

Static SIMS Detection of Gold and Gold Cyanide Complexes on Carbon Using Crown Ether Enhancement

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Determination of the nature of adsorbed gold cyanide species on activated carbon is difficult with presently available surface analysis techniques. Efforts toward the development of new, more specific analytical techniques are described in this paper. It is shown that static secondary ion mass spectrometry can be used for the detection of gold on carbon surfaces and for the identification of cyanide species present. The method described relies on two features: (1) the instrumentation employed utilizes pulsed secondary ion extraction, which mitigates the buildup of surface charge (a major problem in the bombardment of carbon) and permits the acquisition of the anion and cation spectra during the same analysis; (2) the surface of the carbon samples is doped with a crown ether, which results in the facile observation of $\text{Au}(\text{CN})_2^-$, $[\text{M} + \text{crown}]^+$ (where M is Na^+ or K^+), and in some cases Au^+ . It is hypothesized that the crown ether facilitates the formation of gold cyanide ions by forming complexes with Na^+ and K^+ present on the surface of the charcoal, thereby loosening or freeing the $\text{Au}(\text{CN})_2^-$.

Sodium cyanide is the main lixiviant for the recovery of gold from gold-bearing ores. Once solubilized, gold can be recovered from solution either by precipitation with zinc powder or by adsorption on activated carbon. While zinc precipitation has been the dominant method, recent interest has focused on the use of activated carbon for the recovery of gold from cyanide leach solutions. At present, there is little agreement on the mechanisms by which aurocyanide is adsorbed onto activated carbon, because of an inability to characterize the relevant chemical species hosted by the surface of activated carbon. Mechanistic investigations have been based on the analysis of solutions in contact with carbon and have produced equilibrium and kinetic information.¹⁻⁶ Adsorption has also been investigated using appropriate model

compounds.²⁻⁴ However, direct information on the gold cyanide species present on the carbon surfaces is lacking.

In the present paper, we describe the direct detection of $\text{Au}(\text{CN})_2^-$ on the surface of carbon used for the adsorption of gold cyanide complexes. The detection scheme was based upon static secondary ion mass spectrometry (SIMS), in which the carbon surface was doped with a crown ether solution and allowed to dry prior to SIMS analysis. The crown ether facilitates the observation of $\text{Au}(\text{CN})_2^-$, most likely by complexing counterions present on the surface of the carbon, thereby facilitating ion formation from $\text{Au}(\text{CN})_2^-$ complexes.

Previous investigations of crown ethers supported the expectation that they might be useful for altering the surface ion chemistry important in a SIMS experiment. Crown ethers have been long known for their ability to complex alkali metal cations in solution^{7,8} and have also been the subject of several mass spectrometric investigations, in which the affinities of different crowns for different cations were evaluated.⁹⁻¹³

Static SIMS has been under investigation because the technique has very good sensitivity for molecular species present on sample surfaces.¹⁴ The sensitivity is augmented by the use of a molecular primary beam, such as ReO_4^- , which is used in the instruments in our laboratory.¹⁵ Another attractive attribute of static SIMS is that it requires minimal sample preparation and minimizes waste generation, which is particularly advantageous when analysis of hazardous samples is required. Finally, static SIMS is capable of accommodating sample types that develop surface charge by using pulsed secondary ion extraction¹⁶ or electron flooding.¹⁷ These techniques make SIMS amenable to virtually any sample type that is vacuum compatible.

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The issue of analyzing gold in refractory or otherwise difficult matrices has been addressed using dynamic SIMS, which is capable of detecting gold at sub-ppm concentrations in a variety of refractory ore types.^{18,19} Speciation of gold has been studied using XPS, but the interpretation of the data has been difficult because of severe charging occurring in the samples studied.^{5,6,20} The analytical efforts to date have not been able to provide information on the identity of the gold species present on sample surfaces. One approach for facilitating the observation of metal species on surfaces is to dope the surface with a complexing agent. This strategy was employed for the imaging of galena (high lead content) samples doped with diisobutyl dithiophosphinate, but the images of the dopant and Pb^+ did not exactly correlate, and hence the chemical nature of Pb on the doped galena surface could not be surmised.²¹ Nevertheless, it was felt that doping the sample surface with a crown ether might work in the present study, because of the presence of substantial quantities of group I cations on the surface.

