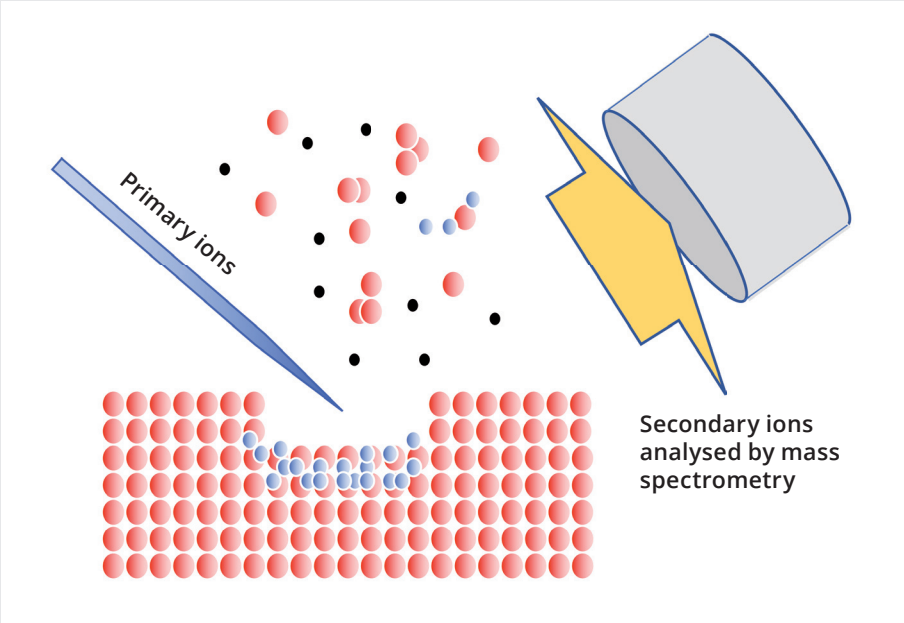
HIDEN ANALYTICAL

SIMS Applications

INTRODUCTION
SIMS Applications

Secondary Ion Mass Spectrometry (SIMS) is an analytical technique where the specimen surface is bombarded by a stream of high energy ions causing sputtering of the surface. The resultant secondary ions are analysed by a mass spectrometer.

This provides highly sensitive compositional analysis with extremely good depth resolution and mass resolved imaging.



Compact SIMS

STATIC SIMS

The most surface sensitive analysis is termed static SIMS. Under conditions where the total dose of ions is under 10^{12} per square cm, only the top monolayer is sputtered. The high surface specificity makes it applicable to measuring contamination and surface chemistry. Static SIMS can readily solve problems associated with adhesion failure, cleaning and surface preparation.

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12. **Battery research** – detection of lithium using SIMS on FIB microscope

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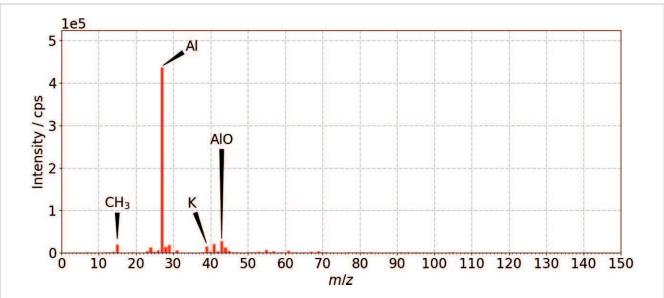
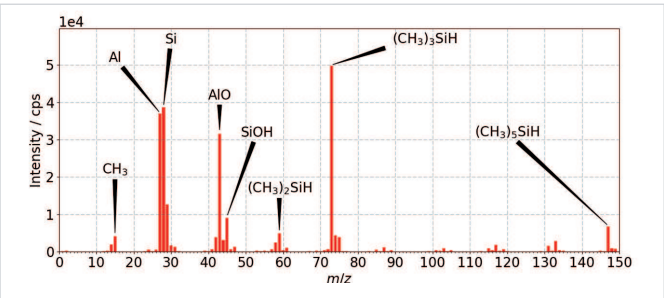
Contamination with silicone

Polydimethylsiloxane (PDMS) is inert, non-toxic and non-flammable and used extensively as a lubricant, in cosmetics, as a food additive [E900] and in sealants. However, it can break down to silicon dioxide (glass) and form an insulating layer in electronics as well as forming a barrier to adhesion when bonding surfaces – it is also difficult to remove. SIMS can easily detect monolayer quantities of this important industrial contaminant.

The positive secondary ion spectra below are from an aluminium foil before and after contact with a protective glove. A residue of PDMS from the glove manufacture has transferred to the foil and is clearly visible from the characteristic silicone peaks at m/z = 59, 73 and 147. The aluminium signal itself at m/z=27 is also significantly attenuated by the coverage of contaminant.



Positive ion Static SIMS of clean aluminium foil before touching with contaminated glove



Positive Static SIMS of aluminium foil after contact with contaminated glove

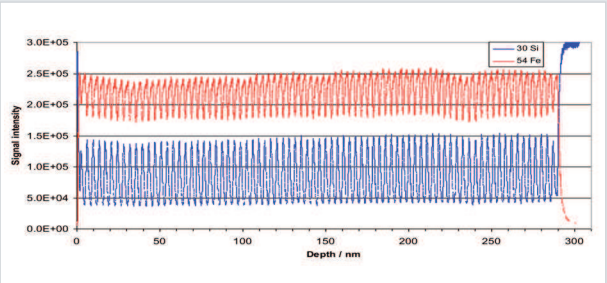
DYNAMIC SIMS

DEPTH PROFILING

When the ion dose exceeds the static SIMS limit (>10^{12} ions cm^{-2}) there is sufficient sputtering to uncover deeper layers of the material. This allows the composition to be determined as a function of depth. SIMS depth profiles are most often used to verify layer deposition and investigate diffusion or the effects of surface chemistry, such as corrosion. The extreme sensitivity and excellent depth resolution of SIMS made the analysis of dopant profiles in semiconductors a natural early application of the technique. These pure materials formed the groundwork for robust quantification and today SIMS finds application across a broad range of industries.

