COMPARISON OF TIME-OF-FLIGHT AND MULTICOLLECTOR ICP MASS SPECTROMETERS FOR MEASURING ACTINIDES IN SMALL SAMPLES USING SINGLE SHOT LASER ABLATION

Ames Laboratory Technical Report # IS-5162

R. S. Houk*, D. B. Aeschliman, S. J. Bajic and D. Baldwin.

Ames Laboratory USDOE
Department of Chemistry
Iowa State University
Ames IA 50011 USA

*Corresponding author.
Tel. 1-515-294-9462 fax 1-515-294-5233
rshouk@iastate.edu

INTRODUCTION

The objective of these experiments is to evaluate the performance of two types of ICP-MS device for measurement of actinide isotopes by laser ablation (LA) ICP-MS. The key advantage of ICP-MS compared to monitoring of radioactive decay is that the element need not decay during the measurement time. Hence ICP-MS is much faster for long-lived radionuclides. The LA process yields a transient signal. When spatially resolved analysis is required for small samples, the laser ablation sample pulse lasts only ~ 10 seconds. It is difficult to measure signals at several isotopes with analyzers that are scanned for such a short sample transient.

In this work, a time-of-flight (TOF) ICP-MS device, the GBC Optimass 8000 (Figure 1) is one instrument used. Strictly speaking, ions at different m/z values are not measured simultaneously in TOF. However, they are measured in very rapid sequence with little or no compromise between the number of m/z values monitored and the performance. Ions can be measured throughout the m/z range in single sample transients by TOF.

The other ICP-MS instrument used is a magnetic sector multicollector MS, the NU Plasma 1700 (Figure 2). Up to 8 adjacent m/z values can be monitored at one setting of the magnetic field and accelerating voltage. Three of these m/z values can be measured with an electron multiplier. This device is usually used for high precision isotope ratio measurements with the Faraday cup detectors. The electron multipliers have much higher sensitivity. In our experience with the scanning magnetic sector instrument in Ames, these devices have the highest sensitivity and lowest background of any ICP-MS device.

The ability to monitor several ions simultaneously, or nearly so, should make these devices valuable for the intended application: measurement of actinide isotopes at low concentrations in very small samples for nonproliferation purposes. The primary sample analyzed was an urban dust pellet reference material, NIST 1648. The ability to provide good detection limits for single laser shots is critical.

EXPERIMENTAL

A CETAC LSX-500 was used for LA. The same LA unit was used with either MS to keep the same basis of comparison. The spot size for the results shown below was 50 μm diameter. Spots as small as 10 μm were used. With a given MS, the experiment started with large enough spot size and sufficient numbers of shots to ensure observation of a signal. The number of shots was then reduced to see if analyte ions could still be measured from single shots. The mass spectrometers were used under operating conditions that maximized M^+ signal for each device during LA.

NIST glass samples were used for setup and optimization. The Urban Dust pellet was prepared by pressing the particulate material into an aluminum planchette. The pellet adhered well enough that an additional binder was not necessary.

RESULTS AND DISCUSSION

TOF Results. Plots of signal versus time for several elements are shown in Figure 3. These isotopes were all measured from the same LA pulses. Starting from the left, shown first are signal pulses for 5 repetitions of 200 shots, then 5 reps x 20 shots, 5 reps x 5 shots, finally 5 reps x 1 shot. Naturally, less signal is seen when fewer laser shots are used. Stable isotopes of Cs and Sr were measured because of interest in their radionuclides ^{137}Cs and ^{90}Sr. These latter isotopes could be measured if present at levels above the stable isobars ^{137}Ba and ^{90}Zr.

Figure 4 gives an expanded view of the single shot transients for ^{238}U and ^{235}U. ^{238}U is easily measured at 5.5 ppm in the sample. ^{235}U should be observed at the same time as ^{238}U. The vertical red lines can be used to identify when ^{235}U is expected. The spikes of various heights for ^{235}U correspond to observation of one, two or three $^{235}U^+$ ions at a time. There aren't enough of these ions to generate a smooth profile.

To determine if the signals at m/z = 235 are significant, the background was measured at m/z = 220. No ions are expected at m/z = 220. However, a few ions of various m/z values leak into the flight tube after the extraction pulse and are seen as a background distributed throughout the m/z range. In four of the five LA pulses, the signal seen at m/z = 235 was higher than the background. Thus, ^{235}U in this sample is just observable. The detection limit for single shots is

estimated to be approximately 40 ppb uranium, assuming ^{235}U is 0.7% of ^{238}U. The detection limit is better than 40 ppb if the uranium has been depleted.