EXPERIMENTAL SECTION

Preparation of Carbon Samples Exposed to Gold Cyanide Solutions. Activated carbon with adsorbed gold was prepared by agitation of 100 mg of 10X14 mesh PICA carbon (coconut shell carbon) in 100 mL of solution containing 1 mg of gold in the form of gold cyanide complex. The solution pH, adjusted with NaOH, was 11.5. Total time of adsorption was 24 h. After adsorption was completed, the carbon was separated by filtration, rinsed with deionized water, air-dried, and stored in a glass vial for future use. The concentration of gold in the solution was analyzed to determine the amount of adsorbed gold. It was found that 80% of the gold was adsorbed, producing a sample containing 8 mg of gold/g of activated carbon.

Preparation of Carbon Samples for SIMS Analysis. The carbon granules were crushed using a mortar and pestle prior to analysis. Normally, one carbon granule was crushed at a time; a typical sample mass was thus on the order of 1–3 mg. A wire sample holder fitted with double-sided tape was then used to “swab” the bottom of the mortar, thereby collecting the crushed carbon sample. Enough carbon was collected to completely cover the double-sided tape.

For the crown ether complexation experiments, 30–70 μL of crown ether/methanol solution (12-crown-4 or 18-crown-6 (Aldrich)) was added to the carbon during crushing. The typical molarity used for the crown ether solutions was in the range of 0.05–0.2 M, although in one study the molarity of the 18-crown-6 was varied from 0.005 to 0.5. The sample was applied either by applying a droplet of the slurry to a sample holder fitted with double-sided tape and allowing it to dry or by swabbing the bottom of the mortar. Either method produced observable $\text{Au}(\text{CN})_2^-$ complexes.

Secondary Ion Mass Spectrometry. The instrument used for the SIMS analyses described in this paper has been described

previously;¹⁶ a brief description will be provided here. The instrument uses ReO_4^- as the primary bombarding particle, which is produced by heating a $\text{Ba}(\text{ReO}_4)_2$ ceramic in vacuum.¹⁵ The ceramic was synthesized in our laboratories and processed in a form that could be used as an ion source. ReO_4^- ions that are emitted upon heating are accelerated to 10 keV. The ion gun was typically operated at 95 pA (the ion current from the gun could be continuously adjusted by adjusting the current passing through the heating element that supported the ceramic). The focusing of the primary ion gun was adjusted so that the sample was just silhouetted on an image intensifier located behind the sample. Thus, most of the primary ion beam is directed onto the target. Typical acquisition required 203 s, and a typical sample had an area of about 0.03 cm^2 ; thus a normal primary ion dose was 4.0×10^{12} ions/ cm^2 , which is below the commonly accepted static SIMS limit.²²

The secondary anions and cations were extracted from the sample target region using pulsed secondary ion extraction.¹⁶ This technique alternately extracts anions and cations from the sample surface by alternating the polarity of the secondary ion extraction lens. The alternating anion/cation extraction mitigates charge buildup on the surface of the sample and thus permits facile analysis of electrically insulating samples. The ratio of [time extracting cations]/[time extracting anions] is adjustable in this instrument, and in the case of the charcoal samples, a value of 6 worked well. The total period for the pulsed extraction sequence was 140 ms, divided as follows: cation extraction, 113 ms; electronic settle time, 4 ms; anion extraction, 19 ms; electronic settle time, 4 ms. This sequence was repeated for each 0.2 u step of the scan of the quadrupole secondary mass spectrometer, which was scanned from 10 to 310 u. The quadrupole was a m/z 2–2000 instrument, manufactured by Extrel (Pittsburgh) and modified in our laboratory. The quadrupole was tuned for unit mass resolution and optimum sensitivity for m/z 81 $^-$ and 198 $^+$ in the SIMS spectrum of tetrahexylammonium bromide.²³

