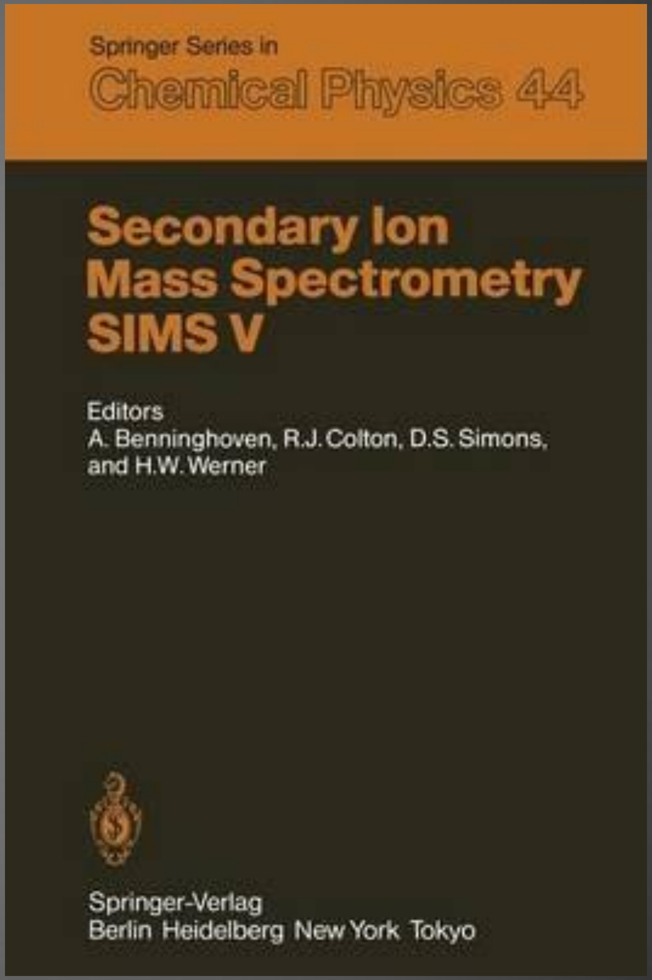
Secondary Ion Mass Spectrometry (SIMS)

SIMS: a desorption/ionization technique

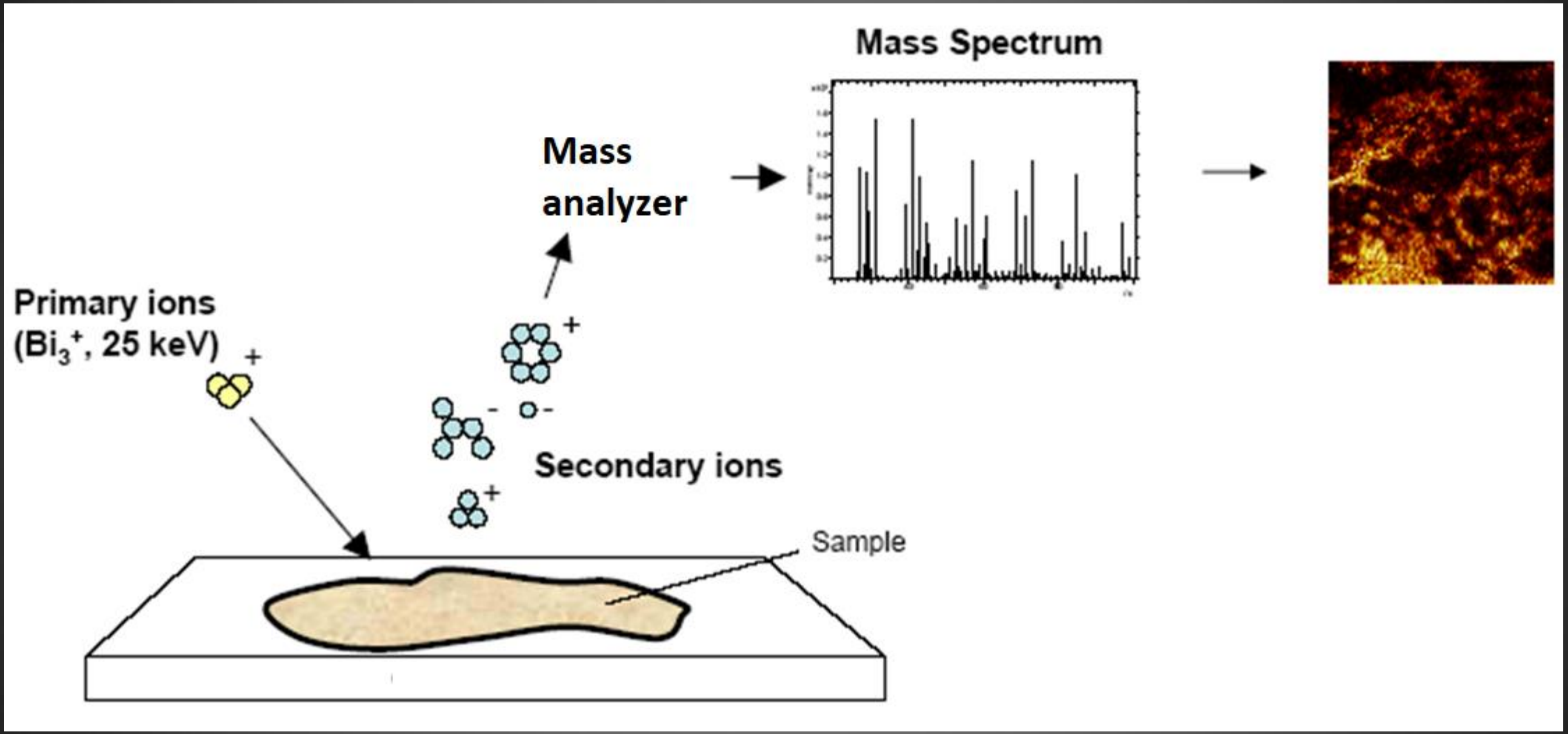
1960s - A. Benninghoven, University of Münster, Germany

(Benninghoven A., Rudenauer F.G., Werner H.W., “Secondary Ion Mass Spectrometry: Basic Concepts, Instrumental Aspects, Applications and Trends”, John Wiley & Sons, 86 (1986).



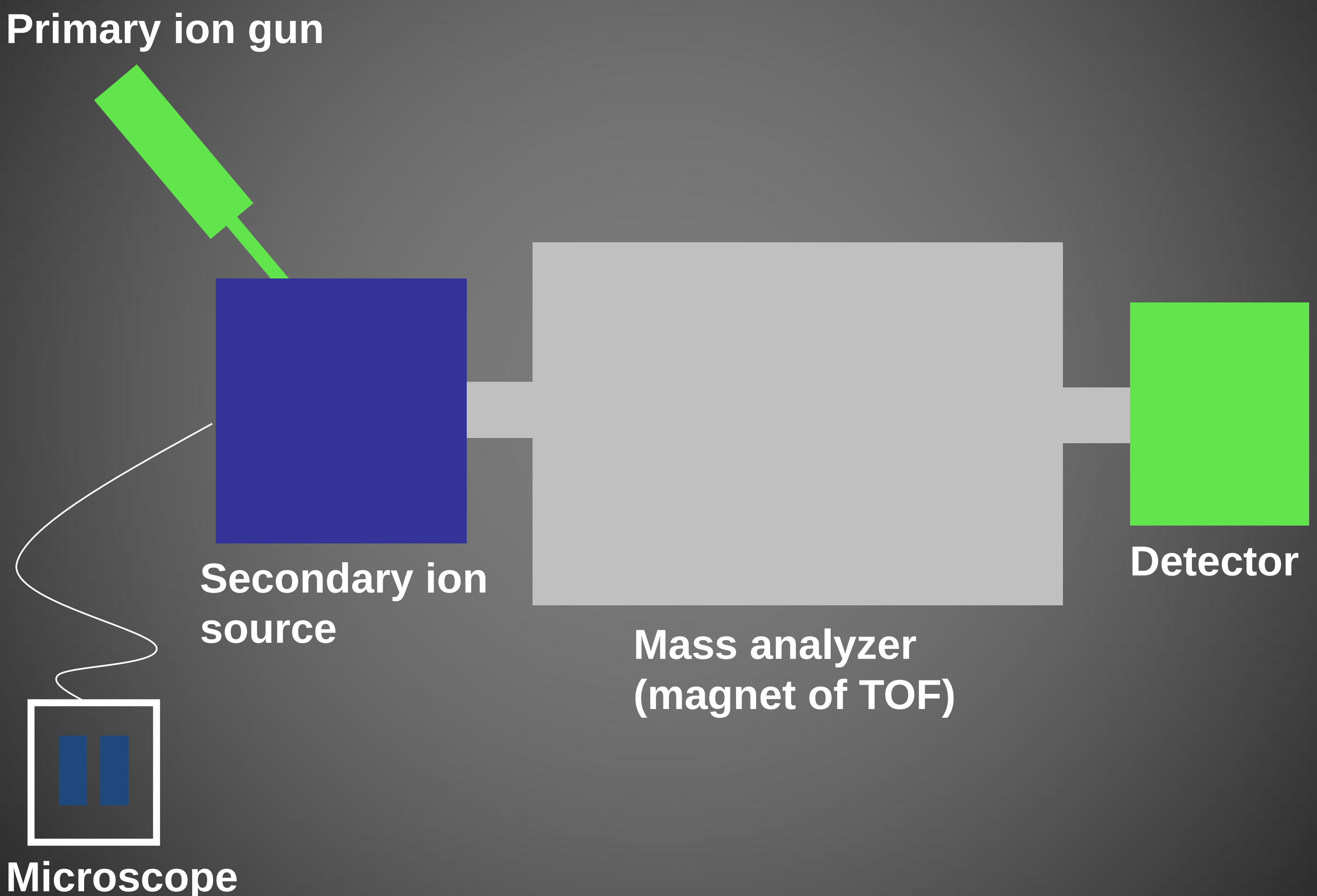
http://masspec.scripps.edu/mshistory/mshistory.php