Multicollector Results. This device had higher signals and lower background than the TOF instrument. Figure 5 shows signal versus time plots for ^{238}U on a Faraday cup detector (see Figure 2) and ^{235}U on an electron multiplier. The device can easily see ^{235}U at 40 ppb in the sample from single laser shots.

In a subsequent experiment, the electron multipliers are used to measure m/z = 234 and 236, corresponding to two trace U isotopes. Figure 6 shows that ^{234}U is readily observed at an estimated concentration of 0.3 ppb. The detection limit is conservatively estimated to be ~ 0.1 ppb. The large spikes on the single shot profiles probably come from large particles from previous ablation events dislodged from the LA cell or transfer tube by the shock wave generated by the laser shot.

The dust pellet sample also contains ions at m/z = 236, which are believed to be $^{236}U^{+}$. Subsequent experiments done in Ames indicate this ion is not merely $^{235}U^{1}H^{+}$. ^{236}U is not abundant enough to be seen reliably from single shots but is just observable from 5 shots (Figure 6). The concentration of ^{236}U in this material is less than that of ^{234}U (0.3 ppb) but otherwise is not known. The single shot profiles for both ^{234}U and ^{236}U represent only a few ions, so the reproducibility is low because of poor counting statistics on small numbers of ions. These low levels are observable because of the remarkably low background with this instrument.

CONCLUSIONS

1. The multicollector magnetic sector instrument can detect actinides from single laser shots at ~0.1 ppb in the sample. This can be done for as many isotopes as there are electron multipliers. However, the magnet setting must be kept the same during the laser transient, so this measurement is restricted to isotopes close in mass. Other actinides, including plutonium, could be measured with similar performance. More isotopes can be monitored at once in individual laser shots with a multicollector instrument than the scanning instrument being used at present in Ames.

2. The TOF instrument can detect actinides from single laser shots only at higher levels, ~40 ppb. However, it can potentially measure different elements in widely different m/z ranges, which might be of use for measuring ^{90}Sr, ^{137}Cs, or other isotopes of concern for dirty bombs. Means for correcting for or removing isobaric, stable isotopes would be necessary for this latter application.

ACKNOWLEDGEMENTS

Ames Laboratory is operated for the USDOE by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the USDOE, Office of Defense Nuclear Nonproliferation, and the Office of Nonproliferation Research and Engineering, NA-22.

The TOF experiments were done at the National Research Council of Canada, Ottawa, Ontario. Ralph Sturgeon and Scott Willie assisted these measurements greatly, as did Flynn Saint from GBC. The multicollector measurements were done at the Geological Survey of Canada, Ottawa Ontario, with help from Conrad Gregoire and Will Doherty.