The observation and abundance of the gold-bearing ions were subject to some variability. For most chips analyzed, CN^- and $\text{Au}(\text{CN})_2^-$ could be readily observed, although for a fraction of the chips (20–30%), these ions were very low abundance or not observable. Furthermore, the abundance of the aurocyanide ions was variable for samples analyzed from the same carbon chip: for example, the abundance of m/z 249 $^-$ ($\text{Au}(\text{CN})_2^-$) varied from 400 to 1500 counts/s in replicate analyses of the same crushed carbon sample. The source of the variability is not instrumental: the abundances of the non-gold-bearing ions were repeatable to within 20% of the mean absolute abundance. An example of this is the abundance of m/z 25 $^-$ (C_2H^-), which ranged from 4000 to 5000 counts/s in the same set of analyses. This variation is consistent with relative standard deviation values (10–30%) for other amorphous samples analyzed using this instrumentation.²⁴ Hence the variability is probably due to inhomogeneous distribution of gold in the carbon samples, since sample preparation was identical for all samples. A consequence of the variability is that the technique is qualitative at this time.

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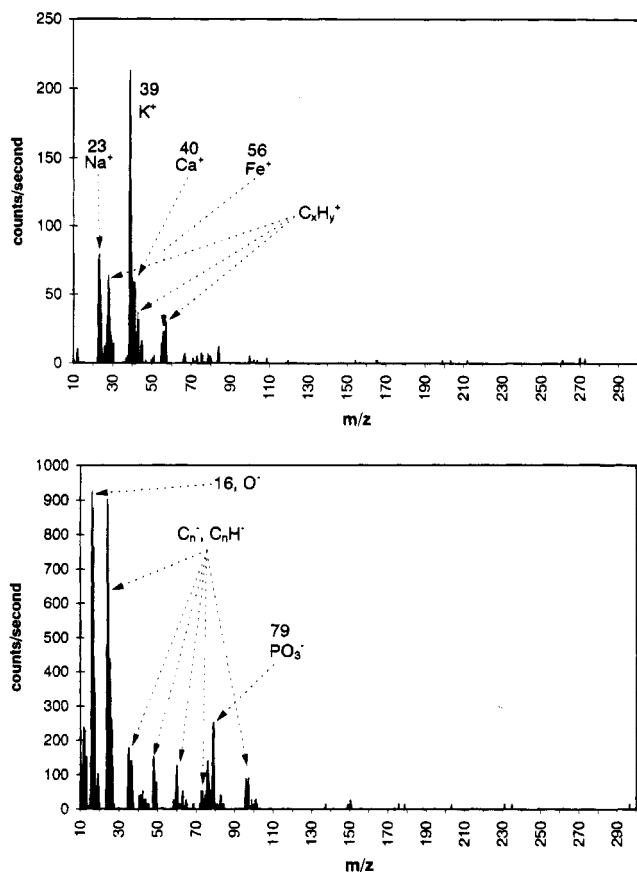


Figure 1. Cation (a, top) and anion (b, bottom) SIMS spectra of carbon.

RESULTS AND DISCUSSION

SIMS Spectra of Unexposed Carbon. The analysis of benchmark carbon was difficult because of surface charging that occurs when carbon samples are crushed and bombarded. This difficulty was reflected in low ion abundances recorded in the SIMS spectra of this sample (Figure 1). Nevertheless the sample charging was manageable using pulsed extraction, such that anion and cation spectra could be recorded (see Experimental Section).

