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Organics at Surfaces, their Detection and Analysis by Static Secondary Ion Mass Spectrometry [and Discussion]

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Organics at surfaces, their detection and analysis by static secondary ion mass spectrometry

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The analysis of the surface chemistry of organic materials or of organic molecules at surfaces presents special problems. Firstly there is the requirement of high chemical specificity and the ability to detect small differences in chemical state. Secondly, organics are very sensitive to damage by the radiation used for the analysis. Over recent years, static secondary ion mass spectrometry (SSIMS) has been developed into a technique which is able to provide the power of mass spectrometry for the chemical characterization of surfaces. Furthermore, the advent of time-of-flight mass spectrometry techniques has enabled very high sensitivity with little sample damage. The power of the technique is illustrated by its application to four areas of surface investigation: the adsorption and reaction of propene at a ruthenium single crystal surface; the interaction of organic lubricants at a synthetic 'gold' surface; the interaction of bioactive molecules at a model cell membrane surface, and the identification of contamination responsible for adhesive failure.

1. Introduction

Surface studies of organic materials or the characterization of complex organic molecules at surfaces has, until very recently, been a neglected area of surface science. There are good reasons for this. The complex chemistry presented at the surface places great demands on the chemical specificity and sensitivity of surface analysis techniques. The fact that most organic materials are insulators and almost all surface analysis techniques rely on the use of charged particles to either probe or analyse the surface presents further serious problems associated with sample charging. Furthermore all organic molecules are very easily damaged by the high energy photon, electron and ion beams used by surface analysis techniques.

The need for effective methods to characterize organic species at material surfaces is, however, urgent. In very many areas of science and technology the organic surface state is of great importance. This has been so for many years in, for example, heterogeneous catalysis, yet the problems of chemical specificity have restricted fundamental surface studies to simple molecules on idealized catalyst surfaces.

The surface state of polymers has become an important area of investigation as a result of the diverse and ever increasing number of applications of such materials. X-ray photoelectron spectroscopy (XPS) has been widely and effectively used to monitor surface chemical composition, contaminants and the results of surface modifications with, for example, plasma discharges. X-ray photons were shown to be the least destructive of the possible analysing radiations especially when used at low flux densities; however, in many cases chemical specificity has not been sufficiently

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precise to enable XPS to be fully informative when the chemistry is complex or when relatively small, although important, changes are being probed.

The analytical demands have increased many-fold with the increasing interest in the surface state and the reactivity of biomedical and conducting polymers. These materials are not only themselves interesting chemically but there is also a need to probe the chemistry of large molecules interacting with their surfaces.

Similar problems have arisen in the lubrication area. Information is required on the mechanism of interaction between the large complex molecules used and the surface of the materials to be lubricated. These interactions generate quite small changes in the chemistry at the surface and are often found to be undetectable by XPS or infrared spectroscopy.

Secondary ion mass spectrometry (SIMS) can be applied as a surface mass spectrometry and has the capacity to overcome many of these problems. Basically a surface mass spectrum may be generated which has the chemical specificity which is associated with organic mass spectrometry.

The basic phenomenology has been described elsewhere (Vickerman *et al.* 1989) and is as follows A high energy (200 eV to several kiloelectronvolts) beam of primary ions or neutrals is directed at the surface of the material of interest and, on collision, energy is transferred to the surface atoms causing interatomic collisions or *collision cascades* down into the bulk of the solid. Some of these cascades branch and return to the surface region at points remote from the original point of impact. If the final collision energy is sufficient, secondary particles are emitted from the surface. The vast majority of these particles are neutral but a small proportion are in the ionized state and can be analysed with a mass spectrometer. It is clear that the technique is inherently destructive, indeed the most widely used version of the technique is *dynamic SIMS*, in which the surface is rapidly eroded away and elemental species are monitored with depth. However, it was shown in the early 1970s by Benninghoven and co-workers that the use of a very low primary beam flux (*ca.* 0.1 nA $\mathrm{cm^{-2}}$, equivalent to less than 10^9 particles $\mathrm{s^{-1}\,cm^{-2}}$; there are about 10^{15} atoms $\mathrm{cm^{-2}}$ in a surface layer) and sensitive ion counting techniques enabled high sensitivity analysis to be performed while removing less than 10^{-4} of a monolayer (Benninghoven 1973). This mode of operation is known as *static* SIMS (SSIMS).