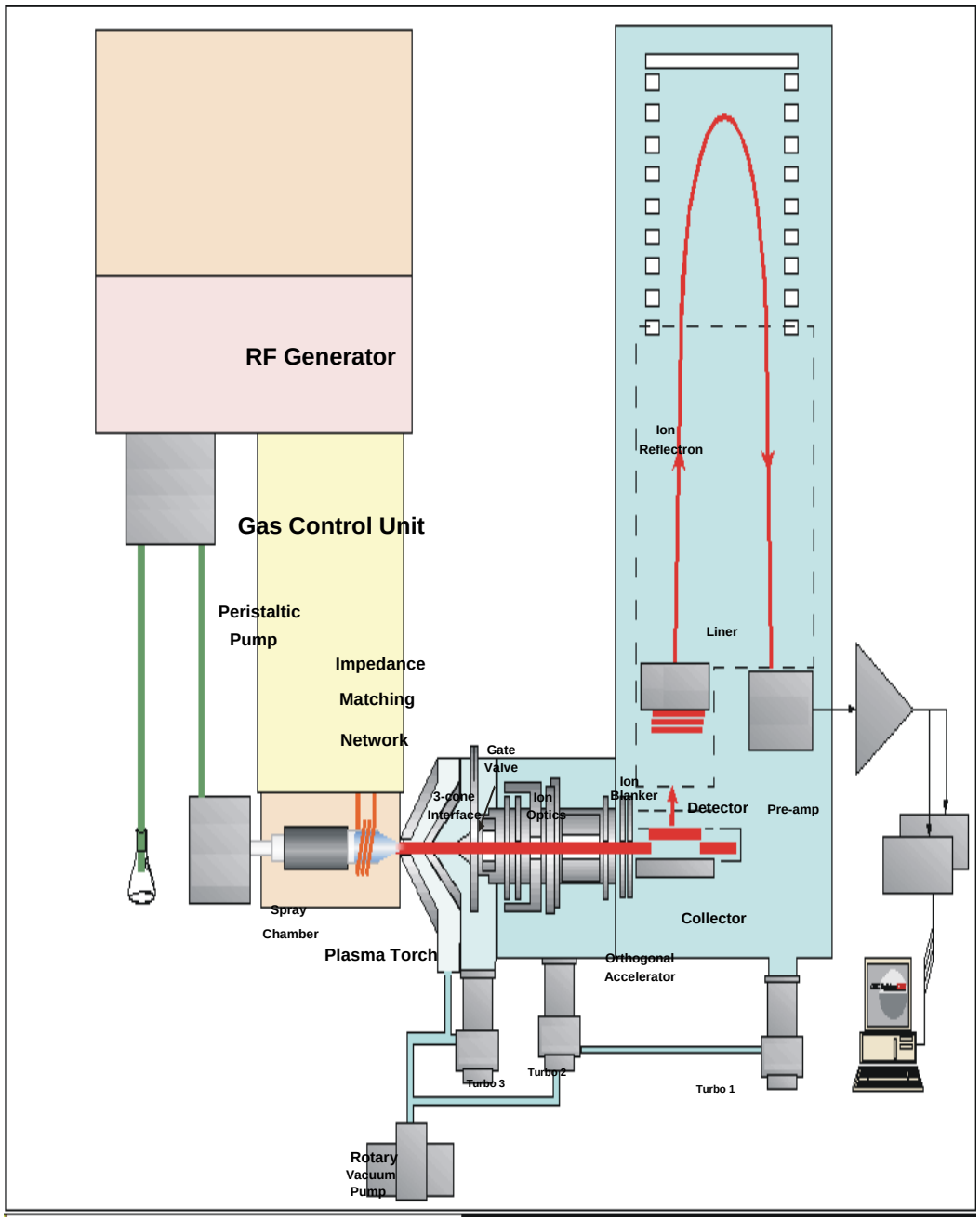
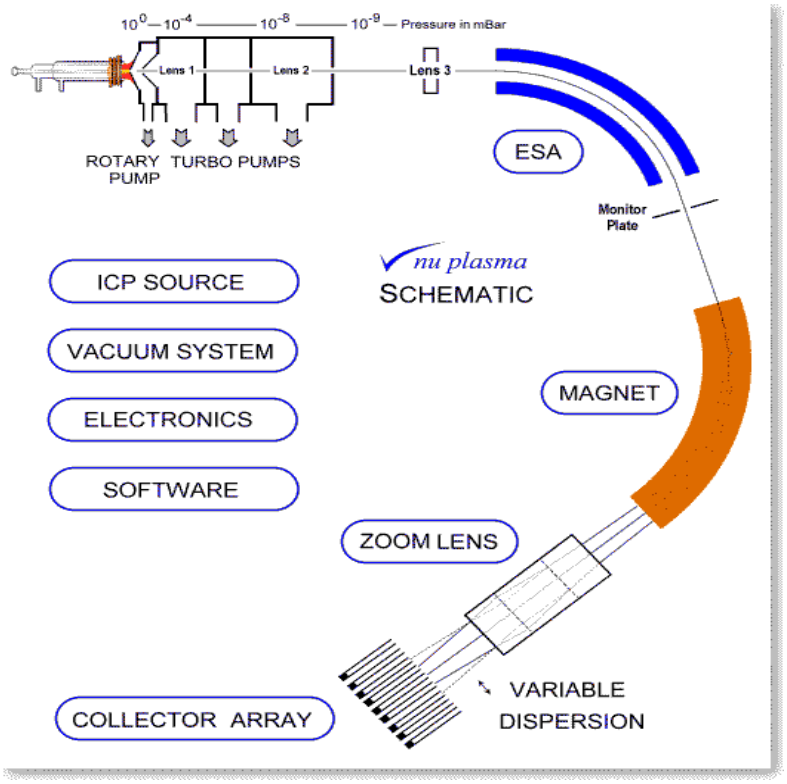


Figure 1. Diagram of GBC Optimass 8000 ICP-TOF-MS. Reproduced with permission of GBC.