The SIMS spectra of unexposed carbon (Figure 1a) was relatively simple: cations corresponding to K⁺, Na⁺, Ca⁺, and Fe⁺ were clearly observed, as were a few low-abundance hydrocarbon ions. These latter ions are observed at odd masses and are common for static SIMS spectra.¹⁴ The anion spectrum is also simple: O⁻ accounts for the most abundant peak, and C_n⁻ and C_nH⁻ ions are also prevalent for $n = 1-5$. The abundance of CN⁻ is low (m/z 26⁻). The ion observed at m/z 79⁻ has been attributed to PO₃⁻, which may be indigenous to the carbon sample (phosphorus is present) or may be the result of the adsorption of trace quantities of atmospheric tributyl phosphate, which is occasionally present in our laboratory.²⁴

SIMS Spectra of Carbon Exposed to Gold Cyanide. The carbon was exposed to the gold cyanide solution (10 mg/L), washed with distilled water, air-dried, and then analyzed using SIMS. The resulting SIMS spectrum was markedly different from that of the unexposed carbon. The absolute ion abundances (both anion and cation) are significantly greater than in the spectra of the unexposed carbon. This observation is partly due to the fact that the exposed carbon samples are not as susceptible to surface charging, which is characterized by the sample deflecting the incoming primary ion beam. At the present time, the physical or

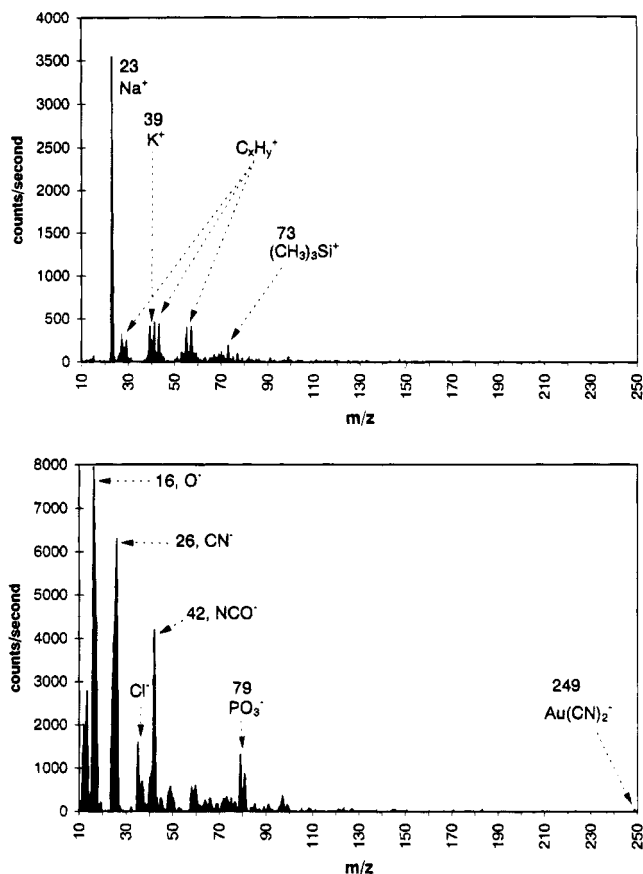


Figure 2. Cation (a, top) and anion (b, bottom) SIMS spectra of carbon exposed to 10 mg/L gold cyanide solution.

chemical properties responsible for exacerbating or mitigating surface charging during primary ion bombardment of carbon have not been identified for carbon samples.

Na⁺ is the most abundant peak in the cation spectrum, which is consistent with the fact that the carbon was exposed to a solution containing a significant quantity of Na⁺ (Figure 2a). The other abundant ions observed in this spectrum are readily explainable in terms of K⁺, hydrocarbon, and siloxane contamination. In the anion spectrum, the abundances of CN⁻ and NCO⁻ were markedly enhanced compared to the spectrum of the unexposed sample, which reflects the fact that the carbon had been exposed to cyanide. A very low abundance ion could occasionally be observed at m/z 249⁻, which is consistent with Au(CN)₂⁻, but the abundance of this ion was too low to be analytically useful.

