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SIMS and ESCA Studies of Possible Sodium Uranate Precursors As Related to Aerosol Characterization From a Simulated HCDA

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Contents

Summary

During the main thrust of the HCDA studies, it was found that sodium uranates, especially Na_3UO_4, were formed when the Na-U-O system was subjected to high temperatures approximating those of the HCDA. Mechanisms through which these rather complicated compounds are formed remain unknown. The purpose of these SIMS and ESCA studies was to detect the formation of any precursor ion species to the sodium uranates.

The main species detected from the Ar^+ excited positive SIMS analyses of oxides in salts of uranium were UO_2^+, UO^+, and U^+.

The main ion detected from the Ar^+ excited negative SIMS analyses was O^-. No Na-U-O complex was observed from the Ar^+ excited SIMS analyses of a $Na_2U_2O_7$ or of a UO_2-Na_2O pellet or from a sodium film deposited on a uranium metal foil.

ESC analyses show peak shapes and binding energies for the $Na_2U_2O_7$ pellet that are different from those for the U-Na foil samples and the UO_2-Na_2O pressed pellet.

The ESCA results agree with theory and support the presence of $U_2O_7^=$ in $Na_2U_2O_7$; however, SIMS analyses show no evidence of possible uranate precursor formation in an Ar^+ sputtered ion beam.

1. Introduction

During the main thrust of the HCDA (hypothetical core-disruptive accident) studies, it was found that sodium uranates, especially Na_3UO_4, were formed when the Na-U-O system was subjected to high temperatures approximating those of the HCDA [1]. Mechanisms through which these rather complicated compounds are formed are unknown [2]. A detailed knowledge of these mechanisms and the rates of their various steps would allow the prediction of production pathways and overall rates, given the accident conditions. Mound has exposed the Na-U-O system to high-temperature conditions in the high vacuum of a mass spectrometer in order to detect precursor ion species to the sodium uranates.

2. Theory

During the most severe hypothetical core-disruptive accidents (HCDA), caused for example by transient overpower (TOP) or loss of flow (LOF), substantial amounts of the reactor fuel, stainless steel cladding, and sodium coolant could be vaporized. The vapor species formed, including PuO, UO, PuO_2, UO_2, UO_3, O, O_2, Na, stainless steel, and the fission products, are expected to be contained initially in gas bubbles within, the sodium coolant. A temperature gradient within the bubble will exist, initially, from probably greater than 2800°C in the gas phase to about 900°C at the liquid sodium walls of the bubble. As the bubble moves away from the primary heat source, cooling will cause condensation and reactions of various vapor species, probably resulting in the formation of an aerosol. In addition, condensation and reactions will occur at the liquid sodium walls of the bubble.

The physical and chemical properties of the aerosol particles are important in predicting the eventual behavior and fate of the aerosol. Physical properties of the aerosol (particle size, density, settling velocity, and coagulation tendencies) are currently being studied, chiefly by vaporization of UO_2. The chemical nature of the aerosol particles, which is determined by the chemical species present in the various temperature regimes transited by the aerosol, must be considered because it could affect the physical properties of the aerosol and would definitely influence the subsequent environmental and biological pathways of any aerosol that might escape from the reactor containment structure.

3. Experimental procedure

3.1. Secondary ion mass spectrometry (SIMS)

3.1.1. MATERIALS

The pellets used for the study were composed of 50% UO_2 - 50% Na_2O by weight. The depleted UO_2 was 99.5% pure. The Na_2O was 98% pure.

The materials were mixed using a mortar and pestle, charged into a 14-mm diameter, graphite-coated die, and hydraulically pressed at 8.61×10^8 Pa in an argon atmosphere glovebox. The moisture level was less than 1.0 ppm, and oxygen level was less than 10.0 ppm.

The uranium metal foils used for the study were 99.9% pure. The sodium metal used was reagent grade, stored under xylene. The uranium metal was cleaned in a 1:1 HCl solution to remove the surface UO_2. The metal foils were rinsed with distilled water and dried with ethanol. The uranium and sodium metal were then passed into an argon atmosphere glovebox. The glovebox conditions were the same as stated above. The sodium metal was trimmed of its oxide coat. The uranium metal foils, which were 3.0 mm wide by 0.5 mm thick, were cut into 25.4 mm lengths. The sodium was then rubbed onto both surfaces of the foils, depositing a thin surface film of sodium.

The U-Na metal foils and the 50% UO_2-50% Na_2O pellets were placed in separate primary and secondary metal containers (double containment) and removed from the argon atmosphere for SIMS and ESCA (electron spectroscopy for chemial analysis) analyses.

3.1.2. METHOD

The two specimens, the 50% UO_2-50% Na_2O pellet and the uranium foil with a thin surface film of sodium, were bombarded with an argon ion beam using SIMS equipped with a 3M mini-beam ion gun and an extranuclear quadrupole mass spectrometer.

The SIMS experiment involved the bombardment of the sample with a 4500 eV argon ion beam and subsequent detection of the secondary ions with a mass spectrometer. The SIMS system was calibrated and optimized for masses exceeding 200 amu. A metal uranium foil with black oxide was used to optimize the system. The secondary ion yields for UO_2 were measured. SIMS spectra were recorded from the pellet and the foil specimens to determine whether any Na-U-O compounds were formed.

3.1.3. RESULTS

For the 50% UO_2-50% Na_2O pellet, the species that were identified between 2 and 140 atomic mass units (amu) were: O^+, Na^+, O_2^+, NaO^+, Na_2^+, NaO_2^+, Na_2O^+, and Na_3O^+ and between 230 and 370 (amu) were: U^+, UO^+, and UO_2^+. Figures 1 and 2 show the spectra and the identification of the species between 2 and 370 amu.

