Elemental Analysis of *Yixing* Tea Pots by Laser-Excited Atomic Fluorescence of Desorbed Plumes (PLEAF)

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Summary

- Two *Yixing* tea pot samples were analyzed by PLEAF.
- The analysis produced no observable damage on the sample surface.
- The elemental profiles of the two samples were identical.
- Major elements were Mg, Ti, Fe, Al, Ca, and Si. No Pb emissions were observed.
- On a single-shot basis, the fluctuation in spectral intensity was around 10% to 15% for Mg and Fe.
- The concentration of some analytes seemed to vary spatially. Si was one example.

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Details of PLEAF analysis of *Yixing* Teaware

Background

Dr. Lawrence Zhang[‡] is an enthusiast in tea culture and teaware collection. He is very experienced in identifying fake teawares. He shared his experience on his personal blog "A Tea Addict's Journal" (http://www.marshaln.com/). He learned of our PLEAF technique for elemental analysis and he wondered if PLEAF could help authenticate teawares. So in May of 2012, he provided us with two Chinese *Yixing* tea pots that were identical in color and shape. He wanted to know if these two pots were identical chemically.

Experimental procedures

The setup for doing PLEAF analysis of the *Yixing* tea pots was shown in **Fig. 1.** Experimental Setup for the PLEAF analysis of *Yixing* tea pots. Left panel: viewed from the top. Right panel: viewed from the right.Fig. 1. The sampled area was indicated by the red spot. This rim position was requested by Dr. Zhang. Each position was sampled by 10 shots. The cap was then manually rotated to expose a new position. About 15 different positions, each 10 shots, were sampled to generate the PLEAF spectra from 260 to 560 nm.

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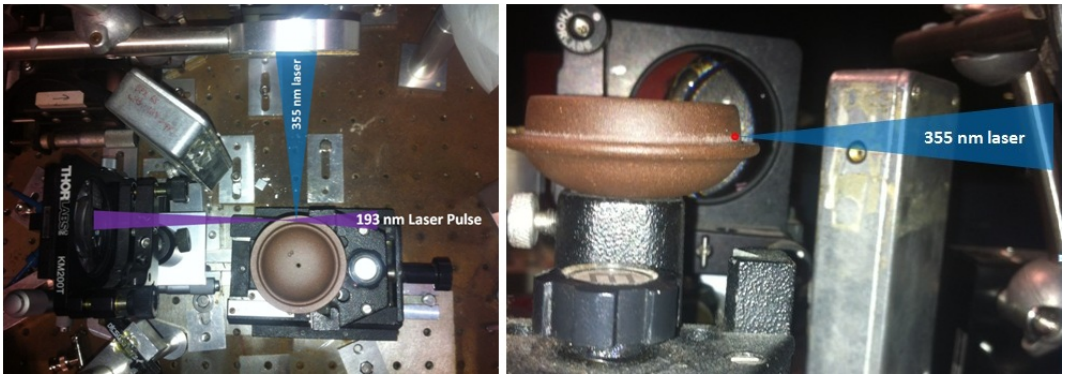

Fig. 1. Experimental Setup for the PLEAF analysis of *Yixing* tea pots. Left panel: viewed from the top. Right panel: viewed from the right. The sampled area was indicated by a red spot (right panel). The first 355 nm laser pulse was 560 mJ cm^{-2} over a spot size of 150 μm. The second 193 nm laser pulse was 25 mJ cm^{-2} over 0.08 cm^2. The Δt between the first and second laser pulse was 200 ns. The ICCD was gated on 40 ns after the 193 nm pulse for 220 ns. ICCD gain value was 255. Spectrometer slit width was 50 μm.

Experimental results

1. No observable damage

Sample damage caused by PLEAF was not observable to the unaided eye. However, due to inexperience with the sample geometry at the beginning, there were two or three places where the sample surface was slightly scorched (darker color). That kind of scorching was completely avoided afterwards.

2. PLEAF spectra and analyte identification

The PLEAF spectra are shown in Fig. 2. The blue and red traces corresponded to *Yixing* sample No.1 and No.2 (coded S1 and S2), respectively.

As can be seen, the spectral features were very similar. We did not see obvious qualitative differences. The quantitative differences were related to the reproducibility of the PLEAF spectra. That will be explained in the next section.

Once the wavelength (X) axis was calibrated, we were able to identify the origin of the emission lines. They corresponded to the following major elements: Mg, Si, Al, Fe, Ca and Ti. The strong 405.8 nm Pb emission line was not detected, as shown in the lower left panel of Fig. 2. Because we did not have matrix-matched calibration standards, the concentration of these elements could not be determined.

