# Comments and Suggestions for TOF-SIMS analysis of Padua ash

Below will be collected questions / advice from various professional and other parties
Comments; Tester Contributor MFMP

**Questions**

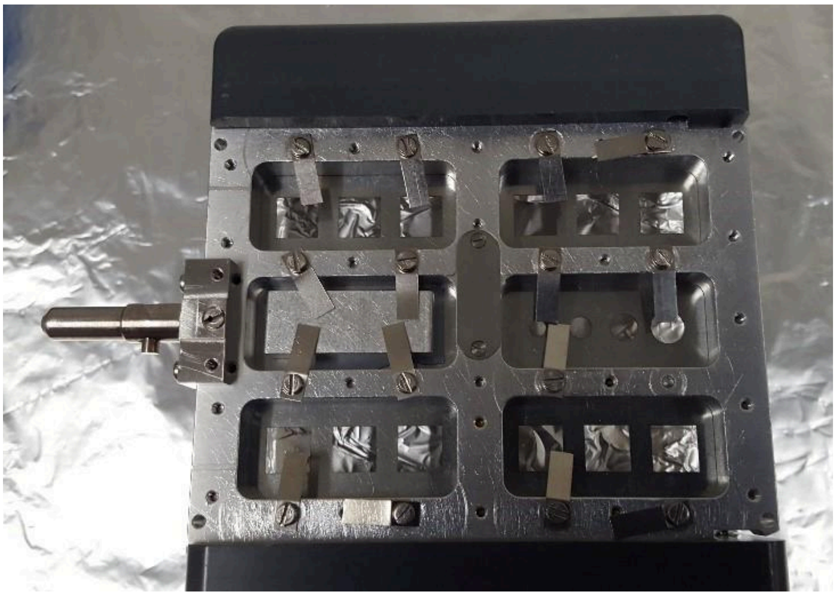
1. **What is the instrument used?**
   **A. We used the TOFSIMS from *iontof* (I think more precisely that it is this model: *https://www.iontof.com/tof-sims-5-product-version-100mm-200mm-300mm.html* )**
2. **What was the ion beam species?**
   **A.The ion used was Bi3+**

3. **Have any other ion beam species been used?**
   **A. only Bi3+ but we have access to Bi+**
4. What is the chance of doubly ionized species ( a MASS++ will appear as a MASS/2 in the data )

5. What is the error in the measurement? (Mass, count rate, ID?)

6. **How the sample was prepared?**
   **A. the sample was just deposited on a carbon tape (the same tape that we use for XPS and SEM experiments)**
   Contributor comment: You should use a Silicon substrate instead

7. **What was the sample support?**
   **A.The sample was just inserted in the TOFSIMS holder (see image)**

