

TOF-SIMS & XPS: PITFALLS TO AVOID WHEN ANALYZING GLASSES

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ToF-SIMS

THE CHALLENGE

One of the recurrent analytical problems encountered in ToF-SIMS is the semi-quantification of element concentrations whose intensity reaches the saturation level of the detector. This is the case, for example, for alkalis in inorganic glasses or silicon in electronic components.

THE SOLUTIONS

One way to solve this problem is to reduce the intensity of the primary ions to avoid saturation of the detector. However, this solution induces a loss of sensitivity on trace elements, compromising one of the strong points of the ToF-SIMS technique. This compromise is therefore not an analytically acceptable option.

To solve this problem, a new technology called EDR* (Extended Dynamic Range) is deployed. This technology extends by a factor of 100 the dynamic range of counting secondary ions while maintaining a linear response of the detection system.

*Patented and marketed by IONTOF.

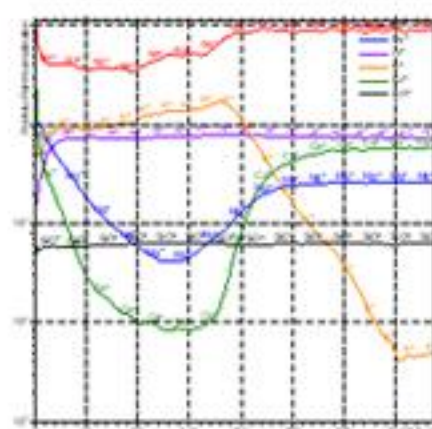
THE STRENGTHS OF TOF-SIMS

TOF-SIMS

- Molecular identification
- Trace analysis ~ppb
- Analyzed z: 1 nm (spectrum) to 10 μm (profile)
- Chemical imaging 2D & 3D
- Resolution: x,y < 100 nm, z < 1 nm
- All solid material UHV compatible

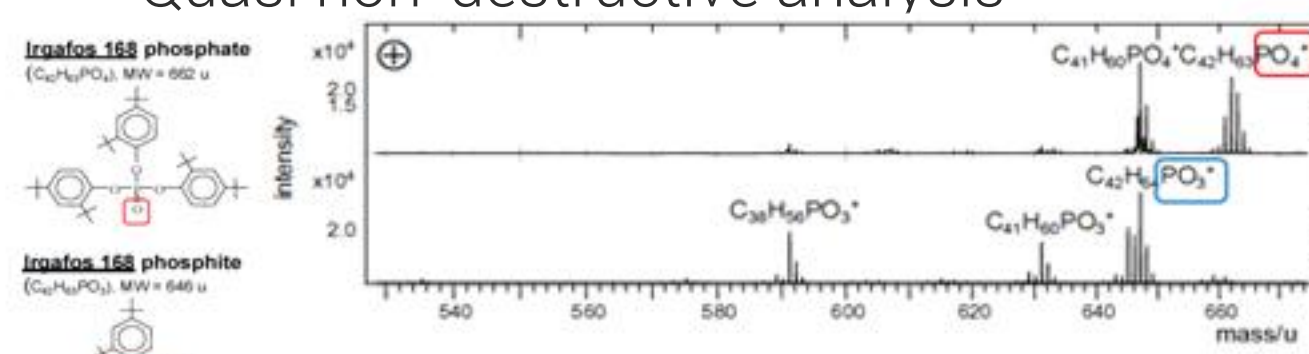
DEPTH PROFILING (O₂⁺, Cs⁺, GCIB)

- Successive analysis and etching
- Elemental in-depth distribution
- Analyzed z: from 1 nm to > 10 μm
- Resolution: z < 1 nm
- Sputtering energy: 250 eV to 2 keV



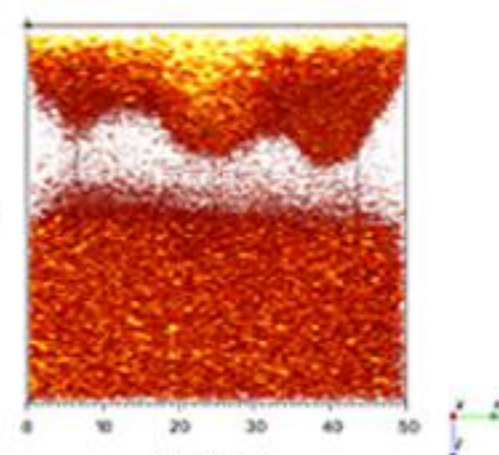
SURFACE SPECTRUM

- Elemental and molecular information
- Sensitivity ~ppb
- Mass resolution > 10 000
- Area analysis: 10 μm to 500 μm
- Quasi non-destructive analysis



SURFACE IMAGING

- Distribution x,y of elements, molecules
- Resolution: x,y < 100 nm
- Area: 5 μm to some mm (macro raster)



WHAT IS EDR?