SIMS Spectra of Carbon Exposed to Gold Cyanide, Treated with 12-Crown-4. The very low abundances of the gold-containing ions in the static SIMS analysis of the exposed carbon were surprising, because the concentration of gold in the sample was relatively high (8 parts per thousand). It was hypothesized that poor ionization efficiency was responsible and hence, means to assist dissociation of ionic complexes on the carbon surface were investigated. 12-Crown-4 was chosen because the compound forms stable adduct ions with Na⁺ in solution and in the gas phase.^{7,9,10} If similar behavior occurred on the surface of the carbon, then Au(CN)₂⁻ present on the surface would be less tightly bound to Na⁺ and more amenable to sputtering as an ion.

The carbon samples were spiked with a 12-crown-4/methanol solution (0.05–0.08 M) and crushed wet using mortar and pestle.

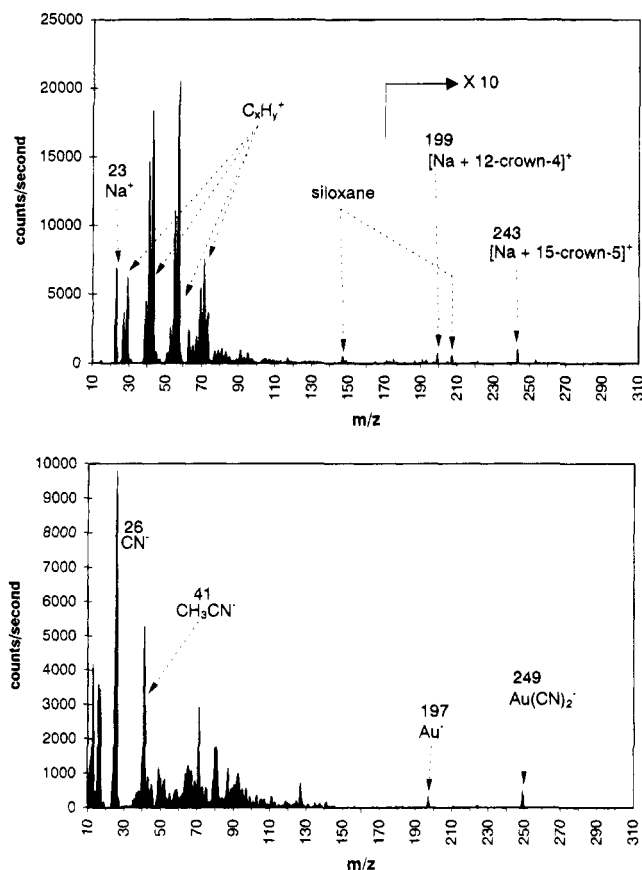


Figure 3. Cation (a, top) and anion (b, bottom) SIMS spectra of carbon exposed to 10 mg/L gold cyanide solution, treated with 12-crown-4 (with 15-crown-5 impurity in (a)).

A droplet of the resulting slurry was then placed on a sample holder that had been fitted with double-sided tape and was allowed to dry. Subsequent SIMS analyses resulted in anion and cation spectra that contained ions that were much more abundant than either the unexposed or exposed carbon samples. m/z 249⁻ and 197⁻ were readily observed in the anion spectrum; these ions must correspond to Au⁻ and Au(CN)₂⁻ (Figure 3b). These ion assignments are supported by control experiments in which carbon samples unexposed to gold (unwashed and washed with water) were treated with crown ether solution and analyzed: m/z 249⁻ and 197⁻ were not observed. The possibility that the methanol might be enhancing the observation of the gold-bearing ions was eliminated by analyzing gold cyanide-exposed carbon crushed with methanol: again, the gold-bearing ions were not observed.