The precise details concerning the mechanism of emission and ionization are far from being understood, it is, however, clear from many empirical studies that the elemental and multiatomic fragment (or cluster) ions emitted closely reflect the chemistry of the surface layer. However, the physics of the process means that emission and ionization occur quasi-simultaneously. The ionization process is thus very sensitive to the electronic state of the parent solid. This is particulary highlighted by the sensitivity of *elemental* ion yields to oxidation state and to the identity of the matrix from which the ions originate. Variations of many orders of magnitude can occur, consequently elemental quantitative analysis is a somewhat complex process. Nevertheless the extreme sensitivity of SIMS to many elements makes the necessary calibration procedures worthwhile. This paper is, however, concerned with the analysis of organics.

In the past, the apparent violence of the SIMS process has suggested to some that the information generated could not bear any relationship to the chemistry of the surface. In this respect it has to be remembered that the ions monitored are emitted remote from the point of impact and the collision energy initiating emission is only a few tens of electronvolts. Many studies using standard compounds and model systems have demonstrated that the SSIMS spectra closely reflect the surface chemistry (Briggs *et al.* 1989). Fingerprint spectra of quasi-molecular ions and associated fragment ions can uniquely define the precise chemistry of the surface.

Quantification of chemistry using characteristic ions should in principle be subject to the same electronic complications of elemental analysis. Data on absolute chemical state analysis are non-existent; however, a few studies of copolymer systems has shown that the use of ion ratios provides good and reliable relative quantification of the copolymer surface composition down to about 0.01 of a monolayer (Briggs 1989).

Although SSIMS does greatly reduce the rate of destruction of the surface layer, it has been found that organic materials are significantly more sensitive to particle bombardment induced damage than are inorganic materials. Briggs and co-workers demonstrated that beyond a total primary beam dose of 10^{13} ions cm^{-2}, surface damage effects became evident in the spectra of polymer materials (Briggs & Hearn 1986). Similarly, Brown *et al.* have shown that primary *ion* beams generate four or five times more damage than primary *neutral* beams (Brown *et al.* 1985). The latter observation has been partly responsible for the use of fast atom bombardment in the analysis of organic materials. The other (predominant) reason has been that the use of neutral primary beams very greatly reduces the serious analytical problems associated with the surface charging which occur when electrically insulating materials are analysed with ion beams.

Until recently, the most widely used mass analyser for SSIMS was the quadrupole, however this suffers from a low overall transmission (less than 10^{-4}), restricted effective mass range and mass resolution, and from the fact that it is a *scanning* instrument. The latter feature means that most of the information is discarded in the process of analysis. Although much very valuable information has been obtained using QuadSIMS instruments, there have been severe problems arising from low sensitivity and the generation of surface damage. Recently the potential of the time-of-flight (TOF) mass spectrometer has been explored (Tang *et al.* 1988; Eccles & Vickerman 1989). This has the advantage of high transmission (greater than 0.1), all ions are collected quasi-simultaneously, it has a very high mass range and mass resolution in excess of $\Delta m/m = 3000$ is obtainable. Overall, compared with a quadrupole based instrument, it has been shown that the TOFSIMS requires 10^{-4} primary beam dose to generate an equivalent spectrum. For organic materials analysis, TOFSIMS is the technique of choice.

2. Experimental

Two different SSIMS systems have been used in the studies described. For the adsorption studies described in §3, a UHV surface science system was used which combined facilities for low-energy electron diffraction, Auger electron spectroscopy, thermal desorption, electron energy loss spectroscopy and SSIMS. SSIMS was performed using a Vacuum Generators MM12-12 quadrupole mass analyser having a mass range of m/z 1–800. A 2 keV Ar^+ primary beam analysis was used at a flux density of 6×10^{-10} A cm^{-2}. At each adsorption temperature spectra took some 15 min to acquire after which the beam was switched off the surface temperature raised and equilibrated before further spectra were recorded.

