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Tandem Mass Spectrometry of Uranium and Uranium Oxides in Airborne Particulates

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A method for detection of uranium in airborne microparticles in real time has been developed. Positive identification of uranium is achieved by isolating UO^{2+} ions and following their reaction with residual oxygen molecules to yield UO_2^+.

The detection of uranium in airborne effluents from nuclear production facilities is of current importance to identify particle emissions from active and inactive plants and to monitor the effectiveness of site remediation efforts.[1] One method that can be used on-line is laser ablation mass spectrometry of individual airborne microparticles.[2] With laser ablation in time-of-flight mass spectrometry, the principal U-containing ions that are observed are atomic U^+, m/z 238, and the two oxide species, UO^+ and UO_2^+, at m/z 256 and 270.[3,4] The U^{2+} ion at m/z 119 can be detected at high laser fluence.[4] The UO^+ ion was used by Stoffels et al.[1] for thermal ionization sector mass spectrometry. In matrixes where there is little isobaric interference, these ions can be formed and detected with high efficiency. However, it has been apparent in various investigations of environmental particles that potential interferences from molecular species with m/z values distributed throughout the range expected for uranium and its oxides are observed for many particles.[5−7] In the present experiments, where individual airborne particles were analyzed by laser ablation mass spectrometry in an ion trap, reactions of the trapped ions with residual oxygen cause the UO_2^+ ion to be the major observed species with UO^{2+} at m/z 127 also being observed. Our attempts to verify the presence of UO_2^+ by ion trap collisional activation have been unsuccessful, due presumably to rapid reaction of collisionally produced UO^+ with neutral species and to the large, 7.8-eV dissociation energy. The purpose of this paper is to report that tandem mass spectrometry of the UO^{2+} ion at m/z 127 via ion−molecule reactions with residual oxygen and monitoring of the associated product ions can be used to verify the presence of uranium in laser ablation mass spectra.

EXPERIMENT

Airborne microparticles were analyzed by laser ablation mass spectrometry in an ion trap mass spectrometer with a direct atmospheric sampling input, as described by Reilly et al.[8] The instrument was modified so that particle aerodynamic size could be measured along with the mass spectrum.[9] Most of the samples for this investigation were particles formed by evaporating droplets nebulized from a solution. Hospitak disposable nebulizers were used to avoid memory effects. For some measurements, solid microparticles were aerosolized directly by blowing a jet of air across a powdered sample. Microparticles containing trace quantities of uranium were generated by nebulizing an aqueous solution. Solutes used included potassium nitrate and 7-amino-1,3-naphthalenedisulfonic acid (ANDSA). Uranyl nitrate in 5% HNO_3, 1000 μg mL^{-1} concentration (ICP standard solution), was added to the solution to attain the desired concentration, ranging from 1 to 1000 μg/g in the dried particles. Salt concentrations in the nebulized solutions were chosen to give dried particles of ∼1-μm diameter. Samples of CaF_2 crystals containing 500 ppm uranium were also measured for comparison.

Laser ablation of the incoming particles was accomplished with an excimer laser with pulses of ∼10 ns in duration, 308 nm in wavelength, and 5 mJ in energy, for a fluence of ∼2 J cm^{-2}. Operation of the ion trap to acquire primary and tandem mass spectra of the laser-generated ions has been described by Reilly et al.[8] ICMS software[10] was used to control the mass scans after a particle had been sampled. MS/MS spectra were obtained either after collision-induced dissociation or ion−molecule reactions. As in our previous experiments, the ion capture voltage on the ring electrode, mass selection, and mass scan range were set up initially and the instrument would then operate autonomously, measuring and storing a mass spectrum for each detected particle.

The mass scan rate of the ion trap mass spectrometer was ∼180 μs amu^{-1}. Therefore, a continuous mass scan between doubly and singly charged uranium ions or oxide ions would require times on the order of 25 ms. The doubly charged ions would have been ejected at the initial part of this interval so ion−