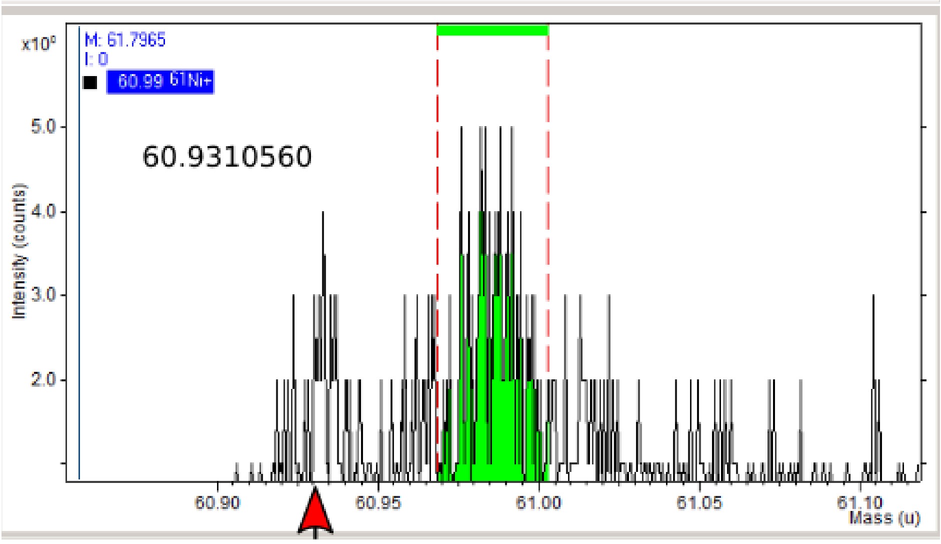


8. **Was it sputter cleaned?**
   Tester comment: “Cs sputtering before the analysis” need to check if it was used

considering the header of the ITA, if not, could be attempted when the TOFSIMS is next booked

9. Q. The ash analysis for Ni-64 indicated no measured 64Ni. Was 64Ni actually measured?
   Contributor comment: Ni64 is less abundant than Ni62.  Given the S/N at m/z 62, then m/z64 would be almost non-existent.
   Need either longer integration times (more sample additions) or higher beam on sample current.  You need ion counts in the 10^5-10^6 range to do this adequately.  The way you tell, if the matrix is say 10^6 counts and you need to see 1PPM ==> one count for that ion.  You should note that the ionization cross section for SIMS varies over 10^4 AND is matrix dependent.  Thus, the spectra often do not reflect the sample.  Alkali earths predominate.
   TOF cannot discriminate ions (it could by beam deflection but not sure that is implemented).
   Tester comment: “longer exposure time” could be attempted when the TOFSIMS is next booked

10. Are you sure you measured the correct peak for 61Ni, the peak presented in the pdf as being for 61Ni looks to be right of the real mass as claimed on Wikipedia (60.9310560)



Contributor comment: As regards the Nickel isotopes, there is not enough signal to definitively reject compound masses (containing more than one entity) - needs longer integration time.
Tester comment: “assignation of  61Ni it has been made automatically by the software” tester will study data more at next opportunity

11. Can you dump the data as a CSV file in full scan mode rather than as nominal masses.
    A. Here is the data as compressed ZIP file https://goo.gl/1qKesR
    MFMP: Here is the data as CSV and ODS https://goo.gl/ue6DcW

12. Q. Can you give a 6Li / 7Li ratio?
    A. Data in 11 would give answer

13. Q. Can you give more data and analysis and conclusions on and around mass numbers 63, 64 and 67 and 69?
    A. Data in 11 would give answer

14. Q. Can you see if the peak at 23 is Na or 7Li16O?
    A. m/z 23 is sodium.
    If Li7O16 the you would also see Li6O16 at m/z 22, which is absent.

15. Q. Can you see if 31P is present and if so, to what degree?
    A. Data in 11 would give answer
    Contributor comment: m/z 31 is present but it is not likely phosphorous.

16. Can you provide negative SIMS spectra?
    A. I'll add a negative spectra next time that I make a measurement.

**Suggestions**

1. The beam needs to be focussed on a smaller spot. There may be too many molecular ions being formed.

2. Sputtering the samples may help i.e. record spectra vs. time.

3. S: You can tune the ionization energy to produce fewer molecules, but then you may create more of the doubly ionized species. Then you need several analysis to see how the peaks change with ionization energy to try to understand what you have. Was several different ionization energy runs attempted?
   Contributor comment: NOT sure how ionization energy can be tuned in SIMS. Unless the TOF instrument has a secondary ionization capability, you cannot tune anything

4. S: Run a sample of the "fuel" to help discriminate any contamination in the testing system
   Contributor comment: You need to run MATCHED pairs, before and after. Otherwise, your cannot determine contamination. Even with this technique, contamination is possible due to materials moving during heating.
   Tester comment: "I think It will help a lot to have the starting material"
   MFMP: Will supply fuel components, Parkhomov Ni and LiAlH4 and mix ratio.

