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A. Waugh, D. Kingham, C. Richardson, M. Goff. A TIME-OF-FLIGHT MASS SPECTROMETER FOR SIMS AND FIELD IONISED NEUTRAL ANALYSIS USING A PULSED LMIS. Journal de Physique Colloques, 1987, 48 (C6), pp.C6-577-C6-582. <10.1051/jphyscol:1987694>. <jpa-00226902>

**HAL Id: jpa-00226902**

**<https://hal.archives-ouvertes.fr/jpa-00226902>**

Submitted on 1 Jan 1987

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## A TIME-OF-FLIGHT MASS SPECTROMETER FOR SIMS AND FIELD IONISED NEUTRAL ANALYSIS USING A PULSED LMIS

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### ABSTRACT

A new surface analysis instrument has been developed using an energy-compensated time-of-flight mass spectrometer. Samples are ionised for analysis either by microfocussed laser irradiation or by sputtering with a microfocussed ( $<0.25\mu\text{m}$ ) mass-filtered beam of  $\text{Ga}^+$  ions from a liquid metal ion source. A framestore-based data system allows the simultaneous capture of both SIMS mass spectra and mass-resolved ion images. Data are presented illustrating both SIMS and Laser Microprobe performance. Data are also presented showing enhanced ion yield from the sputtering of a gold tip, due to field ionisation of sputtered neutrals.

### I. INTRODUCTION

In order to make best possible use of the relatively small number of secondary ions sputtered from a thin surface layer by a microfocussed ion beam it is necessary to use a mass spectrometer with parallel detection of all masses, rather than a tuned spectrometer such as a quadrupole or magnetic spectrometer. An energy compensated time-of-flight mass spectrometer was devised by Poschenreider /1/ and is well suited to this purpose /2/. We have combined such a spectrometer with a microfocussed ion gun using a liquid metal ion-source /3/ which has been developed to give a pulsed beam of nanoseconds duration. The instrumentation is also fitted with a Q-switched Nd:YAG laser using second or fourth harmonic radiation (532 or 266nm) which can be focussed to a few microns diameter, as an alternative way of ionising sample materials.

### II. INSTRUMENTATION

The instrument (Figure 1) is constructed as a fully bakeable UHV system in a high-stability chamber with a sample stage capable of  $<50\text{nm}$  resolution when the liquid-metal ion gun is operated as a continuous beam. The 'Poschenreider' spectrometer is the same as we have used previously for the 'FIM100' atom-probe field ion microscope /4/ with the addition of a variable iris to control the spectrometer acceptance angle.

The liquid-metal ion gun is currently fitted with a gallium liquid metal ion source operating at up to 30kV. The gun has condenser and focus asymmetric einzel lenses, a Wien mass filter with sufficient resolution to separate  $^{69}\text{Ga}^+$  from  $^{71}\text{Ga}^+$ , octupole stigmators and scan rods. Auxiliary internal deflector plates can be used to chop the beam. (5 to 50ns pulses can be selected by computer control) by scanning it across an aperture. A spatial resolution of <50nm has been achieved using a continuous beam and <0.25  $\mu\text{m}$  using a pulsed beam. The ion beam can be pulsed at up to 20kHz.

Time-of-Flight SIMS spectra are collected using a time-to-digital converter with 1ns resolution (LeCroy 4208). Digital delay generators can be used to veto signals from unwanted intense peaks (eg alkali metals) to avoid saturating the acquisition system, if necessary. A fast CAMAC processor is used to sort the data and transfer it periodically to a PDP 11/73 incorporating a digital frame-store. The datasystem can either just acquire mass spectra with acquisition times of typically 10-100 seconds, or can simultaneously acquire both a mass spectrum and multiple mass-resolved secondary ion images of  $64^2$ ,  $128^2$  or  $256^2$  pixel resolution, with acquisition time typically around 120 seconds. Due to the parallel detection of the time-of-flight spectrometer, images can include ions at different masses (eg all the isotopes and all the cluster-ions containing a given element). While SIMS spectra are acquired by accumulating secondary ion counts over many primary ion pulses, Laser Microprobe data are generated using a single-shot laser pulse with analogue acquisition using a 200MHz, 8 bit 32,000 channel transient recorder. The laser beam is focussed using a mirror microscope objective which can also be used for viewing the sample via an eyepiece or a TV camera: this is also connected to the digital framestore, allowing optical micrographs to be recorded on disk if required.

