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Characterization of copper chloride cluster ions formed in secondary ion mass spectrometry

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Abstract

The surfaces of copper chloride salts were investigated using three different secondary ion mass spectrometry (SIMS) instruments: a quadrupole instrument equipped with an ReO_4^- primary ion, a time-of-flight (ToF) instrument equipped with a Ga^+ primary ion, and an ion trap instrument equipped with ReO_4^-. The research was conducted to identify copper chloride species sputtered from the surface of the copper chloride salts and to attempt to relate these species to the composition of the salt. Rich anion spectra were recorded using all three instruments for $CuCl_2$ and CuCl, which were dominated by $CuCl_3^-$ and $CuCl_2^-$. Other copper chloride adduct ions were also observed at higher masses. An examination of these ions revealed Cu primarily in the +1 and +2 oxidation state, irrespective of the oxidation state of the original salt. The presence of the Cu(+1)-bearing ions originating from the Cu(+2) salt has been attributed to reduction processes occurring during the bombardment event. However, oxidation processes must also be occurring, because Cu(+2)-bearing ions are observed in the spectra of the Cu(+1) salt. In contrast to the anion spectra, the only Cu-bearing cations contained in the $CuCl_{(1,2)}$ spectrum were acquired using the quadrupole- and ToF-SIMS corresponded to Cu^+ and low abundance Cu_2Cl^+ and $Cu_3Cl_2^+$ [(all Cu(+1)]. $CuCl_{(1,2)}$ were further investigated using the ion trap SIMS instrument: in these analyses, abundant cation clusters could be observed in addition to Cu^+. The ions have been grouped into one of four categories: highly oxidized, one e^- oxidized, redox neutral, and reduced. The most abundant species were redox neutral [e.g. $(CuCl_2)_2CuCl^+$)] and one e^- oxidized (e.g. $(CuCl_2)_3^+$). (Int J Mass Spectrom 178 (1998) 19–29) © 1998 Elsevier Science B.V.

Keywords: SIMS; Cluster ions; MS/MS; Ion trap; Copper chloride

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1. Introduction

This report describes the characterization of the copper chloride salts using secondary ion mass spectrometry (SIMS). This study is motivated by several factors. First, the relationship between gas-phase species produced by SIMS and the structures extant on the surface is a largely unresolved issue. SIMS is a relatively nondestructive technique; however, bombardment-induced damage does occur. Normally, a spectrum consists of ionic species that are unchanged by the analysis and species that have been substantially modified (i.e. damaged). The spectra of sodium nitrate [1], sodium tetrafluoroborate ($NaBF_4$) [2], and some perrhenate salts [3] are excellent examples of this phenomenon, in that they are salts that display

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Dedicated to the memory of Al Nier.

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substantial surface damage after a relatively small primary ion dose. For this reason, the interpretation of SIMS spectra of salts must be conducted with care, and the need for more research into gas-phase ion formation processes is clearly indicated.

A second motivation for the current investigation is the growing interest in inorganic salt analysis. The pioneering work of Gard et al. [4] and Johnston and Wexler [5], who independently developed "on-the-fly" laser desorption mass spectrometry particle analysis instruments, has shown that many environmental particles are primarily inorganic [6]. The ability to relate secondary ion, or laser desorption spectra, to condensed phase species is critical to this work because the samples are so small that any alternative analytical technique would not be practical.

A third motivation is that metal speciation at solid surfaces is a significant issue, but there are few means by which it can be probed. The subject is important because it bears on the contaminant mobility and the eventual contaminant disposition in the environment [7]. Furthermore, metal toxicity is profoundly affected by speciation. Because surface species are likely to be the most accessible, this regime is critical to understanding mobility and toxicity issues. Yet, analysis in this region remains problematic because of low contaminant concentrations, the perturbing nature of most interrogation techniques, the lack of sensitivity, high background signal, and difficulty in interpreting resultant data. Recently, encouraging results generated using laser desorption have demonstrated that meaningful speciation information can be derived from inorganic surfaces [8].

