The role of SIMS in cultural heritage studies

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Abstract

Secondary ion mass spectrometry (SIMS) is a highly sensitive chemical analysis technique available in variants, which are top monolayer specific (static SIMS) or which can extract micro-volume analyses or depth profiles (dynamic SIMS). The technique offers ppm or even ppb atomic sensitivity for the consumption of extremely small sample volumes. In the area of cultural heritage, SIMS has been applied to a diverse range of problems including technology and authenticity, origin and provenance, degradation processes, such as corrosion and weathering, and conservation. In this paper, the basic attributes and limitations of the technique are described. An outline is given of applications to glasses (obsidian dating, conservation of stained glass and Venetian glass), metals (simulated archaeological bronzes), pigments and human remains, focusing on conservation problems such as the assessment and suppression of corrosion, other degrading processes, identification of materials using speciation. The topic of ultra low energy SIMS, newly applied to cultural heritage materials, is briefly described.

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1. Introduction

At first sight the requirements of secondary ion mass spectrometry (SIMS) and of chemical analysis in the area of cultural heritage appear to be diametrically opposed. SIMS is a destructive analytical technique – in the sense that sample material is consumed during the analysis (as with all forms of mass spectrometry). In addition, like many forms of ion beam analysis (IBA), electron microscopy and electron spectroscopies, the SIMS instrument can usually accommodate only a small sample with maximum linear dimensions of some mm. A larger artefact will need to be sampled in some way before SIMS analysis is possible. Finally, SIMS is a high or even ultra high vacuum technique, and depends on good vacuum over the sample for many aspects of its data quality. Therefore, the sample must be vacuum compatible. In fact, the latter requirement still allows samples as diverse as oil paint and obsidian to be analyzed so this limitation is not so great.

On the other hand, SIMS offers unique combinations of attributes which warrant its use under appropriate circumstances [1]. A superficial
description of the technique often runs something like “high depth and lateral resolution (nm and 10’s nm, respectively), molecular specificity and fingerprinting, trace analysis in the ppm–ppb range”. It is worth noting that although these specifications can undoubtedly be achieved individually, they are often mutually incompatible and even require different instruments for their attainment. Indeed, the achievement of ppb sensitivity is rare, and probably only possible under ideal demonstration-like circumstances. Nevertheless, it is in combinations of properties that SIMS has its strengths, and also in complementary use with other analytical techniques. In this paper, therefore, we will first outline the SIMS technique, and then give examples of applications highlighting complementary aspects.

2. Basic concepts of SIMS

In a SIMS analysis, the sample is bombarded in vacuo with a mono-energetic mass filtered focused ion beam (primary ions) with energy in the range 0.2–30 keV depending on the application and the instrument. The deposition of kinetic energy in the solid (or occasionally liquid) surface by the impact of a primary ion initiates a short-lived (~1 ps) phenomenon known as a collision cascade (Fig. 1(a)) in which the atoms in a volume of around $10^3$ nm$^3$ around the track of the ion are in violent motion. (Exactly the same process will take place around a scattering event in RBS, or at the ends of the tracks of implanted ions in IBA generally (Fig. 1(b))). Some of the energy may return to the surface in such a way as to break atomic bonds and liberate atomic or molecular species into the vacuum. A fraction of these is ionized (or may be ionized after emission using a laser or electron impact in a related technique – secondary neutral mass spectrometry (SNMS)) during the emission process (secondary ions), collected by an electric field and focused into a mass spectrometer. SIMS can be divided into two different techniques: static SIMS (SSIMS), which is a highly surface specific mass spectrometry tool offering organic and inorganic fingerprinting as well as atomic compositional analysis, and dynamic SIMS which is capable of depth profiling and bulk analysis. Both branches of the technique are capable of trace analysis below (often well below) 0.1% atomic. In the case of static SIMS this is combined with virtually non-destructive sampling of the top one or two atomic layers only. For dynamic SIMS, typically ppm sensitivities can be achieved across the periodic table for the consumption of $<10^{-13}$ cm$^3$ of sample per data point. Both static and dynamic SIMS can be used to generate chemical images with lateral resolution approaching 10 nm using a liquid metal ion gun (e.g. 30 keV Ga$^+$ primary ions), or down to ~1 μm using primary ions from a gas source. Primarily because of the low sampled volume per pixel in the image at the extreme resolution in the former case, sensitivity will be reduced to ~10% atomic at best.