SIMS: principles



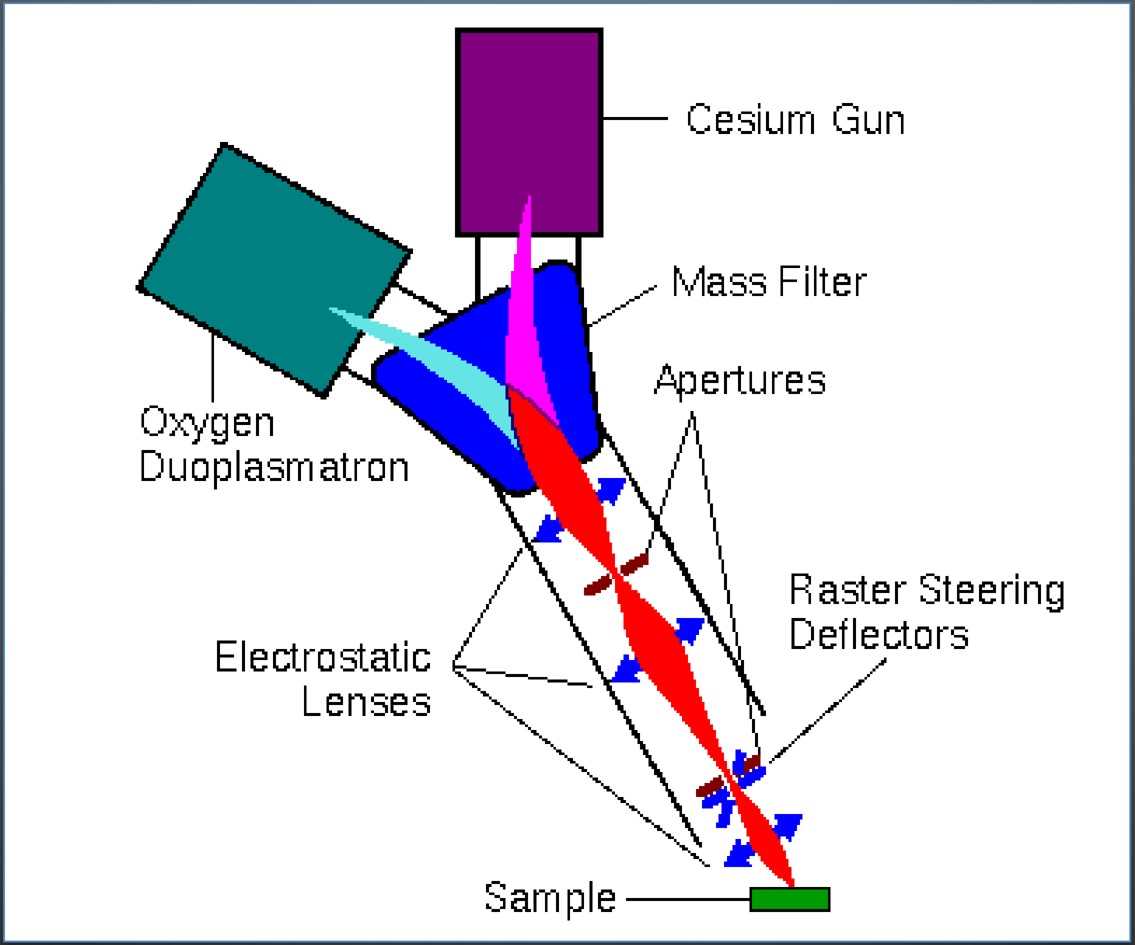
http://www.si-ontario.utoronto.ca/Presentations/sjovall_presentation.pdf