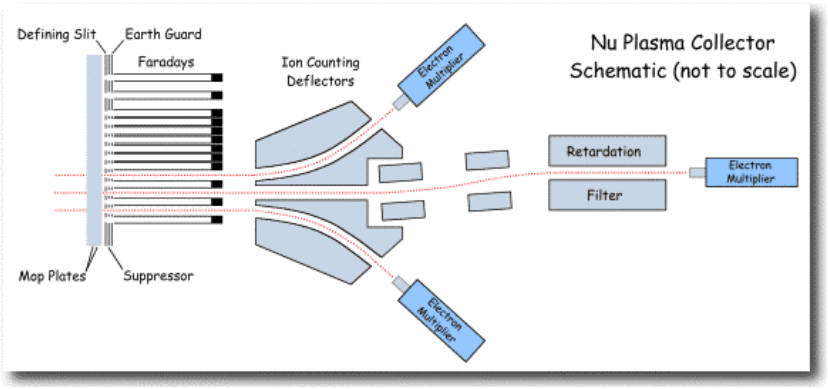


Figure 2. NU Plasma 1700 ICP multicollector MS.
Top: entire instrument.
Bottom: close up of detectors showing Faraday cups and electron multipliers.
Reproduced with permission of NU Instruments.

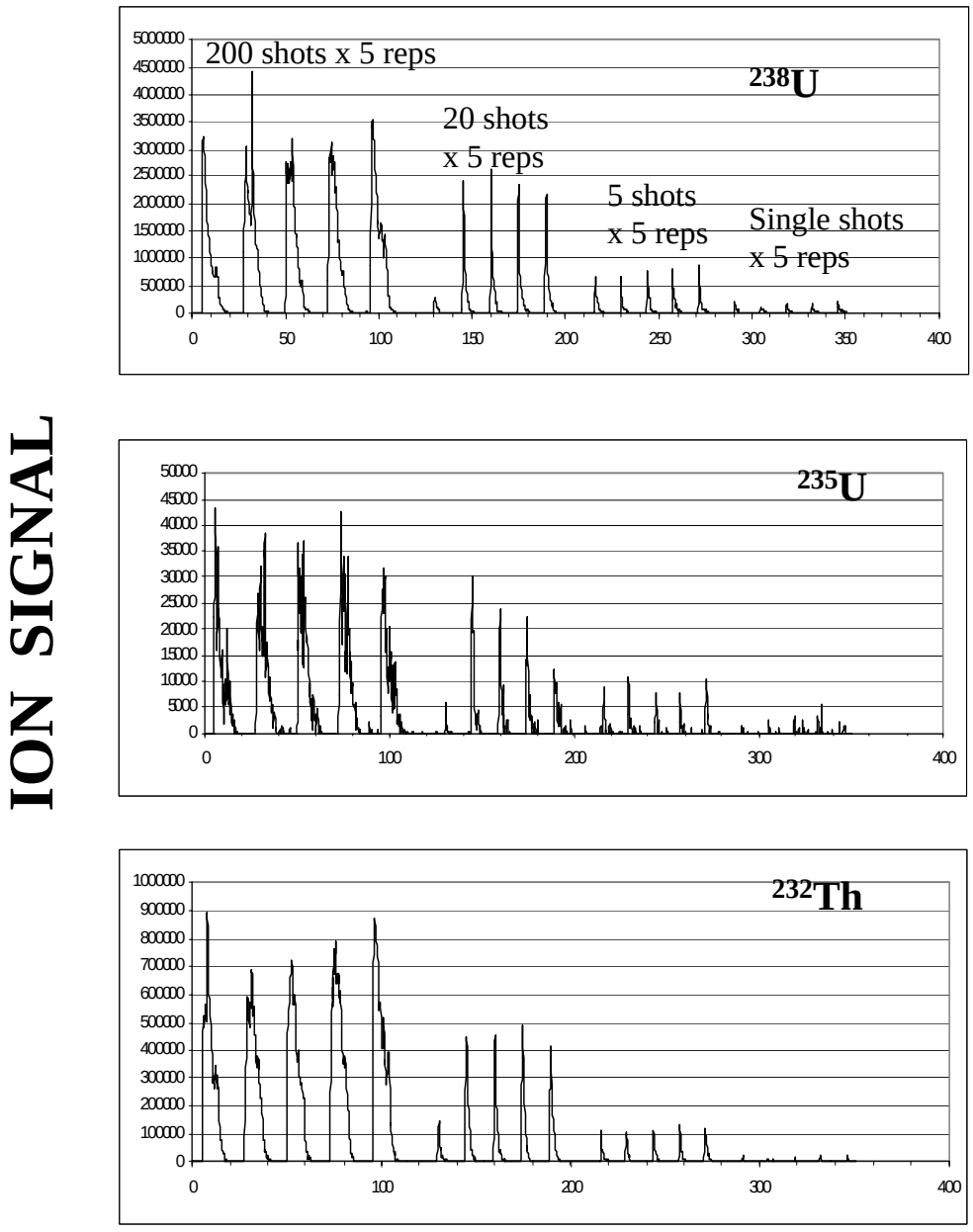


Figure 3. Time profiles obtained from LA of dust pellet using ICP-TOF-MS. The various isotopes shown were monitored from the same LA transients.