At the energies used in most SIMS experiments, the area of surface damaged by each ion impact has linear dimensions ~10 nm. The criterion for

![Fig. 1. (a) Schematic of the sputtering process and the collision cascade in SIMS. (b) Similar processes occurring at the ends of tracks or at scattering sites in IBA. Note that the track length in the electronic stopping region is many times greater in general than the dimensions of the damaged region.](image-url)
static SIMS is that the probability of sputtering from a pre-existing impact site must be low. This constrains the total primary ion dose per experiment to \( \ll 10^{13} \) ions cm\(^{-2}\). For dynamic SIMS it is necessary for the primary beam to create average steady state conditions at the sample surface. Otherwise, quantification and useful intercomparison of the data are impossible. The regime of dynamic SIMS lies beyond ion doses of \( 10^{16}–10^{17} \) ions cm\(^{-2}\) therefore. Such steady state conditions may, however, be impossible to achieve, especially if the sample surface is rough, or becomes rough under ion bombardment, or if the bulk sample chemistry changes significantly on a depth scale comparable with the SIMS depth resolution.

In SSIMS primary species such as inert gas ions (general purpose) and metal ions – Ga\(^{+}\), In\(^{+}\) (high lateral resolution imaging) are used. Recently, there has been much interest in the use of cluster ions, e.g. Au\(^{m+}\), C\(_{60}\)\(^{+}\), to promote cluster ion emission for high molecular weight fingerprinting. In dynamic SIMS, inert and metal ion species are used too, but the most common primary ions in use are O\(^{+}\), O\(^{-}\) and Cs\(^{+}\). These reactive species are used primarily to control the chemical properties of the altered layer which forms at the surface of the sample if and when equilibrium bombardment conditions are achieved. Very briefly, oxygen ion bombardment creates a few nm (depending on beam energy) of material with strong bonds and localization of electrons around the implanted oxygen atoms. This can enhance the emission of positive (and negative) ions by several orders of magnitude, greatly increasing the sensitivity of the technique. Oxygen is also useful for stabilizing ion yields against changes in chemistry with depth, particularly where the material contains high but varying concentrations of electronegative species such as oxygen itself. Caesium promotes negative ion emission both through its effect on reducing the work function and in the increased electron availability in a caesiated surface. It is also useful in positive ion analysis when using MCs\(^{+}\) and MCs\(^{+}\) secondary ions can greatly reduce the matrix effect in analysing for atomic species M. O\(^{-}\) is used for insulator analysis to minimise charging effects, otherwise the sample may be bombarded coincidently with electrons to achieve charge compensation.

3. Quantification and sensitivity

A key parameter for SIMS of both types, and one which must be determined explicitly or implicitly for quantification, is the ionization probability \( z \) for the analyte species \( X \). This is defined as

\[
z_X^\pm = \frac{n_X^\pm}{n_X^+ + n_X^- + n_X^0},
\]

where \( n_X^\pm \) is the total number of positive or negative ions of species \( X \) emitted and \( n_X^0 \) is the total number of neutrals sputtered for the same primary ion dose. \( z \) is determined by the electronic interaction of the departing particle with the perturbed sputtering site and varies strongly from one elemental (or molecular) species to the next. It may also be strongly influenced by the sample chemistry at the sputtering site (SIMS matrix effect) and by the (local) primary ion impact angle (hence the sensitivity to surface topography). In practice this means that SIMS is dependent on careful replication of measurement conditions, and the use of reference materials for quantitative accuracy and precision. \( z \) is very difficult to determine independently because the overall (species dependent) efficiency (collection, transmission, detection) of the spectrometer is unknown in general. A more practical parameter is the useful yield \( \tau \), the product of \( z \) with the spectrometer efficiency, where

\[
\tau_X^\pm = \frac{N_X^\pm}{n_X^+ + n_X^- + n_X^0},
\]

and \( N \) is the detected count for \( X \). This parameter can be measured for a reference material, and, indeed, forms the underlying basis of the relative sensitivity factor method for quantification which is described later. Across instruments, analyte ions, and matrices \( \tau \) varies by many orders of magnitude, with a maximum \( \sim 0.1 \). Fig. 2 shows how the detection limits in SIMS are related to the
sputtered volume per data point for useful yields in the range $10^{-1}$–$10^{-5}$. It is assumed that it is necessary to collect a minimum of 10 counts for statistical significance.

