An edited version of this article appeared in International Laboratory News October 2003

Surface Mass Spectrometry – for the Masses!

by Dr John Eccles Commercial Director, Millbrook Instruments Limited

The bulk composition of liquids, gases and solids is routinely analysed by mass spectrometry. But what happens when the analysis needs to establish the identity of contaminant present only on the surface? Or when there is a need to analyse a surface coating of nanoscale thickness without interference from the substrate?

One option is to swab or dissolve the surface to take the material into solution for subsequent analysis. As well as the inconvenience of this method, and the potential it brings for cross-contamination of the small quantities involved, any spatial information about the distribution of the material is lost. However, knowing the shape of a contaminated area could have yielded vital clues to its origin. As a simple example, the evaporation of droplets of liquid would lead to circular residues, but linear boundaries would suggest a shadowing or masking of the surface during contamination. Removing material for *ex situ* analysis also does not distinguish between particulate contamination and the same amount of material present as a continuous layer, yet the surface properties would be entirely different in the two cases.

As well as saving time in sample preparation, it would be far more effective to perform an *in situ* localized mass spectrometric analysis directly on the surface itself. The technology to do this does exist, and is known as Secondary Ion Mass Spectrometry or SIMS. In a SIMS analysis, the surface is bombarded by high-energy ions (known as the "primary" ions) that initiate collision cascades among the surface atoms [Figure 1]. As a result, some atoms and clusters of atoms are ejected from the surface. Some of these atomic fragments are ionized (the "secondary" ions), and these can be collected and identified by mass spectrometry. Although the primary ion penetrates to a depth of several nanometres below the surface, ions are only emitted from the first 2-3 atomic layers of the sample, which gives the SIMS technique its high surface specificity.

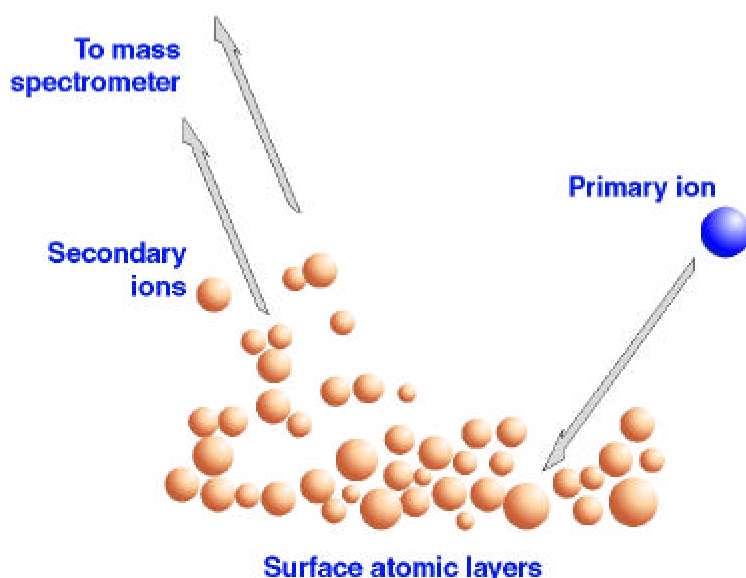


Figure 1 In the SIMS process, a surface is bombarded with high energy ions. This produces secondary ions, characteristic of the surface atomic layers, which are identified by mass spectrometry.

The real power of the SIMS technique comes with the refinement of focusing the primary ion beam to allow localized analysis. Raster scanning of the focused beam means that a full image of the surface can be built up a point at a time. The high sensitivity of SIMS, and the excellent signal to noise characteristics of the data makes this a very fast process, and image times are typically

measured in seconds rather than minutes. With a focused beam, it is also possible to control the current density of the primary beam on the surface. Using a low current density removes the minimum amount of material necessary for analysis, typically less than 1% of the original surface layer. A higher current density will result in the deliberate erosion of the sample, allowing an investigation of what lies below the original surface. This means it is straightforward to assess whether a species is present as a superficial contaminant or integrated into the surface itself. In the former case, the contaminant spectrum will soon disappear under the etching action, but in the latter case it will persist or even increase in intensity during etching. More sophisticated analysis means it is possible to etch well-defined craters to monitor changes in the sub-surface composition with depth, or to profile through thin films and coatings to establish their thickness.