### III PERFORMANCE OF THE INSTRUMENT

#### III. 1. SPECTRAL AND IMAGING PERFORMANCE

Examples showing spectral and image information obtained with the new instrument are shown in figures 2, 3 and 4. Figure 2 shows trace amounts of molybdenum (as  $\text{Mo}^+$ ,  $\text{MoH}^+$  and  $\text{MoOH}^+$ ) and cobalt, as well as hydrocarbons, on the surface of an alumina catalyst particle removed from a reaction vessel; the  $^{27}\text{Al}^+$  has been truncated severely (19000 counts full scale) in the figure.

Figure 3 shows simultaneously-acquired time-of-flight SIMS images of  $\text{Fe}^+$ ,  $\text{Ni}^+$ ,  $\text{Cr}^+$  and  $\text{Si}^+$  from a metallographic section of an oxidised nuclear fuel-can. (courtesy Central Electricity Research Laboratories)

Figure 4 shows an example of a laser-induced mass spectrum from a polymer - a molecular-weight standard of polystyrene with a distribution of  $(\text{C}_8\text{H}_8)_n$  chains centred on  $n=6$ . Although fragmentation of the chains to give  $\text{C}_x\text{H}_y^+$  ions of masses < 200amu was observed, the parent molecular ions were very clearly observed with an intensity distribution reflecting that in the sample material.

#### III. 2. FIELD IONISATION OF SPUTTERED NEUTRAL ATOMS

In general only a small percentage of atoms sputtered in SIMS experiments are ionised, and strong differences are observed between different elements. To achieve higher and more uniform sensitivity it is necessary to post-ionise the