Figures 3 and 4 are similar to the preceding two figures except they are mass spectra taken from a uranium foil with a "thin film" of sodium on the surface. The species identified between 2 and 140 amu were: O^+, Na^+, NaO^+, Na_2^+, NaO_2^+, and Na_2O^+, and between 230 and 370 amu were: U^+, UO^+, and UO_2^+. In Figure 3 a reasonable identification of mass 51 and 115 cannot be made although it is strongly suspected that a memory effect from a previous indium specimen was responsible for the 115 peak. Mass 51

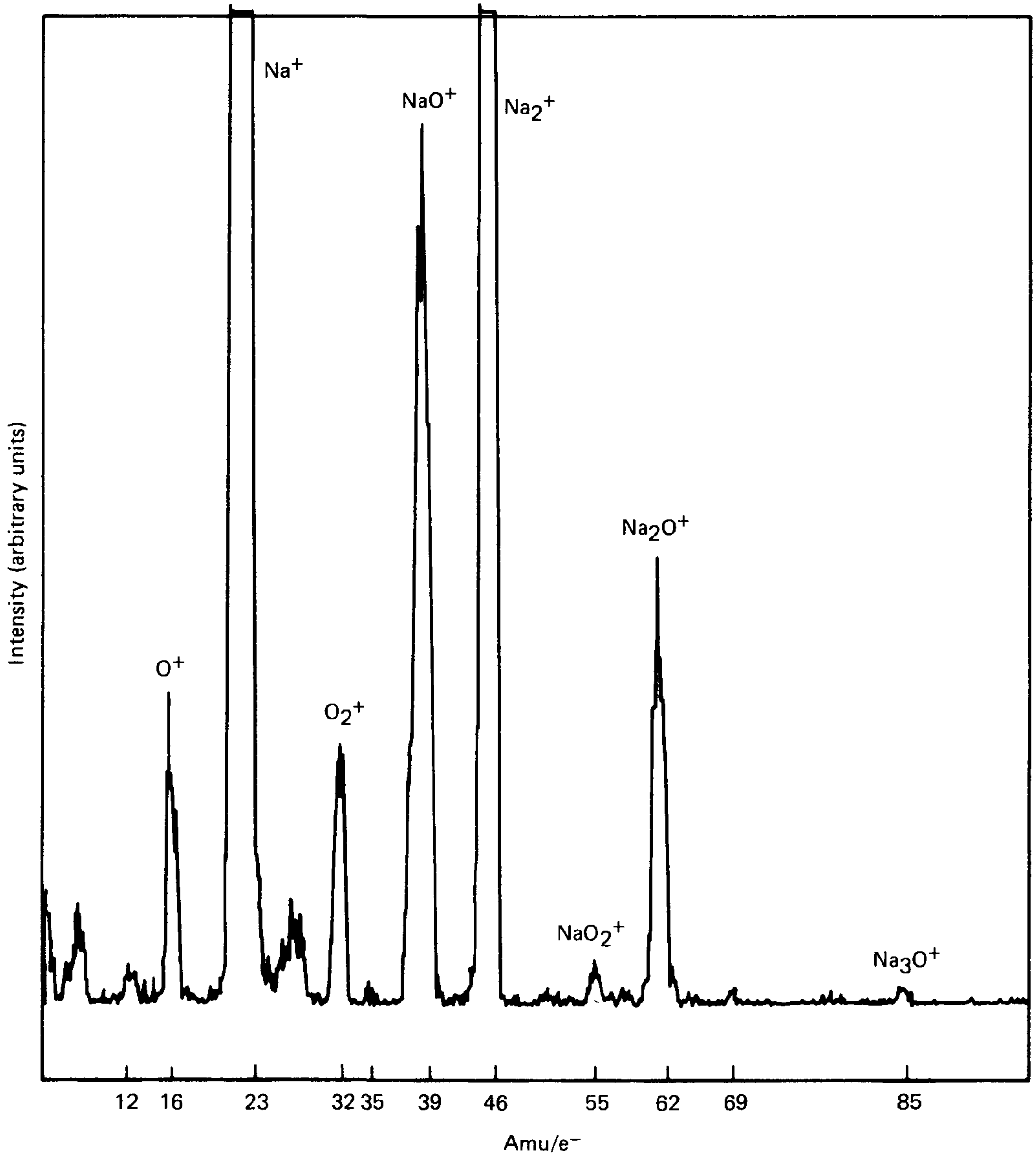

FIGURE 1 - Positive SIMS spectrum of 50% UO_2-50% Na_2O pellet from 0 to 150 amu/charge units.

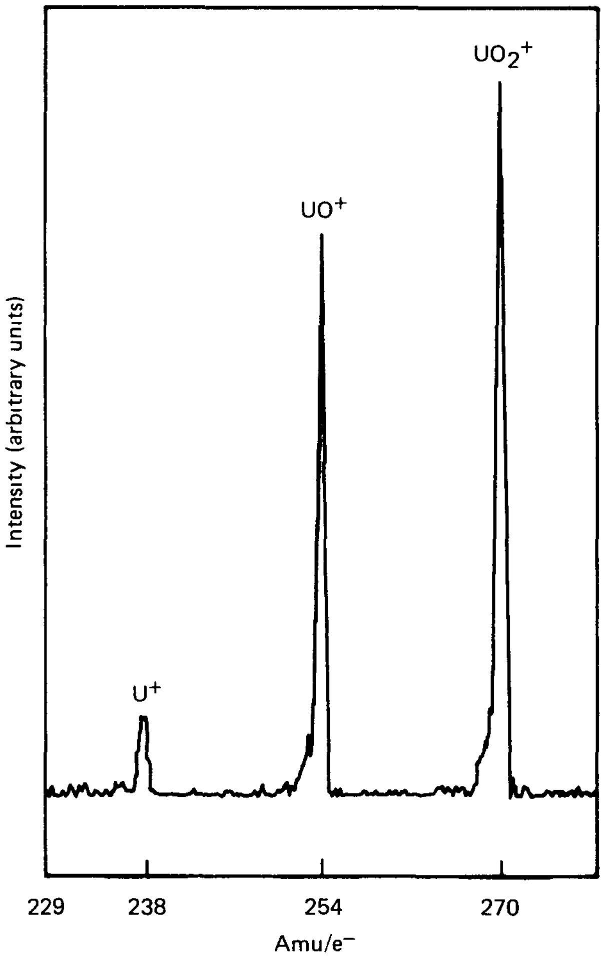

FIGURE 2 - Positive SIMS spectrum of 50% UO_2-50% Na_2O pellet from 229 to 369 amu/charge units.

corresponds to vanadium, the presence of which cannot be explained. It could also be a doubly charged molecular ion such as $Na_3O_2^{++}$ which would appear at mass 50.5.