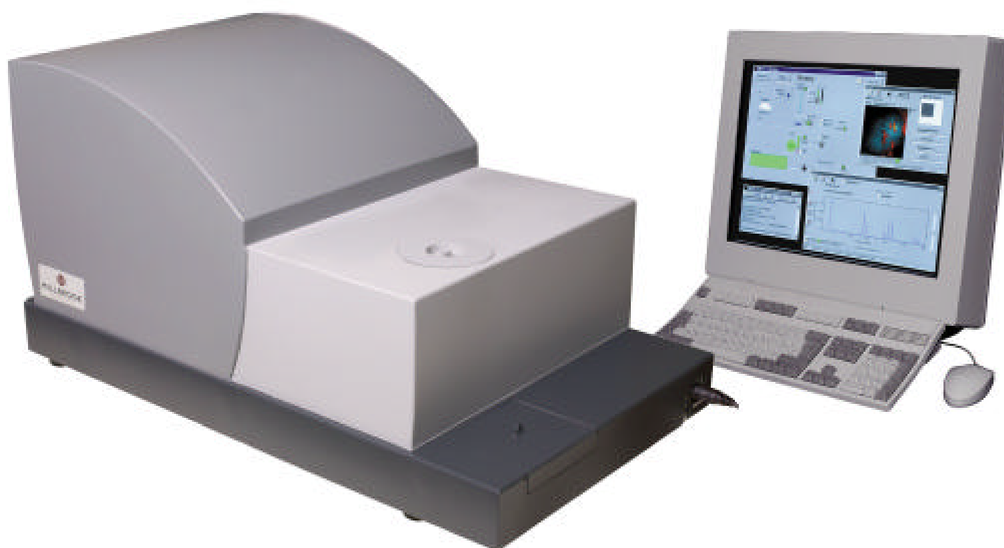


Figure 2 An example of a low-cost, automated desktop surface analysis instrument – the MiniSIMS from Millbrook Instruments.

It can be seen that SIMS is a fast and direct analysis technique. The information it generates is of growing relevance as surface modification and thin film coatings are increasingly used to impart specific functionality to a surface. However, the installed base of SIMS instruments around the world is still relatively low, mainly because of the high costs traditionally associated with the technique. An on-site SIMS analysis capability used to mean a substantial investment in terms of the capital cost of the instrumentation. The costs of the supporting service facilities and maintenance, together with the salaries of experienced personnel required for its operation, meant that ongoing costs were correspondingly high. Overall, the high analysis cost per sample made SIMS uneconomic as a routine analysis technique for all but the highest value products and processes. Fortunately, recent years have seen the development of low-cost instrumentation such as the MiniSIMS developed by Millbrook Instruments [Figure 2]. Operation is straightforward via a Windows™ interface, with the dedicated computer also monitoring instrument performance. This type of instrumentation is designed to allow high throughput analysis by less experienced operators. It is sufficiently compact to be treated as a mobile instrument, and one that can be operated remotely via a modem link. This is very useful where the need for analysis is shared by several locations within a company.

This type of desktop instrumentation harnesses the power of the SIMS technique in a form and at a price that allows its widespread use. Not surprisingly, it does not offer the same ultimate performance specification or flexibility in analysis as the much more expensive conventional SIMS

systems. Instead, by reducing the cost of a SIMS analysis by up to 90%, the instrument makes it cost-effective to generate SIMS data in a wide range of situations, providing information about materials that would be difficult or impossible to obtain by other analysis techniques. An example of a typical analysis performed using this type of desktop SIMS instrument will illustrate both its strengths and its versatility. The material in question was a magnesium alloy, which had been coated with a molybdenum-based coating of 0.2 μm in thickness.