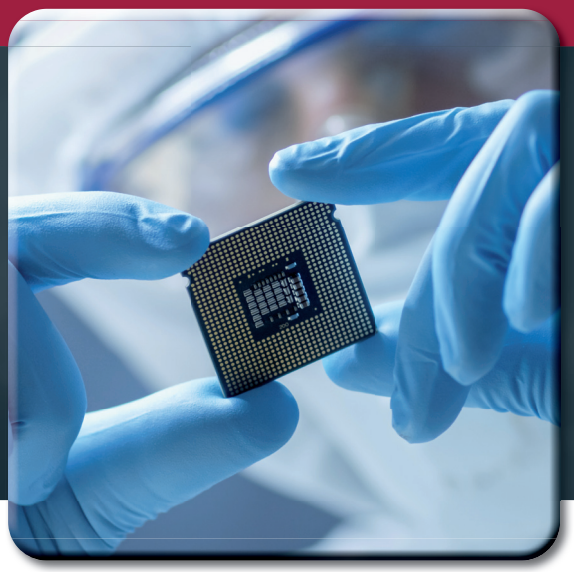
DEPTH RESOLUTION

In the static SIMS case the depth resolution is the uppermost atomic monolayers. In dynamic SIMS, the depth resolution is improved by reducing the impact energy, and therefore the penetration and mixing caused by the bombarding ions such that nanometre features can be resolved.



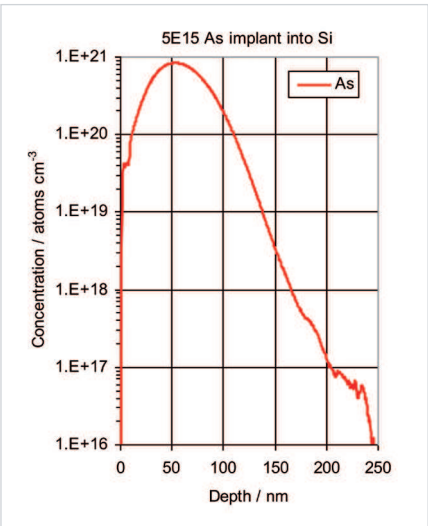
Positive ion SIMS depth profile of a Si/Fe neutron mirror comprising 80 pairs of silicon and iron layers, each layer 1.8nm thick. Analysed using 1.5 keV O_2+ primary ions with oxygen flooding.

Electronic materials

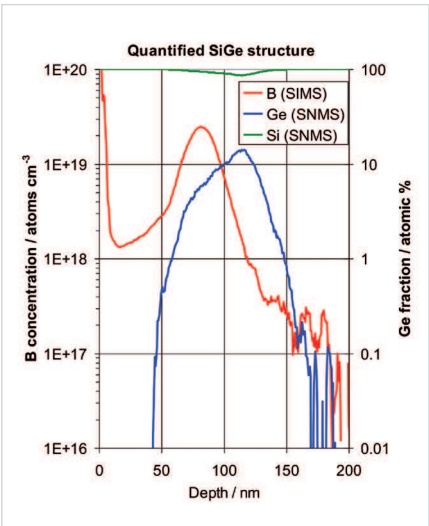


Ion implantation and diffusion is used to deliver dopants into semiconductors, SIMS accurately measures the dopant concentration for process development and monitoring.

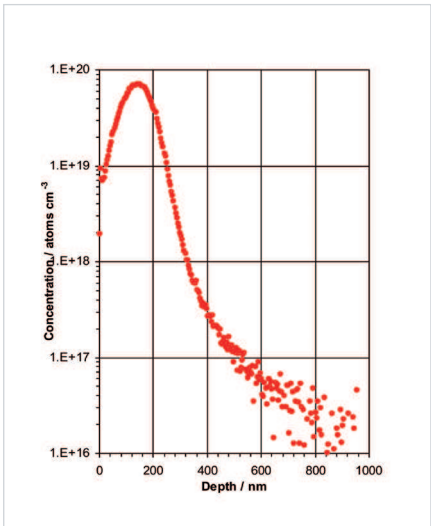
The examples below show quantified depth profiles in silicon substrates



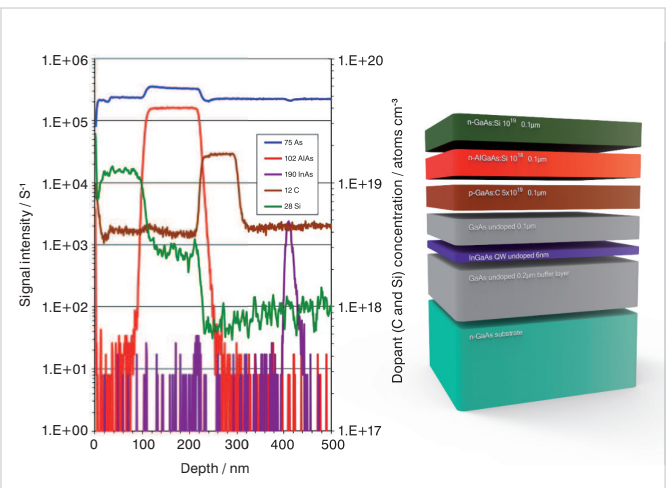
Arsenic ion implant in silicon
Cs+ primary ions negative secondary ions



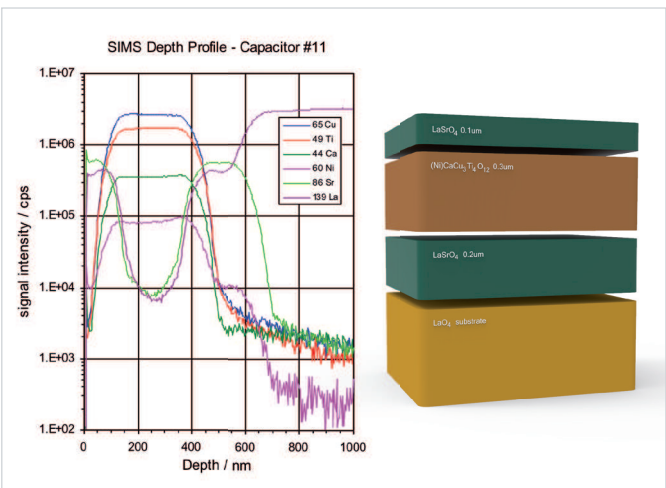
CVD grown SiGe layer structure
O_2+ primary ions positive secondary ions



Boron ion implant in silicon
O_2+ primary ions positive secondary ions

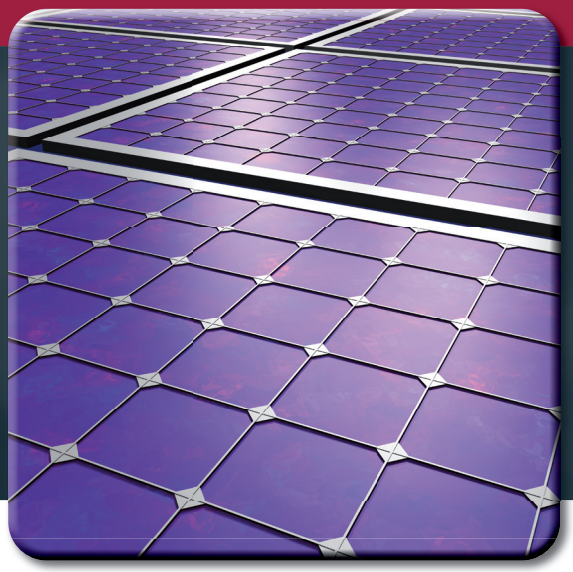


III-V MBE grown quantum well structure analysed using Cs+ primary ions.