SIMS: instrumentation



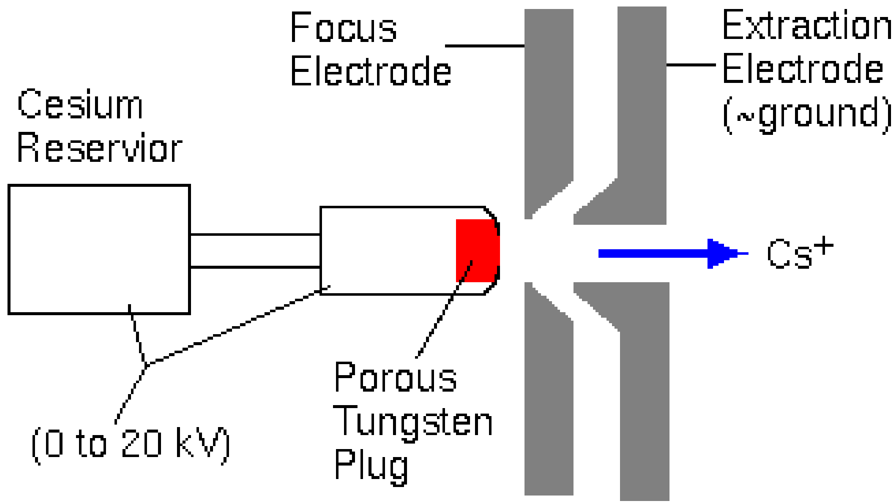
Generation of primary ions: ion guns

- Cs^+, O_2^+, Ar^+, Be^{3+}, Ga^+, C_{60}^+, etc.
- Most used: Cs^+, O_2^+

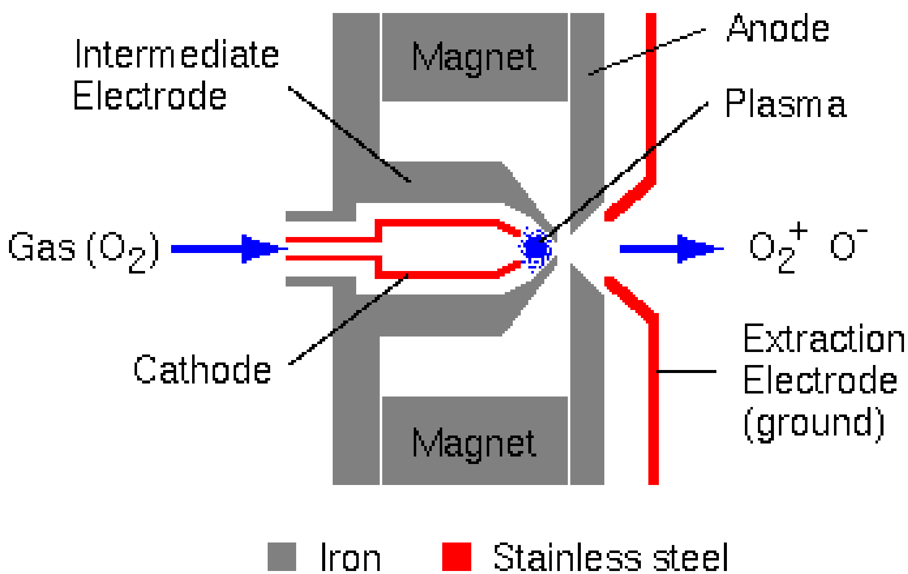


http://pprco.tripod.com/SIMS/Instrumentation.htm

Cesium Surface Ionization Source

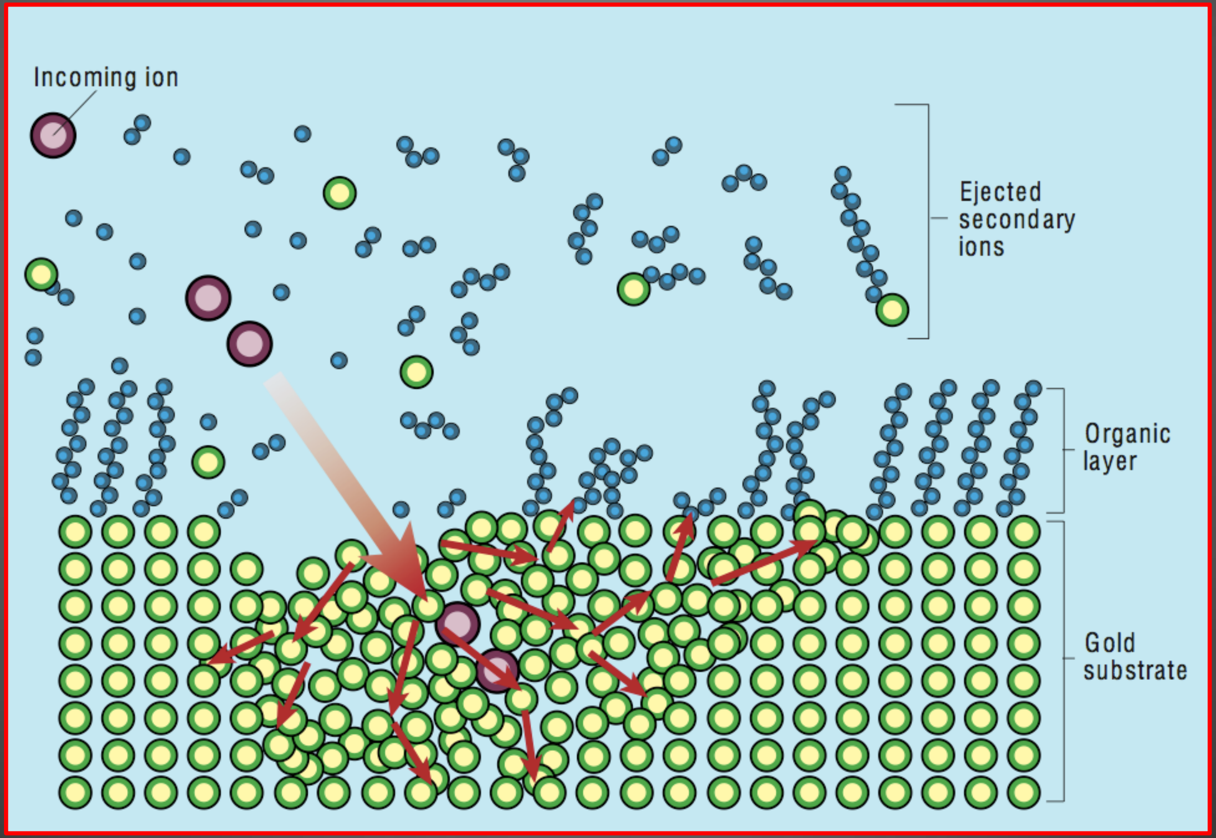


Duoplasmatron



http://pprco.tripod.com/SIMS/Instrumentation.htm

- sample: analyte deposited on a conductive solid support
- secondary ions (+/-) are “sputtered” from the surface

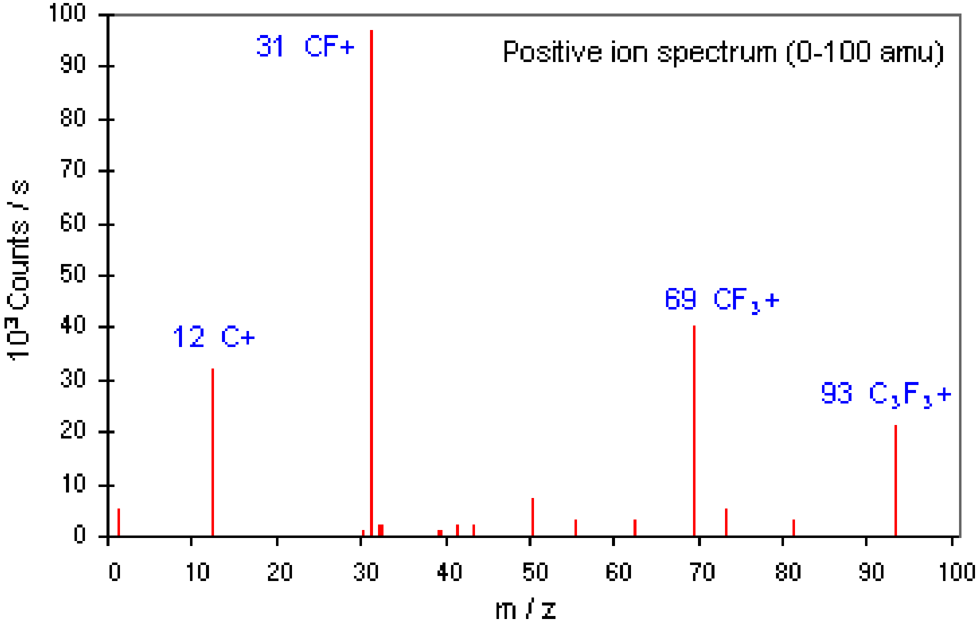


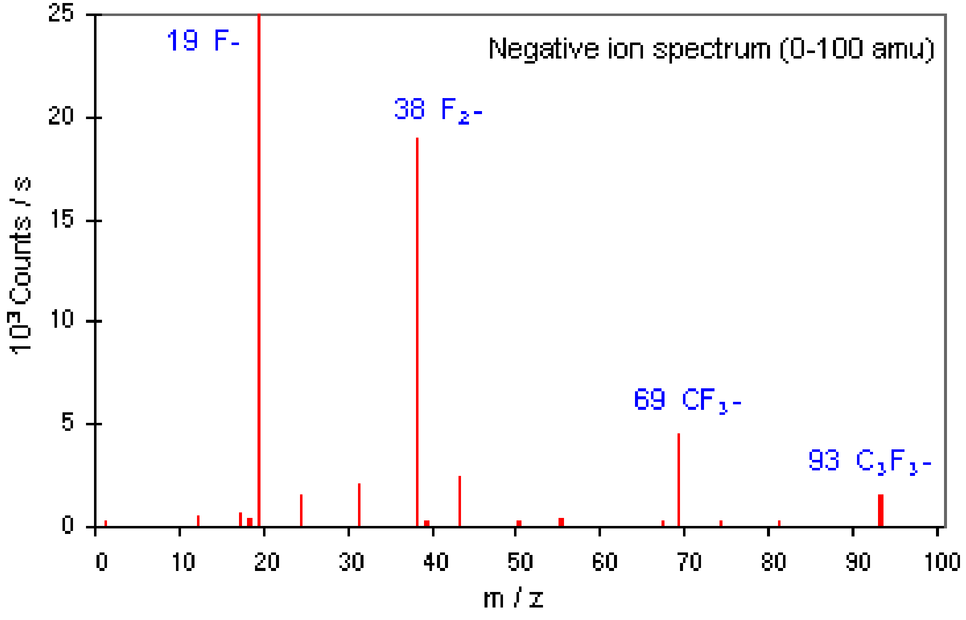
Castner, D. G., *Nature* **2003**, 422 (6928), 129-130

Mass analyzers

- Magnetic sectors or time-of-flight
- Positive or negative ions may be detected
- Secondary ions are small (<1000 Da) due to the high impact

Examples: Static SIMS spectra from the surface of PTFE (polytetrafluoroethylene)