In practice, the detection limits shown in Fig. 2 may not always be achieved because of background counts due to ions species originating from the vacuum or the sample at the same mass as the analyte.

There is no ab initio method for calculating $x$ so, in common with many other analytical techniques, it is necessary to use reference materials to quantify SIMS data. This is usually done using the relative sensitivity factor (RSF) method. Because of the strong matrix effects in SIMS, and the consequence that, at high concentrations, an analyte species may affect its own ionization probability, accurate quantification (within 1–2%) is only possible in general for species with overall concentrations below $\sim 1\%$ (dilute species). The relationship between the SIMS ion yield and impurity concentration needs to be established with great care at higher levels. The RSF method is based on the argument that the useful yield of a species representative of the matrix – the matrix channel (e.g. Si$^+$ or O$^+$ from Si bombarded with O$_2^+$) will react in the same way as that of the analyte species to (small) perturbations in the measurement – e.g. differences in distance from the edge of the sample holder, changes in surface potential and primary ion current, so that changes in the ratio of the ion intensities is more representative of changes in concentration of the analyte. It is important to understand that this behavioural similarity will probably break down at the surface, and also that a matrix species with a similar energy and angular emission spectrum to the analyte species should be chosen (e.g. if the analyte species is a molecular ion containing two atoms then the matrix species should be similar). Then the concentration $C_X$ of impurity $X$ in the unknown sample can be determined from

![Fig. 2. Detection limit represented by a signal of 10 counts versus sample volume sputtered per data point with useful yield as a parameter. The normal range of SIMS depth profiling is between $10^{-13}$ and $3 \times 10^{-12}$ cm$^3$, and that of SSIMS imaging is between $3 \times 10^{-18}$ and $3 \times 10^{-16}$.](image)
\[ C_X = C_{X(\text{ref})} \frac{N_X}{N_{X(\text{ref})}} \frac{N_{mc(\text{ref})}}{N_{mc}}, \]  

where \( C_{X(\text{ref})} \) is the concentration of \( X \) in the reference material, \( N_X \) and \( N_{mc} \) are the counts recorded for \( X \) and matrix channel ions respectively in the unknown, and \( N_{X(\text{ref})} \) and \( N_{mc(\text{ref})} \) are similar signals from the reference material.

In SIMS depth profiling the raw data are acquired as a plot of secondary ion count (or count rate) versus time. Provided the erosion rate is constant, time may be converted to a depth scale either by applying a previously measured erosion rate for samples of the same type, by measuring the SIMS crater depth with a surface profilometer or similar device. If the sample is stratified, it is unlikely that the erosion rate in different layers will be the same, and a piecewise approach may be required. A valuable combination of parameters achievable in SIMS depth profiling is a high depth resolution and accuracy, combined with trace element detection. Depth resolution is the ability to distinguish between adjacent features separated by a small depth increment, and may be as good as 1 nm (for beam energies below 1 keV). It is more usual to see primary beam conditions which give depth resolution between 3 and 10 nm in archaeometric profiling. Finally, it is worth remembering that the depth resolution can never be better than the surface roughness on the crater bottom.

### 4. Selected applications in cultural heritage studies

In the area of art and archaeometry, SIMS has been applied successfully to a wide range of materials, including pigments [2,3], glasses [4–13], metal alloys and tarnishes [14–17], and human remains such as teeth [18]. Here we describe in more detail the use of both dynamic and static SIMS for some selected applications.

#### 4.1. The dating of obsidian artefacts

Glassy materials, for example obsidian [5–8], stained glass [4,9,10] and Venetian glass [11–13] have all been studied successfully using SIMS depth profiling. These matrices present a number of challenges to the analyst, including a large variation in the glass composition itself, the fact that the material is insulating, and most surfaces of real interest are weathered and therefore rough and even porous. SIMS has been used to measure the in-diffusion of atmospheric and soil species such as water, the leaching out of alkali metals, and the effectiveness of conservation measures. High silica glasses such as obsidian can be good subjects for fairly high depth resolution quantitative depth profiling. Obsidian is a favourable case because artefacts were often produced from it by conchoidal fracture which leaves a gently curved but locally smooth surface [7]. Weathering of the material tends to leave localized pits [5] rather than crizzling, and these can be excluded from the analyzed area.