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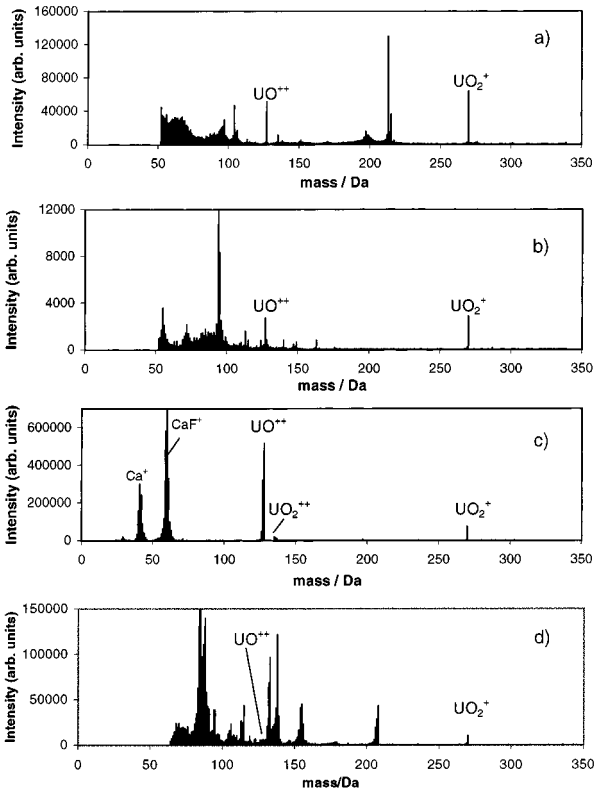

Figure 1. Primary mass spectra of uranium in particles of different substances, averaged over many particles: (a) ANDSA plus 16.8 μg/g U; (b) potassium nitrate plus 1.25 mg/g U; (c) calcium fluoride plus 500 μg/g U; (d) NIST SRM 2710, Montana soil, 25 μg/g U.

molecule reactions involving these ions would be negligible after this time. Already-formed intermediate species could continue to react until they were ejected, however, resulting in a lower measured population for these ions than would be obtained under steady-state conditions. Accordingly, mass scans after isolation were sometimes started close to the m/z value of a target species to analyze for transient species with high reaction rates. Most of the measurements were made with the residual air partial pressure of 4×10^{-5} Torr, corresponding to an oxygen concentration of 2.8×10^{11} cm^{-3}. In some experiments, additional air or water vapor was added to the trap to influence the reaction rates.

RESULTS AND DISCUSSION

This section is presented in two parts. First, primary mass spectra are used to identify uranium ion reactants, intermediates, and products as well as measure their decay rates. In the second part, MS/MS measurements are used to determine the reaction mechanism and demonstrate a sensitive and positive method of identification of uranium in complex matrixes that should prove useful in environmental analysis.

Primary Mass Spectra. Primary mass spectra of uranium in several arbitrarily selected matrixes, ANDSA, potassium nitrate, and calcium fluoride, are shown in Figure 1a–c, respectively. In addition, the average mass spectrum of particles from NIST Standard Reference Material 2710, Montana soil, is shown in Figure 1d. The uranium concentration for this material is reported to be 25 μg/g (uncertified). Two prominent masses observed in these matrixes were attributed to uranium: UO_2^+ at m/z 270 and

