally Au).

2) Sample size maximum 15 mm across surface, and maximum 6 mm thickness.

D. Costs; accessible time

We charge 4.800,- SEK per workday. However, in one day we can normally measure either a) approx. 60 surface distribution pictures of different elements; or b) approx. 6 "complete" analysis spectra (alternatively a large amount of "finger print spectra") or c) approx. 6 depth profiles down to 1-2 µm depth, for 4 elements at a time.

During the year 1980-81 we can accept up to 25 working days for KBS, provided the order is made at least a couple of months in advance. Smaller jobs (1-2 work days) we can accept at about 2 weeks' notice. When ordering more than 10 work days a certain discount on the price can be made.

5. Institute of Physics, Uppsala University.

Person to contact: U Gelius, telephone 018-15 54 00

Equipment: XPS, Scanning AES, SIMS

XPS of own construction with high sensitivity and resolution

Depth profiling using SIMS and "sputter profiling" AES

Lateral resolution in AES 1 μ

Waiting time and price: Cannot be quoted since the consultant services are not yet available (June 1980)

Commentary: Long-term cooperation projects are preferred to short one-day-works. However, there is a positive attitude also to shorter analytical jobs.

6. Swedish Silicate Research Institute, Gothenburg.

Person to contact: R. Carlsson, telephone 031-18 48 57.

This is mentioned as one of the many places places where SEM, X-ray fluorescence, and electron microsond investigations are performed. Large experience from work with ceramics and glasses is at hand. The X-ray detection covers a larger wave-length-region than normally which is important for glass studies, since several lighter elements can be analyzed.

Equipment: A. X-ray fluorescence spectrometer.

Elements from F and upwards in atomic mass can be detected.

Sensitivity down to 10^{-3} weight per cent (for lighter elements considerably lower sensitivity).

Waiting time: Shorter works: normally 1 week

Price: 500 SEK/h for instrument

205 SEK/h for operators

155 SEK/h for specimen preparation

Government agencies are entitled to a 30% discount

B. Electron microsond

Energy dispersive analysis covering atomic masses F and upwards

Wave length dispersive analysis covering Bor and upwards

Sampling depth 1 μ

Depth resolution 0.1 - 1 μ

C. Sweep electron microscope (SEM)

Resolution 7.5 nm (possible) - 15 nm (standard)

7. Dept of Physics, Chalmers University of Technology, Gothenburg.

Persons to contact: G. Dunlop, telephone 031-81 01 00
H. Nordén

Here is mentioned one of the many electron microscope equipments that are available in the country (probably the most modern one).

Equipment: JEM 200 CEX combined sweep- and transmission electron microscope
Resolution SEM 4.0 nm
TEM 0.3 nm point to point

Energy dispersive X-ray fluorescence analysis is available

Waiting time: 1 week for shorter works

Price: Not decided but calculated to be in the range 400 - 500 SEK/h

8. Physics Department, Loughborough University, Loughborough, England.

Person to contact: Mike Walls

Here is a Surface Analysis Service (see encl. 2) available especially designed for consultant work in Europe. Of particular interest in this context is that the group has a large experience from working with glass through the five-year cooperation with

Pilkington Research Laboratories at Pilkington Glass Industries.

Equipment:	(see also encl. 2) XPS + Scanning AES From January 1981 a SIM's unit will also be available Two AES equipments with depth profiling analysis through sputter-AES Lateral resolution 5 μ and 0.5 μ respectively
Waiting time:	< 7 days possible for shorter work
Price:	300 - 350 £/day (approx. 3.000 SEK/day) Written report is supplied. Fixed price can be guaranteed in advance.

9. Physical Electronics Division of Perkin-Elmer Munich, West Germany.

Person to contact:	Dr Goretski Dr R. Olsen
Equipment:	XPS, Scanning AES, SIMS See further enclosure 3.

15. ACKNOWLEDGEMENT

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