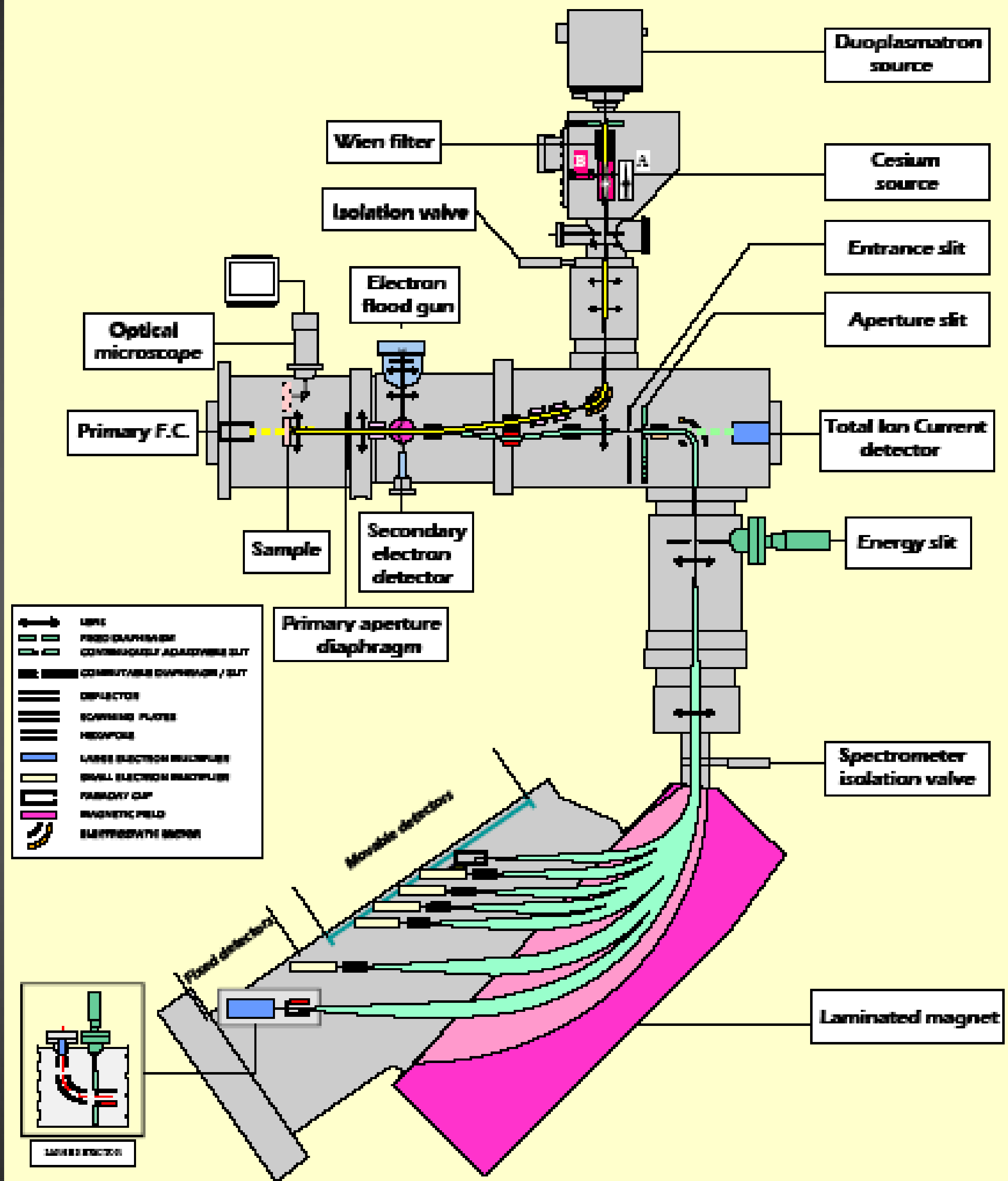




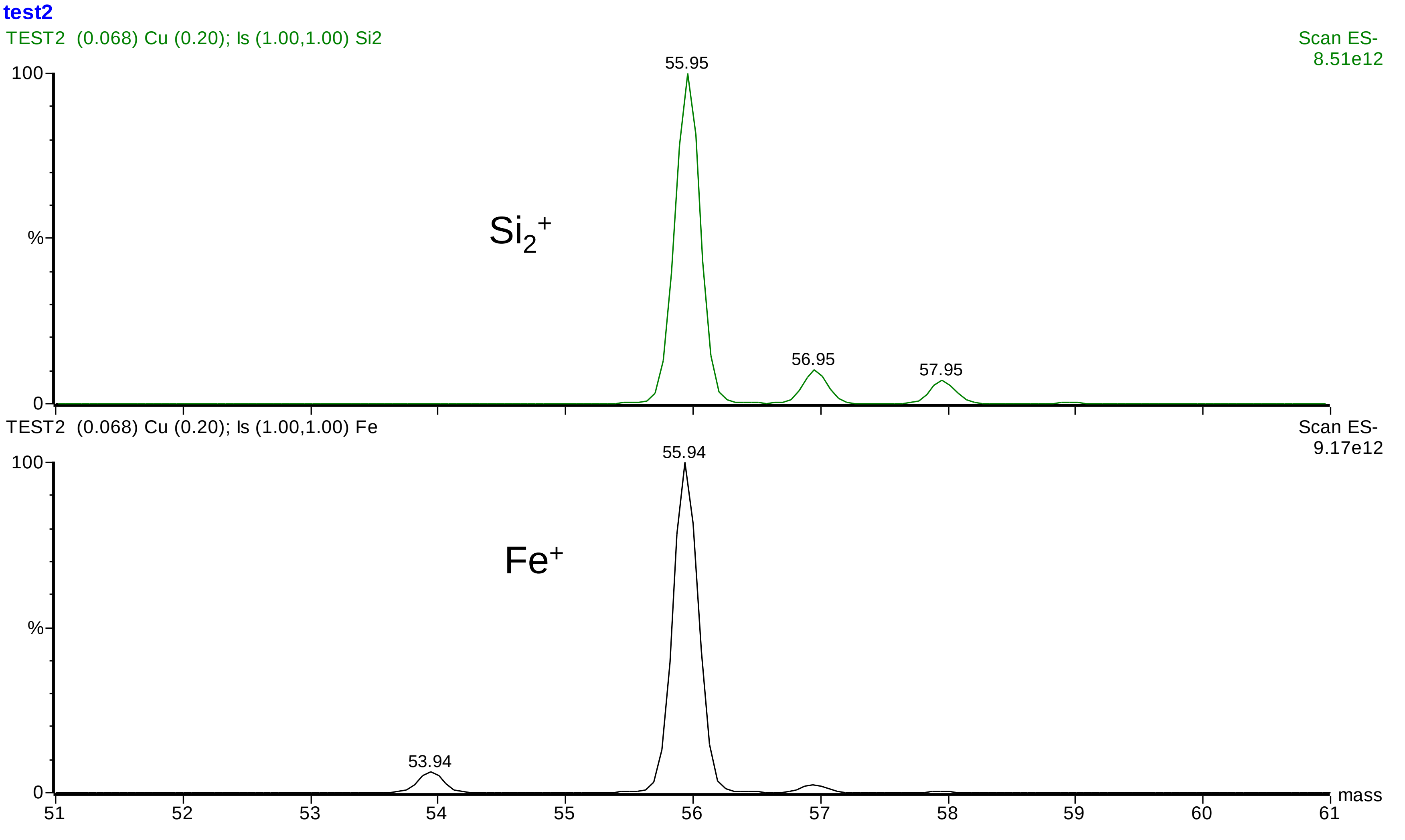
Magnetic-sector SIMS

NanoSIMS 50, based on a double focusing **magnetic sector**, allowing the **parallel detection of five elemental or isotopic masses.**