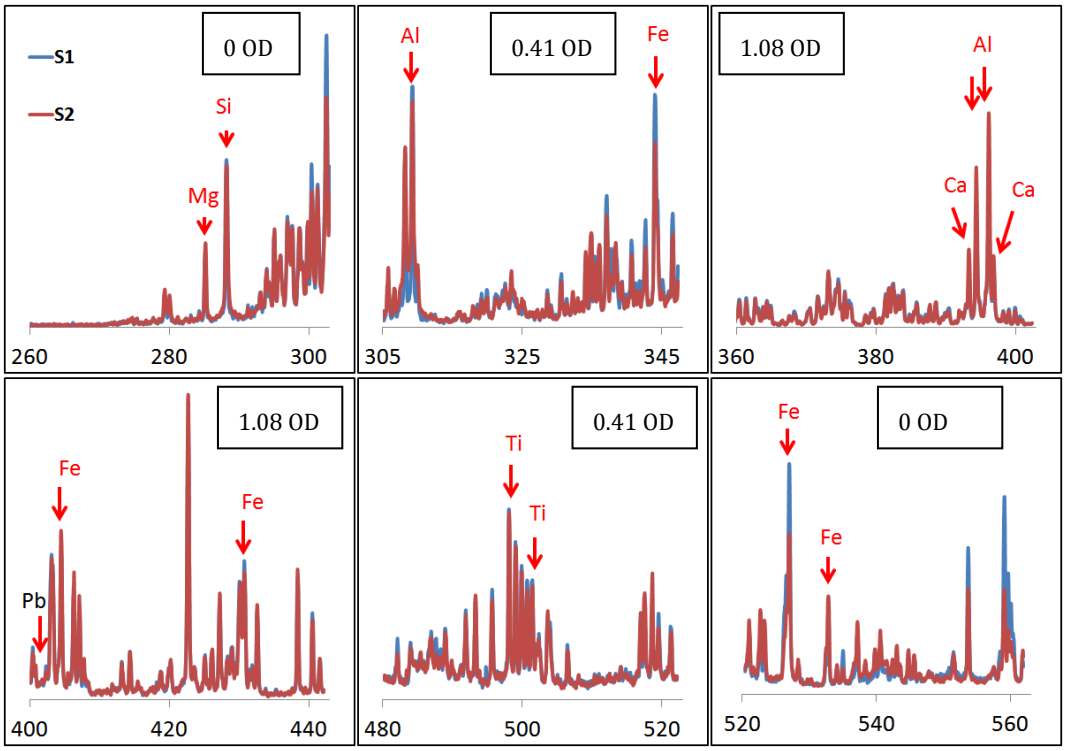

Fig. 2. Panoramic spectra of *Yixing* sample No.1 and No.2. Each spectrum was the accumulation of 10 shots. Vertical axis was the normalized signal intensity. Neutral optical filter, with OD value shown, was used to avoid

ICCD saturation. Spectral features highlighted in the panels are Mg 285.21, Si 288.16, Al 309.28, Fe 344.06, Ca 393.37, Al 394.4, Al 396.15, Ca 396.85, Pb 405.8, Fe 404.58, Fe 430.79, Ti 498.17, Ti 501.4, Fe 526.95 and Fe 532.8 nm emission lines.

3. Reproducibility of PLEAF spectra

Spectral reproducibility was one of the key factors that determine the reliability of PLEAF data. Three single-shot PLEAF spectra, with spectral area normalized to one, were shown in Fig. 3. They represented the maximum, average, and minimum intensity at the Si 288.16 nm spectral position. As can be seen, except for the Si line, most spectral intensities were quite reproducible. We selected three emission lines, Mg 285.21, Si 288.16, and Fe 302.4 nm lines. Their intensities varied from shot to shot. The variation decreased when we averaged over *n* shots. We plotted the intensity fluctuation (in %) as a function of *n* (Fig. 4). As can be seen from Fig. 4, for Mg and Fe, the intensity fluctuation was about 10 – 15 %, and signal averaging did not significantly reduce the fluctuation. This suggests that the single-shot signal reproducibility of PLEAF was about 10 – 15% for *Yixing* analysis. Signal averaging by sampling different depths or different positions probably introduced other variations due to spatial inhomogeneity of analyte contents. This kind of behavior was observed for most other emission lines shown in Fig. 3. The Si 288.2 nm signal, however, was more exceptional. Intensity fluctuation dropped from 30% at 1-shot to 18% at 5-shot average. We believe the 30% fluctuation at 1-shot was not due to instrumental variations because all other emission lines exhibited 10-15% fluctuations only. A more probable reason was significant spatial

inhomogeneity of Si contents in the sample.