In the lower mass region of the anion spectrum, abundant CN⁻ is observed as before, but the abundant NCO⁻ at m/z 42⁻ has been supplanted by an abundant m/z 41⁻, which may correspond to CH₃CN⁻, although other assignments cannot be ruled out. The appearance of an abundant m/z 41⁻ is related to the presence of the crown ether, as this ion was also observed in the 18-crown-6 spectrum (Figure 4b).

The appearance of the cation spectrum (Figure 3a) was also significantly different: a higher mass cation was observed at m/z 199⁺, which corresponds to [Na + 12-crown-4]⁺, and another cation was observed at m/z 243⁺. The m/z 243⁺ is interpreted in terms of [Na + 15-crown-5]⁺, where the 15-crown-5 is an impurity in the 12-crown-4. GC/MS analysis of the 12-crown-4 revealed the presence of 15-crown-5, but at a concentration <1% 12-crown-

4, which is not consistent with the abundance of [Na + 15-crown-5]⁺ in the SIMS analysis (comparable to that of [Na + 12-crown-4]⁺). The abundance of the [Na + 15-crown-5]⁺ relative to [Na + 12-crown-4]⁺ probably reflects higher Na⁺ affinity of 15-crown-5 in solution^{7,8} or in the gas phase.¹⁰ No kalliated crown adducts were observed, because Na⁺ is by far the dominant group I cation on the surface. We estimate the ratio of Na⁺ to K⁺ to be about 17 by comparing the absolute abundance of Na⁺ in the spectrum of the gold cyanide-treated carbon (Figure 2a) with the abundance of K⁺ in the spectrum of the untreated carbon (Figure 1a). (Note that it was not possible to directly compare the m/z 23⁺ abundance with that of m/z 39⁺ in the spectrum of the 12-crown-4 + gold cyanide treated sample, because m/z 39⁺ has a substantial component corresponding to C₃H₃⁺ which could not be resolved.)

In the lower mass regions of the cation spectra, abundant hydrocarbons are observed. A simplistic explanation for the presence of these abundant ions is that they are derived from the crown ether, but there is little evidence for oxygen in these ions (e.g., the abundance of m/z 45⁺ (normally C₂H₄OH⁺) is low). Further, it is difficult to rationalize C₃, C₄, and higher ions in terms of the crown ether, whose repeating unit is (C₂H₄O). Alternative explanations are that the hydrocarbon ions are either derived from an atmospheric source or are indigenous to carbon surfaces. The observation of these ions may be facilitated by the presence of the crown ether.

SIMS Spectra of Carbon Exposed to Gold Cyanide, Treated with 18-Crown-6. The carbon exposed to gold cyanide was crushed wet with an 18-crown-6 solution, because it was felt that more abundant complex ions might be observable using a larger crown, which is capable of efficiently complexing K⁺ and more efficiently complexing Na⁺. Au(CN)₂⁻ was observed in the anion spectrum, as was CN⁻ and CH₃CN⁻ (Figures 4b and 5b). The abundances of these ions were similar to those observed in the spectra of carbon doped with 12-crown-4. In the cation spectrum, adduct ions corresponding to [Na + 18-crown-6]⁺ and [K + 18-crown-6]⁺ were observed at m/z 287⁺ and 303⁺ (Figures 4a and 5a). The lower mass region again contained very abundant hydrocarbon ions.

It was surprising that the 12-crown-4 worked as well as the 18-crown-6 in promoting the sputtering of Au(CN)₂⁻, because the larger ligand is known to be a more effective complexing agent.^{8,10} An equimolar solution of both crown ethers (0.049 M) was applied to a carbon chip, which was then crushed and analyzed. This experiment showed that 18-crown-6 was indeed much more effective at complexing Na⁺ than 12-crown-4: the ratio of [Na + 18-crown-6]⁺/[Na + 12-crown-4]⁺ was at least 49.