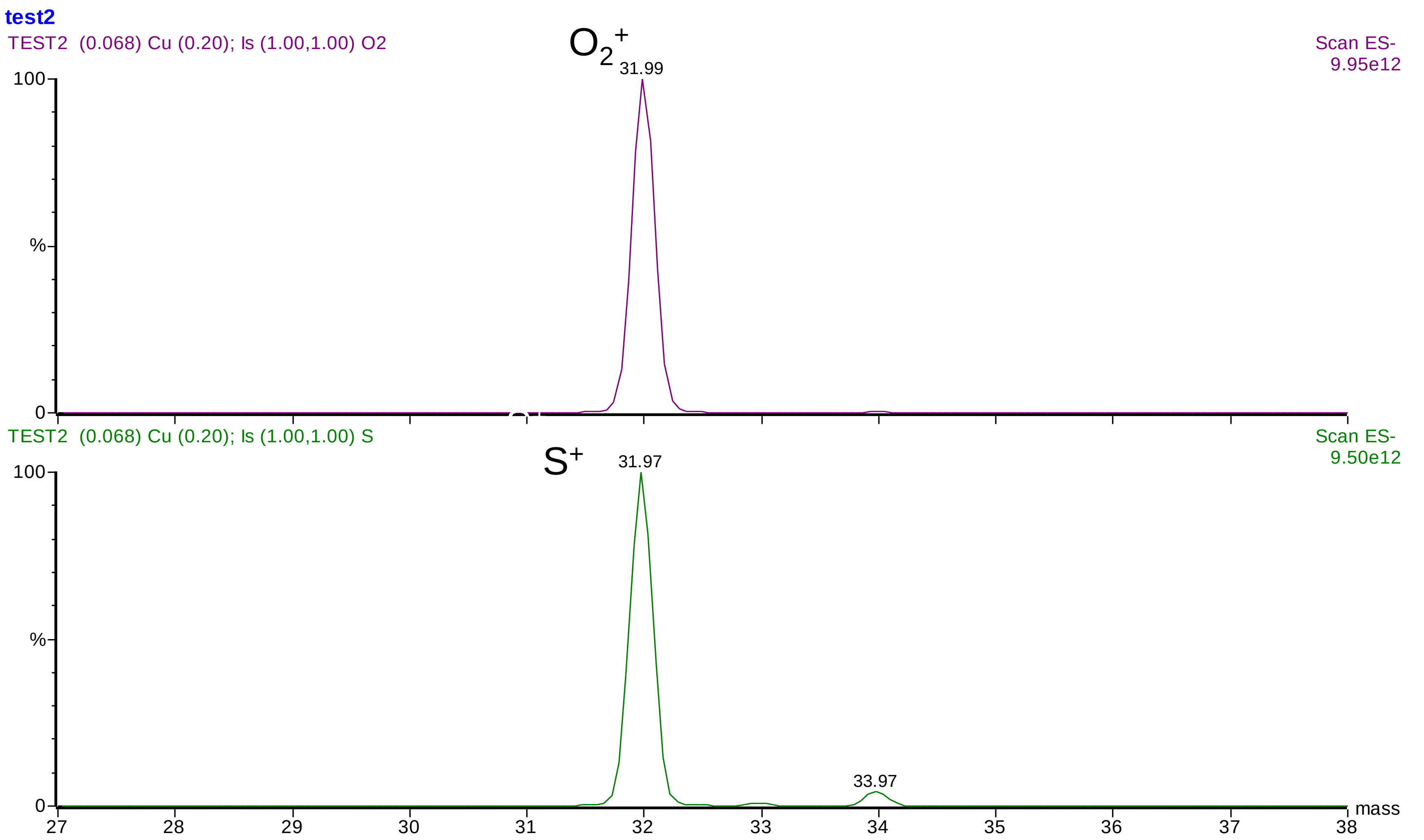
www.cameca.com


Duoplasmatron source
Wien filter
Cesium source
Isolation valve
Entrance slit
Electron flood gun
Aperture slit
Optical microscope
Primary F.C.
Total Ion Current detector
Sample
Secondary electron detector
Energy slit
Primary aperture diaphragm
Spectrometer isolation valve
Movable detectors
Laminated magnet

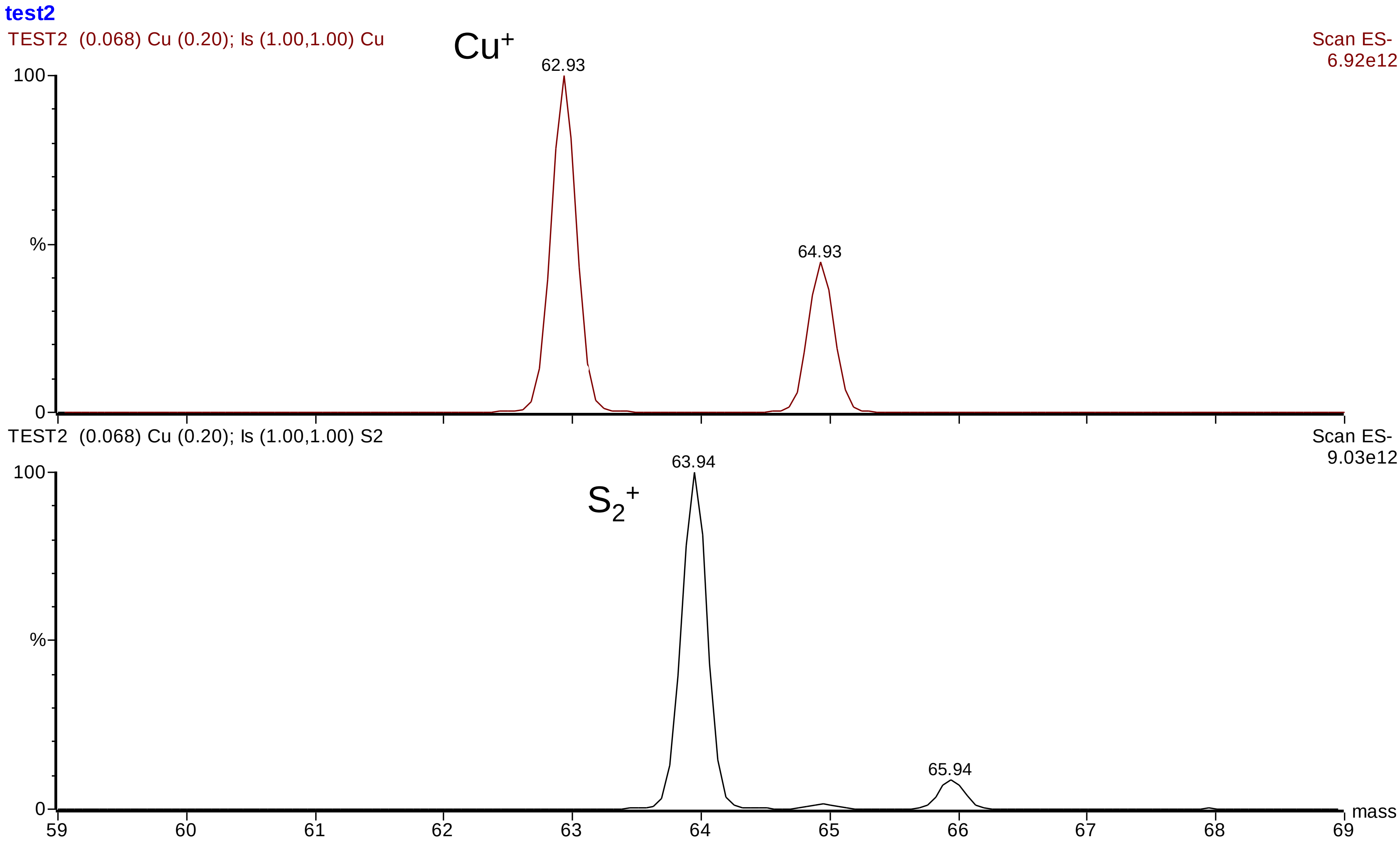
General features of SIMS: importance of isotopes



General features of SIMS: importance of isotopes



Importance of mass accuracy



SIMS variants:

Statics SIMS	used for monolayer elemental analysis **Primary ion beam up to 0.3 mm wide**
Dynamic SIMS	used for obtaining compositional information as a function of depth below the surface **Primary ion beam up to 0.3 mm wide**
Imaging SIMS	used for spatially-resolved elemental analysis **Microprobe imaging: primary beam 2 µm**

Research Article

SURFACE and INTERFACE ANALYSIS

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(www.interscience.com) DOI 10.1002/sia.2904

Differentiating calcium carbonate polymorphs by surface analysis techniques – an XPS and TOF-SIMS study

Ming Ni[a] and Buddy D. Ratner[a,b*]