We have been applying SIMS to the characterization of a variety of inorganic surfaces [9]. Historically this approach has been difficult because of surface charging, and the low abundance of *molecular* species sputtered from the surface of interest. Several new technological approaches have been applied in our laboratories that have made the technique more amenable to the determination of metal species sputtered from inorganic surfaces. Pulsed secondary ion extraction has provided a viable means for overcoming troublesome surface charging that plagues the analysis of refractory, nonconducting surfaces [10]. A polyatomic, primary anion source was developed [11] that is more efficient at sputtering molecular secondary ions when compared with atomic sources [1b]. In addition, an ion trap SIMS was developed, which has demonstrated improved detection of high mass secondary ions. This is a consequence of both better high mass sensitivity in the ion trap mass spectrometer and collisional stabilization from the He bath gas [12]. This combination proved to be highly effective for the identification of *bis*(alkylamine)mercury complex ions formed on the surface of mercury nitrate salts.

We have applied three different types of SIMS instrumentation to the characterization of copper chloride surfaces. Copper chloride was chosen because it is a toxic metal and because it bears an oxidation state similarity to Hg, which is an element of interest in our laboratory. Furthermore, the generation of Cu-complexes from solution [13] and the gas phase [8,14] have been studied, which permits some basis for comparison. The combination of SIMS instrumentation used in this study allows for the analysis of the copper chloride surfaces using both atomic and polyatomic primary beams and for the secondary ions to be formed in both high and low pressure environments.

2. Experimental

2.1. Quadrupole SIMS instrument

The quadrupole SIMS instrument used in these studies is based on an Extrel (Pittsburgh, PA) triple quadrupole mass spectrometer with 19-mm rods and a mass range of 500 u. A schematic diagram of the instrument has been published previously [1b], but a brief description is given here. The instrument is equipped with an ReO_4^- primary ion gun [11], which was designed in our laboratory, and consists of an ion source, a three element electrostatic zoom lens, and beam steering electrodes positioned immediately after the exit aperture of the lens. These components are mounted on a 12-in. spherical vacuum chamber, with a 35° angle between the primary ion gun and the mass spectrometer. This placement of the primary gun allows the primary beam to pass through the center of the spherical chamber. A microchannel plate image intensifier is mounted directly opposite the ion gun, to assess beam focusing and positioning. The ReO_4^- gun is operated at an ion energy of 5.25 keV, between 100 and 300 pA of primary ion current. The base pressure in the instrument is on the order of 2×10^{-7} Torr.

Sample targets consisted of a stainless steel wire, flattened on one end: this would accommodate a 2×3 mm rectangle of double-sided tape, which was used to adhere the copper chloride powder samples. CuCl and $CuCl_2 \cdot 2H_2O$ (J.T. Baker, Phillipsburg, NJ) were used as target powders. The loaded sample was attached to a direct insertion probe for analysis. When the $CuCl_2 \cdot 2H_2O$ was evacuated in the insertion lock, the salt quickly turned brown. This results from the dehydration of the dihydrate: anhydrous $CuCl_2$ is brown. Hence, $CuCl_2$ was what was investigated for Cu(+2). When the sample target was inserted into the mass spectrometer, it intercepted the primary ion beam, and this could be observed on the image intensifier. Typical values for the area of the target in the beam were on the order of 0.03–0.04 cm^2. A typical flux density was 3.6×10^{-10} ions/cm^2 s.

The secondary ion extraction lens was operated in a "pulsed extraction" mode [10], which means that anions and cations are alternately extracted from the secondary ion source. This extraction system, when coupled to the quadrupole mass analyzer, permits the acquisition of the anion and cation spectra in an interlaced fashion. The extraction time for each polarity was adjustable, and the ratio (cation extraction time/anion extraction time) used in the present experiments was 2.0. The actual time required for a single cation/anion extraction cycle was 80 ms, which consisted of 49.3 ms cation extraction; 3 ms electronic settle time; 24.7 ms anion extraction time; 3 ms electronic settle time. This sequence was repeated at 0.2-u intervals from m/z 10 to m/z 400. A typical dose was on the order of 9.3×10^{11} ions/cm^2.