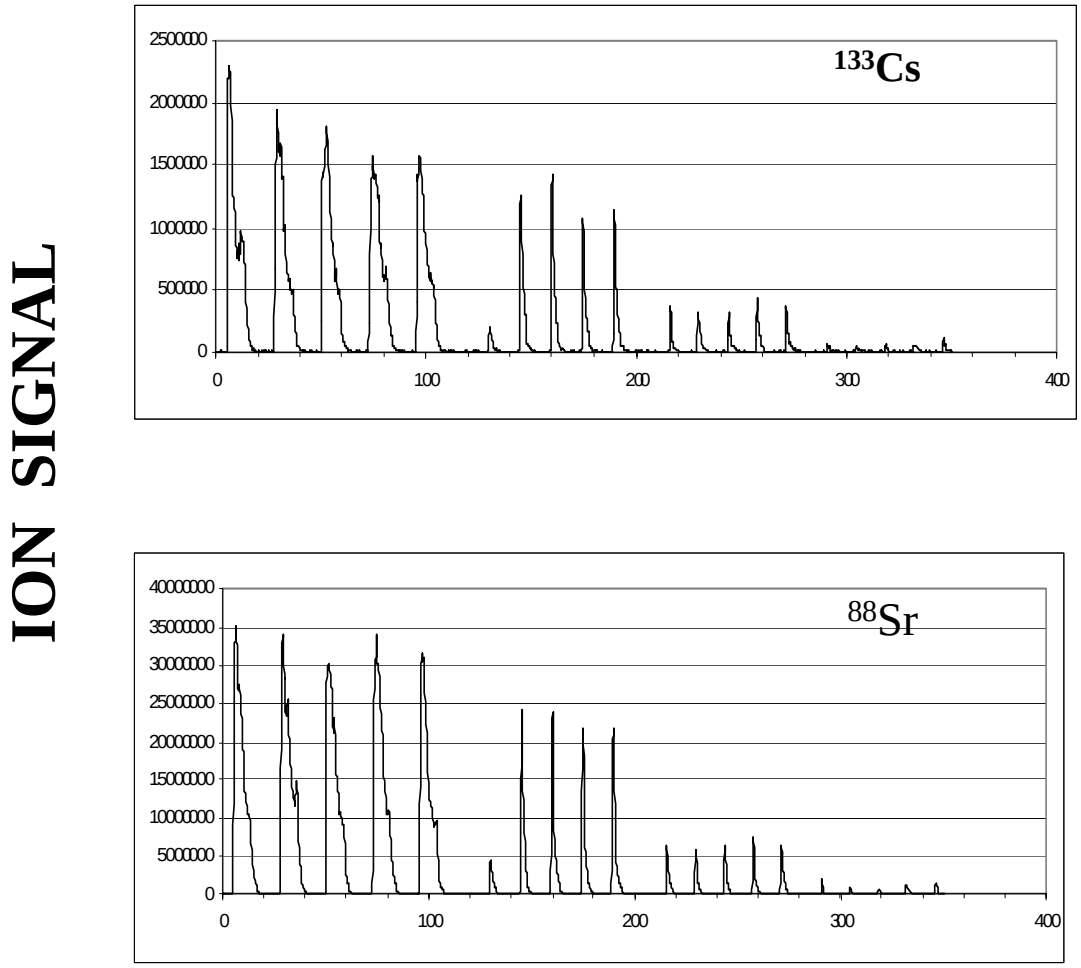


Figure 3 continued.