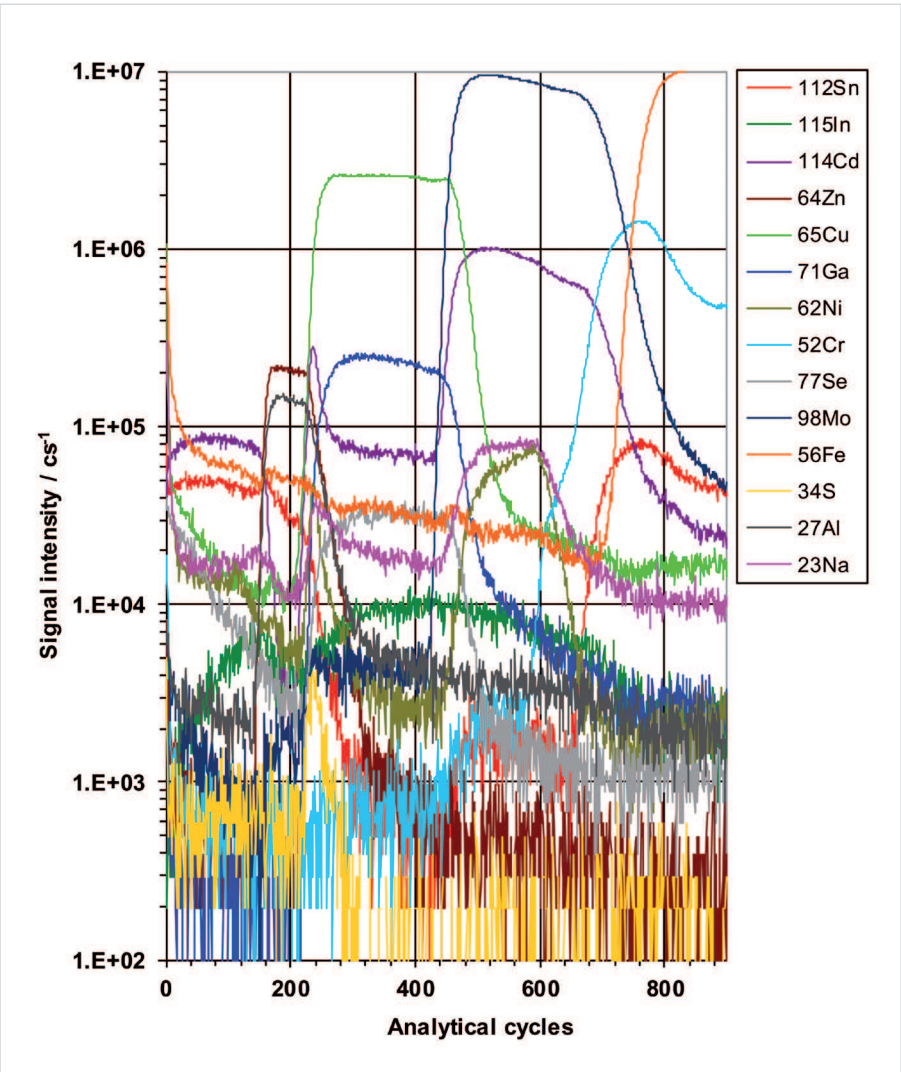
High dielectric strength capacitor structure

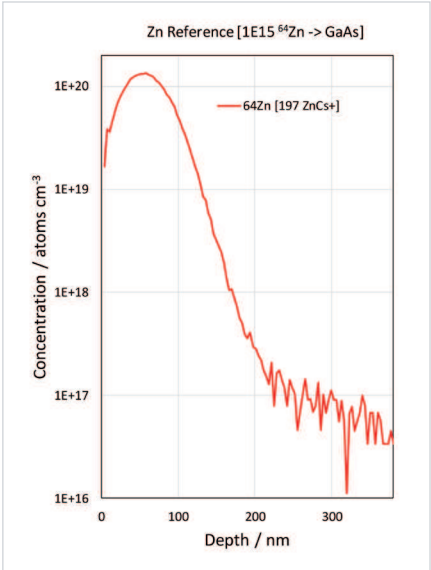
Flexible solar cell



Depth profile through a Copper Indium Gallium Selenide (CIGS) solar cell showing high dynamic range and good depth resolution.

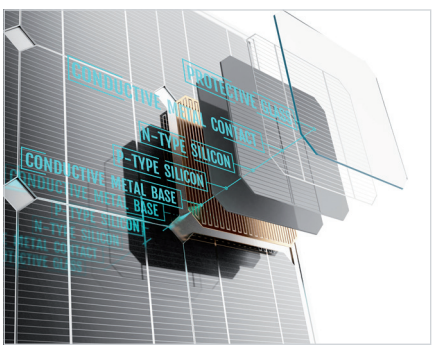
The depth scale is left as analytical cycles, showing that high data density can be achieved even when a large number of elements are detected. The overall depth is around 4 microns.