The studies described in §§4–6 were carried out by TOFSIMS using a VG IX 23S spectrometer of the Poschenrieder design and equipped with a pulsed liquid metal ion source (Eccles & Vickerman 1989). A 30 keV Ga^+ primary ion beam (pulse length 20 ns) was used at an incident angle of 38° to the surface normal. The secondary ions were accelerated to ± 5 keV for the analysis by applying a bias to the sample. For each sample, both positive and negative secondary ion spectra were collected using a total primary ion dose of 1×10^{11} ions cm^{-2}.

3. Adsorption and reaction of propene on ruthenium

The adsorption of simple molecules such as CO, NO, O_2, etc., on single crystal surfaces has occupied many surface science investigators, however, defining the chemistry of interaction of more complex molecules with surfaces is not straightforward. There are the questions concerning both binding site and chemical transformation which are difficult to clarify when a significant number of atoms are involved in the molecule. Both thermal desorption and vibrational spectroscopy via reflection absorption infrared (RAIRS) or electron energy loss spectroscopy (EELS) can provide very helpful information. The advent of SSIMS has provided a further powerful technique to probe such systems. The adsorption of CO on single crystal metal and small metal particles has been extensively studied by SSIMS and shown to be in complete agreement with data derived from other techniques (Brown & Vickerman 1986; Gillet *et al.* 1985). Adsorbate structure, coverage and chemical transformations can all be monitored using the data.

The detail of the adsorption of more complex organic molecules such as ethene, propene and butene is being explored successfully using SSIMS (Sakakini *et al.* 1987). A study of the adsorption and reaction of propene on a Ru(0001) surface demonstrates the power of SSIMS in this area. The exposure of a clean annealed Ru(0001) surface to 1 langmuir of propene at 150 K results in two distinct regions of interest in the positive SSIMS spectrum. The first is the CH_x^+ region, $m/z = 12$–15 and the second being attributable to $RuC_3H_x^+$, $m/z = 138$–146. Although both regions provide information on the adsorption process we only consider the latter here. The spectrum observed is shown in figure 1*a*. This is complex because of the seven isotopes of Ru and the fact that some surface reaction has already occurred. If propene adsorbed completely unreacted, a spectrum for $RuC_3H_6^+$ would result having the isotope pattern of Ru displaced up the mass scale by $m/z = 42$ (figure 1*b*). This has been shown to occur for ethene and propene on gold passivated surfaces. Surface reaction modifies the spectrum. It is possible to isolate certain individual m/z peaks as being solely attributable to possible surface species. The peak at $m/z = 146$ can only arise from molecularly adsorbed propene; $m/z = 145$ is uniquely associated with C_3H_5, probably propylidyne; $m/z = 131$ will indicate the presence of adsorbed C_2H_3, ethylidyne. Using these assignments it is possible to monitor surface coverage and reaction as a function of temperature.

Clearly the data suggest that at 150 K propene adsorbs both molecularly and some dissociation occurs. Vibrational spectroscopy confirms this suggesting di-σ adsorption (Ransley *et al.* 1990). As temperature is raised there is a rapid fall in molecular propene coverage to 250 K as monitored by the ratio of the $RuC_3H_6{}^+$ (I_{146}) to the ^{102}Ru isotope, $I_{146}/^{102}Ru$ (figure 2). Concurrently there is first a rise and then a fall in the $I_{145}/^{102}Ru$ ratio suggesting a dehydrogenation to form surface propylidyne and this further dissociates to form ethylidyne between 200 and 230 K as monitored by $I_{131}/^{102}Ru$. Finally this species further dissociates to form surface CH_x. Further details of the adsorbate sites involved can be obtained from studies of

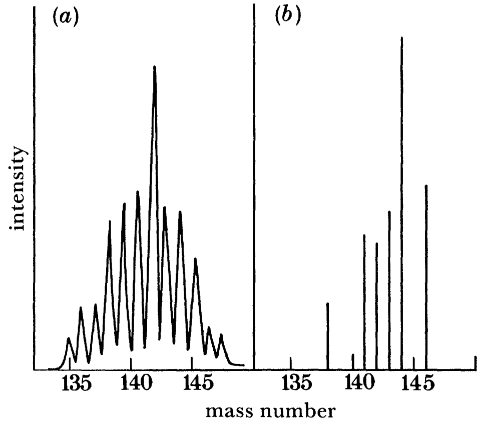

Figure 1. (*a*) Positive secondary ion spectrum in m/z range 138 to 146 resulting from the adsorption of propene on a Ru(0001) surface at 150 K. (*b*) The expected SSIMS isotope pattern for molecular adsorption of propene on Ru(0001).