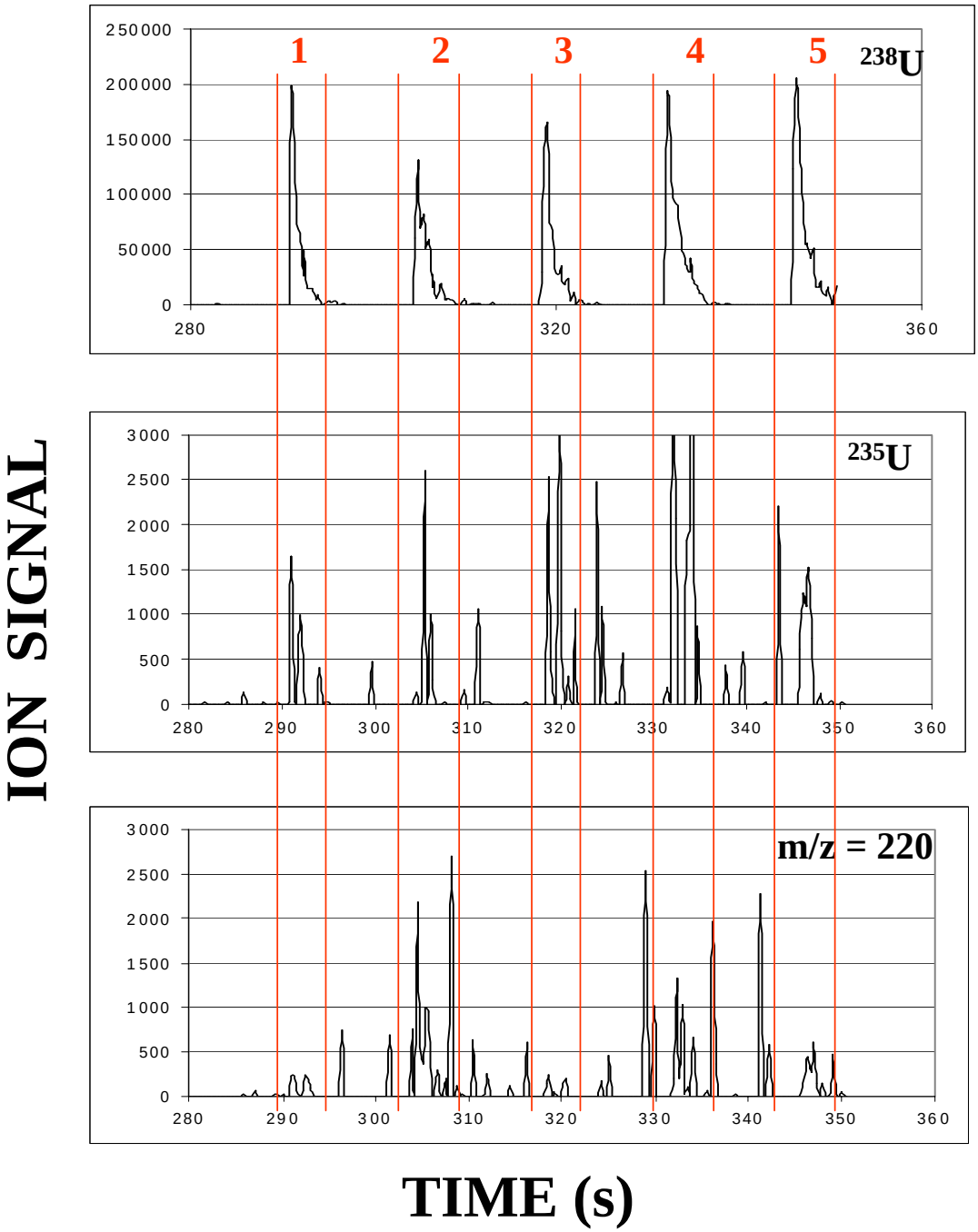


Figure 4. LA-ICP-TOF-MS of dust pellet. Close up of single shot region For 5 shots from from far right side of Figure a. Red lines indicate times when U^+ ions are observed due to ablation of sample.
^{235}U is present at ~ 40 ppb.