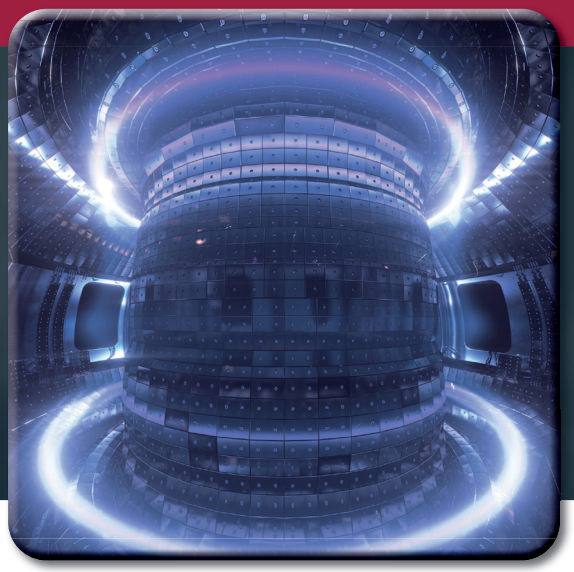


Zinc in GaAs

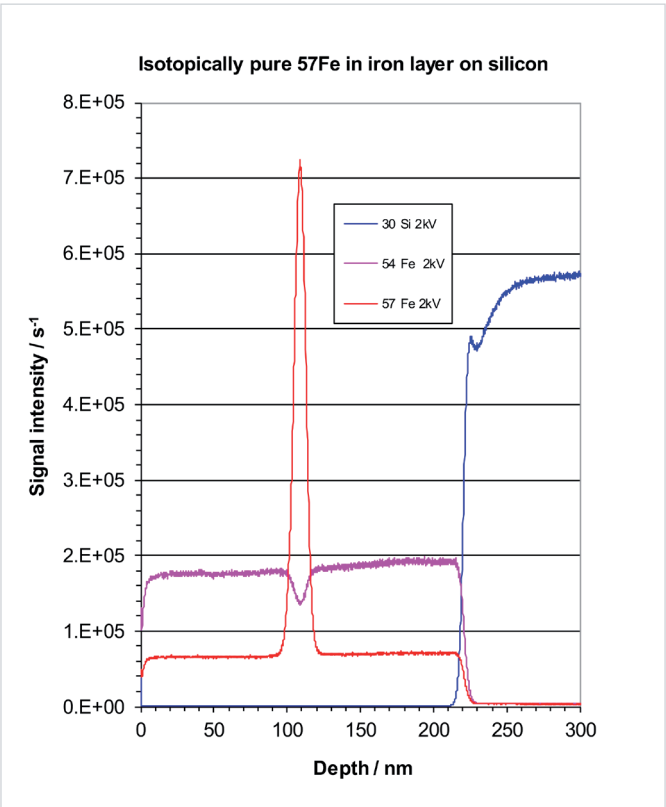
Using caesium primary ions, the species of interest is measured as a molecule together with a Cs+ ion. For some elements, such as Zn, the ion ZnCs+ is actually more sensitive than detecting either Zn+ or Zn- ions.

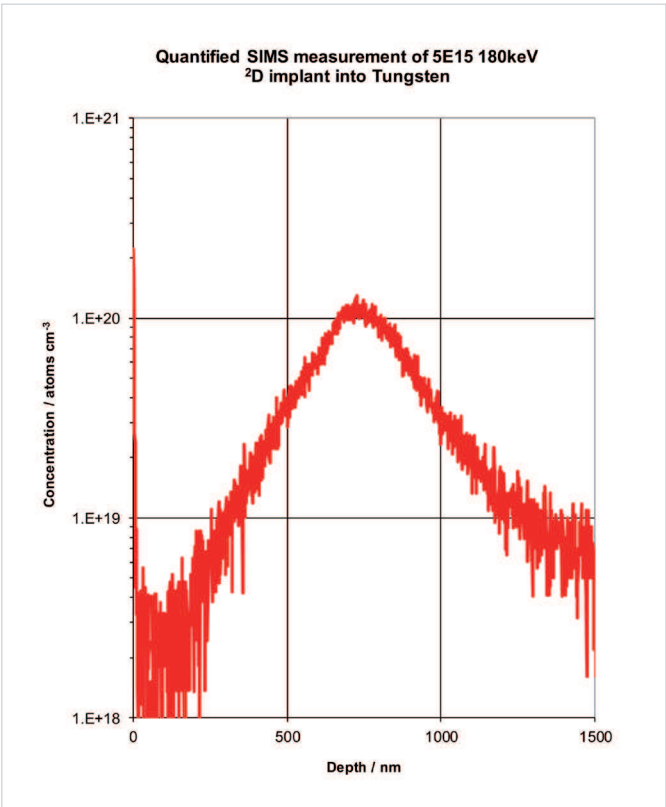


Isotopically labelled material



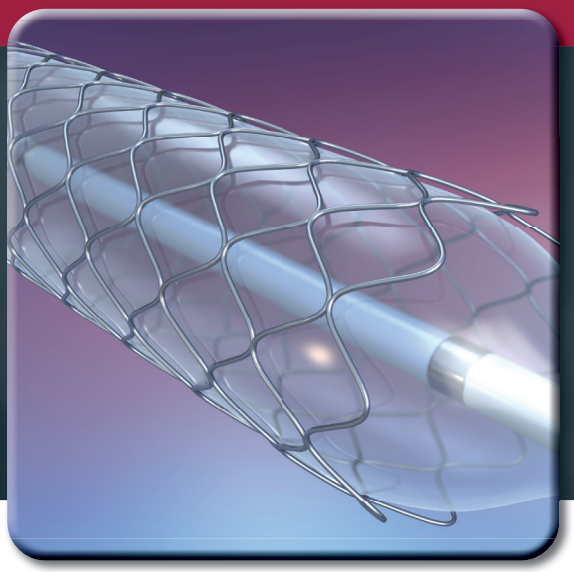
Being a mass spectrometry technique, SIMS can determine the isotopic composition of a material. This is particularly useful when investigating diffusion within layers. Here a very sharp isotopically pure ^{54}Fe layer is clearly defined with excellent depth resolution, grown within a thicker layer of natural isotopic abundance.





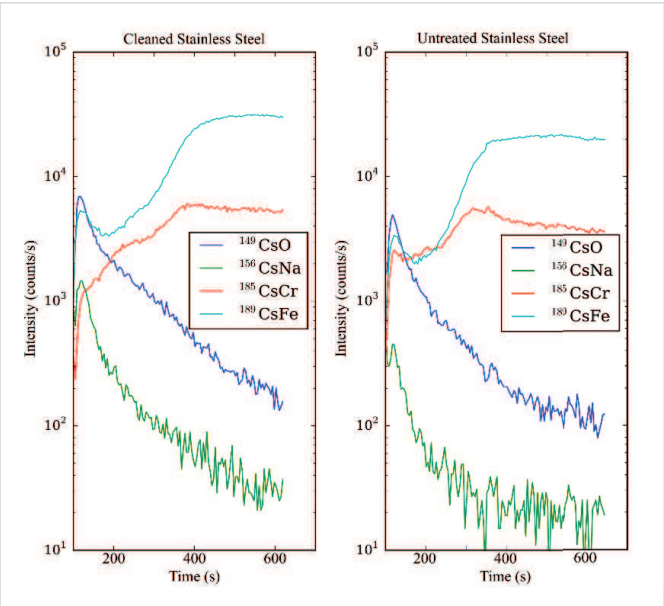
Nuclear fusion produces very high energy protons which implant in the reactor walls. Here SIMS has been used to detect deuterium implanted into tungsten as a simulation for the material effects in a fusion reactor wall.