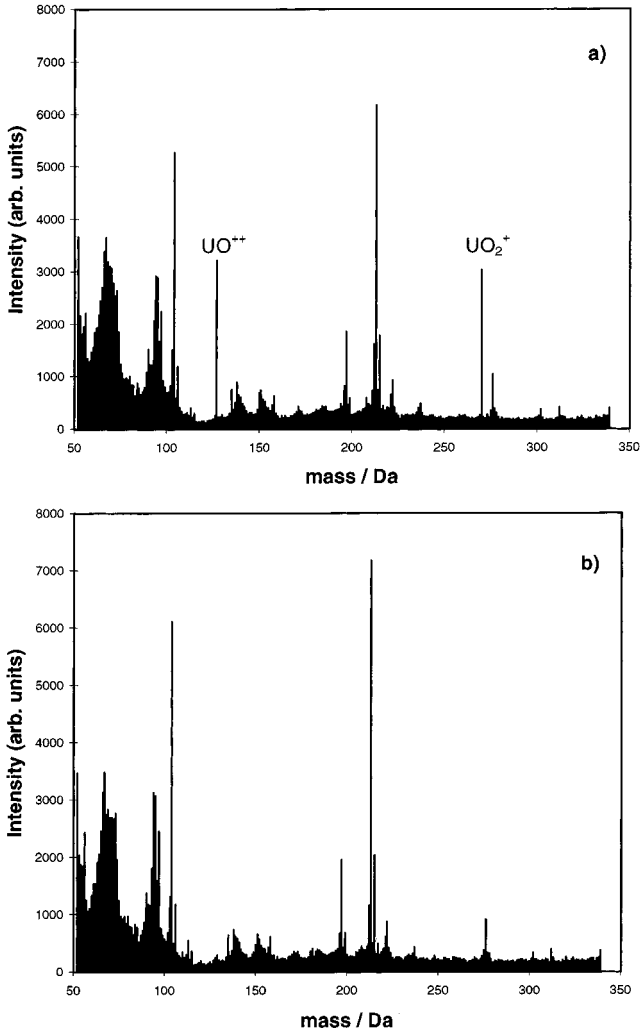

Figure 2. Primary mass spectra of uranium in ANDSA, average of several hundred particles with mean diameter of 0.7 μm: (a) ANDSA plus 1.8 μg/g U as uranyl nitrate; (b) blank.

UO^{2+} at m/z 127. Minor ions at m/z 287, UO_2OH^+, and m/z 135, UO_2^{2+}, were sometimes observed in the primary spectrum. The uranium contributions to the mass spectra were qualitatively similar for all matrixes studied here. However, the sensitivity or detection limit depended strongly of the matrix, being ~3 orders of magnitude worse for potassium nitrate than for ANDSA particles.

To explore the limit of detection, measurements were made on ANDSA particles at lower uranium concentrations as well as blank determinations. In Figure 2a, we show the mass spectrum obtained from several hundred particles of ANDSA with 1.8 μg/g uranyl nitrate added, measured individually with 5-mJ pulses at 308 nm but averaged for the plot. Only particles between 0.5 and 1.0 μm in diameter were included. The geometric diameter was calculated from the measured aerodynamic diameter with the assumption that the particles were spherical with a density of 1.5 g cm^{-3}. The mean diameter of the particles was 0.7 μm with a standard deviation of 0.15 μm. The mass of a 0.7-μm particle is 0.3 pg so the average detected uranium for this size particle was less than 0.6 ag. A similar measurement with no uranium added is shown in Figure 2b. The ultimate uranium detection limit is thus in the subattogram range in a favorable matrix.

Table 1. Ion−Molecule Reaction Decay Constants, at 4×10^{-5} Torr Air Pressure

ion	decay const (s^{-1})	time const (ms)	ion	decay const (s^{-1})	time const (ms)
U^{2+}	330	3.0	UO^{+}	260	3.8
UO_2^{2+}	160	6.2	UO^{2+}	8	120
U^{+}	220	4.6			

The various uranium ions could have been produced either by the laser ablation/ionization event or by ion−molecule reactions with the background gas since not all of the ambient air was removed and the ions were stored for tens of milliseconds before they were ejected. TOF spectra from uranium carrying algae-[3] and uranium-containing ANDSA particles[4] were used to determine which ions were created during the ablation/ionization event ($t = 0$ ions). Ions ablated from particles examined using time-of-flight mass spectrometry would not have enough time (less than a few microseconds) to react with background gases before their extraction into the flight tube; therefore, uranium-containing ions in the TOF spectra were created during and just after the laser pulse. The predominant ions in the TOF spectra were U^{2+},[4] U^{+}, UO^{+}, and UO_2^{+} [3,4] (A mass at m/z 119, U^{2+}, was present but not identified in the algae spectra). The $t = 0$ ions in the ion trap should have the same composition and distribution as those observed in the TOF spectra. Presumably, the other ionic species observed in the ion trap spectra, UO_2^{+}, UO_2^{2+}, and the occasionally seen UO_2OH^{+}, were created in the ion trap by reaction of $t = 0$ ions with the background gas. (See first row in Figure 4.)

While the U^{2+}, U^{+}, and UO^{+} ions could not be detected in a normal ion trap scan, it was possible to observe them and measure their decay when the intrinsic delays were minimized by starting the mass scan close to the ion of interest. To measure the decay of particular ions in the ion trap, the trapping potential was set so that the masses below the mass of interest were ejected. A delay between the laser pulse and the start of the scan was then varied and intensity of the ion was observed. Decay rates measured at the residual air partial pressure of 4×10^{-5} Torr are presented in Table 1. The rapid decay rates show that under normal scanning conditions where a wide mass range was scanned, the U^{2+}, U^{+}, and UO^{+} ions created by the laser pulse would not be observable. When the RF trapping potential was set so that masses below m/z 120 were ejected from the trap, the disappearance of the UO^{2+} and UO_2^{2+} ions confirmed that U^{2+}, m/z 119, was the source of the UO^{2+} and UO_2^{2+}. This was not surprising since U^{2+} is the only doubly charged ion created by the laser pulse. UO_2^{+} was only observed to decay when the trap depth was small enough to permit collisional detrapping. The most notable feature of Table 1 is the relatively slow decay rate of UO^{2+}. This slow decay together with the stability of UO_2^{+} account for the prominence of the two ions in the primary ion trap mass spectra. It is also apparent that the end product of the decay of the $t = 0$ uranium ions is eventually UO_2^{+}.