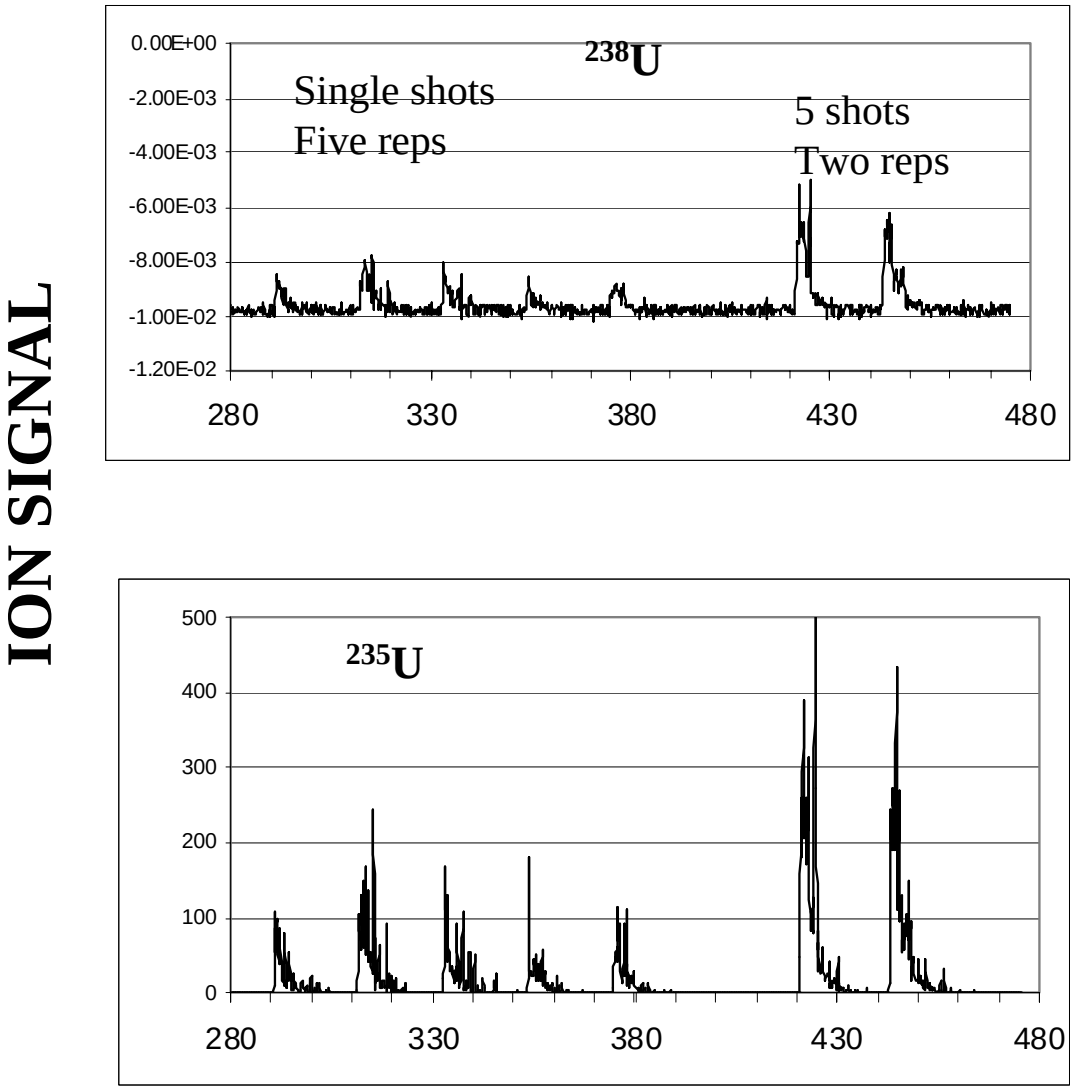


Figure 5. LA of dust pellet with ICP multicollector MS. ^{238}U is monitored with a Faraday cup, ^{235}U with an electron multiplier.