Surgical stent



Stents are wireframe scaffolds, typically laser cut from stainless steel, use to hold narrowed arteries open. Inserted via a catheter, the mesh is placed in the narrow area and expanded using a small balloon which is then withdrawn.

Surface condition of the stent is very important and SIMS can be used to examine the nanometre thick protective chromium dioxide layer which naturally forms on the material. The depth profiles below show how treating with a chlorine based disinfecting product leaves the surface iron rich and open to corrosion, potentially causing failure or tissue damage.



LIMIT OF DETECTION

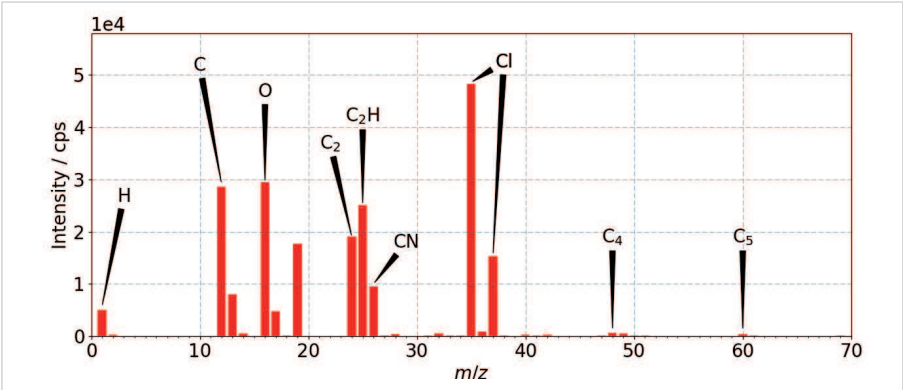
SIMS is the surface analysis technique with the best limit of detection (LOD), often providing ppm and even ppb measurement. If no interfering signals are present, the actual limit of detection depends on the ionisation probability of the sought species, the transmission of the instrument and the analyte volume. Thus, as first two parameters are fixed, if the volume is very small, there will be insufficient atoms present for detection. By collecting the data as images, the pixel sizes can be summed laterally or over a number of cycles to effectively increase the analyte volume and improve the LOD. This means that lateral and depth resolutions can be mutually traded to optimise an analysis for the most desirable parameter

SIMS Workstation

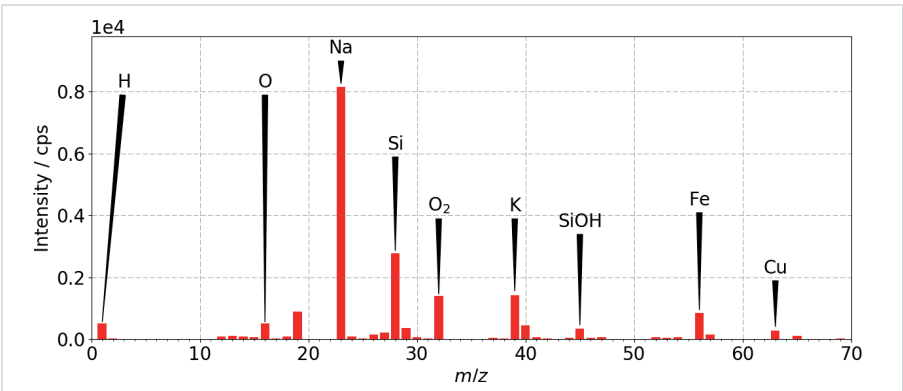
Stents may be coated with polymer layers for protection or to elute drugs into the region to prevent future blockage. Static SIMS can detect and characterise this layer.

ION BEAM POLARITY AND CHEMISTRY

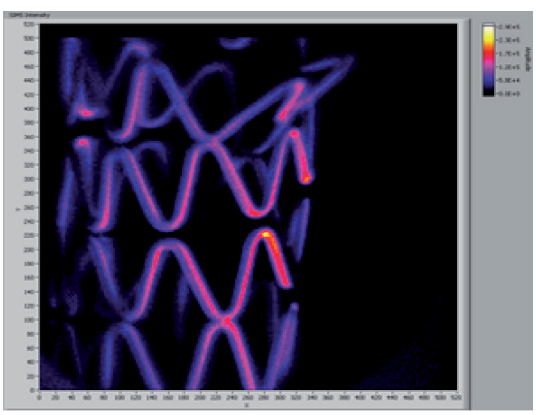
The secondary ions emitted from the specimen usually have a favoured polarity. For instance, alkali metals are emitted as positive ions and halogens as negative. The probability of ion formation is also enhanced by using oxygen for electropositive elements and caesium for electronegative elements. In addition, caesium can be used in the CsM+ mode, where the element of interest, M, is detected as a molecule with Cs. The CsM+ mode is an excellent means of detecting and quantifying metal oxides and other materials where both electropositive and electronegative elements are sought.



The negative secondary ion spectrum shows the hydrocarbon coating with Cl present.



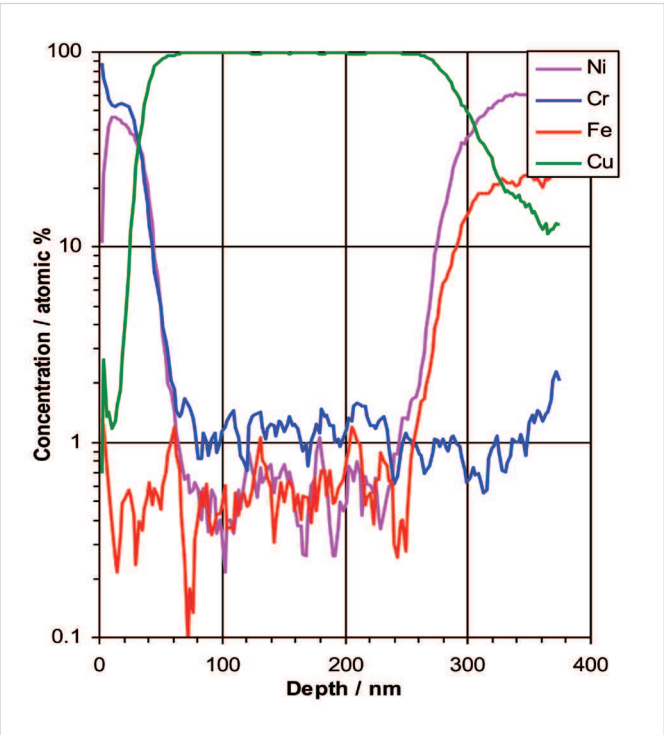
Positive secondary ion spectrum from coated stent showing very small amounts of Fe and some Si present.