Measurement of the depth to which water has diffused into the obsidian fracture surface was originally proposed as a method of dating by Friedman and Smith [19]. Microscopic examination of the outer edge of a transverse section reveals a band of contrast due to a change in refractive index of the material between the hydrated and unhydrated material – the so-called hydration rim. The thickness of the surface region, together with a simple Fickian diffusion model for water form the basis of the dating method. However, there is often very poor agreement between dates estimated in this way, and radio-carbon dating of artefacts which should be a similar age. Moreover, recent comparison of dates obtained from the same samples by different laboratories have revealed serious disagreements [7]. Anovitz et al. [6] and Riciputi et al. [7] have claimed that the optical measurement is itself subjective and it has been known for some time that the diffusion model is too simplistic. SIMS depth profiles for hydrogen, representative of the water content of the surface, were obtained from hydrated reference materials and from obsidian artefacts [6,7]. The data were taken in a modified Cameca 4F instrument using \(^{16}\text{O}^-\) ions at 12.5 keV. The authors were careful to choose smooth parts of the surface for profiling, and to establish that the hydrogen yield was proportional to the water concentration up to levels in excess of 10% by weight.
Typical H profiles obtained by Anovitz and Riciputi are shown in Fig. 3, labelled with the date (CE) obtained from radio-carbon dating of appropriate artefacts in the same mound. The s-shaped profile is characteristic of a non-linear (concentration dependent) diffusion behaviour for the water, rather than the linear diffusion usually assumed. Profiles from different samples, all with a fairly high level of hydration showed broadly similar shapes, indicative of increasing diffusivity with increasing water content. Using the depth at which the profile had decreased to half its height as a characteristic, the authors show that there was a generally poor correlation between the decay regions of the profile and the optically measured thickness of the hydration rim (Fig. 4, where the filled and open circles show obsidian hydration date (OHD) measurements from two different labs). Using a diffusion model of the form

$$t^* = Dx,$$

where $t$ is time, $D$ is a constant and $x$ is the depth at half height (in this case), and applying the constraint that $x = 0$ when $t = 0$, Riciputi et al. [7] show a good correlation between ages calibrated from the SIMS depth at half height and the $^{14}$C date for associated artefacts. This is shown by the open triangles in Fig. 4. Anovitz et al. [6] propose a new non-linear diffusion model for intrinsic dating, based in part on fitting to calibrated SIMS profiles. Similar results were obtained by Stevenson et al. [8] who compared SIMS with infra-red photoacoustic measurements, on rims with much lower levels of hydration below 1% (apparently no molecular water), but of similar thicknesses. They used a PHI 6300 quadrupole SIMS instrument and Cs$^+$ ions at 5 keV. Note that there are large differences in the near surface profile shape in the two studies, with Stevenson's work showing extremely high surface spikes and the work of Anovitz and Riciputi showing surface dips. This is probably due to the use of Cs$^+$ and O$^-$ ions in the two studies, together with differences in quantification procedures. For example, the division of an analyte channel point by point by a matrix channel will usually produce a fictional dip or spike at the surface. This could result in difficulties in defining the depth at half height between data acquired on different instruments, or using different primary beams.

4.2. Depth profiling of stained glass

Other glass profiling is more problematic than the obsidian case, because of the rough surfaces
produced by weathering and corrosion. It is unlikely in the extreme that these will sputter uniformly, and almost certain that the roughness will evolve during sputtering. Where such effects are reproduced deliberately, it is easy to show that there is little or no correlation between changes in the secondary ion intensities and changes in chemical composition. Indeed, the Si$^+$ signal from pure silicon bombarded with O$_2^+$ ions may vary by more than a factor of 2 as the surface roughens [20]. Dynamic SIMS data from rough surfaces must therefore be interpreted with caution and supported by information from other techniques. Even this is not straightforward – it has to be remembered, for example, that in Auger and XPS sputter profiles, the signals are characteristic of the surface composition, whereas the SIMS measurement is of the sputtered flux itself. It is perfectly possible for the surface level of a species to increase whilst its proportion in the sputtered flux decreases. On a uniform material it is well known that, under steady state sputtering conditions, the particle ratios (neutrals plus ions) in the sputtered flux are identical with those in the bulk, but the composition of the top nm or so will be depleted in high sputter yield species.