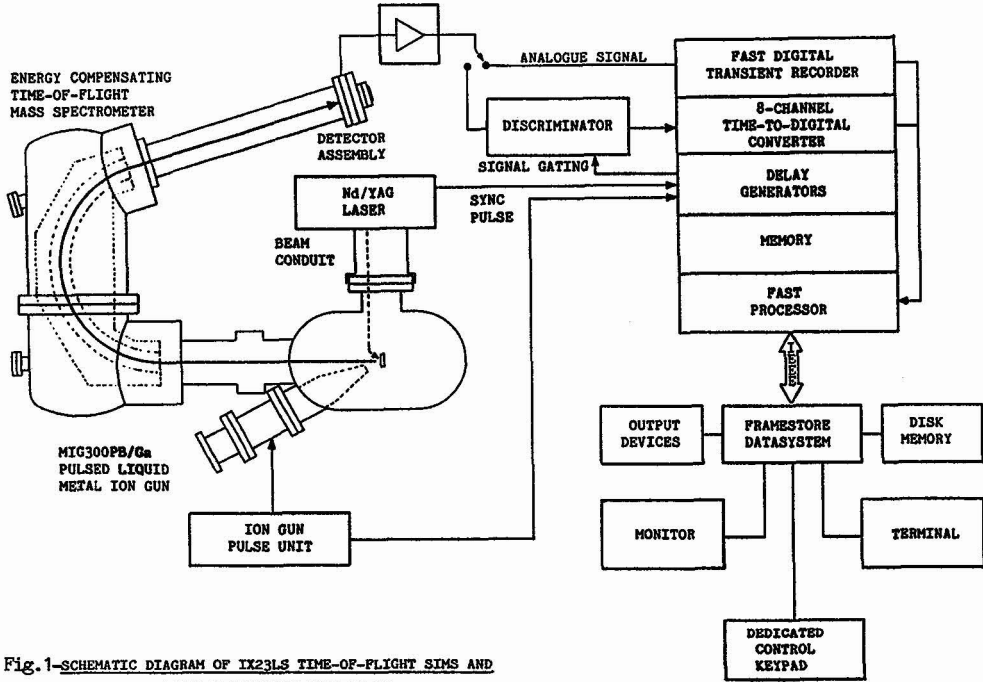


Fig.1-SCHMATIC DIAGRAM OF IX23LS TIME-OF-FLIGHT SIMS AND LASER MICROPROBE INSTRUMENT

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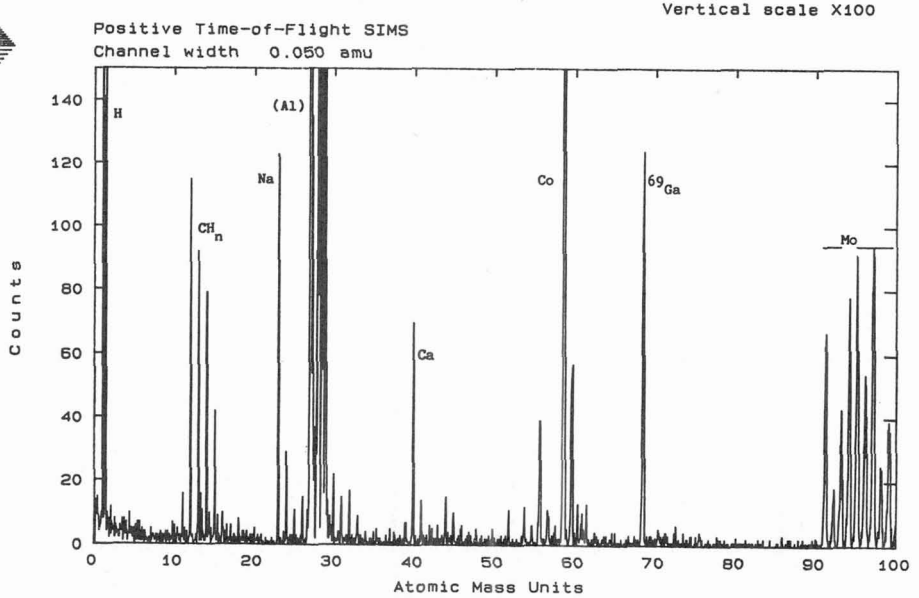


Fig. 2 - Alumina catalyst particle after exposure to reactants.

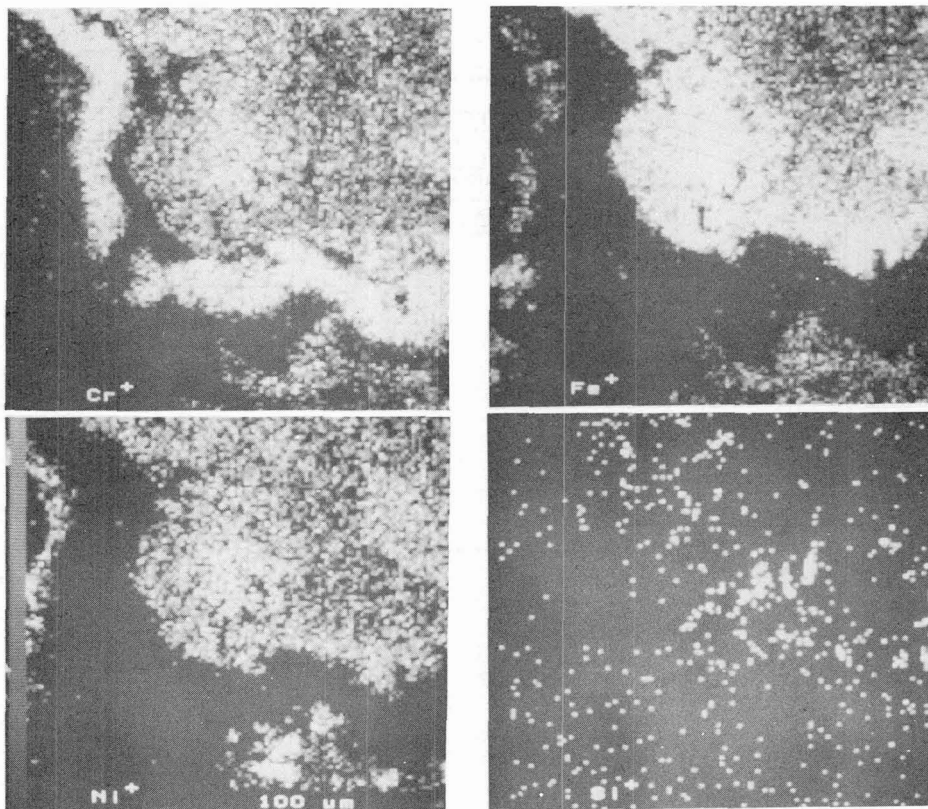


Fig. 3 - Cr<sup>+</sup>, Fe<sup>+</sup>, Ni<sup>+</sup> and Si<sup>+</sup> images from a section of an oxidised fuel can