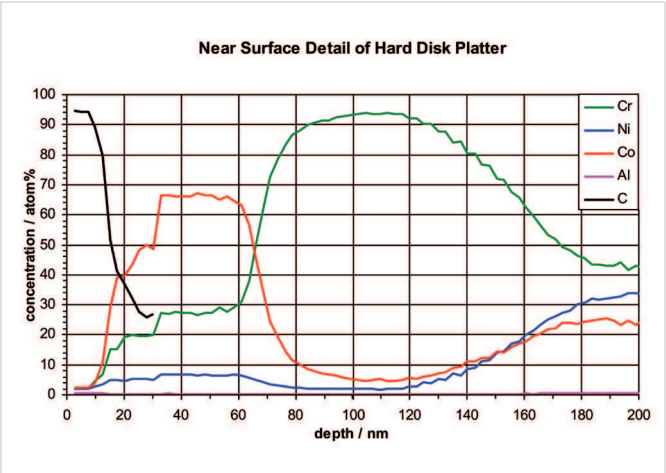


Negative secondary ion image of the coated stent displays a very uniform polymer layer.

SNMS of magnetic storage materials

SNMS provides excellent depth resolution and quantification to analyse the layer structure of the hard disc head material (left) and the active region of the platter surface itself (right).





SPUTTERED NEUTRAL MASS SPECTROMETRY SNMS

Sputtered Neutral mass Spectrometry separates the ionisation event from the sputtering and thus overcomes the matrix effect which makes high concentration quantification difficult in conventional SIMS analysis.

The MAXIM spectrometer uses a high efficiency electron impact ioniser to detect the sputtered neutral flux after secondary ions have been removed by means of an external deflector.

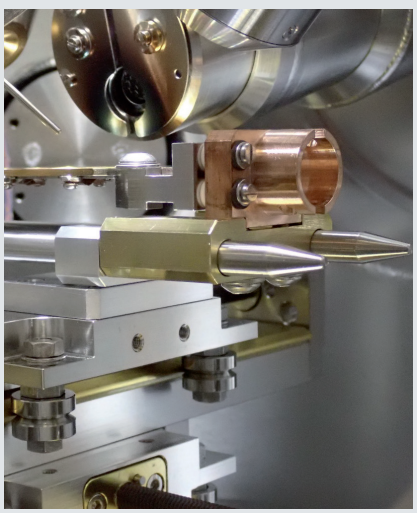
With no significant matrix effect there is no need for matrix matched reference materials, as is the case with SIMS, and easily available alloys may be used to determine global sensitivity factors.

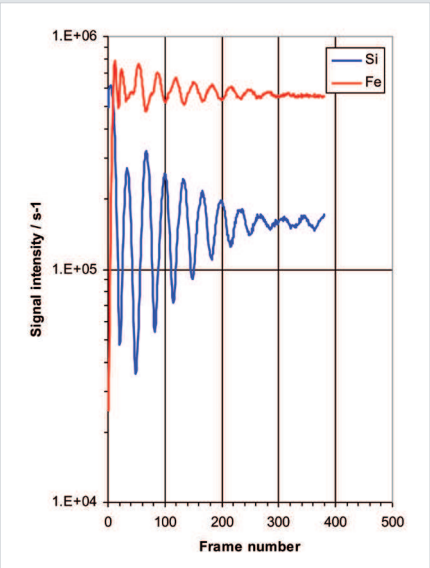
OXYGEN FLOOD

Low energy beams give improved depth resolution but can also induce surface topography. A directional jet of pure oxygen is provided over the sample surface, fully oxidising the surface via a stainless steel capillary.

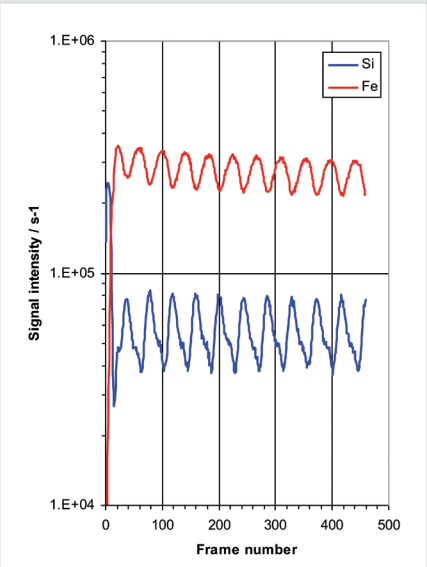
The gives enhancements in sensitivity for the analysis of electropositive species such as metals and semiconductor dopants, as well as reductions in surface roughness in low beam energy, high depth resolution analyses.

The examples show the improvements in surface topography given by the use of the localised oxygen flood in a 3.6 nm multilayer Si/Fe sample.





Without oxygen flood depth resolution decays.

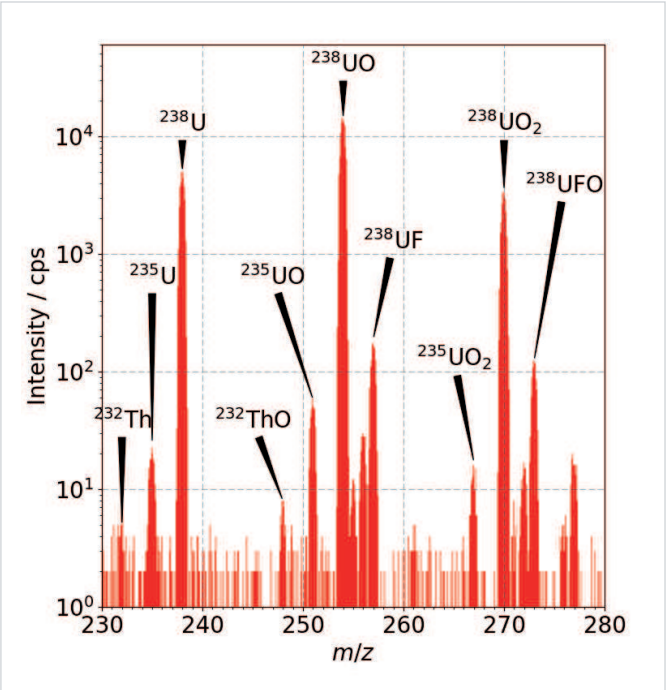


With oxygen flood depth resolution is maintained.