Schreiner et al. extracted quantitative SIMS profiles from lightly weathered medieval glass (free from efflorescence and significant roughness) to examine the leaching of many glass constituents (including minor components such as Na and Ba) from the surface [9]. They show that careful account must be taken of the change in erosion rates through the weathered layer into the bulk in producing an accurate depth scale. They also account for the increased Si$^+$ signal in the weathered layer on the basis of the higher erosion rate. The effect this has on the ion intensities of the leached elements is corrected by the RSF quantification procedure they used. However, there is a problem with their absolute levels, particularly in the bulk as the total of K and Ca amount to $10^{24}$ atoms cm$^{-3}$ – a density in excess of 64 g cm$^{-3}$.

In their study of factors in the deterioration of early medieval glasses from Monselice’s hill, Bertoccello et al. [10] used a variety of techniques – SIMS, XPS, SEM-EDS, micro-Raman and Mössbauer spectroscopy, and recognize many of the problems, using the strengths of one technique to support the weaknesses of another. In the case of a very deeply leached glass, where the alkali metal signals in the SIMS profile were still rising after many hours of sputtering, they use SEM-EDS on a cross-section to show that the leaching is as deep as 40 μm.

4.3. Crizzling of Venetian glass

Controlled experiments may be undertaken by simulating a glass or a metal alloy and exposing it to the environment whilst testing conservation measures. Under these circumstances it is possible to use SIMS without worrying about sampling irreplaceable material, but it is also the case that the environmental influence must be accelerated (by using higher than natural temperatures or humidity for example) in order to see an effect on a reasonable timescale. This will always give rise to some concern that the processes being studied are different from naturally occurring ones, and therefore tests of conservation methods may not be relevant to a real artefact. Nevertheless, much valuable information can be obtained in this way. One example is the studies by McPhail et al. of the crizzling of Venetian glass [13]. Crizzling, or glass disease/sickness is a major conservation problem with ancient or antique glasses where high levels of soda or potash were added to bring the flow temperature down to a level where the glass could be worked with the available furnace technology (and also to produce an acceptably lucid appearance in some cases) [11]. Such glasses are susceptible to attack by water vapour and the alkali metals are leached out leaving a sol–gel structure in place of a glass network. When the humidity falls, the surface will lose water and develop a network of fine cracks and a flaking surface, allowing deeper penetration of water and an increasingly destructive cycle as the humidity rises and falls over time. Fig. 5 shows a 17th/18th century goblet of white Venetian glass with red overlay which has suffered severe damage through this process. McPhail et al. measured the bulk composition of a set of Venetian glasses using EPMA and inductively coupled plasma atomic emission spectroscopy (ICP) and synthesized glass
of similar composition. These glasses were exposed to accelerated weathering at moderately elevated temperatures and humidities, and the physical effects of crizzling (surface shrinkage and cracking on dehydration etc.) were reproduced. Fig. 6 shows SIMS depth profile measurements of as-produced and weathered surfaces made on an Atomika 6500 quadrupole SIMS instrument using 10 keV O$_2^+$ ions at normal incidence with co-bombardment using 2.7 keV electrons focused into the 250 µm square SIMS crater for charge compensation. The data were quantified using RSF’s from Corning B reference glasses.

Fig. 6(a) shows the as-produced surface. The elevated signal for Si in the top 100 nm may be an indicator of early attack by the air and a consequently enhanced erosion rate (cf. work of Schrei ner et al. [9]). A similar effect is observed in the Al and Ca channels. Fig 6(b) shows the effects of leaching after weathering at 50 °C at 80% RH for 72 h. The minimum Na level has fallen by a factor of 50 or so, and effects are observed over a depth of 400 nm. The loss of K from the near surface is also evident. Again, the Si, Ca and Al channels provide evidence of a higher SIMS erosion rate in this region. Fig. 7 shows the dependence exhibited by alkali metal concentrations on the humidity level during the weathering process. McPhail et al. recommend the use of SIMS to investigate diffusion of “replacement” ions into the glass surface.

Fig. 5. Severely crizzled 17th or 18th century Venetian white glass goblet (Courtesy: V.L. Oakley, V & A collection of glasses and ceramics).

Fig. 6. SIMS depth profile of metal ions from the surface of simulated Venetian glass: (a) as produced surface, (b) after weathering at 50 °C at 80% RH for 72 h. Severe leaching of Na and K is evident (Courtesy: D.S. McPhail, after [13]).

Fig. 7. Na profiles measured from different humidity levels for the same exposure. Alkali leaching shows a clear correlation with RH (Courtesy: D.S. McPhail, after [13]).
following chemical treatment, and have shown that mono-functional silane compounds can provide chemical protection at the glass surface with a single hydrophobic molecular layer. In this way, short-term aging (at least) can be arrested by a factor of 10 [12].