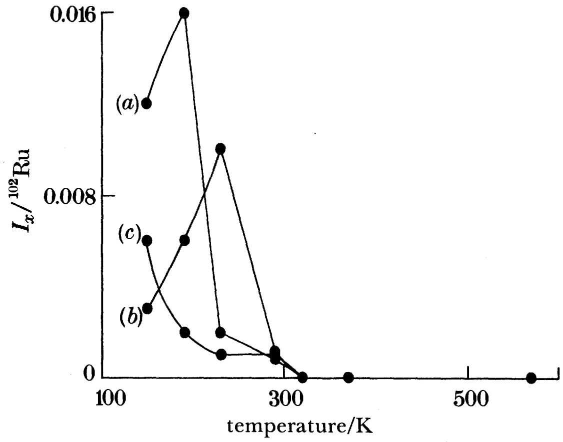

Figure 2. The variation of the positive secondary ion ratios associated with the coverage of adsorbed propene, $I_{146}/^{102}$Ru; the coverage of propylidyne $I_{145}/^{102}$Ru; the coverage of ethylidyne $I_{131}/^{102}$Ru. (*a*) $x = 145$, (*b*) $x = 131$, (*c*) $x = 146$.

the relative intensities and variation of the $RuC_6H_x^+$ and $Ru_2C_6H_x^+$ species. These conclusions are supported by both RAIRS and EELS studies. The two studies provide powerful evidence of the value of combining vibrational and mass spectral data to obtain a clear understanding of these surface transformations.

4. Lubricants on synthetic gold flake

Organic lubricants, such as fatty acids, are an essential ingredient in the manufacturing process by which copper–zinc metal is turned into synthetic gold for use in the printing industry. The quality and properties of the final product (e.g. hydrophobicity, stability) are very sensitive to the efficiency of attachment of the lubricant molecules to the surface of the flakes. Such attachment, which takes place

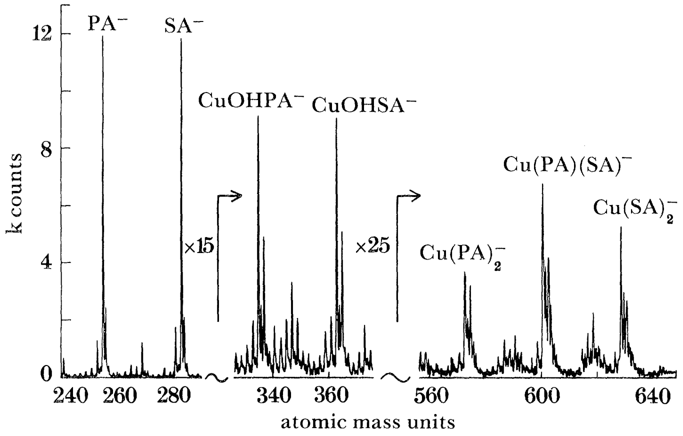

Figure 3. Negative secondary ion spectrum recorded for synthetic 'gold' flake with fatty acid lubricants.

with monolayer/submonolayer coverage, is difficult to monitor using conventional wet chemistry methods (e.g. solvent extraction, liquid chromatography). In contrast, the required information can be obtained quickly and directly by SSIMS. SSIMS has been used to study both standard and novel lubricants on a wide range of flake specimens. The technique provides routine analytical information (e.g. lubricant uptake etc) in addition to affording a means by which flake–lubricant interactions can be directly studied. For example the nature and extent of intact molecular attachment can be monitored, whilst the degree of full or partial dissociation can be investigated.