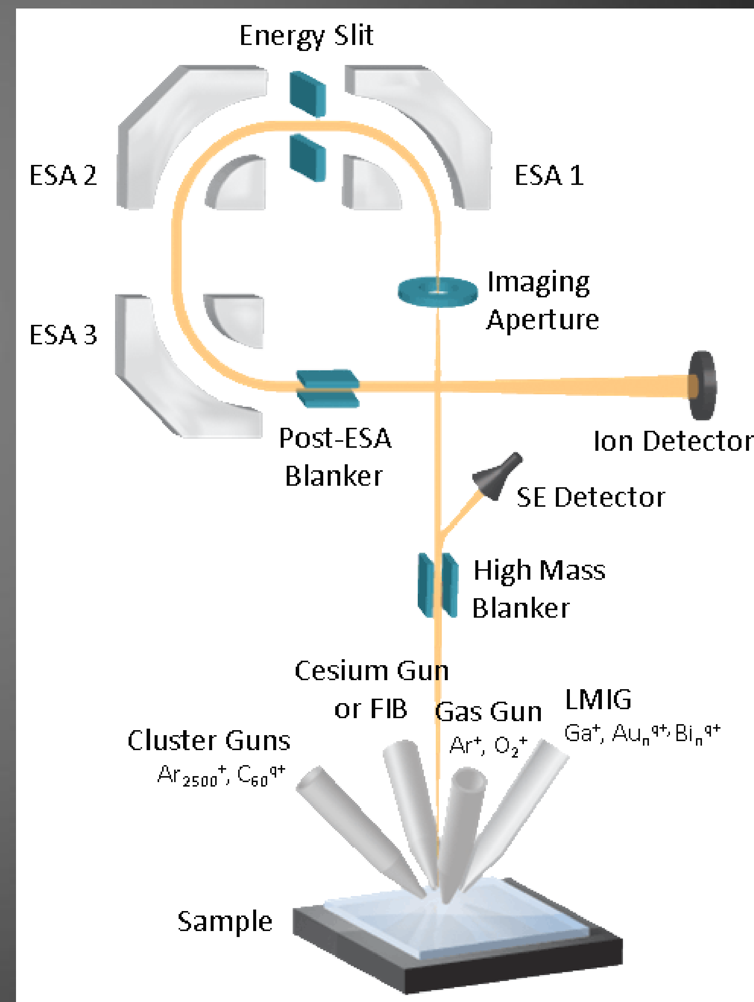
Calcium carbonate has evoked interest owing to its use as a biomaterial, and for its potential in biomineralization. Three polymorphs of calcium carbonate, i.e. calcite, aragonite, and vaterite were synthesized. Three conventional bulk analysis techniques, Fourier transform infrared (FTIR), X-ray diffraction (XRD), and SEM, were used to confirm the crystal phase of each polymorphic calcium carbonate. Two surface analysis techniques, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS), were used to differentiate the surfaces of these three polymorphs of calcium carbonate. XPS results clearly demonstrate that the surfaces of these three polymorphs are different as seen in the Ca(2p) and O(1s) core-level spectra. The different atomic arrangement in the crystal lattice, which provides for a different chemical environment, can explain this surface difference. Principal component analysis (PCA) was used to analyze the TOF-SIMS data. Three polymorphs of calcium carbonate cluster into three different groups by PCA scores. This suggests that surface analysis techniques are as powerful as conventional bulk analysis to discriminate calcium carbonate polymorphs.

Experimental: SIMS

SIMS data were acquired using a Model 7200 Physical Electronic instrument (PHI, Eden Prairie, MN) with an 8 keV Cs^+ primary ion source.

Data were taken over a mass range from *m*/*z* = 0–200 for both positive and negative secondary ions.

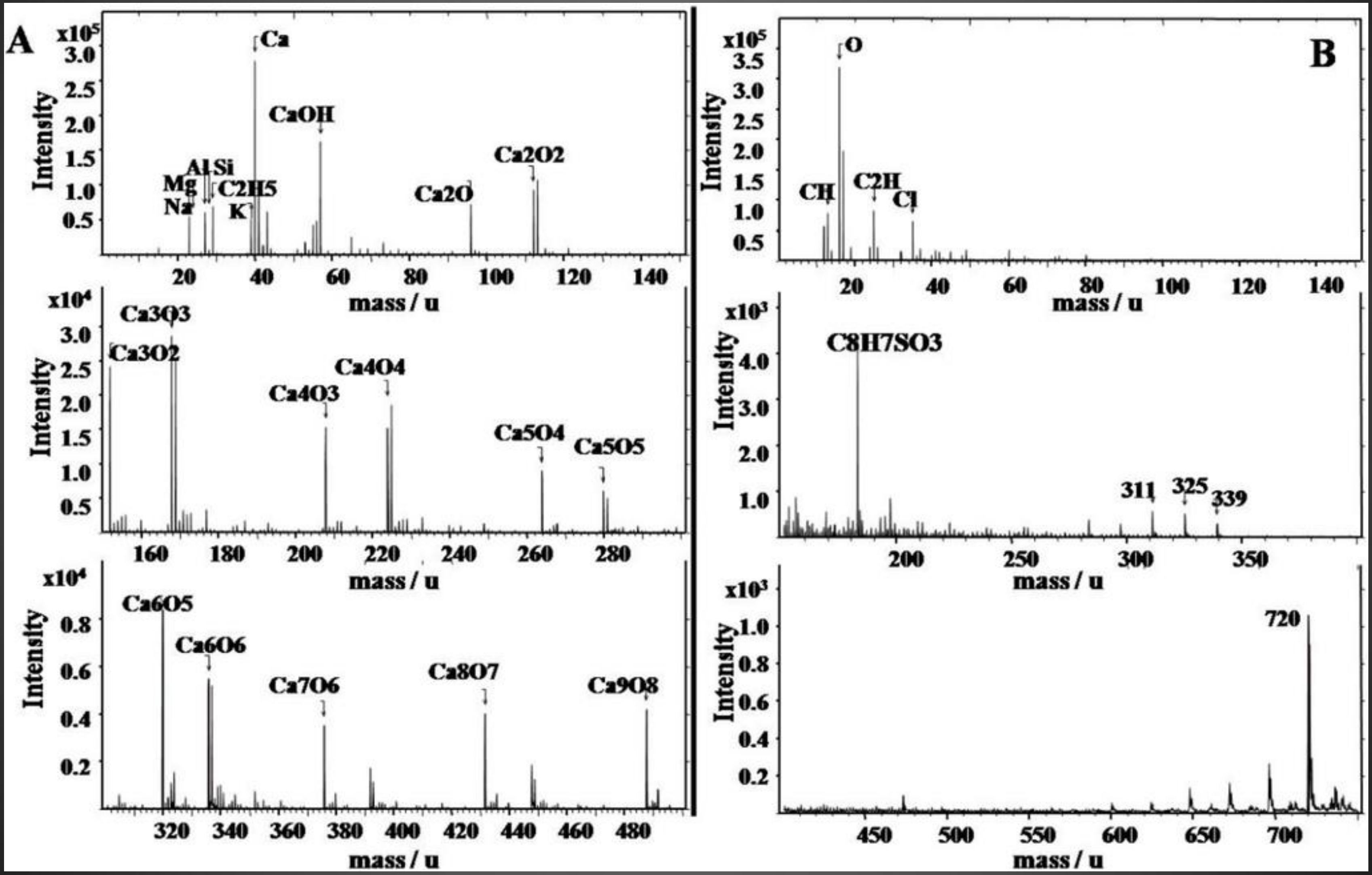
The differences between the expected and observed masses were less than 20 ppm.



https://www.phi.com/surface-analysis-equipment.html

$CaCO_3$ positive ions

$CaCO_3$ negative ions



http://www.mdpi.com/1660-4601/11/12/13084/htm

Application: NanoSIMS - An Analytical Tool for Trace Metal Detection in Bone and Liver from Haemodialysis Patients

John Denton, Francois Hillion, Francois Horreard, Alan G. Cox, University of Manchester, UK, CAMECA, Paris, FR, Centre for Analytical Sciences, University of Sheffield, UK.

Purpose of study:

Use the CAMECA NanoSIMS 50 as an ion microprobe for the analysis (mapping) of specific elements in bone and liver.

Sample: tissues derived from an end stage renal haemodialysis patient receiving both aluminium and iron.

•Renal dialysis patients develop elevated levels of phosphorous → hyperphosphatemia, a severe metabolic disorder.