The role of the crown ether concentration was evaluated by analyzing carbon chips that had been crushed in 50 mL of 18-crown-6 solutions having concentrations ranging from 0.0049 to 0.49 M. At the lowest concentrations, a very low abundance [Na + 18-crown-6]⁺ ion could be observed, but no Au(CN)₂⁻. Thus, insufficient 18-crown-6 defeats attempts to observe Au(CN)₂⁻. When 0.049 or 0.18 M crown solutions were used, good abundances of the [Na + 18-crown-6]⁺ and Au(CN)₂⁻ were observed. The higher concentration crown solution appeared to work better, but the precision of the measurements do not permit a firm conclusion to be drawn at this time. Interestingly, when a 0.49 M solution was used, the abundances of the complex ions were markedly decreased, perhaps because the organic had thoroughly

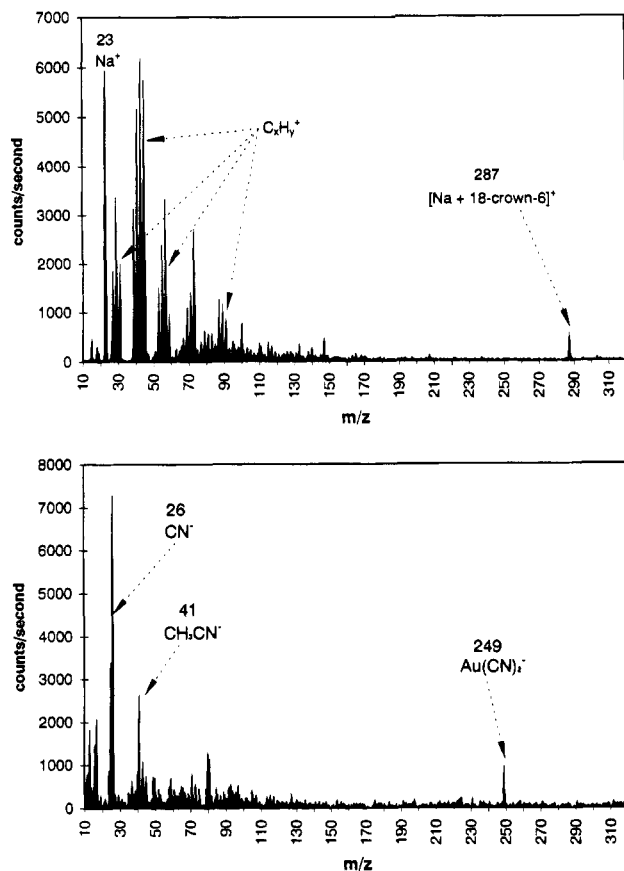


Figure 4. Cation (a, top) and anion (b, bottom) SIMS spectra of carbon exposed to 10 mg/L gold cyanide solution, treated with 18-crown-6.

coated the surface and thus obscured ions originating from the carbon surface.

Discussion. The 18-crown-6 and 12-crown-4 results show that $\text{Au}(\text{CN})_2^-$ may be readily observed on carbon surfaces by treating the surface with a crown ether. It is hypothesized that the crown ether enhances the sputtering of $\text{Au}(\text{CN})_2^-$ and other ions by complexing the group I cation, thereby weakening $\text{MAu}(\text{CN})_2$ compounds present on the carbon surface (where $\text{M} = \text{Na}^+$ or K^+), and facilitating subsequent formation of gas-phase $\text{Au}(\text{CN})_2^-$ upon sputtering with ReO_4^- . The observation of $[\text{M} + \text{crown}]^+$ is consistent with this hypothesis, which if correct generally implies that secondary ion sputtering can be facilitated by manipulation of the surface chemistry.