The efficient attachment of a 50:50 mixture of palmitic and stearic acids has been verified in one case from the negative secondary ion spectrum shown in figure 3. Signals characteristic of the fatty acid quasi-molecular anions (diagnostic of the intact molecules) were observed at m/z values of 255^- ($PA^- = CH_3(CH_2)_{14}COO^-$) and 283^- ($SA^- = CH_3(CH_2)_{16}COO^-$). The equal intensity of these two signals clearly shows that the actual surface uptake of palmitate : stearate is in the same proportion as that of the bulk lubricant mixture. In addition, throughout the spectrum (figure 3), copper–lubricant complex ions were evident corresponding to $CuOH(PA)^-$, $CuOH(SA)^-$, $Cu(PA)_2^-$, $Cu(PA)(SA)^-$ and $Cu(SA)_2^-$. Higher mass negative ion clusters and positive ion species, e.g. $Cu_2(PA)^+$ and $Cu_2(SA)^+$, were also observed (not shown). The detection of such an array of copper–lubricant cluster ions implies the strong interaction of copper at the surface of the flakes with the lubricant molecules in agreement with infrared studies.

In addition to assessing lubricant coverage, SSIMS has been able to directly monitor the surface presence of contaminant species which inhibit the production of high quality flakes. Signals indicative of the sub-monolayer attachment of phthalate species ($HOOCC_6H_4CO^+$) and in particular unsaturated fatty acids [$CH_3(CH_2)_nCH = CH(CH_2)_mCOO^-$] have been observed (figure 4). Initial studies correlating secondary ion intensities with hydrophobic properties have suggested that the enhanced surface presence of these unsaturated fatty acids is partly responsible for the poor quality of some flake products. Reduced hydrophobicity in such cases is attributed to the inability of the unsaturated acids to close pack on the surface of the flakes as effectively as the saturated molecules.

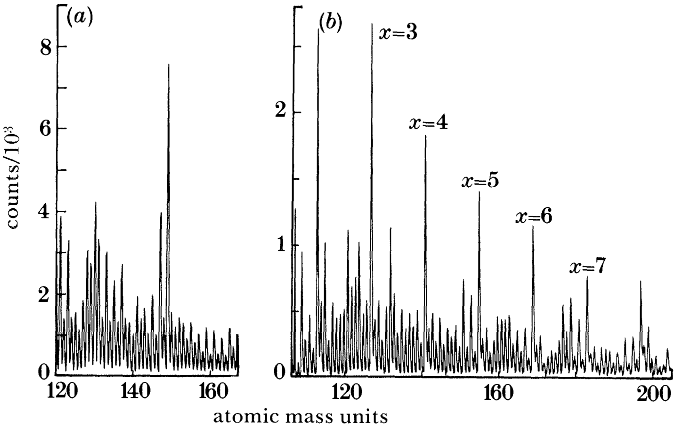

Figure 4. (*a*) Positive and (*b*) negative secondary ion spectra recorded for synthetic 'gold' flake showing contaminants. (*a*) $HOOCC_6H_4CO^+$, (*b*) $CH_3(CH_2)_x(CH)_2COO^-$.

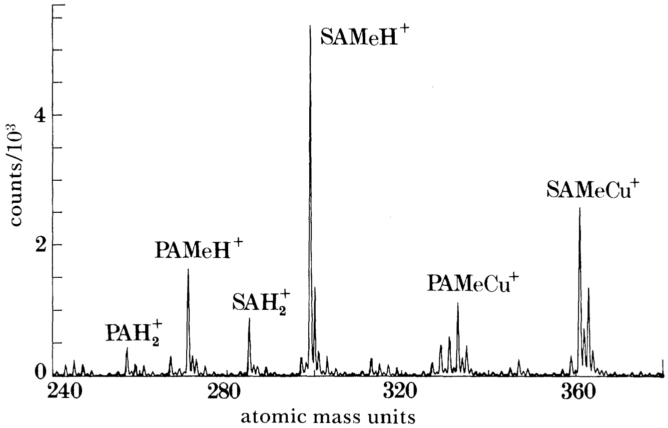

Figure 5. Positive secondary ion spectrum recorded for synthetic 'gold' flake with fatty acid ester lubricants.