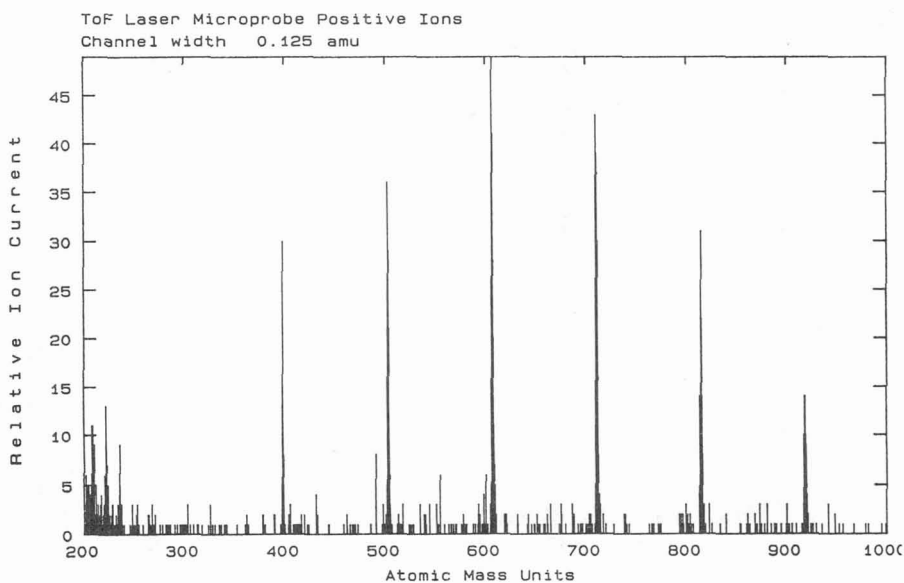


Fig.4 - Polystyrene with nominal Mol. Wt. 600.

sputtered neutrals /5,6/ using electron impact or laser-induced ionisation, although complete ionisation is only achieved with tuned laser systems /7/. We report here an alternative technique using field-ionisation of sputtered gold atoms from a blunt gold tip. It is of course well established in the atom-probe that field-ionisation provides an excellent way of completely ionising atoms near a surface. A gold tip was electropolished in dilute HCL: glycerol and mounted at room temperature in the instrument. At 5kV a weak continuous signal due to field-ionisation of residual gases and water vapour was observed, (background pressure was  $10^{-8}$  mbar during this experiment). When the pulsed  $\text{Ga}^+$  ion-beam was focussed on the tip and a time-of-flight 'SIMS' spectrum obtained, peaks due to  $\text{Au}^{++}$ ,  $\text{Au}^+$ ,  $\text{Au}_2^+$  and  $\text{Au}_3^+$  were observed. (Under normal SIMS conditions the  $\text{Au}^+$  ion yield from sputtered gold is extremely low, and the  $\text{Au}^{++}$ ,  $\text{Au}_2^+$  etc would be negligible. Small peaks at mass 16 ( $\text{O}^+$ ), 213 ( $\text{AuO}^+$ ) and 229( $\text{AuO}_2^+$ ) were initially observed: these decreased proportionately with time, as did the background due to continuous ionisation; both were restored each time the tip voltage was raised. The spectra were acquired in 60 seconds with 10KHz pulse repetition rate.

#### IV DISCUSSION AND SUMMARY

The time-of-flight SIMS instrument described here has demonstrated the acquisition of sub-micron resolution mass-resolved images with sensitivities at least an order of magnitude better than any previous instrument known to the authors. A laser microprobe attachment gives very rapid analytical information, with high sensitivity over the whole mass range of elements.

The demonstration of the field-ionisation of sputtered neutrals described here raises the possibility of a number of new experimental techniques:-

- 1) Analysis of tips too blunt or too delicate to be analysed by conventional APFIM or Laser Atom-Probe
- 2) Quantitative or semi-quantitative measurements of the composition and distribution of fragments sputtered by ion impact from samples that can be prepared as tips.
- 3) Quantitative or semi-quantitative analysis of materials deposited or adsorbed on a support tip.
- 4) By varying the ionisation field, to find the threshold value for ionisation of different species, it should be possible to probe the population of excited states of sputtered neutrals and neutral clusters.