Initially, a SIMS analysis of the extreme surface of the material was performed using a large (3 mm diameter) defocused primary ion beam and the minimum analysis time needed to obtain a spectrum. The information depth under these conditions is of the order of 1 nm, with less than 1% of the surface layer removed during the analysis. The positive secondary ion spectrum [Figure 3a] shows no clear evidence for molybdenum as would have been expected from the coating. Instead, the spectrum shows two clear peaks at m/z = 73 and 147. These ions $(CH_3)_3Si^+$ and $(CH_3)_3SiOSi(CH_3)_2^+$ are characteristic of the common contaminant polydimethylsiloxane (PDMS). This spectrum illustrates the value of a mass spectrometric technique, which does not simply detect the element silicon, but identifies that this is present as a silicon-based polymer. The fragment ions contain information about the polymer end-group and repeat unit, and similar but distinct spectra are obtained from different members of the siloxane family [see Reference for further details].

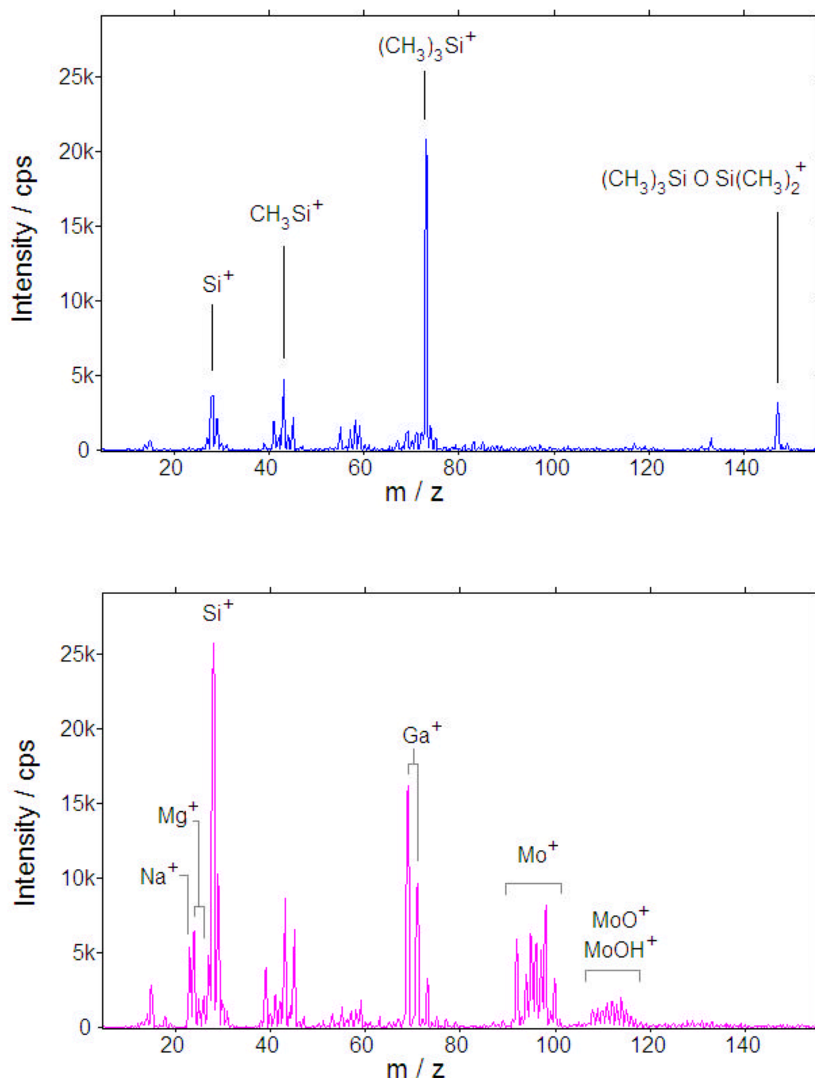


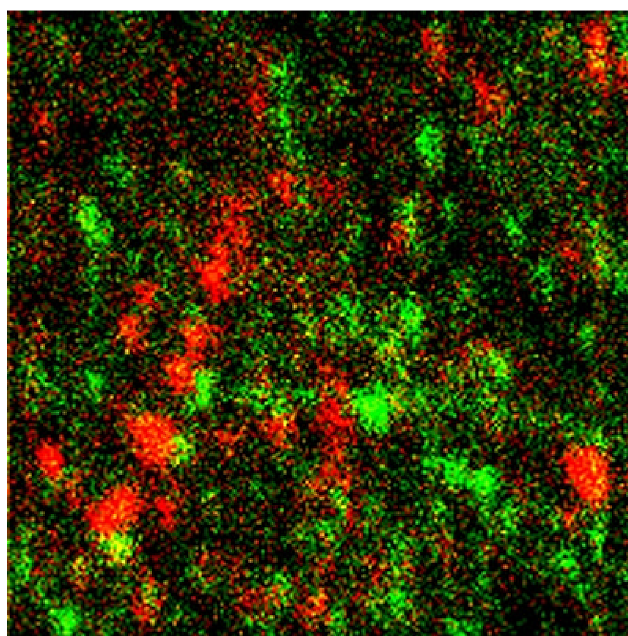
Figure 3 The positive SIMS spectrum acquired from (a) the original surface and (b) the surface after a short period of etching. This demonstrates that the as-received surface is contaminated with a thin, continuous layer of polydimethylsiloxane. Each spectrum was acquired in less than 30 seconds.

The continuity of the siloxane contaminant at a millimetre scale was demonstrated by images (not shown) of the distribution of the characteristic ions identified above. The superficial nature of the

siloxane was proved by its rapid disappearance under continuing primary ion bombardment of the surface due to the etching action of the ion beam. The initial spectrum shown in Figure 3a therefore also illustrates the surface specificity of the SIMS analysis, a thin siloxane contaminant layer being sufficient to obscure the material underneath. Other techniques, for example Energy Dispersive X-Ray analysis (EDX or EDS), have a much greater information depth and so the surface layer contributes only a tiny amount to the resulting spectrum. The presence of a siloxane layer like this might therefore go undetected, yet a surface coverage as low as 10% would be sufficient to seriously degrade the strength of an adhesive bond to the surface.