Static SIMS has also been effectively used for the analysis of flake surfaces with attached lubricants of modified or unknown composition. As outlined earlier the SIMS technique allows such information to be obtained rapidly and non-destructively in contrast to traditional methods of chemical analysis. Thus in the case of one flake product with high quality surface properties, the presence of a 30:70 mixture of the methyl esters of palmitic and stearic acids was immediately established from the secondary ion spectra. In the positive ion mode (figure 5) signals were observed corresponding to the ester quasi-molecular cations ($271^+ =$ PAMeH$^+$, $299^+ =$ SAMeH$^+$) and copper–ester complexes (PAMeCu$^+$, SAMeCu$^+$). In the negative ion spectrum (not shown) signals characteristic of MeO$^-$, PA$^-$, and SA$^-$ were detected.

5. Bioactive molecules at membrane surfaces

Static SIMS is becoming increasingly important for the characterization and development of materials and devices used in pharmaceutical applications. For example, in the field of drug delivery the technique provides a unique insight into the

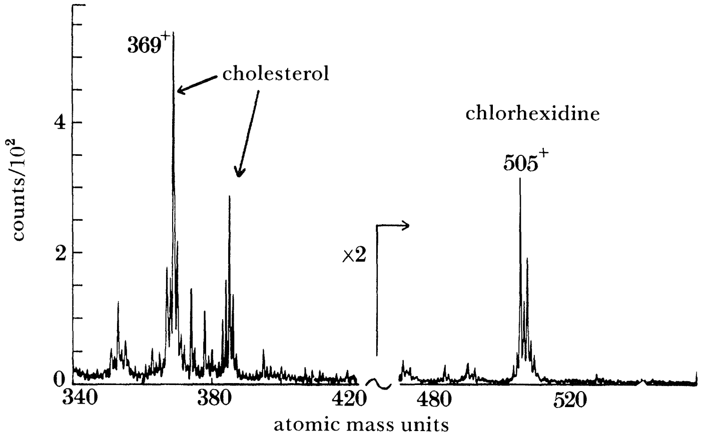

Figure 6. Positive secondary ion spectrum recorded for a model cholesterol membrane with chlorhexidine.

relationship between surface chemical composition and surface versus bulk drug levels. Such an understanding is important for controlling the rate of drug release (Davies *et al.* 1988).

For some drugs their surface active behaviour is an integral facet of their *in vivo* performance. One mechanism by which such surface active drugs can function is to replace biomolecules constituting bacterial cell membranes eventually leading to cell disruption. Static SIMS, in conjunction with liquid ultraviolet photoelectron spectroscopy, liquid UPS (Archer & West 1990) has recently been used in this laboratory to investigate the interaction of the antibacterial agent chlorhexidine $[(ClC_6H_4NHC(NH)NHC(NH)NH)_2(CH_2)_6]$ with the model cell membrane cholesterol. *In vivo*, cholesterol is a major structural component of cell membranes. The presence of submonolayer quantities of chlorhexidine at the membrane surface was monitored by the detection of the diagnostic quasi-molecular cation cluster at $m/z = 505-510^+$ (figure 6) in addition to the associated array of fragment ions (not shown). These are easily distinguishable from the cholesterol signals at 369^+ $(M-OH)^+$ and $383-387^+$ $(M,\ M \pm H_n)^+$. This general ability of SSIMS to uniquely characterize and identify biomolecules with high sensitivity is extremely valuable from the aspect of detection alone.

The technique, however, may be extended to providing an insight into the interaction of bioactive molecules with cell membranes. In the case of the chlorhexidine–cholesterol model system the very pronounced surface active behaviour of chlorhexidine was observed. Such information was obtained by the analysis of a range of chlorhexidine–cholesterol solutions where the surface versus bulk levels of the chlorhexidine were monitored. This investigation was undertaken above the solution concentration at which cholesterol micellates, in the absence of other agents, to form a rigid structure. This work was carried out in tandem with liquid UPS to verify that the solid solution films analysed in the UHV SIMS experiment were representative of the dynamic fluid state which exists *in vivo*. The similar results obtained by the two techniques suggest that this is the case. The molecular specificity of SSIMS is particularly well suited to this type of study where the surface levels of chlorhexidine can be assessed by measuring the relative intensity variation of the SSIMS signals diagnostic of the two components (e.g. 505^+ versus 369^+). The