MS/MS SPECTRA

Using the methods of ion trap tandem mass spectrometry, we were able to isolate the ions at m/z 127 and subsequently analyze the product ions formed by reaction of the precursor with the background gas. In Figure 3, we show a sequence of measurements with varying time delays between isolation of m/z 127 and the scan of the reaction product spectrum. The growth of UO_2^{+} with time is evident. The ions at m/z 127 react with the background O_2 to eventually yield UO_2^{+} at m/z 270 and O_2^{+} at m/z 32 (not shown in Figure 3). Intermediate species in this reaction, particularly UO_2^{2+} and UO^{+}, were sought by starting the mass scan just below the mass of interest. Only UO_2^{2+} was detected in these experiments. A small concentration of UO_2^{2+} can be seen at m/z 135 in the delayed scans of Figure 3.

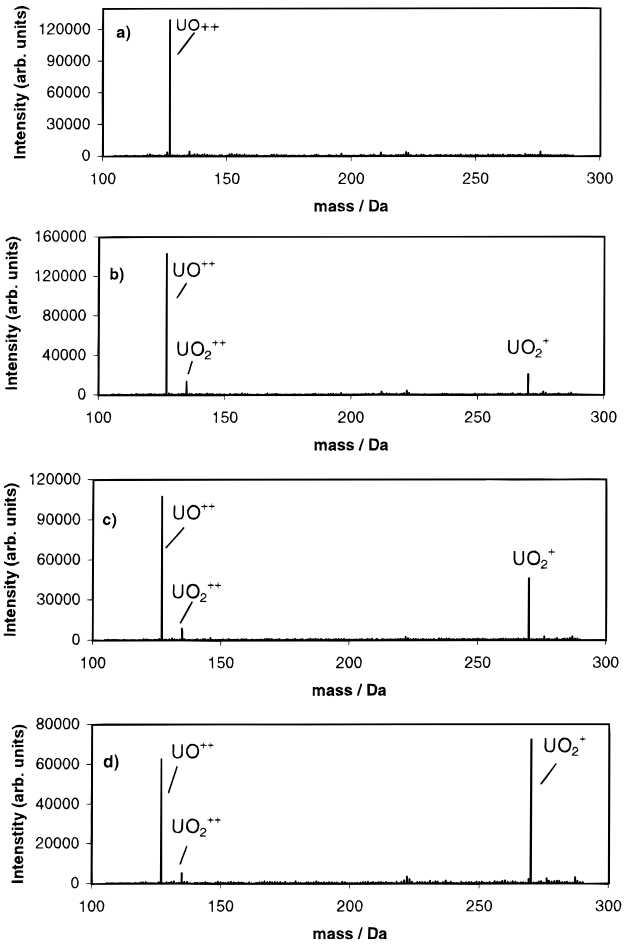

Figure 3. MS/MS experiments showing increase of UO_2^{+} with time from isolated UO^{2+} ions. The concurrent growth of O_2^{+} is not shown here because ions with m/z below 100 were not trapped in these scans. The times from the laser pulse until the appearance of ions at m/z 127 for the four scans were, from top to bottom, 5.7, 60.7, 145.7, and 255.7 ms.

In the present experiment, where ambient air was admitted into the vacuum system along with the airborne particles being analyzed, there was only partial control of the composition of the molecular background in the ion trap. We therefore must speculate to some degree on the background reactants. Since all of the products and intermediates contain oxygen, only oxygen-containing reactants need be considered. O_2 and H_2O seem the most likely candidates. MS/MS experiments on m/z 127 while water vapor was admitted to the vacuum chamber showed production of significant amounts of UO_2OH^{+} as well as UO_2^{+}. Since UO_2OH^{+} was rarely detected in our experiments when water was not deliberately added, we suggest that O_2 is the primary

background gas reagent. This is further confirmed by the measured decay rate for U^+. If one assumes this decay is due to reaction with O_2 exclusively according to the following reaction,

$$U^+ + O_2 \rightarrow UO^+ + O \quad (1)$$

and that 20% of the background air is composed of O_2, then the rate constant for reaction 1 is 8×10^{-10} cm^3 s^{-1}. This agrees very well with the rate constant of 8.5×10^{-10} cm^3 s^{-1} given by Johnsen and Biondi[11] for the same reaction and helps to confirm O_2 as the primary reactant in the background gas.