2.2. Ion trap SIMS instrument

An ion trap SIMS instrument constructed in our laboratory was also used to record the secondary ion mass spectra of the copper chloride salts. The instrument has been described in detail previously, but is briefly described here [12,15]. The ion trap mass spectrometer is a modified version of the Finnigan (San Jose, CA) ITMS running Teledyne Apogee software. The ion trap used a 4.5-keV ReO_4^- primary beam and an offset detector. Both the primary ion beam and the direct insertion probe are coaxial with the ion trap, with the gun located behind one end cap, and the probe behind the other. The ion trap end cap corresponding to the direct insertion probe was modified with a larger (5 mm) aperture covered with a 90% pass grid. The system base pressure without He bath gas was 5×10^{-7} Torr. The pressure with the He bath gas was approximately 8.5×10^{-5} Torr. The ion trap was operated at room temperature.

The $CuCl_{(1,2)}$ powders were prepared for analysis in a manner identical to that described for the quadrupole: the powders were adhered to the top of a small metal sample holder (a no. 18 nail) using double-sided tape. The loaded sample holder was then pressed into the top of a direct insertion probe.

The ReO_4^- primary ion gun was operated at an ~435-pA primary ion current during these experiments. The ion gun aperture in the end cap was 1 mm in diameter, which defined the area on the sample target irradiated by the primary ion beam (7.85×10^{-3} cm^2). The primary ion beam only irradiated the sample surface during the ionization portion of the acquisition. These parameters were used to calculate a flux density of 3.5×10^{11} ions/cm^2 s while the beam was on target.

The low mass cutoff of the trap corresponded to 40 u for the single stage mass spectrometry measurements; the trap was scanned from 40 to 640 u using the mass selective instability technique [16]. For most experiments, this resulted in degraded mass spectrometer performance as a result of too many ions in the trap. The problem was overcome by ejecting the most abundant (Cu^+) ion from the trap, which was accomplished by applying a 10 V filtered noise field (FNF) [16] at 226–233 kHz to the end caps during sample irradiation (ionization).

Tandem mass spectrometry (MS/MS) measurements were also made using the ion trap: to acquire these data, the envelope of isotopic ions corresponding to the parent of interest was isolated in the trap by applying an FNF, notched at the appropriate frequency components, to the end caps during ionization. Once isolated, the envelope of isotopic ions was caused to fragment by application of supplementary "tickle" frequencies (the same frequencies used in the isolation) to the end caps; typical excitation voltage used was on the order of 1 V.

2.3. Time-of-flight SIMS instrument

Time-of-flight (ToF) SIMS analyses were performed using a Charles Evans & Associates TRIFTTM ToF-SIMS (Redwood City, CA) instrument [17,18]. CuCl and $CuCl_2 \cdot 2H_2O$ particles were mounted in one of two ways: (1) they were placed on an Si wafer, and pinned into place using a tungsten mesh; or (2) they were pressed into indium foil. The mounted samples were then placed in the sample holder of the instrument and admitted to the source, where they were analyzed at a base pressure of approximately 5×10^{-9} Torr. When the particles were analyzed, an 80×80 μm area was scatter rastered using the primary ion beam in a pulsed fashion. The temporal width of a single pulse was 16.28 ns, and the repetition rate was 10 kHz. The primary ion used was 12 keV Ga^+ for cations, and 18 keV Ga^+ for anions, operated at a dc ion current of 600 pA. This information was used to calculate a flux density of 9.5×10^9 ions/s cm^2. Analysis time for a single sample required approximately 2 min, and hence the total dose imparted to the samples was on the order of 1.1×10^{12} ions/cm^2.