Figures 5 and 6 show the SIMS spectra obtained from an $Na_2U_2O_7$ pellet. The species identified between 2 and 140 amu were: Na^+, O_2^+, and NaO^+, and between 230 and 370 amu were: U^+, UO^+, and UO_2^+ An attempt was made to try to identify a mass peak in the vicinity of Na_3UO_4 (mass 371) and $Na_2U_2O_7$ (mass 634). In neither case could a significant mass peak be identified above background.

The main species detected from the Ar^+ excited negative SIMS analyses was O^-. One would expect that anionic uranium oxide species would be the precursors of the uranates formed in a HCDA. However, no anionic species other than O^- were detected in the negative SIMS spectra. The reason for this is not apparent at this time. Perhaps some anionic species were formed but their concentrations were below the detection limit of the instrument. In this regard, Laser Microprobe Mass Analyzer (LAMMA) studies are planned in order to detect anionic species. The laser experiment involves the bombardment of the sample with a high powered pulse of UV light with subsequent detection of the positive and negative spectra. The LAMMA technique produces temperatures in the plasma on the order of 5000 to 10,000 K during laser bombardment of the sample. This approach is more analogous to the HCDA simulation accomplished at Mound and is expected to be a more applicable technique than SIMS. As a consequence, anion yields should be higher relative to positive ion yields, and the chances of observing precursors to the uranate salts produced in a simulated HCDA are increased. This result should in turn provide additional information about the mechanisms involved in a simulated HCDA.

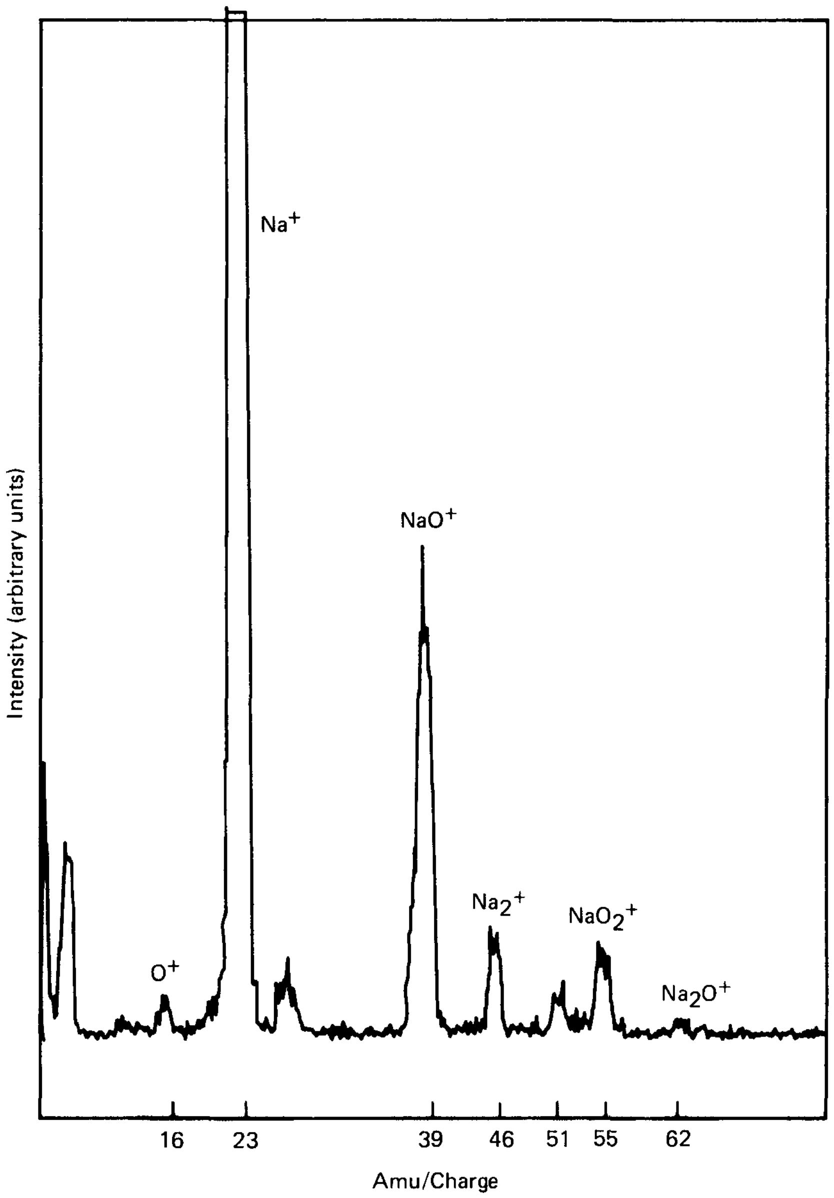

FIGURE 3 - Positive SIMS spectrum at a U foil with a thin film of Na from 0 to 150 amu/charge units.