4.4. SIMS line scanning

In general, the use of SIMS on a cross-section seems to have much to recommend it. In many cases, the section may be polished, and the effects of surface roughness avoided. Moreover, if there is a layer structure which is conformal with the surface roughness (which may be confirmed using SEM on the section) a line scanning technique could be used to build up a statistically precise “depth” profile by post-acquisition shifting of the individual lines prior to summing the data down the line stack. The penalties of this approach are summarized largely by Fig. 2, but it is easy to relate the beam diameter to the consumed volume and see whether sufficient sensitivity can be combined with the required resolution. An example of SIMS line scanning in a different context is given by Stermer et al. [18] who used large amplitude linescans to correlate areas of dark staining on sections and surfaces of medieval human teeth with high levels of Mn absorbed from oxides in the soil at the burial site.

Fig. 8 shows the use of SIMS line scanning to obtain a “depth profile” of a very thick corrosion layer [21]. It would be impractical to depth profile such a layer conventionally.

4.5. Imaging of paints and pigments

One of the major advantages of SSIMS resides in its potential to characterize and image both inorganic and organic analytes, thereby representing one of the few methods of closing the traditional gap between the fields of organic and inorganic analytical chemistry. This capability has been demonstrated in work by Van der Weerd et al. [3], which focuses on the deterioration of lead pigmented paint layers. Small crater like holes or protrusions which are present across the entire surface of The Anatomy Lesson of Dr Nicolaes Tulp (Rembrandt van Rijn, 1632), have been the subject of many studies. In cross-section, the protrusions are seen as irregularly shaped areas consisting of whitish opaque and more transparent parts. A general characteristic is the difference in granulometry between the paint layer and the protruding mass. The original mineral matter of the paint seems to have disappeared – as if dissolved – leaving a transparent gel-like mass behind. Early hypotheses of their origin proposed that the craters were formed as a result of exposure to a fire in 1723, where heat caused organic particles to migrate in the not yet completely dry paint. An extended microscopic study by Van der Weerd, using UV–VIS, FTIR, SEM and SIMS, however points to chemical changes perhaps unrelated to fire damage. Finely divided, layered materials, seen under SEM, suggest that the precipitation of newly formed compounds has taken place. In most cases small red particles are present in or around the protrusion, which have been identified as Pb3O4. Imaging secondary ion mass spectrometry in positive and negative ion mode was performed using a 25 keV In+ primary ion beam. The surface of the sample was charge compensated with electron pulses in between the primary ion beam pulses. Results demonstrate high concentrations of stearic and palmitic acid (both fatty acids), lead and lead salts inside the protrusions showing that aggregation of lead soaps and ionomers is taking place (Fig. 9). Lead soaps are not introduced into the paint as such, but have developed as a result of the aging of lead white oil paint. Carboxylic acids derived from oil medium and lead ions, which become available.
due to the degradation or dissolution of lead containing materials, e.g. lead white or lead acetate. SIMS revealed also the presence of chlorine in the protrusions. The reason for its presence is somewhat unclear but the hypothesis is that it could be a normal contamination of 17th century lead white, because the production process is far from well defined [3]. Recent surveys have shown that the occurrence of protrusions is much more common than first thought and has been observed in paintings from the 15th through 20th century and seems to be a common defect in oil paintings [22].

4.6. The identification of pigments through speciation

The images also indicate the possibility of obtaining molecule specific information. SSIMS has emerged as a promising technique in this context [23]. Its potential advantage for obtaining molecule specific information lies primarily in the use of a low flux ion bombardment resulting in relatively high molecular ion yields, although the overall ion yield may be low. The latter problem can be resolved by using a mass analyzer with high transmission, such as a time-of-flight mass spectrometer, therefore obtaining a good sensitivity. In addition the use of polyatomic projectiles offers in principle significant potential to increase the molecular information in SSIMS. It has been demonstrated that bombardment of binary salts with polyatomic instead of atomic primary ions gives a substantial gain in the total ion current by a factor 4–10 depending on the analogue under study, hence resulting in a substantial increase in the molecular specificity of the mass spectra [24].