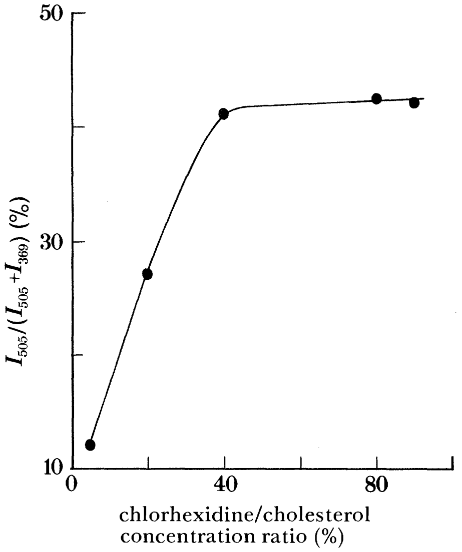

Figure 7. The variation of the positive ion ratio $I_{505}/(I_{505}+I_{369})$ with bulk concentration chlorhexidine for cholesterol–chlorhexidine model system.

surface coverage versus bulk concentration relationship as shown in figure 7 (i.e. $I_{505}/(I_{505}+I_{369})$ versus C), can be interpreted thermodynamically to yield information on the energetics of formation of the two-component surface structure. For chlorhexidine the shape of the graph indicates that it is highly favourable for this species to exist in the surface layer.

The relationship shown in figure 7 also gives an indication of the minimum dose of chlorhexidine required for maximum antibacterial effect. The results show, in agreement with liquid UPS, that the equilibrium surface concentration of chlorhexidine is attained at low concentrations and is not enhanced above this level. In general such knowledge of minimum effective dose is very important from the aspect of toxicity. The molecular specificity of SSIMS potentially can be further exploited to investigate the complex interrelationship of such ideal two-component systems with the presence of other biomolecules, e.g. lipids, to more closely model the situation which exists *in vivo*.

6. Adhesive failure

Static SIMS can also sensitively study fractured adhesive interfaces to try to identify the chemical reasons, if any, behind premature failure of the corresponding adhesive joints. This is particularly relevant in the light of the widespread and important commercial applications of adhesively bonded structures, e.g. fibre–resin composites and aluminium–epoxide systems. In one such case the premature failure of an alloy–epoxide composite specimen was investigated by SSIMS. The presence of significant quantities of the polymer polydimethylsilicone $[(CH_3)_2SiO]_n$ at the fracture interface was immediately established from the secondary ion spectra. In many similar cases these contamination levels are at or below the detection limits of electron spectroscopy which, in any event does not generally have the required chemical specificity to unequivocally identify such organic species. For this sample, in the positive ion mode (figure 8), species such as $(CH_3)_3Si^+$, $(CH_3)_3SiOSi(CH_3)_2^+$, and

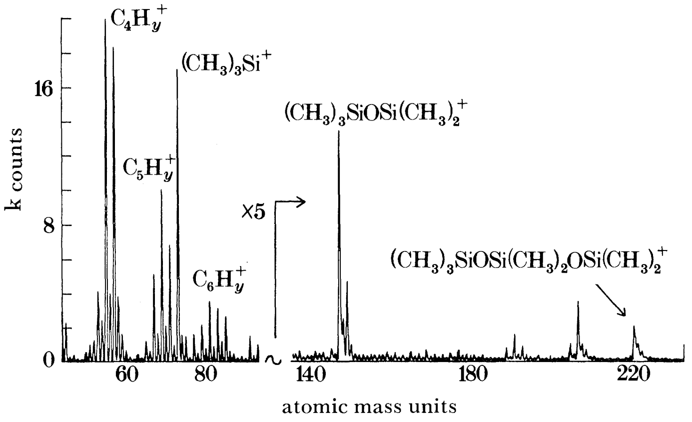

Figure 8. Positive secondary ion spectrum of the fracture interface of a failed adhesive joint.