New ToF-SIMS technology is suitable for inorganic analysis. Negative and positive ions are detected simultaneously.

Positive-mode profile with Cs⁺ etching gun, MCs⁺ cluster formation on the surface:
(M⁰ + Cs⁺ -> MCs⁺)

'Quantitative' profiles:
 $Y_{MCs^+} / Y_{Cs^+} \propto C_M$

Y_i: Ionic yield of x
C_i: Concentration of x

For glasses, Na is often the predominant ion detected, it's basically highly overestimated. It's by tracking the NaCs⁺ ion that the true value of [Na] is obtained.

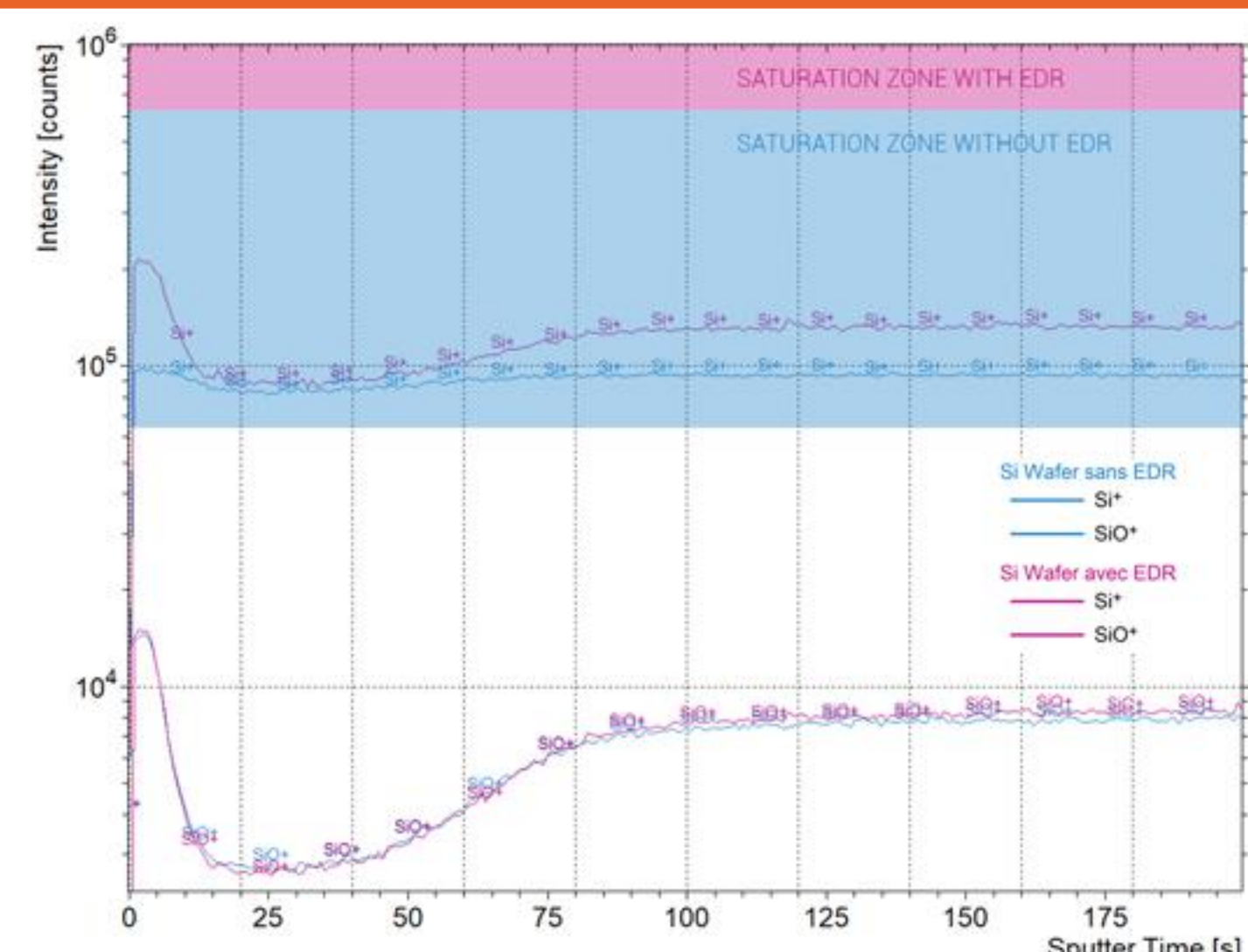
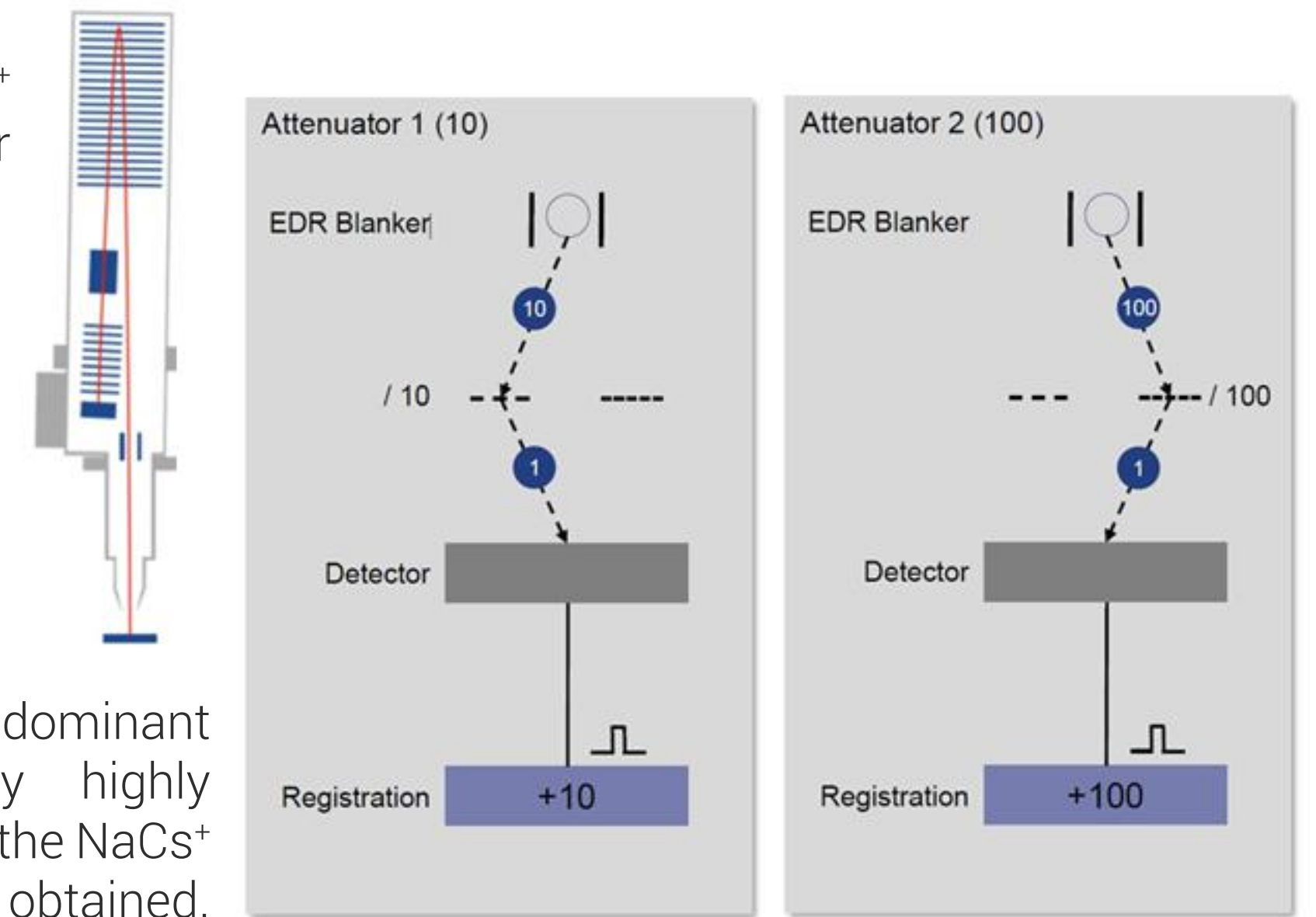


Figure 1: ToF-SIMS profiles of a silicon wafer with and without EDR

The ToF-SIMS profile of a silicon wafer (Figure 1), is collected with and without EDR.