The spectrum that emerges after a short period of etching shows the characteristic isotope pattern of molybdenum [Figure 3b] (the gallium comes from implantation and re-sputtering of the incident primary ions, in this case 6 keV Ga^+). The spectrum also shows silicon (at least in part residual silicon from the siloxane) and sodium, another common contaminant. Unexpectedly, the spectrum also shows magnesium. An image [Figure 4] of the sodium shows this is present as a patchy distribution. An image [also Figure 4] of the magnesium distribution in the same area also shows a patchy distribution, but it can be seen this is not coincident with the sodium.

Figure 4 SIMS images of a 1 mm x 1 mm area of the etched surface, showing the lateral distribution of sodium (Na+ in red) and magnesium (Mg+ in green) contamination. Each image was acauired in 15 seconds.



The obvious explanation for the magnesium distribution would be that the molybdenum coating is not continuous so that the magnesium alloy substrate is visible through the defect areas of the coating. An alternative explanation is that additional magnesium is present as a contaminant on top of the molybdenum coating. Again, it is obvious that the resultant properties of the coating would be very different in the two situations. The way to resolve this ambiguity is to employ the third mode of analysis, depth profiling. This involves controlled etching of a small area over one of the magnesium patches whilst continually monitoring the intensity of selected ions [Figure 5] arising from the base of the crater as it advances into the material. The period during etching through the molybdenum-based coating is indicated by the Mo^+ ion intensity remaining high, and the intensity of the Mg^+ ion is zero during this period. At the expected time, the coating-substrate interface is reached, causing the Mo^+ intensity to fall and the Mg^+ signal to rise steeply. This profile analysis proves that the magnesium visible at the surface of the material is a further surface contaminant rather than a discontinuity in the coating.