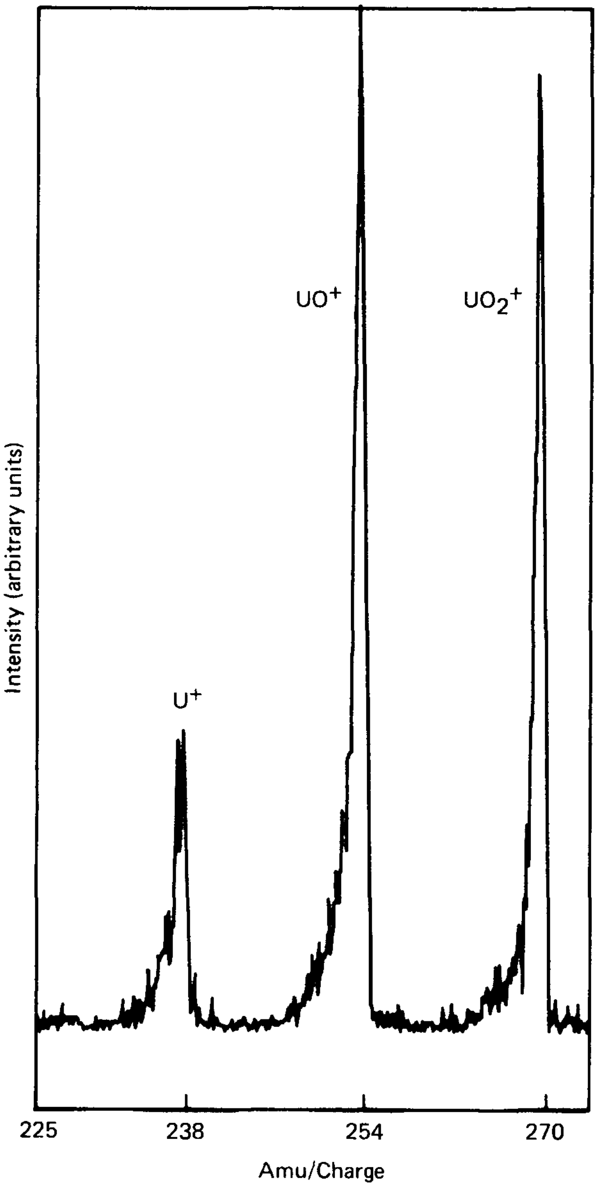

FIGURE 4 - Positive SIMS spectrum at a U foil with a thin film of Na from 225 to 365 amu/charge units.

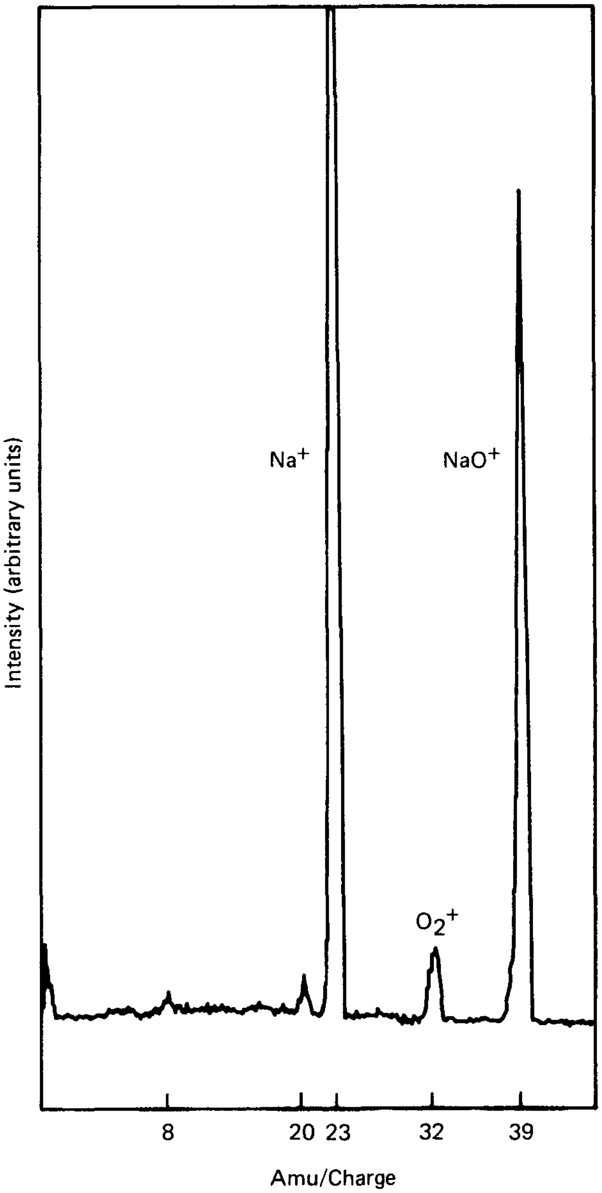

FIGURE 5 - Positive SIMS spectrum of a $Na_2U_2O_7$ pellet from 0 to 150 amu/charge units.

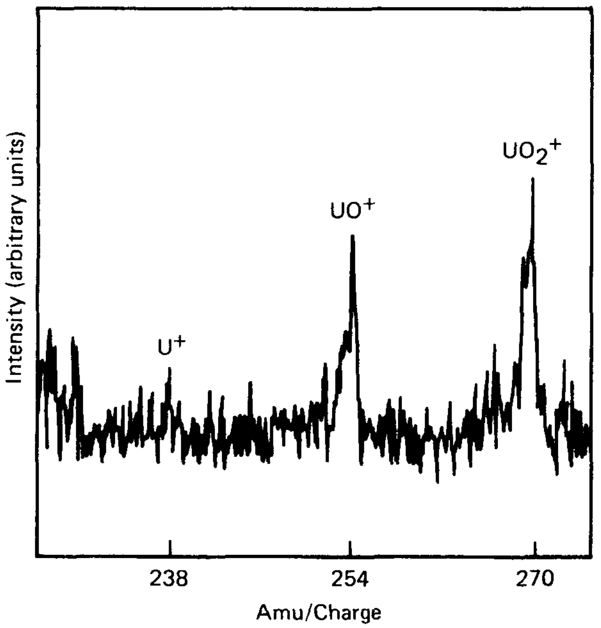

FIGURE 6 - Positive SIMS spectrum of a $Na_2U_2O_7$ pellet from 225 to 365 amu/charge units.

3.2. Electron spectroscopy for chemical analyses (ESCA)

3.2.1. MATERIAL

The materials and samples used were the same as those used for the SIMS analyses.

3.2.2. METHOD

The analytical technique ESCA involves the interaction of x-ray photons having a constant energy, hν, with bound electrons in a sample, having a binding energy E_B. Via the photoelectric effect, these bound electrons are promoted into a continuum outside the sample as photoelectrons with a kinetic energy, E_K. By measuring the various values of E_K for photoelectrons ejected from a sample, one can determine by simple subtraction ($h\nu - E_K$) the binding energy E_B for all the energy levels of atoms or molecules in the sample.

A qualitative analysis of the elements present on the surface is accomplished by measuring values of E_B to within a few electron volts; the oxidation state of an element is characterized by determining E_B to within a couple of tenths of a eV. Semiquantitative surface atom concentrations are ascertained by measuring the photoelectron peak heights and adjusting for the sensitivity of the instrument to the different elements. The x-ray source used in the following results was a magnesium anode, which has a $K_{\alpha 1,2}$ line with an energy of $h\nu = 1253.6$ eV. The electron energy decoder used to determine E_K was a pair of hemispherical electrostatic plates.

The ESCA spectra discussed in this report were measured from samples in high vacuum (approximately 1×10^{-7} torr pressure). For the compounds of interest the technique is nondestructive.