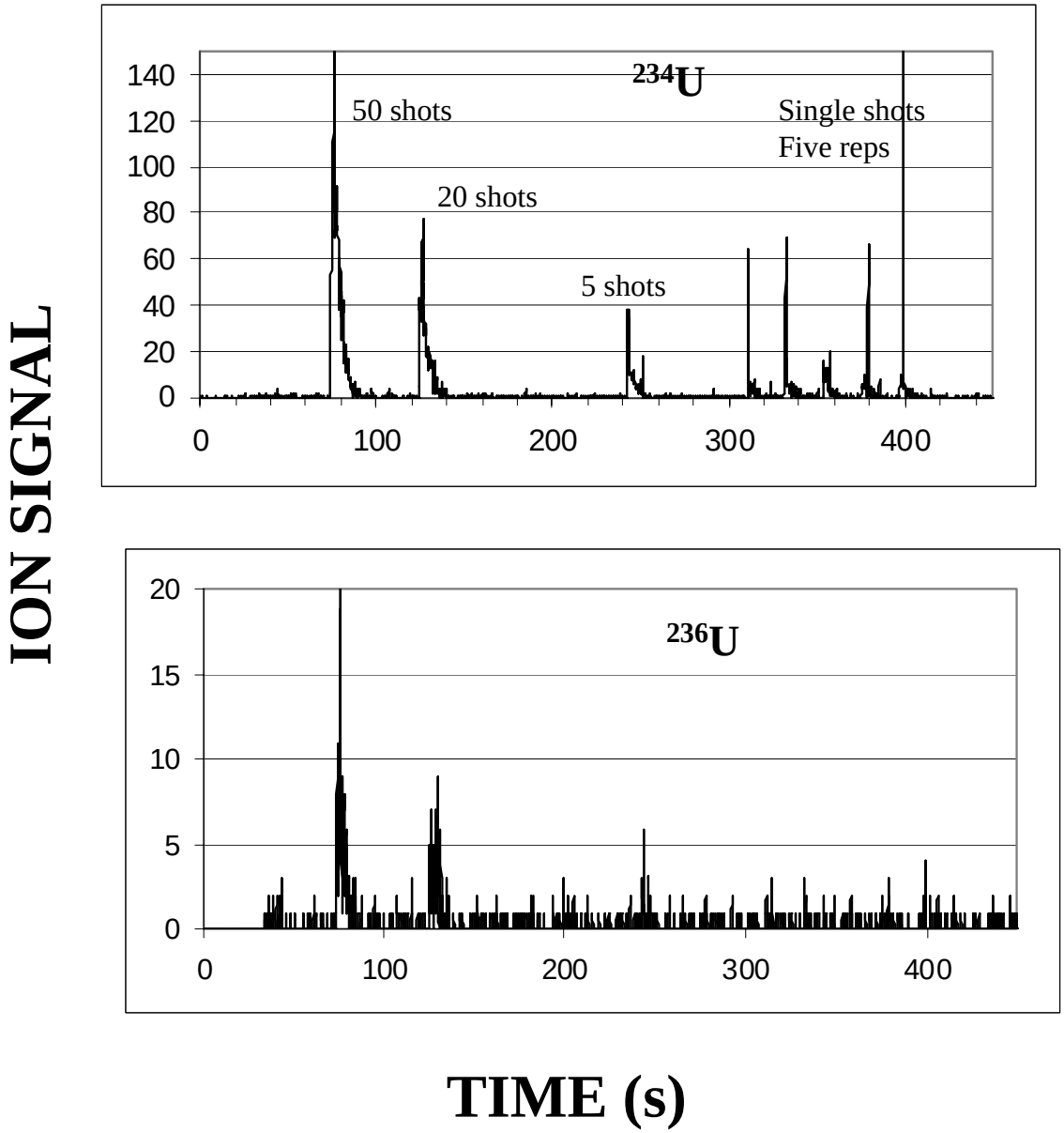


Figure 6. LA of dust pellet with ICP multicollector MS. Both isotopes are monitored with electron multipliers. ^{234}U is present at ~ 0.3 ppb.

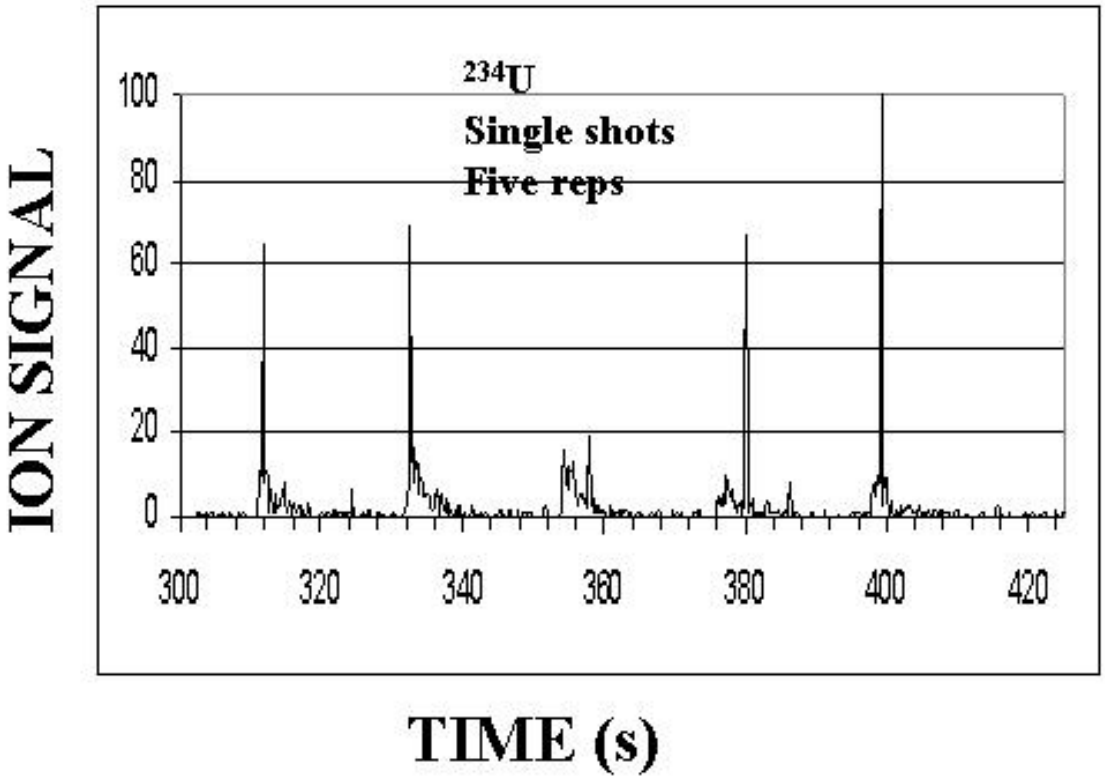


Figure 6 continued.