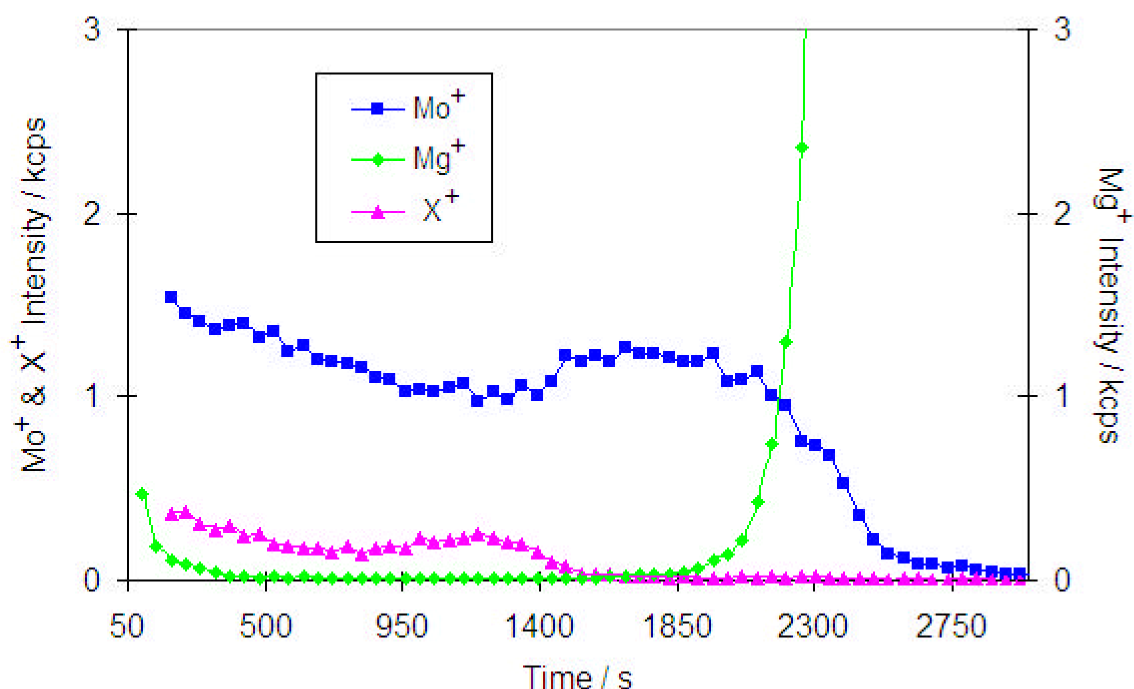


Figure 5 The SIMS depth profile acquired by continuous etching through the 0.2 μm molybdenum-based coating to the interface with the magnesium alloy substrate. The identity of the other major component [labelled X] of the coating has been withheld for reasons of customer confidentiality.

In the above example, the three-dimensional analysis capability of the MiniSIMS led to a very detailed picture of the identity and distribution of the contamination, vital information to help establish its origin. In addition, the analysis gave important information about the composition and thickness of the surface coating itself. For the monitoring of product quality against known standards, correct design of the analysis protocol would mean this information is sufficient in itself. In other situations, a SIMS analysis could be complemented by analysis using other techniques, building up the complete picture of the sample from several viewpoints. In either case, the availability of cost-effective desktop instrumentation such as the MiniSIMS makes analysis of the true surface much more accessible in a much wider range of application areas.

Reference

Spectral Differences and their Interpretation for the Identification of Common Polymers
A.J. Eccles, T.A. Steele & D. Briggs
Proceedings SIMS XII, Eds. A. Benninghoven et al., Elsevier Amsterdam 2000 p. 781

About the Author

Dr John Eccles has over 20 years experience in the chemical characterisation of surfaces. After a Natural Sciences (Chemistry) degree at Cambridge, he went on to a PhD in secondary ion mass spectrometry (SIMS) with John Vickerman's group at UMIST. From here he worked in the UK scientific instrument industry as SIMS product manager, and completed a part-time MBA to broaden his commercial skills. In 1995, he was one of the co-founders of Millbrook Instruments Limited. Millbrook was set up with the specific goal of designing and producing an inexpensive and easy to use surface analysis instrument. This desktop instrument - the MiniSIMS - has won several major awards in both Europe and the USA for its innovative design. It has succeeded in making surface analytical techniques accessible and affordable to a much wider user base.