The samples used for this study were the same as those used for the SIMS analyses, namely a 50% UO_2-50% Na_2O pellet, a 100% $Na_2U_2O_7$ pellet, and a uranium metal foil with a "thin film" of sodium on the surface.

3.2.3. RESULTS

The ESCA spectrum from the foil specimen that had a thin film of sodium (Figure 7) shows clearly the presence of uranium on the surface. The high resolution spectrum of the uranium 4f peaks (Figure 8) shows the presence of the characteristic shake-up peaks* at 6.8 eV above the binding energies of the 4f doublet, strongly

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*A shake-up peak is a photoionization process due to excitation accompanying ionization.

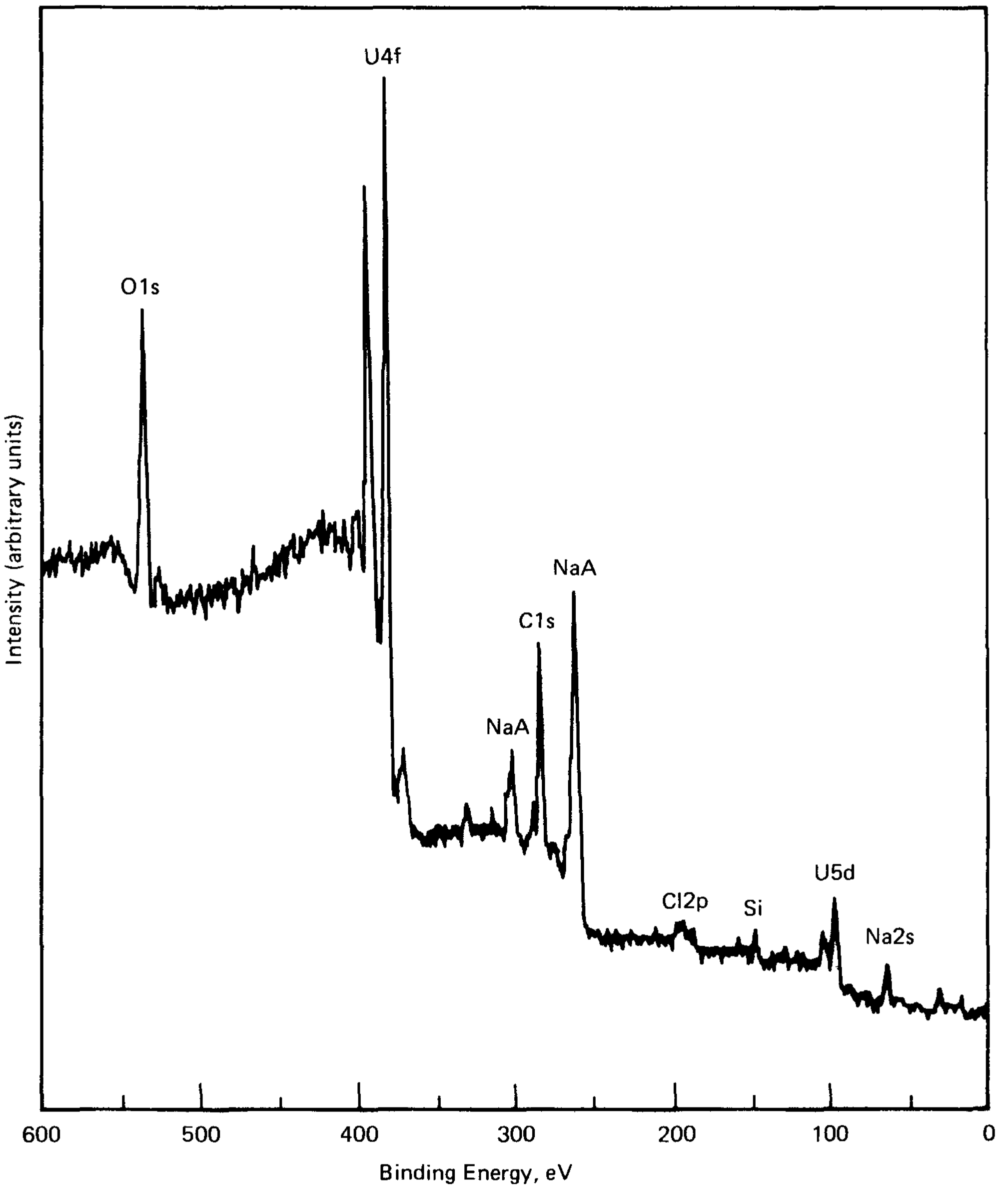

FIGURE 7 - ESCA overall spectrum of a U foil with a thin film of Na.