$(CH_3)_3SiOSi(CH_3)_2OSi(CH_3)_2^+$ were detected in addition to the array of signals associated with the adhesive itself ($C_xH_y^+$). This polymeric material, which is normally used as a lubricating/release agent, is a known adhesion inhibitor and its presence in this case is likely to be the primary reason for adhesive failure.

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Discussion

M. Grasserbauer (*Technical University of Vienna, Austria*). How would Dr Vickerman evaluate the use of Cs^+ primary ions in addition to Ga^+ and Ar^+ ions for molecular surface analysis?

J. C. Vickerman. In principle, there should be no problem using Cs^+ (especially in SSIMS mode). Possible changes in surface chemistry induced by the use of Cs^+ must, however, be borne in mind when interpreting the spectra.

M. Grasserbauer. In general, how would Dr Vickerman assess the potential of SIMS for quantitative analysis of mixtures of organic materials?

J. C. Vickerman. The use of ion ratios has been shown to be reliable and should overcome most electronic effects on absolute ion yields.

M. Grasserbauer. How much surface material is removed during the acquisition of a SIMS image?

J. C. Vickerman. This is very dependent on a number of factors such as image magnification, primary ion current, image acquisition time, sample nature, etc. For example, increasing the magnification such that a smaller area is being analysed results in a greater consumption of surface material. In quadrupole SIMS, it is not possible to go beyond a magnification of about × 1000 before exceeding the SSIMS limit (defined as the removal of 0.01 of a monolayer). In time-of-flight SIMS, imaging within the SSIMS régime can be achieved up to magnifications of about × 10000.

M. Grasserbauer. How does Dr Vickerman rate the practical value of high mass resolution in SSIMS?

J. C. Vickerman. High mass resolution is not required for the majority of practical analyses, however there are cases where mass overlap can be a serious problem for the detailed interpretation of spectra from complex organics. High mass resolution is obviously advantageous in such cases.

K. E. Cooksey (*US Office of Naval Research, European Office*). How effective is SIMS likely to be for studying the adsorption of organic macromolecules to clean surfaces placed in aquatic environments?

J. C. Vickerman. SIMS should be very effective for the analyses of such surface-adsorbed materials. Our studies have shown that the fragmentation patterns of molecules are usually very distinctive fingerprints, and can be used to monitor their presence and modification.

R. F. C. MANTOURA (*Plymouth Marine Laboratory, U.K.*). Has Dr Vickerman investigated environmental samples (e.g. adsorbed pollutants), and how do the results compare with pyrolysis GCMS?

J. C. VICKERMAN. We have studied pollutant and contaminant molecules at surfaces. Although some simple examples have been published, many remain commercially confidential. The spectra are rather different from those of pyrolysis GCMS.

B. EVANS (*Pilkington Technology Centre, U.K.*). Is Dr Vickerman completely certain that the presence of metal-organic adducts in the mass spectrum does indicate the presence of strong bonding between the metal surface and the organic species?

J. C. VICKERMAN. Our evidence from model systems indicates that spectral features consisting of metal-organic components indicates a bonding between the organic molecule and the metal surface. Note, in the case of our particular examples, the presence of metal-organic bonding, as indicated by SIMS, is confirmed by X-ray photoelectron spectroscopy analysis of the same surfaces (data supplied by R. H. West, CSMA, UMIST).

B. EVANS. Does Dr Vickerman rule out the formation of the metal-organic adducts in the gas phase?

J. C. VICKERMAN. The possibility of reactions between emitted metal species and organic fragments in the gas phase above the sample would appear to be very remote under SSIMS conditions.

W. J. ALBERY (*Molecular Sensors Unit, University of Oxford, U.K.*). Can Dr Vickerman explain why the SIMS image obtained for the well-bonded CF-epoxy composite (mixed red/green bands) is different to that of the poorly adhering sample (sharp red/green bands), and what would be observed on the molecular level in the well-bonded case?

J. C. VICKERMAN. In the well-bonded case, the red/green mixing in the secondary ion image arises from the fracture of the composite within the resin, leaving epoxy-adhesive bonded to the fibres. This contrasts with the poorly adhering case where a clean fracture takes place between the carbon fibres and the resin. For the well-bonded case, it may be possible, to observe carbon–oxygen–epoxy bonding at the molecular level.