Although SIMS does not provide direct spectral information on adsorbed surface species, the present observations are consistent with the notion that gold is extant as the $\text{Au}(\text{CN})_2^-$ complex on the carbon surface. A less likely alternative is that Au and CN^- are independently present on the carbon surface and then combine to form $\text{Au}(\text{CN})_2^-$ in the "selfedge" region upon ion bombardment. This type of process would be similar to the formation of M_2^+ ions observed by Rabalais and co-workers ($\text{M} = \text{alkali metal}$).²⁵ We do not favor clustering as an explanation for $\text{Au}(\text{CN})_2^-$, because if this were occurring, then $\text{Au}(\text{CN})_2^-$ should be observable irrespective of the presence of the crown ether. The fact that the crown ether promotes $\text{Au}(\text{CN})_2^-$ sputtering also suggests strongly that $\text{Au}(\text{CN})_2^-$ is tightly complexed on the surface with sodium.

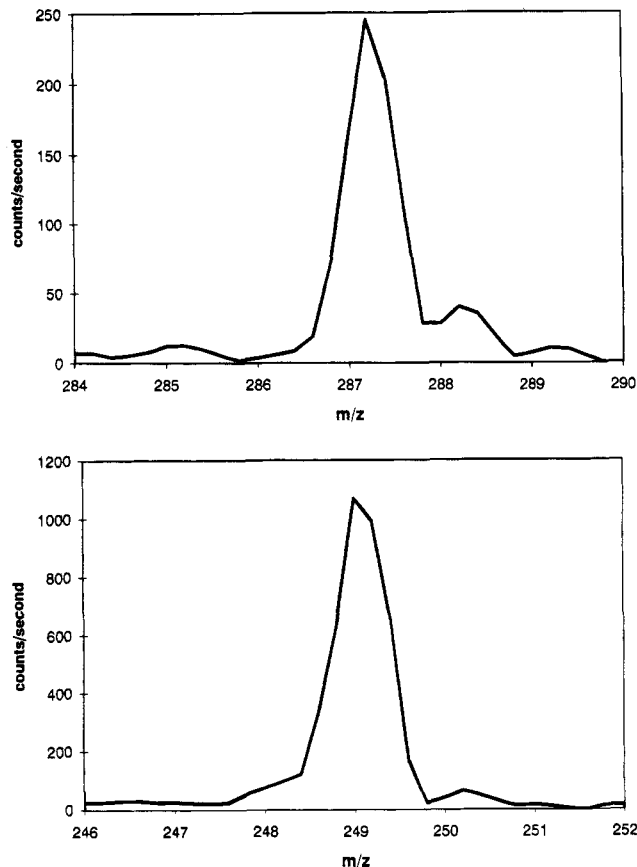


Figure 5. Partial cation (a, top) and anion (b, bottom) spectra of carbon exposed to 10 mg/L gold cyanide, treated with 18-crown-6.

The presence of crown ethers on the carbon surface also appear to promote the formation of Au^- (Figure 3b). One explanation for the auride ions is that nascent or actual $[\text{Na} + \text{crown}]^+\text{Au}^-$ complexes are formed on the carbon surface; the component ions are then sputtered into the gas phase upon SIMS bombardment. This idea is supported by the fact that crown ethers are known to promote the formation and stabilization of Au^- in the presence of sodium.⁷ A second plausible explanation is that Au^- is formed by a SIMS-induced decomposition of $\text{Au}(\text{CN})_2^-$. This draws support from the SIMS spectrum of $\text{KAu}(\text{CN})_2$, which contains Au^- . A third possibility is that Au^- is formed directly from SIMS bombardment of Au^0 ; however, this does not account for the enhancing effect of the crown ether. At the present time, Au^0 cannot be identified in the presence of $\text{Au}(\text{CN})_2^-$ on carbon surfaces, but an improved understanding of the relationship between the two ionic species may permit this distinction in the future.

ACKNOWLEDGMENT

The authors thank Marnie Cortez for assistance with SIMS data acquisition, and Cathy Rae for GC/MS analysis. This work was supported by the U.S. Department of Energy, Idaho Operations Office Contract DE-AC-07-76IDO1570.

Received for review January 17, 1995. Accepted April 6, 1995.*

AC950053C

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* Abstract published in *Advance ACS Abstracts*, May 15, 1995.