THE RESULTS

- without EDR, the silicon profile is in the saturation zone, its intensity is thus underestimated which induces a loss of quantitative information.
- with EDR, the saturation zone has been pushed back for silicon, its profile is no longer saturated and those of other ions like SiO₂ remain unchanged.

EDR technology is the solution for the semi-quantification of elements in inorganic glasses.

XPS

THE CHALLENGE

The etching source in XPS analysis is used, among other things, to determine the depth profile quantification of materials. The choice of the etching source impacts significantly the elemental quantification, concerns mainly light alkaline metals in glasses, which diffuse during profiling. This quantification is a key element in the manufacturing process: it allows to link the macroscopic properties of materials to their atomic or molecular architecture.

THE SOLUTIONS

To access the depth elemental quantification, the XPS community relies on two different depth profiling methods, using either a monoatomic argon source or an argon cluster source. The use of an argon cluster source helps to limit the diffusion of light elements during profiling, and gives access to more reliable elemental quantification data.

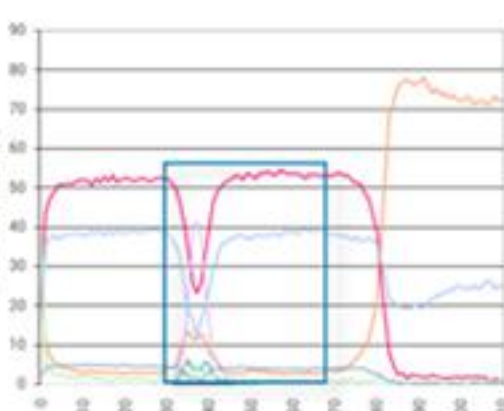
THE STRENGTHS OF XPS

XPS

- Semi-quantitative elemental analysis
- Detection limit ~ 0,1% at.
- Analyzed z: 3-10 nm (spectrum) to 3 μm (profile)
- Chemical speciation, depth distribution, chemical imaging
- Resolution: x,y 3 μm, E 0,47 eV
- All solid material UHV compatible

DEPTH PROFILING

- Successive analysis and etching
- Elemental in-depth distribution
- Analyzed z: from 3-10 nm
- Resolution: z few nm
- Sputtering energy: 5 keV to 20 keV
- Ar₅₀₀⁺ to Ar₃₀₀₀⁺



SURFACE SPECTRUM

- Elemental and chemical informations
- Detection limit ~ 0.1% at.
- Energy resolution: 0.47 eV
- Analysis area: 27x27 μm² to 300x700 μm²
- Non-destructive analysis

SURFACE IMAGING

- Distribution x,y of elements
- Resolution: x,y ~ 3 μm
- Area: 250x250 μm² to some mm²