3. Results and discussion

Three different types of SIMS instruments were employed in the present study. Quadrupole and ion trap SIMS instruments, each equipped with the polyatomic ReO_4^- primary particle, were used in studies conducted at the Idaho National Engineering and Environmental Laboratory. The ion trap instrument operates at a higher pressure than the quadrupole instrument, and the secondary ions are long-lived in the trap. Hence, the opportunity exists for thermalization of secondary ions in the ion trap, which can facilitate observation of ions that are difficult to see in the quadrupole. Conversely, the ion trap is also subject to space charge effects and ion–molecule reactions; because these phenomena are not factors in the quadrupole instrument, the spectra acquired using the quadrupole tend to be cleaner and easier to interpret. The third type of instrument employed was a ToF-SIMS, equipped with a Ga^+ primary ion gun. It is believed that the surface penetration of this particle is somewhat greater than the penetration of the ReO_4^-, and consequently, a different sampling region may be accessible using this instrument. In addition, the ToF analyzer does not have a drop-off in sensitivity for higher mass ions, as does the quadrupole.

3.1. Secondary cations

Analysis of $CuCl_{(1,2)}$ using the quadrupole and ToF-SIMS instruments produced predominantly Cu^+ and a small group of isotopic ions that corresponded to Cu_2Cl^+ (m/z 161, 163, and 165) and $Cu_3Cl_2^+$. These ions are interpreted straightforwardly in terms of Cu in the +1 oxidation state, which was in agreement with the oxidation state of CuCl, but not particularly reflective of the Cu(+2) salt. By contrast, subsequent analysis of $CuCl_{(1,2)}$ using the ion trap SIMS instrument yielded a rich spectrum, containing many clusters of isotopic ions. The origin of the cluster cations has been the source of some speculation. Two possibilities are envisioned: first, the cluster cations could be sputtered intact into the gas phase; second, they could be the products of gas-phase ion–molecule reactions. Ion ejection experiments using the ion trap do not support the ion–molecule reaction hypothesis. Ion isolation of any of the cluster ions could be easily accomplished using the FNF notched at the appropriate mass: if the cluster ions were the product of the ion–molecule reactions, then ejection of the parent would result in disappearance of the product ion, and this did not occur.

Because the clusters are not likely to be the product of ion–molecule reactions, the questions of why they

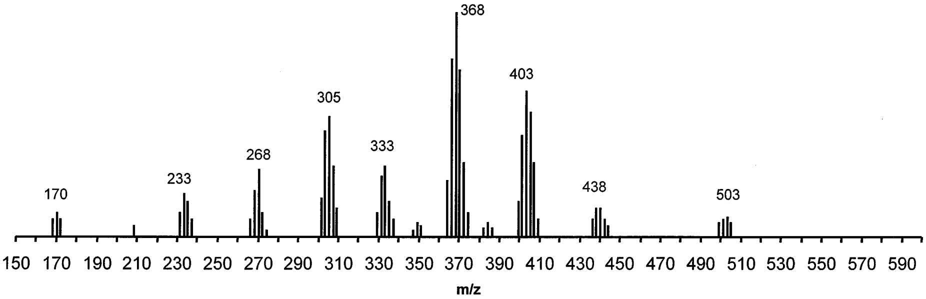


Fig. 1. Cation spectrum of $CuCl_2$, acquired using the ion trap SIMS instrument. The surface was bombarded for 50 ms, during which time an FNF was applied that ejected the two Cu^+ isotopic ions from the trap.

are only observed in the ion trap is raised. The appearance of the cluster cations may be due to collisional stabilization available in the He bath gas of the trap, which can reduce the amount of internal energy in the secondary ions. This phenomenon has been noted previously [19].

No substantial mass spectral differences between the $CuCl_2$ and CuCl salts could be observed using the trap. The most abundant ion was Cu^+ in both cases, and isotopic cation clusters were observed out to *m/z* 535. The abundant Cu^+ created problems in the ion trap associated with space charging because of too many ions. This problem was eliminated by ejecting Cu^+ from the trap, by applying an FNF tuned to the frequencies of the Cu^+ isotopic ions during sputtering (ionization). Reasonable resolution of the copper chloride isotopic ion envelopes was achieved using this approach (Fig. 1), but did not eliminate the problem completely for a full scan: apparent ions are observed between the isotopic ions (e.g. *m/z* 302, 304, and 306 in Fig. 1), which are caused by the data system recording signal above background at these masses. However, careful ion isolation of individual isotopic envelopes showed that these signals were artifacts of the space charging problem and the data system (Fig. 2, top).