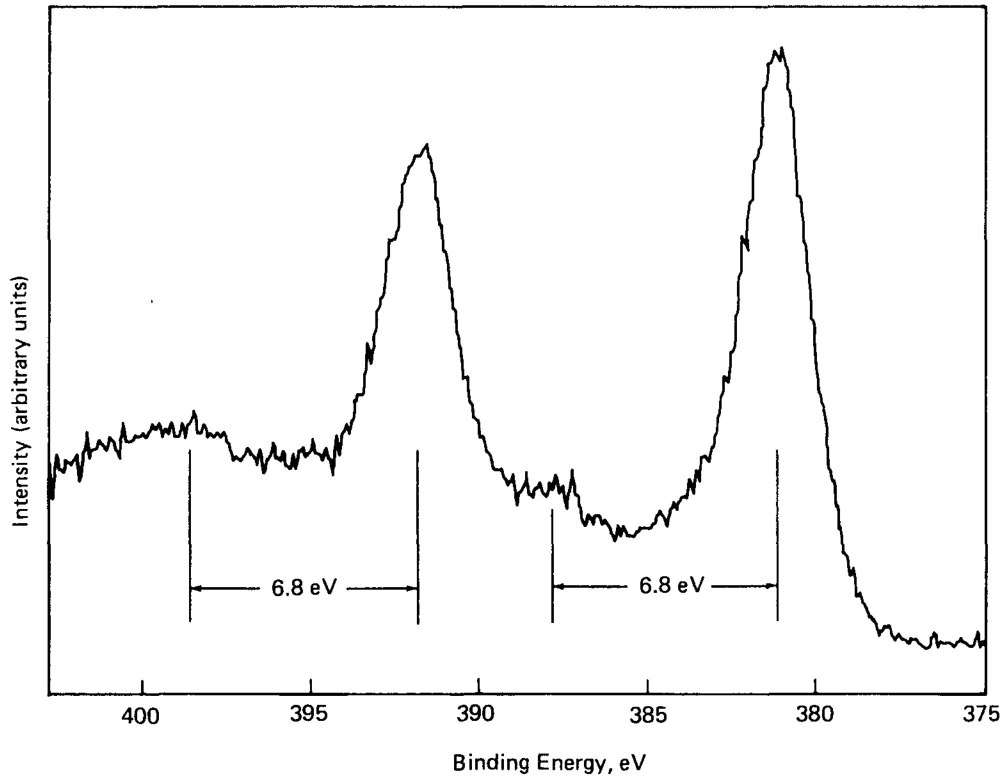

FIGURE 8 - ESCA U 4f spectrum of a U foil with a thin film of Na.

suggesting that the uranium is tied up with oxygen as UO_2. The high resolution oxygen spectrum from this same specimen (Figure 9) clearly shows multiple oxidation states of oxygen, indicating that an oxide of sodium is also present.

The pressed sodium oxide and uranium oxide pellet was sputtered with 1-keV Ar ions for approximately 1 hr. The 4f peaks of uranium were visible (Figure 10) but constituted a minor component of the ion bombarded surface. The high resolution of these 4f peaks (Figure 11) shows evidence of the shake-up peaks characteristic of UO_2.

A third specimen, the sodium uranate pellet, was also run on the ESCA instrument. The overall spectrum (Figure 12) shows the expected elements present. The high resolution spectrum of the uranium 4f peaks (Figure 13) does not show the presence of the "shake-up" peaks at 6.8 eV above the 4f peaks. This confirms that UO_2 was not present in this pellet, which was an expected result. The shift of all the high resolution peaks to the left (higher binding energy) indicates the specimen was charging during analyses.

4. Discussion and conclusions

Peaks greater than mass 270 were carefully searched for during SIMS analyses of both the U-Na metal foil and the 50% UO_2-50% Na_2O pellet. At no time was a Na-U-O combination peak observed. Great care was taken to locate the Na_3UO_4 peak at mass 371, but it was not detected throughout these analyses.

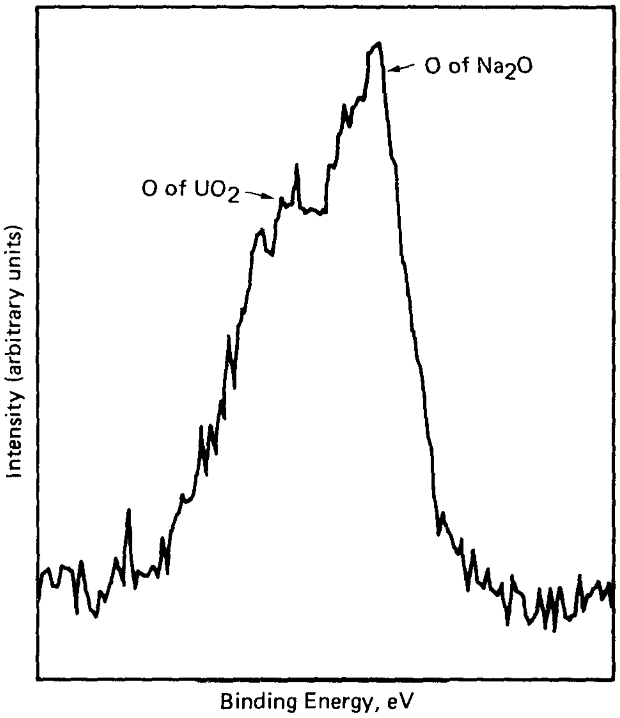

FIGURE 9 - ESCA O 1s spectrum of a U foil with a thin film of Na.

A pressed pellet of $Na_2U_2O_7$ was examined to determine a standard SIMS spectrum for this compound. Attempts were made to identify mass peaks in the vicinity of Na_3UO_4 (mass 371) and $Na_2U_2O_7$ (mass 634). In neither case could a significant peak be identified above background.

These data indicate that precursor ion species Na-U-O were not formed by ion bombardment, at least at 5 keV. Various oxides of sodium and uranium were observed; however, a combination of sodium and uranium was not detected throughout these SIMS experiments. From these data we conclude that precursor ion species containing Na-U-O do not form upon 5 keV Ar^+ ion bombardment. Even in the presence of excess oxygen that was provided by a capillary tube to the surface of the specimen during bombardment, expected precursor species were not observed.

One very likely explanation for not observing any Na-U-O species in the SIMS was that, if formed, these species would leave the sample surface with such a large amount of internal energy that fragmentation into atoms would be essentially instantaneous. Ion or electron beam methods may yet prove to be a viable way to investigate sodium uranate precursors, but lower energy beams (tens to hundreds of eV rather than 5 keV) would have to be used to produce species vibrationally "cool" enough to remain associated long enough to be detected.

Another reason could be that precursors are neutral species and since SIMS analyses detect positive and negative species, these neutral species would not be observed. A number of mechanistic possibilities exist. Reactions of neutrals occur in the condensed phase after vaporization.

$$(1) \quad Na_2O + UO_2 \longrightarrow Na_2^+ + UO_3^=$$

Followed by ion-molecule reaction such as:

$$(2) \quad UO_3^= + Na_2O \longrightarrow Na + Na^+ + UO_4^{\equiv}$$

The condensed phase species may act to solvate and stabilize the intermediate ions produced such as $UO_3^=$.