Nuclear materials

The isotopic sensitivity, and ability to analyse small particles, makes SIMS the ideal technique for the study of nuclear materials.

The spectrum below was measured from a uranium containing glass (under 1% wt.) using a 5keV oxygen primary ion beam and 500eV electron beam charge compensation. The ^{235}U fraction is determined to be 0.55 ±0.02%; less than the 0.72% abundance expected from natural material.



QUANTIFICATION

DEPTH

SIMS depth profile data is collected as a function of sputter time which comprises the time taken for individual raster scanned frames and the number of frames in an analytical cycle. The most usual way to calibrate the depth scale is to measure the depth of the crater at the end of analysis (either using a surface profilometer or optical technique) and assume a constant sputter rate. In heterogeneous materials, different sputter rates can be applied for each component.

CONCENTRATION

The intensity scale is converted to concentration by comparison to a reference sample whose composition is well known. This can be a specially prepared material or a previously measured sample. It is even possible to use SNMS (built into many Hiden SIMS spectrometers) to calibrate in the high concentration region which can then be used to quantify low level impurities in SIMS.

DIRECT COMPARISON

In many cases it is unnecessary to fully quantify a measurement, instead the depth profiles can be directly compared to observe differences. This approach can work extremely well detecting changes from the norm in a production environment.

IMAGING

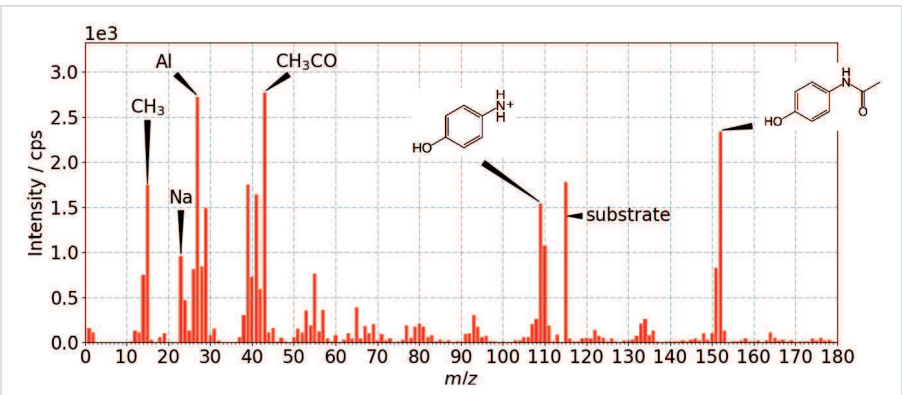
As the primary ion beam is scanned across the sample in a raster pattern, secondary ions are collected as a function of position allowing a mass resolved image to be produced at every cycle within a depth profile, so imaging is actually the primary method of data collection.

The lateral resolution of an image depends on the primary ion beam spot size, the ultimate being when a SIMS detector is mounted on a focussed ion beam microscope (FIB) when resolutions of 10s of nm are possible.

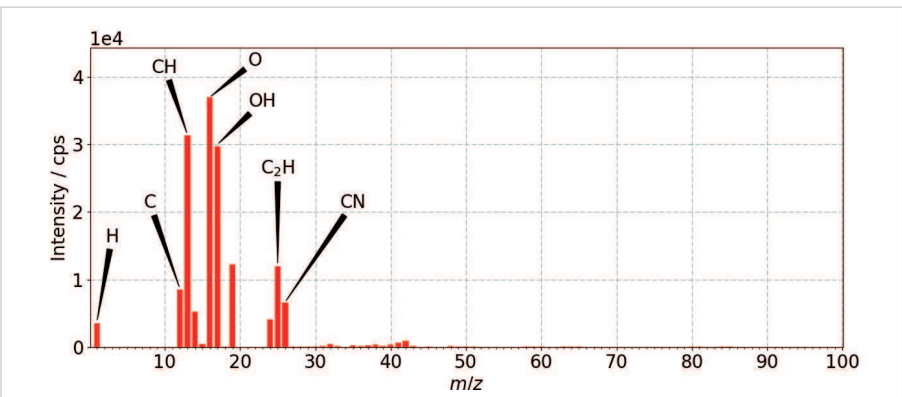
Pharmaceuticals

SIMS can be used to confirm the presence of a drug or to make brand identification where different formulations exist; a branded product may contain additional substances or a counterfeit product could show contamination.

The presence of binding, dehydrating or filling agents can also provide a unique fingerprint. In the example below, Al and Na come from the pill forming material. The high sensitivity of the analyser allows very low beam currents to be employed, keeping below the static SIMS limit preserves the high mass fragments required for unequivocal identification.



Positive secondary ion mass spectrum from generic paracetamol deposited on indium substrate.



Negative secondary ion mass spectrum.

POWDER ANALYSIS

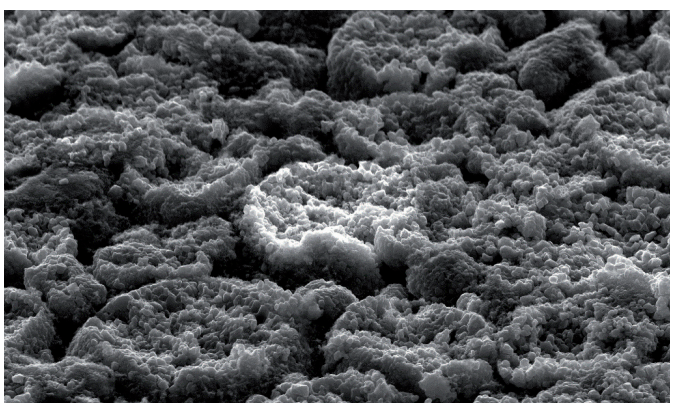
Powders may be analysed using SIMS, both for bulk composition and core-shell structure. Powders can be mounted using either conductive adhesive tape, dispersion, pill formation or pressing into indium sheet.

Battery research

The EQS spectrometer provides SIMS detection for focused ion beam (FIB) microscopes, with excellent sensitivity for light elements (sub ppm sensitivity for lithium).

Additionally, isotopically pure materials can be used for diffusion studies.