The cations were identified on the basis of mass and relative abundances within the isotopic envelopes. The ions were assigned to one of four groups, according to whether the ion was oxidized or reduced compared with $CuCl_2$ (Table 1). In the discussion below and in Table 1, the mass denoted corresponds to the principal isotopic ion [20].

3.1.1. Redox neutral cations

The most abundant cluster of isotopic ions had a principal isotopic ion at *m/z* 368, and corresponded to $(CuCl_2)_2CuCl^+$; this composition requires neither oxidation nor reduction of the starting $CuCl_2$, and hence is termed *redox neutral*. Other ions belonging to this family include $(CuCl_2)_3CuCl^+$ (*m/z* 503) and $(CuCl_2)CuCl^+$ (*m/z* 233). These ions were studied using the MS/MS capability of the ion trap. In these experiments, the parent isotopic ion cluster is isolated using an FNF with a "notch" corresponding to the

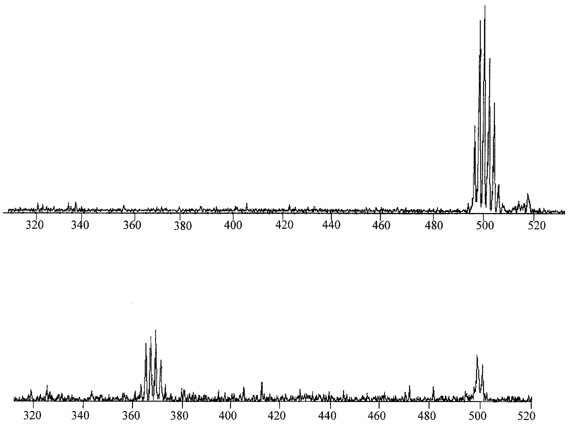


Fig. 2. MS/MS of $(CuCl_2)_3CuCl^+$ using the ion trap SIMS. Top, isolation of $(CuCl_2)_3CuCl^+$ using the FNF of the ion trap. Bottom, fragmentation of $(CuCl_2)_3CuCl^+$, forming $(CuCl_2)_2CuCl^+$.

Table 1
Interpretation of secondary cations sputtered from $CuCl_2$, using the ion trap SIMS

	Reduced	Redox neutral	One e^- oxidized	Highly oxidized
n	$(CuCl_2)_nCu^+$	$(CuCl_2)_nCuCl^+$	$(CuCl_2)_n^+$	$(CuCl_2)_nCuCl_3^+$
0	Cu^+ (63, note 1)	Not observed	N.A.	7% (170)
1	Not observed	20% (233)	Not observed	50% (305)
2	30% (333)	100% (368)	20% (268)	10% (438)
3	Not observed	9% (503)	70% (403)	Not observed
4	Not observed	Note 2	1% (538)	Note 2

Abundances are reported to one significant figure relative to the base peak (m/z 368). Values in parentheses correspond to the mass of the principal isotopic ion.

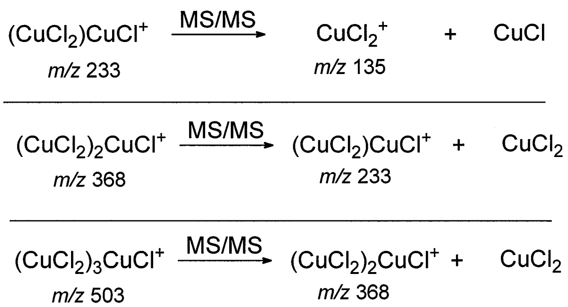
Note 1: Cu^+ is observed as the base peak in the spectrum, but was ejected to facilitate observation of other isotopic ion clusters.