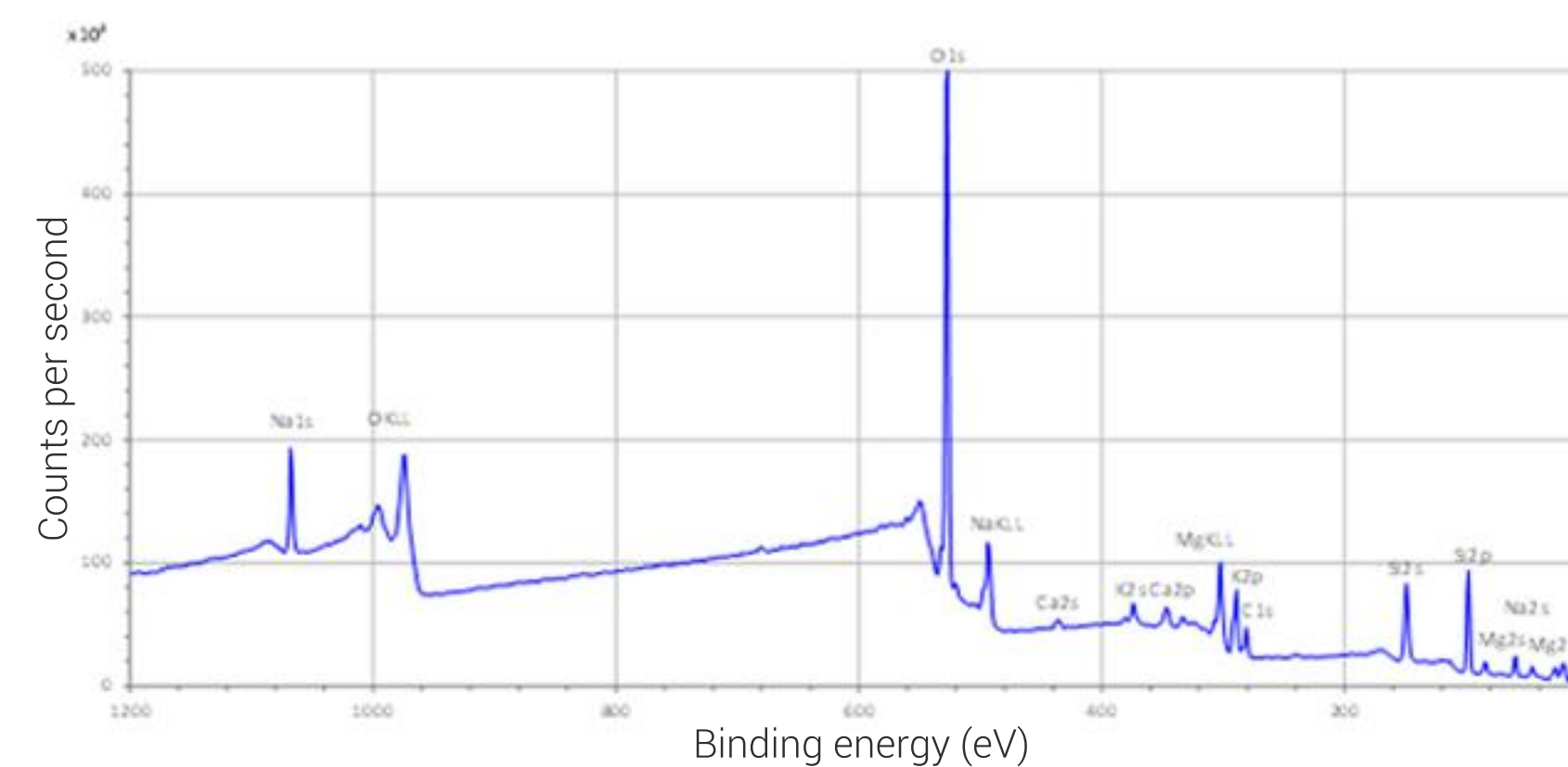
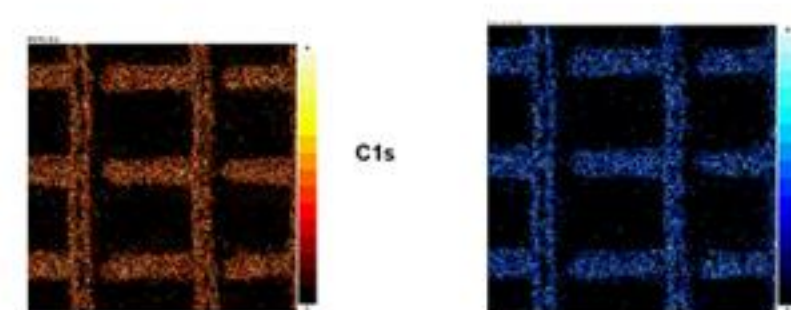


Figure 1: XPS spectrum of the extreme surface of soda-lime glass

The XPS spectra of the extreme surface (Figure 1), collected with a monochromatic AlK_α source, highlights the presence of soda-lime glass elements (Na, O, Ca, Si, Mg).