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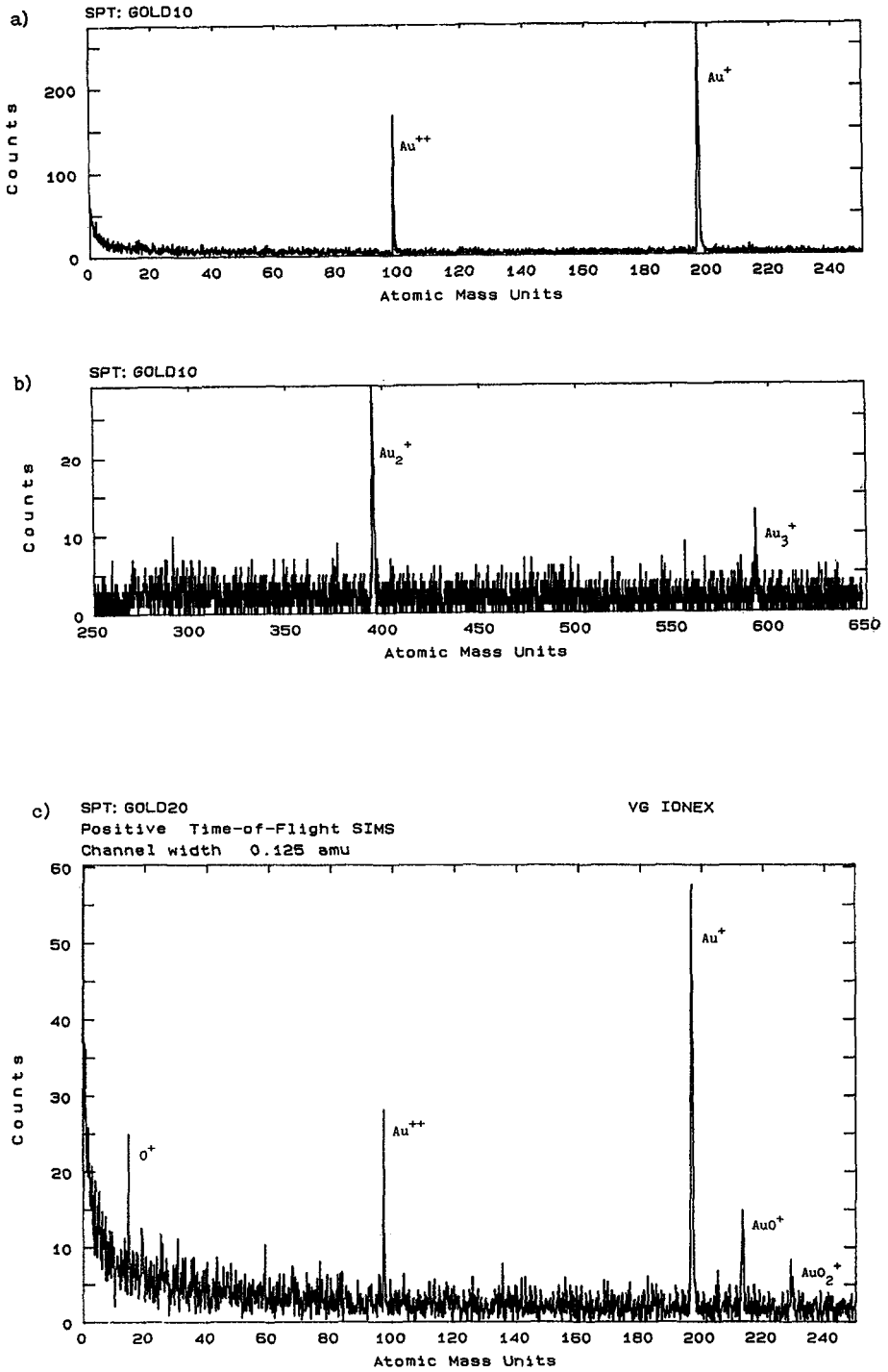


Fig.5-Gold ions and clusters from tip sputtered by 20 kV Ga<sup>+</sup>.