In a feasibility study by Van Ham et al. [25] the possibilities of TOF SSIMS were explored to characterize pure inorganic pigments used in paintings by means of molecular information. The main objective in the identification of pigments is to extract information about their historical origin for authenticity studies and possible need for restoration. The characterization of a pigment can require different levels of sophistication, ranging from the identification of its colour to its chemical formula. In the latter case one may need to obtain molecule specific information as some pigments contain the same elements but have a different chemical formula. Verdigris, a copper acetate ((CH₃COO)₂Cu·2Cu(OH)₂), was selected as one of the examples in the study. The pigment powder was pressed into a pellet and spectra were taken during 300 s with a raster of 300×300 µm² using a Ga⁺ primary ion beam. The mass spectra demonstrate clearly the acetate component of the pigment, herewith allowing to make a distinction with another commonly used green pigment, malachite, a copper carbonate (CuCO₃·Cu(OH)₂). In the positive ion mode (Fig. 10(a)), the CH₃⁺ signal is unusually intense and prevalent peaks refer to the monomeric and dimeric adducts. Interestingly, the detection of ions such as (CH₃COO)Cu·Cu⁺ refers to the presence of the Cu(I) form or its generation during the primary ion bombardment. The Cu(OH)₂ component of the pigment can be readily traced back by the signals Cu₂OH⁺ and Cu₂O·Cu⁺. The corresponding intensity is lower than for the acetate-related ions. The relative contribution of the oxide-related ions is rather limited. In the negative
ion mode, the Cu acetate component is detected as molecular ion and as adduct with acetate anions (Fig. 10(b)). The relative contribution of the oxide related ions is rather limited.

4.7. Ultra low energy SIMS

Surface analytical techniques are evolving rapidly, especially under pressure from the demands of modern materials science. For example, the requirement to analyze ultra-shallow ion implants and sharp multi-layer structures at the leading edge of semiconductor technology has lead to the development of SIMS instrumentation which can use focused ion beams with energies in the range 200 eV–1 keV routinely [26]. The potential of such instruments in archaeometry is, as yet, untested. Ultra low energy SIMS (uleSIMS) brings both nm, or even sub-nm depth resolution, and the capability to depth profile the top few nm of a sample (impossible at higher beam energies because of the transient width). An example of a possible application would be to use the technique to examine thin corrosion layers on surfaces, and observe their...

Fig. 10. Positive (a) and negative (b) ion mass spectra recorded from a pellet of verdigris using TOF SSIMS.
evolution over a timescale of hours, days or weeks without using artificial aging techniques. This, in turn, would allow the effectiveness of cleaning and unobtrusive reversible coating techniques to be evaluated, and the earliest stages of corrosion to be monitored.

At these low energies, special equipment is required to produce the high current density focused beams required for depth profiling. The work described here was carried out using an Atomika 4500 SIMS tool, equipped with floating low energy ion guns (FLIG™) designed for this purpose [27]. The instrument has already been used to characterize passivating oxides on NiCr and NiCrFe alloys [28]. The purpose of this study was to see if ulSIMS could detect early stages of oxidation on archaeological alloys with the ultimate objective of characterizing and testing passivation and unobtrusive protective measures.

Preliminary work was carried out on a tin bronze which is part of a set of reference materials (BCR-691) [29]. SIMS has been used to examine these samples previously [30]. In this experiment, a sample was polished and exposed to air to oxidise overnight.

The certified tin-bronze composition is shown in Table 1. Only the elements in bold are certified. The material was supplied as $35$ mm x $2$ mm

<table>
<thead>
<tr>
<th>Elements</th>
<th>Tin bronze</th>
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<tbody>
<tr>
<td>Cu</td>
<td>Main composition</td>
</tr>
<tr>
<td>Sn</td>
<td>$70 \pm 6$</td>
</tr>
<tr>
<td>Pb</td>
<td>$2.04 \pm 0.18$</td>
</tr>
<tr>
<td>As</td>
<td>$1.94 \pm 0.20$</td>
</tr>
<tr>
<td>Zn</td>
<td>$1.57 \pm 0.25$</td>
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Fig. 11. Optical micrograph of polished tin-bronze surface (45° tilt) taken in situ in the Atomika 4500 SIMS instrument. Scale bar is 300 $\mu$m in each direction.

Table 1: Certified values and uncertainties for the tin bronze of CRM 691 in $gkg^{-1}$ [29].