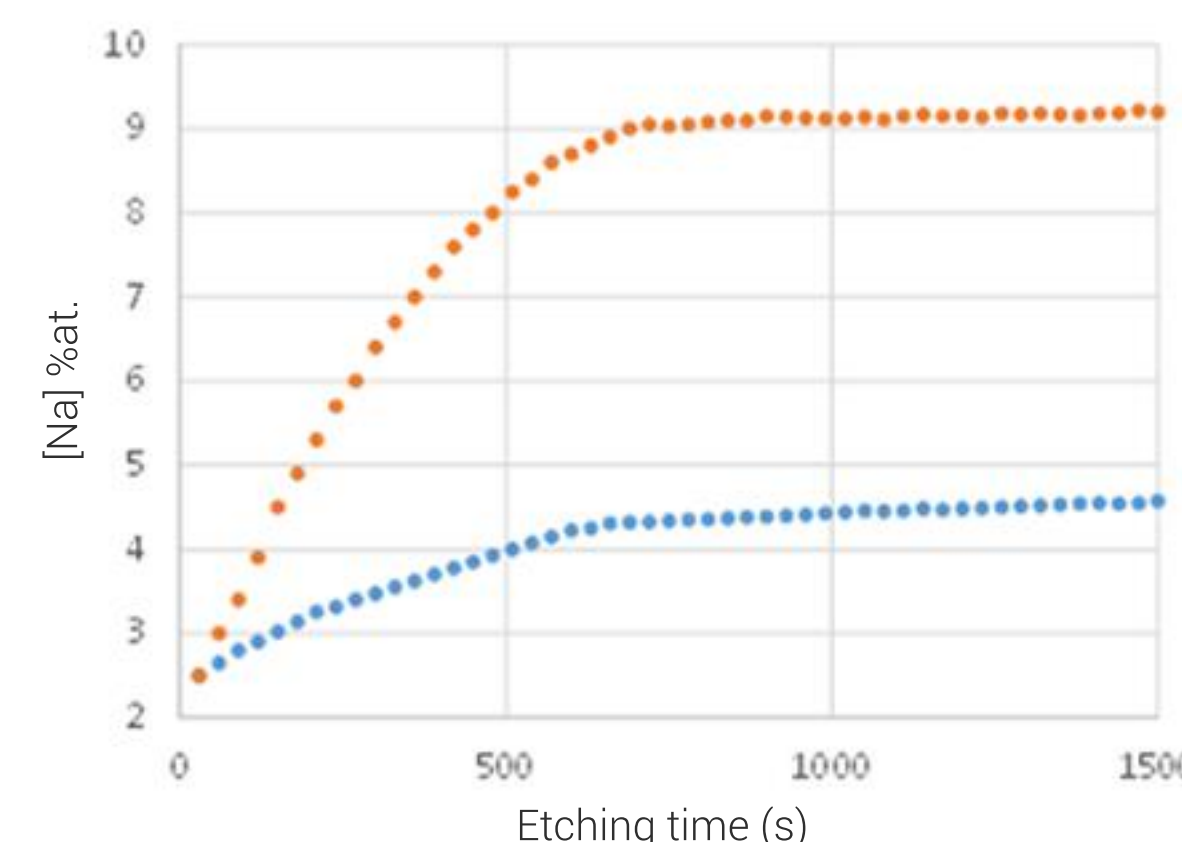


Figure 2: Sodium profile: monoatomic source Ar⁺ vs clusters Ar

The depth distribution of Na, the element most often impacted by diffusion phenomena, was followed by profiling with an Ar⁺ monoatomic source and with an Ar₅₀₀⁺ argon cluster source (Figure 2).

THE RESULTS

- with the monoatomic source, the [Na] measured in the glass volume (after 500 seconds of etching) is close to 4.5 atomic %. It's clearly lower than expected for a soda-lime glass ([Na] around 9 atomic %). Numerous studies in the literature describe a decrease in [Na] near the extreme surface when the etching is performed with a monoatomic Ar⁺ source. This decrease has been explained by the accumulation of positive charges in the region close to the extreme surface, thus repelling the highly mobile Na⁺ ions in the glass matrix, creating a Na depleted zone.
- with the Ar cluster source, the [Na] measured at the plateau is close to 9.2 atomic %, in perfect agreement with the expected composition. These results indicate a negligible migration of Na during profiling. This reduction in migration could be explained by the difference in energy of the Ar ions in the two profiling modes: while Ar ion carries an energy of 5 keV with the monoatomic source, the energy carried by each atom constituting the cluster is 40 eV, i.e. 125 times lower.

The GCIB etching source is the optimal method for a reliable glass core alkalis quantification.