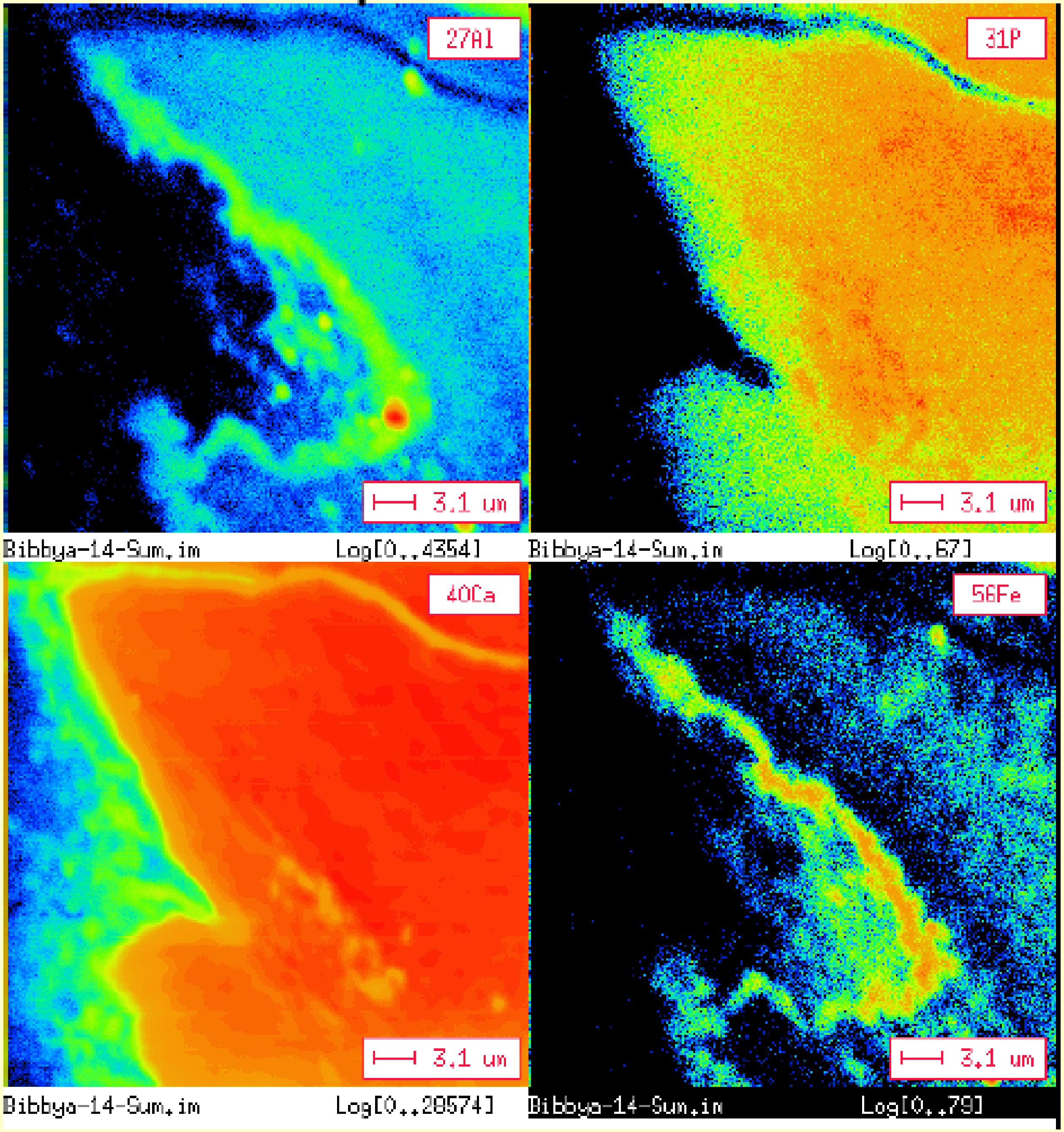
•Oral phosphate binders (e.g. $Al(OH)_3$) are used to block absorption of dietary phosphate to counteract hyperphosphatemia.

•$Al(OH)_3$ results in serious toxic effects, e.g. development of anemia.

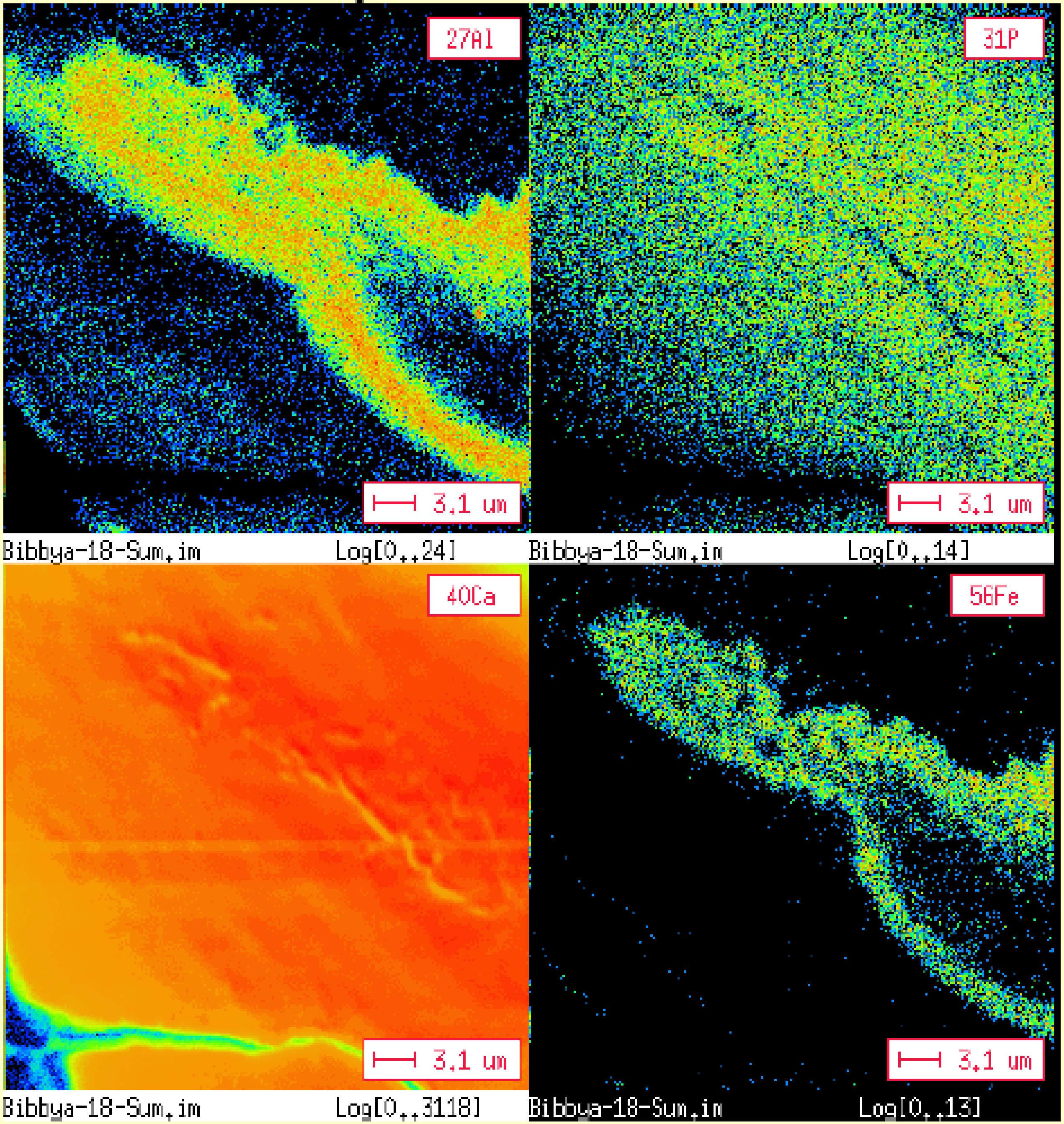
•Iron supplementation in the form of whole blood transfusion therapy can be used to counteract anemia.

•Tissue samples: i) liver biopsy, ii) trans-iliac bone biopsy from an end stage renal disease, from a hemodialysis treated patient.