Fig. 12. SIMS depth profiles from a sample of archaeological tin bronze, polished and then exposed to atmosphere overnight. (a) Average positive ion profiles from 1 mm square area, (b) average negative ion profiles. Rise in metal clusters ion intensities shows oxide–metal interface. Overall eroded depth is estimated to be $\sim10$ nm.
thick discs. For SIMS analysis 7×7 mm rectangles were cut with a diamond saw. One of these was polished with P1000 SiC paper until no machining marks were visible under an optical microscope. The marks from the P1000 paper were then removed with 0.06 μm liquid silica polish (colloidal silica suspended in ethylene glycol, Kemet Ltd.). Although the resulting surface appeared shiny to the naked eye, the inhomogeneity of the material and resulting roughness is evident from the optical micrograph Fig. 11. Samples were ultrasonically cleaned in ultra propan-2-ol for 3 min prior to air exposure.

All SIMS data were acquired using the following conditions: beam energy 500 eV; scanned area 1×1 mm; primary beam (positive ions) 40 nA O$_2^+$, angle of incidence 0° to surface normal; primary beam (negative ions) 12.5 nA Cs$^+$, 50° to normal. Depth scales on the profiles were estimated from sputter yields in other materials for now.

Fig. 12 shows positive (a) and negative (b) ion profiles from a relatively large area – 1 mm square.

Fig. 13. (a) Mn$^+$ image showing manganese-rich grains in the sample surface. (b) Positive ion profile from one of the grains (labelled “+” in the image) compared to the average profile from the whole area. (c) Negative ion profile from grain labelled “–”, similarly compared.
These will be averaged over many different grains. However, reducing the acquisition (gated) area made no difference to the main features of the profile, indicating fairly similar surface chemistry on each grain. The positive ion signals show surface enhancement (except for Mn) typical of oxidation. Other SIMS measurements showed that Na was present as a surface contaminant. The relative behaviour of Cu and Mn suggests that Cu is enriched on the surface, and this was observed, especially on Mn-rich grains. The negative ion signals show a rise in metal and inter-metal cluster ions (Cu$_7^+$ and SnCu$^-$) shortly before a fall in oxygen containing species suggesting that such ions might be used to determine the position of the oxide–metal interface.

The grain structure of the material is sufficiently coarse that it is possible to extract individual profiles from grains of differing composition using the checker-board gating feature of the instrument. Fig 13(a) shows the Mn image from a 1 mm square area, and Figs. 13(b) and (c) respectively show some channels from positive and negative ion profiles from Mn-rich grains compared with the surface average. The Mn$^+$ signal is more than an order of magnitude higher from the Mn-rich areas, and there is also an increase in the Sn$^+$ signal. The Cu$^+$ signal is again indicative of surface enrichment, but in the presence of surface oxide, this is inconclusive. However, the Cu$_7^+$ signal is also relatively enhanced at the surface, compared to the average level — probably confirming Cu enrichment over the Mn-rich grains. This may be an effect of the polishing, especially if the Mn containing regions are harder and have become coated with Cu transported from softer regions.

Much further work is required to interpret and compare such data, but it is clear that the effect of a few hours oxidation under unaccelerated conditions is easy to observe with the uleSIMS.

5. Conclusions

If high sensitivity, molecular specificity, or spatially resolved chemical information is required from a vacuum compatible sample, then the use of dynamic or static SIMS should be considered. SIMS measurements are most useful when there are different examples of the same sample to examine, especially if there is a natural or artificial process which has been applied to the sample in different degrees. It is even better if there are reference materials available – not just because quantification can be attempted, but also for instrumental setting-up, and checking for artefacts.

One area not touched on here is the use of SIMS for isotope ratio measurements. Isotope ratios may give important clues as to provenance, and may also be used for dating. SIMS is perhaps the only technique which can measure isotope ratios accurately from a few cubic microns of material, and indeed from adjacent grains/phases in the same sample.

SIMS (like many other analytical techniques) has only been characterized in detail on a small number of sample types. Characterizing the technique (optimum experimental conditions, erosion rates, ion yields, surface behaviour, uniformity of sputtering, effects of roughness, effects of ion beam induced surface topography, determining which matrix channels to use etc.) must be done, at least in part, for every new sample type attempted.

Having discussed the capabilities and limitations of SIMS and its role in the cultural heritage field, it should be kept in mind that in general hardly any applied analysis depends on the application of a single analysis tool. Very often it is by using a wide range of techniques and exploiting the synergy of complimentary data that complex problems can be solved.

References