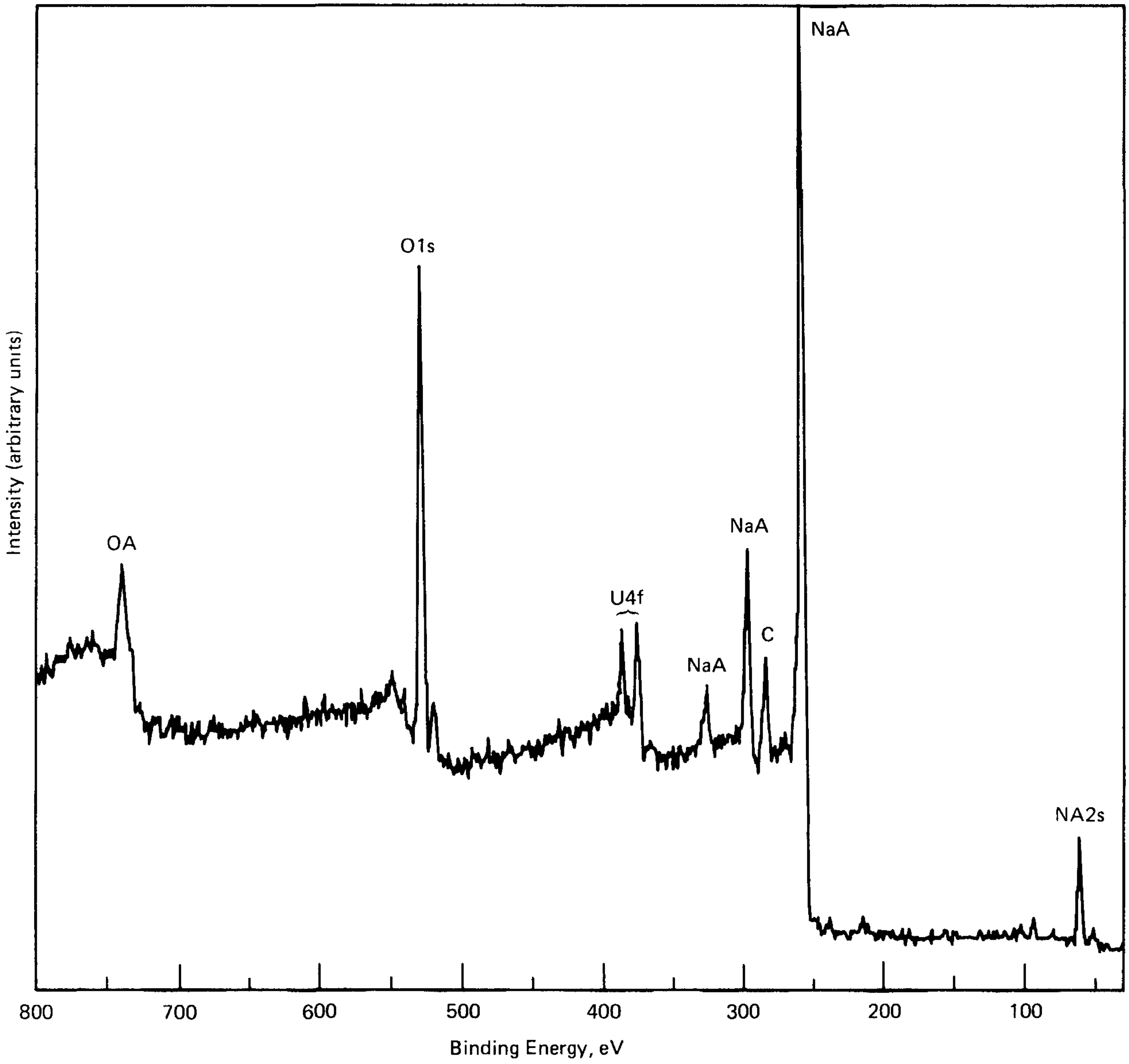

FIGURE 10 - ESCA overall spectrum of 50% UO_2-50% Na_2O pellet.

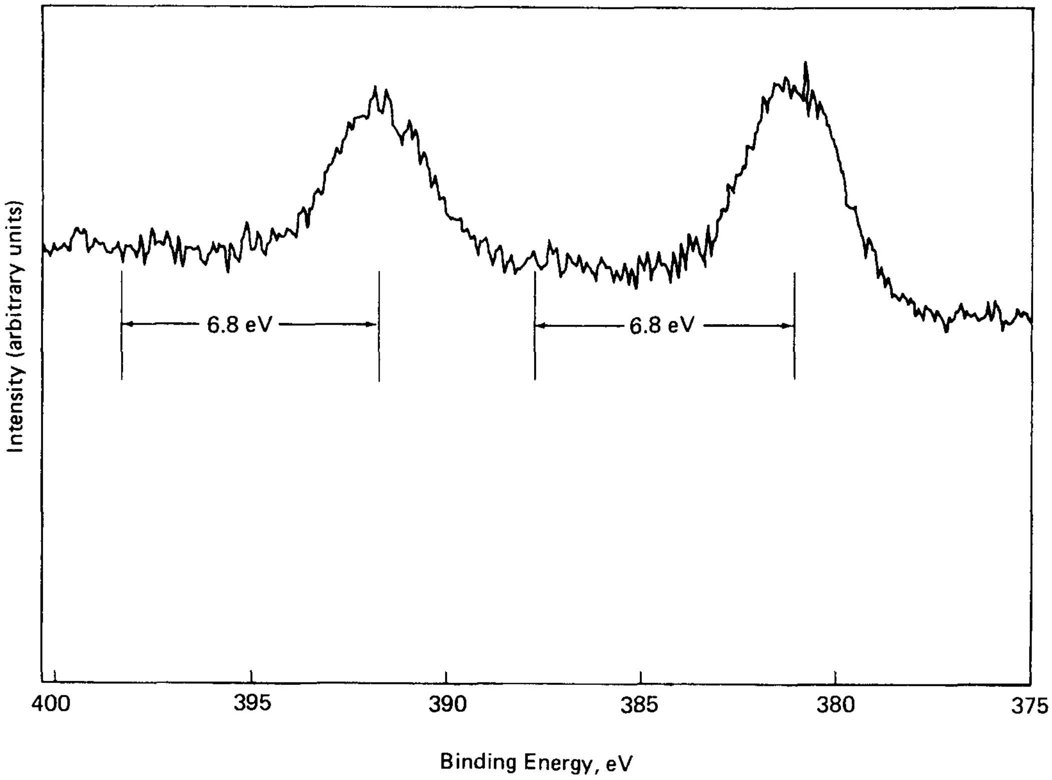

FIGURE 11 - ESCA U 4f spectrum of 50% UO_2-50% Na_2O pellet.