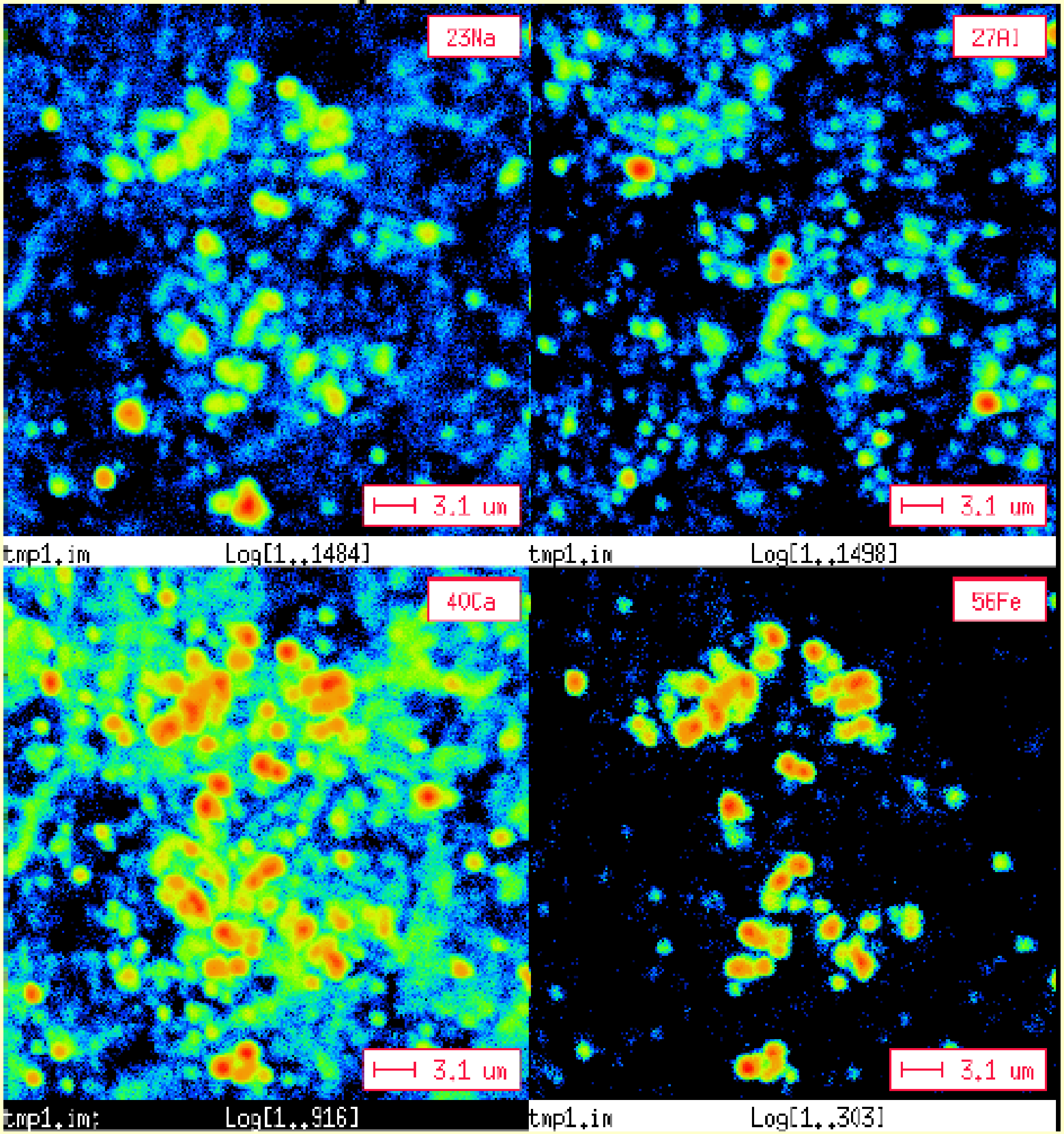
Ion map 1 *Bone*



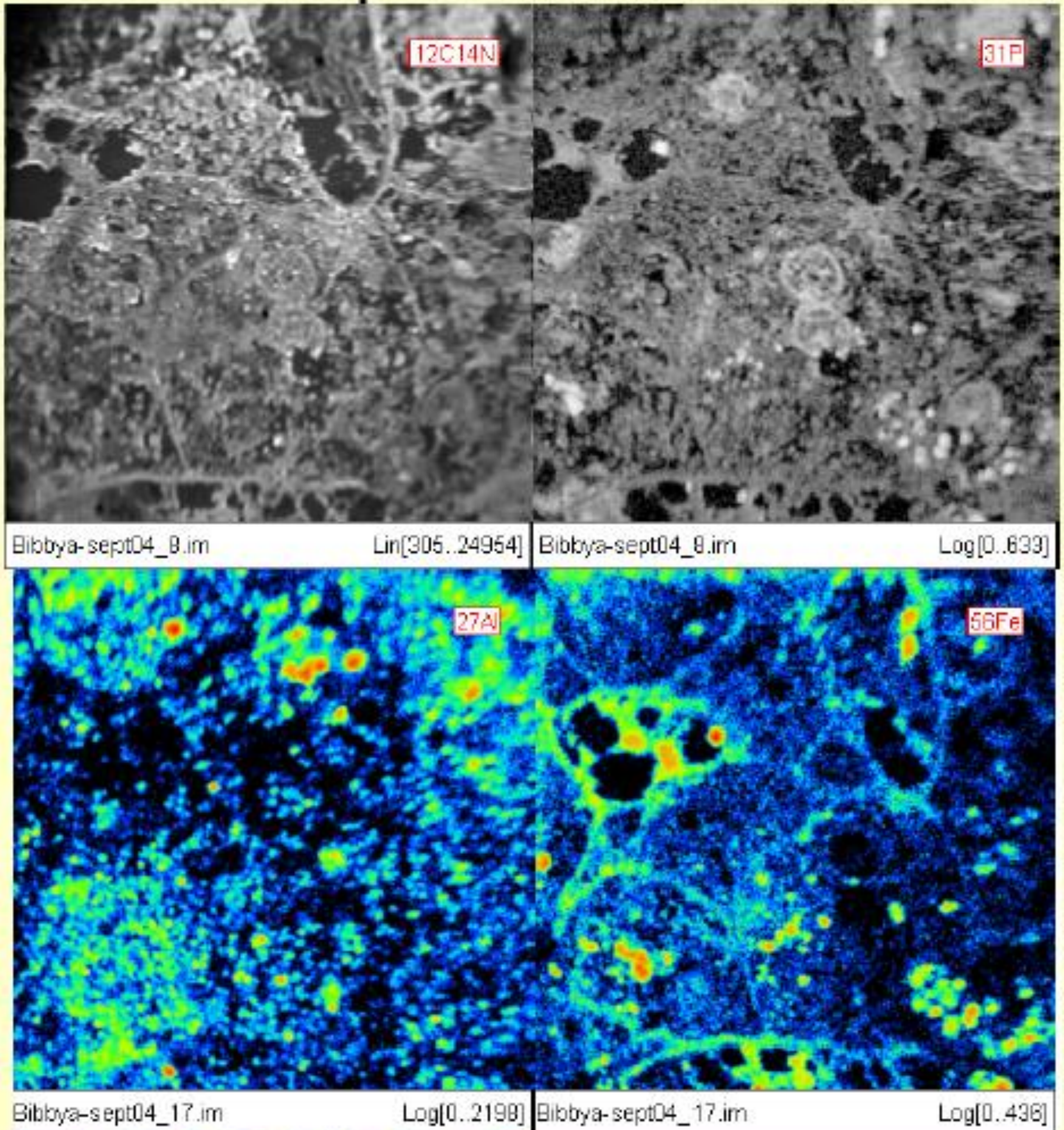
Ion map 2 *Bone*



Ion map 3 *Liver*



Ion map 4 *Liver*



Conclusions of the study

Trace levels of both aluminium and iron in liver and bone tissue were detected with high spatial resolution: a correlation was found.

The ion mapping of cellular components containing carbon, nitrogen, sulphur and phosphorous gives a clear visualization of the different tissue composition.

The use of stable isotopes as tracers offers a powerful and quantitative technique in cellular biology.

Conclusions on SIMS

Useful for elemental analysis at different depths
Good for imaging elements in their x-y (z) positions
Different guns for different applications
Microprobe gives very detailed representation of sample surface
Applications in all fields

But:
Impossible to know masses of complete molecules
Different instruments may give different spectra for same sample
More quanlitative than quantitative
Very expensive

Questions

1. Static SIMS gives information about the _______________ of a sample, while dynamic SIMS characterizes the ______________ of a sample. Examples of _____________ ions include Cs^+, O^-, C_{60}^+.

1. If a mass spectrometer equipped with a magnetic analyzer at constant field detects Ca^{2+} with a radius of 40 cm, what radius would be necessary for Li^+ ?