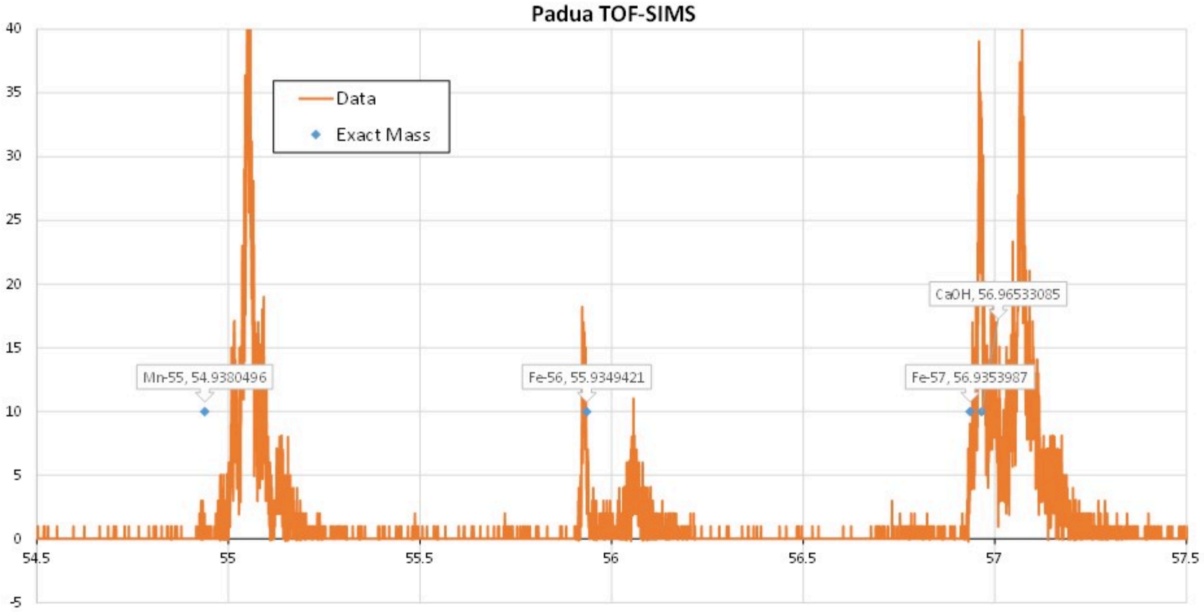
**Notes**

1. SIMS can see Li, but it will also have interferences from [6Li, 7Li] [H, D] and 12C++ and 14C++ and 12CH2++ etc.

2. m/z 73 is interesting as it could indicate (CH3)3Si+ - a contaminant. If true, it does not bode well for trace analysis.
   Contributor comment: The peak at mass 73 might also result from Al2O3 (mass 74) due to calibration error or drift of the TOF measurement?

## Analysis

By “DAK”



This is an expanded area of the SIMS data taken from the ash of the Padua sample. Note the numerous peaks at the nominal masses. The peak at m/z 57 was especially interesting. If it were Fe-57, then the ratio of Fe56/Fe57 would be very far off. However, note that the exact mass for Fe56 is very close to correct (also for Co59, indicating that the calibration was OK - blue diamonds show the expected position), whereas the exact mass for m/z 57 is too high. This indicates that it cannot be Fe57 but is more likely a complex ion of CaOH, whose calculated mass is shown. Also, note the large number of peaks with mass excess (mass greater than nominal). In this mass range this is unusual and can be attributed to hydrocarbon peaks.

A similar analysis can be done at m/z 63-65 for copper. The ratio of nominal masses is incorrect. However, closer inspection indicates that the masses are not copper but hydrocarbons as they all show mass excess.

Thus, just looking at nominal mass would lead one to believe that transmutation had occurred as the hydrocarbon and molecular ion peaks would provide incorrect ratios for elements in this range. That is why SIMS needs to be analyzed VERY carefully. In this case, one is mostly looking at background with no evidence of transmutation.