The following sets of reactions represent the three most plausible paths from UO^{2+} to UO_2^+ in the MS/MS experiments of m/z 127:

$$UO^{2+} + O_2 \rightarrow UO^+ + O_2^+$$

$$UO^+ + O_2 \rightarrow UO_2^+ + O \quad (2)$$

$$UO^{2+} + O_2 \rightarrow UO_2^+ + O^+$$

$$O^+ + O_2 \rightarrow O_2^+ + O \quad (3)$$

$$UO^{2+} + O_2 \rightarrow UO_2^{2+} + O$$

$$UO_2^{2+} + O_2 \rightarrow UO_2^+ + O_2^+ \quad (4)$$

Pathway 2 can be rejected as being dominant since no UO^+ intermediate was observed in the MS/MS experiment, yet this species was readily observable immediately after the laser pulse. An upper limit for the decay rate for the first reaction in pathway 2 is 0.9 s^{-1}, based on our estimated signal-to-noise ratio and the measured decay rates of UO^{2+} and UO^+. This is 1 order of magnitude smaller than the measured decay rate of UO^{2+}. Pathway 3 may also be rejected as the dominant path since setting the trapping potential so that m/z 16, O^+, was immediately ejected from the trap had no observable effect on the rate of production of O_2^+. To confirm that (4) must be the principal reaction pathway, an MS/MS experiment on m/z 127 was carried out with resonant ejection of m/z 135, UO_2^{2+}. The UO_2^+ product was strongly suppressed in this experiment. MS/MS experiments on m/z 135 showing production of O_2^+ and UO_2^+ were further confirmation.

A reaction scheme that is consistent with our experimental observations is shown in Figure 4. The four species shown on the top line are generated during the laser ablation/ionization event, either by the laser pulse or subsequent collisions as the plume expands. Following the ablation, the stored ions react with residual oxygen, with U^{2+} converting rapidly to UO^{2+}, and with U^+ and UO^+ converting to UO_2^+ with a high enough rate that they are not detectable in the conventional ion trap mass scan. The relatively inert UO^{2+} slowly converts to UO_2^+ in a two-step reaction with UO_2^{2+} as an intermediate.

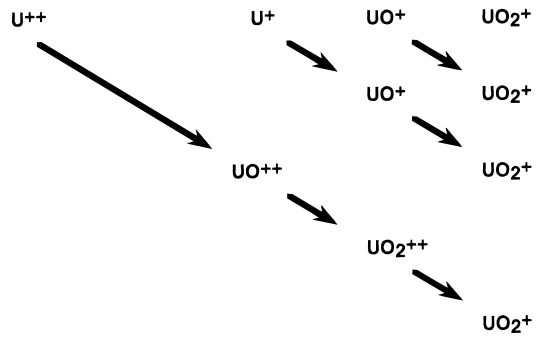

Figure 4. Reaction pathways in the ion trap MS/MS analysis of uranium. Ions in top line formed during laser ablation; ions below formed by reactions of stored ions with residual O_2.

CONCLUSIONS

We have shown that uranium can be detected at the attogram level or better in microparticle samples by laser ablation ion trap mass spectrometry, with UO_2^+ being monitored. However, the detection efficiency strongly depends on the particle matrix. The method may be useful as an on-line monitoring system to determine the fraction of uranium-containing particles in the atmospheric environment. Together with other information from the mass spectra, it might be possible to identify the origin of the particles. If isobaric interferences are encountered, positive identification of uranium can be assured by following the ion−molecule reaction of isolated UO^{2+} ions with residual oxygen molecules in the ion trap to yield UO_2^+ ions. In our experiments, approximately the same level of UO^{2+} as UO_2^+ was observed in the primary mass spectra, so comparable detection limits should be achievable after isolation of UO^{2+} in the MS/MS determination. It is possible to alter the concentration of reagent molecules in the trap to vary the rates of the reactions and reaction products to further enhance the analytical power of the method. However, the kinetics of the ion−molecule reactions that were observed to take place in the trap were favorable for tandem mass analysis with no alteration in measurement conditions.

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