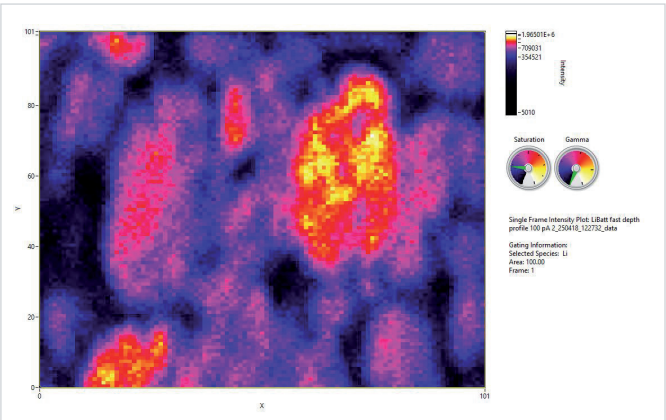
Hiden EQS on Zeiss Crossbeam 340.



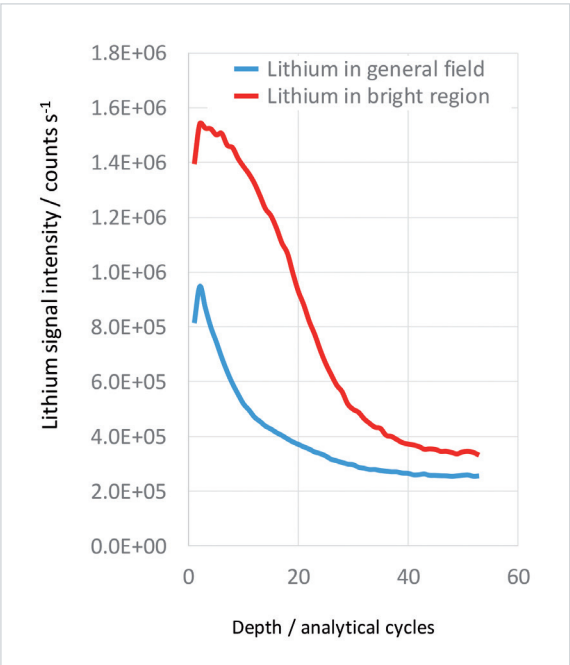
Lithium battery analysis The micrograph shows a 50µm field of view of a cathode surface.

SEM imaging of an aged battery cathode shows bright regions.

SIMS imaging of this region shows the bright areas to be lithium rich.



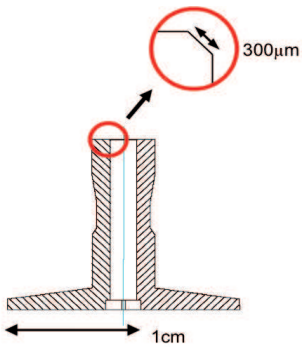
SIMS of cathode ^{7}Li mass resolved SIMS image of the cathode surface showing a distinct lithium rich area (research of Hochschule Aalen).

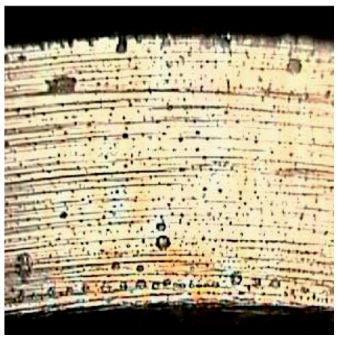


Contamination

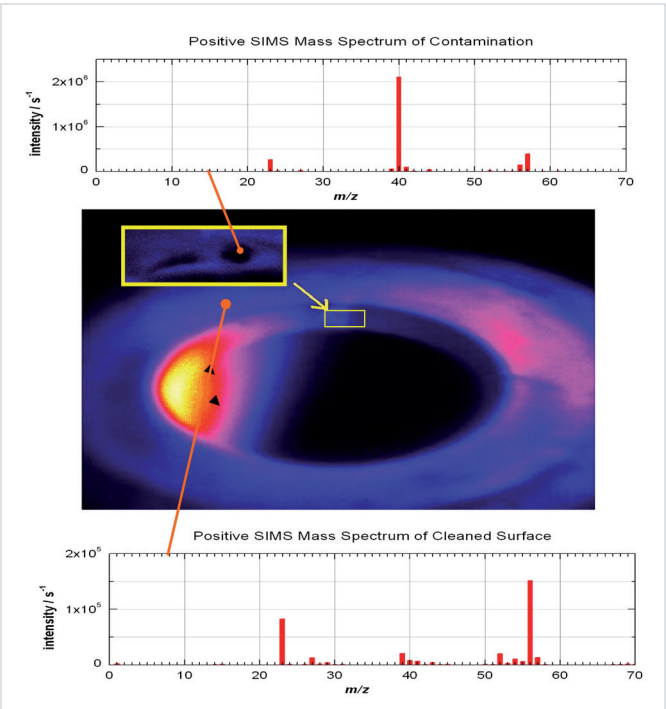
Visible staining was observed on internal angled face of a diesel engine injector component.

The stain was too thin to be detected by EDX.





Contamination on Diesel Injector Component



The mass resolved image shows the distribution of ^{56}Fe. The inset identifies the region where the stain was observed; as the Fe signal is masked by the surface contaminant.

A mass spectrum taken on the clean base surface shows the composition to be mainly Fe and Cr (with some Na from handling). A similar spectrum from the stain is dominated by the ^{40}Ca signal with the metal signals being significantly reduced.

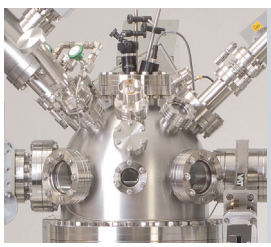
The stain is positively identified as being Ca based and originating from use of bio-diesel. This known possible fuel contaminant is limited by EU regulations to 5 mg/kg (summed with the Mg content).

Hiden**APPLICATIONS**

Hiden's quadrupole mass spectrometer systems address a broad application range in:

GAS ANALYSIS

- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

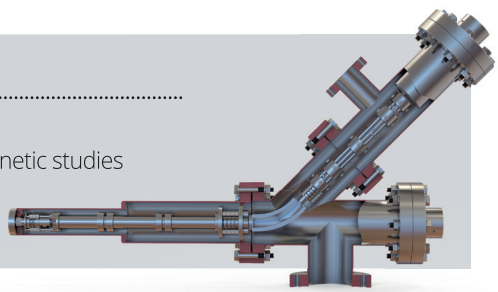


SURFACE ANALYSIS

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging – 3D mapping

PLASMA DIAGNOSTICS

- plasma source characterisation
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species



VACUUM ANALYSIS

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

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