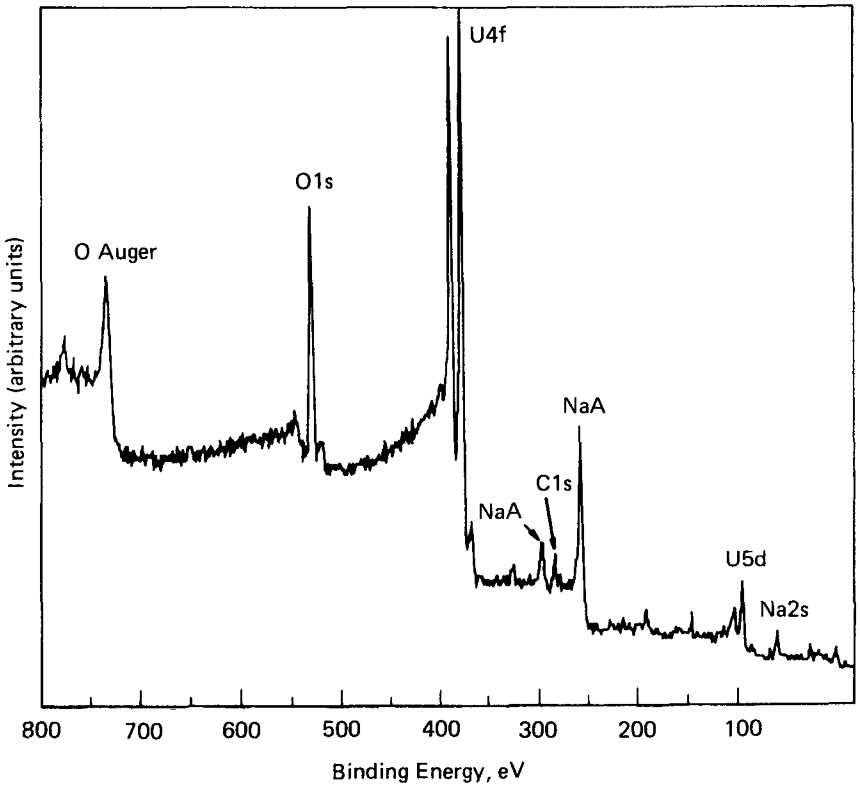

FIGURE 12 - ESCA overall spectrum of $Na_2U_2O_7$ pellet.

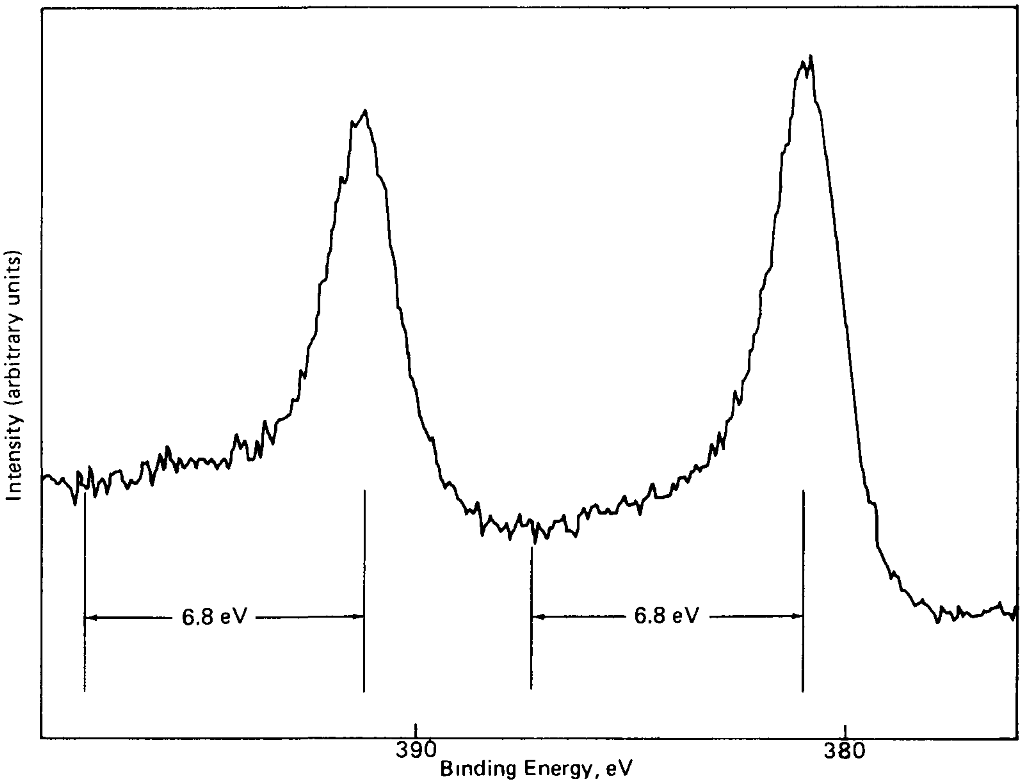

FIGURE 13 - ESCA 4f spectrum of $Na_2U_2O_7$ pellet.

Gas phase reactions of neutral species could occur but solvation of the intermediate species cannot occur, and charge separation is not energetically favored in the gas phase. The other possibilities include ion-molecule reactions in the gas phase. Probably all three processes are occurring upon irradiation of the sample with laser light in the HCDA. The mechanism that predominates is unknown at the present time, and more experimental work is needed to gain some insight into the gas phase ionic intermediate role in product formation.

This does not necessarily suggest that the Na-U-O precursors are not formed under conditions milder than a 5 keV ion beam and could possibly be detected with a lower energy technique that more closely simulates the laser-induced HCDA system.

A recommended technique would be to evaluate the samples from the study in a Laser Microprobe Mass Analyzer (LAMMA).

5. Recommendations for future work

An experiment that could provide valuable information about HCDA precursors would be to measure the neutral species. This could be accomplished by heating the samples with the laser, converting the neutrals to ions with electrons and analyzing the ions in a quadrupole mass spectrometer. Another approach would be to create the neutrals with the laser, then pass them through a R.F. plasma and analyze the species in the UV, visible, and infrared regions using an Optical Spectroscopic technique.

6. Acknowledgement

We would like to thank J. Hoenigman, of the University of Dayton, for the SIMS and ESCA analyses. We would also like to thank W. D. Moddeman for his assistance in the interpretation of the SIMS and ESCA data.

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