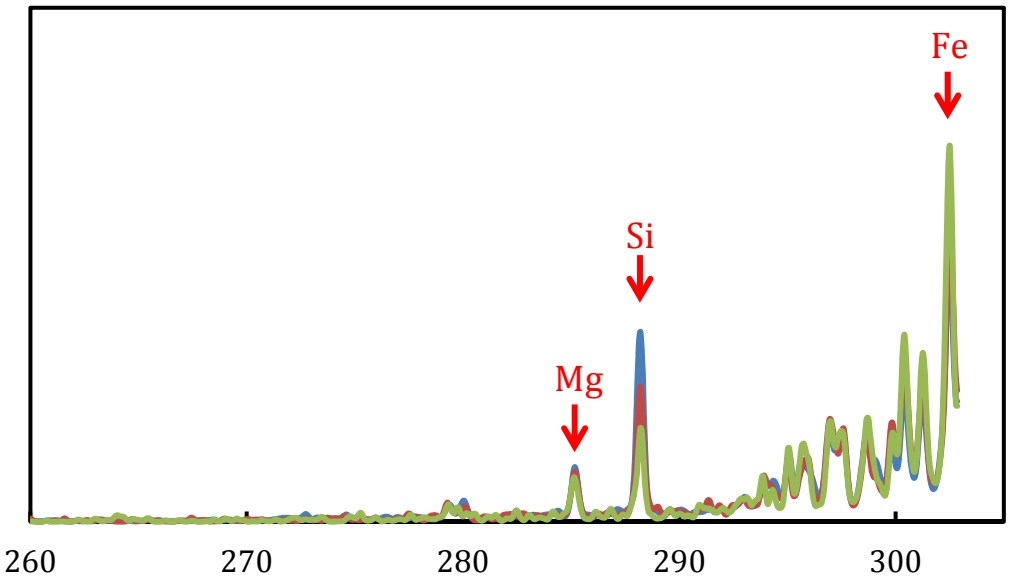

Fig. 3 Comparison of three representative single-shot PLEAF spectra. All spectra had area normalized to 1. The Si signal fluctuated within the minimum (green) and maximum (blue) bracket. Highlighted lines were Mg 285.21, Si 288.16, and Fe 302.4 nm lines.

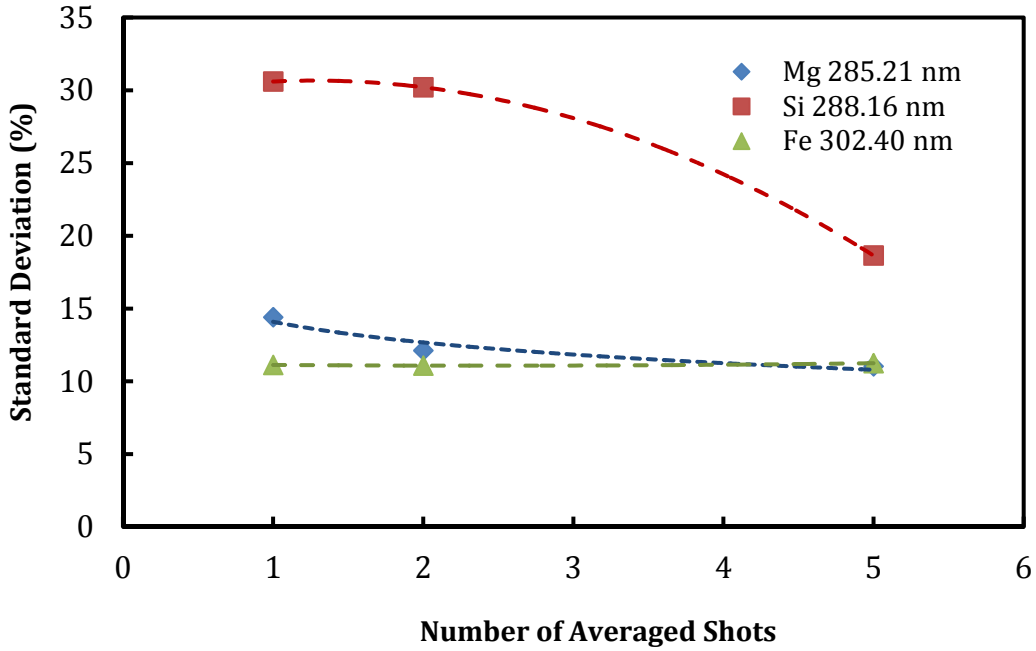

Fig. 4 Standard deviation (%) versus number of averaged shots for the Mg 258.21 (blue diamond), Si, 288.16 (red square) and Fe 302.4 (green triangle) nm lines. Corresponding trend lines were also plotted.

4. Conclusion

PLEAF elemental analysis was performed on two *Yixing* tea pots. The analysis caused no observable damage to the sample surface. Both samples gave similar elemental profile. The major elementals were Mg, Ti, Fe, Al, Ca, and Si. No Pb signal was detected.

Single-shot PLEAF spectra were reproducible to within 10 – 15 % for Mg, Fe and most other analytes. Single-shot signal fluctuation for Si was higher, about 30%. This was probably due to significant spatial inhomogeneity of Si contents in the *Yixing* tea pots.