Note 2: the high mass limit of the ion trap was approximately 640 u, which would preclude observation of these species.

mass of the parents (see Sec. 2), and then caused to undergo collisional activation by applying a second FNF with a "spike" at the same frequency (Fig. 2). In this manner, it was shown that $(CuCl_2)_3CuCl^+$ and $(CuCl_2)_2CuCl^+$ each eliminate $CuCl_2$ in a process that does not alter the Cu oxidation state of either the product ions or neutrals (Scheme 1). In contrast to the higher mass homologues, $(CuCl_2)CuCl^+$ does not eliminate $CuCl_2$, but rather eliminates only CuCl to produce $CuCl_2^+$ (m/z 135): this process results in a reduced neutral (to Cu(+1)) and an ion that contains Cu(+3) (see below).

3.1.2. One-electron oxidized cations

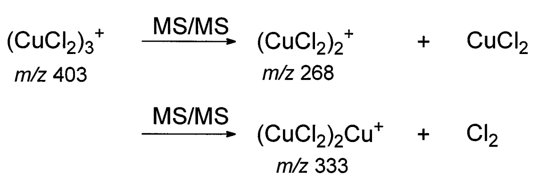
Three cations were observed in the ion trap that were interpreted in terms of $(CuCl_2)_n^+$ ($n = 2$–4), formed by the loss of one electron from neutral $CuCl_2$ clusters, and analogous to molecular ions formed by electron ionization. The second most abundant cluster of isotopic cations observed in the ion trap corresponds to $(CuCl_2)_3^+$ (m/z 403). MS/MS of this isotopic ion cluster showed that it eliminated $CuCl_2$ to form $(CuCl_2)_2^+$, and also eliminated Cl_2 to form the reduced species $(CuCl_2)_2Cu^+$ (Scheme 2). MS/MS was attempted unsuccessfully on $(CuCl_2)_2^+$; we were unable to input sufficient energy into this ion to cause fragmentation. MS/MS on $(CuCl_2)_4^+$ was not attempted because the ion was not present in sufficient abundance.



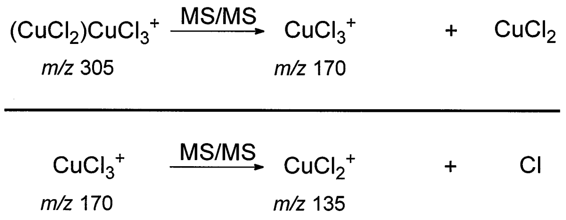
Scheme 1. MS/MS fragmentations of redox neutral cations, observed in the ion trap.

3.1.3. Highly oxidized cations

Two clusters of isotopic ions observed in the ion trap were interpreted in terms of highly oxidized copper chloride species; the compositions were $CuCl_3^+$ and $(CuCl_2)CuCl_3^+$. For $CuCl_3^+$, Cu can be interpreted as being in the +4 oxidation state. For $(CuCl_2)CuCl_3^+$, the Cu atoms can occupy the +2 and +4 oxidation states, or both Cu atoms in the +3 state could be envisioned. Although copper in higher oxidation states is not common, Cu(+3) and (+4) salts have been isolated in the condensed phase [21]; consequently, we believe that formation of these ions



Scheme 2. MS/MS fragmentations of one-electron oxidation-formed cations, observed in the ion trap.

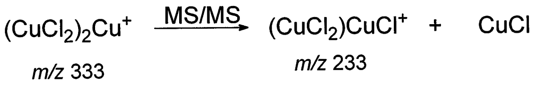


Scheme 3. MS/MS fragmentations of highly oxidized cations, observed in the ion trap.

in the isolation of the He bath gas of the ion trap is not beyond the realm of comprehension. MS/MS of $(CuCl_2)CuCl_3^+$ resulted in elimination of $CuCl_2$, to produce $CuCl_3^+$ (Scheme 3). MS/MS of $CuCl_3^+$ resulted in the elimination of Cl, to produce $CuCl_2^+$. This latter result is consistent with the idea that all three Cl atoms are bound to Cu, which would require Cu(+4).

3.1.4. Reduced cations

Two ions in which copper is present in the +1 state were observed: Cu^+, and $(CuCl_2)_2Cu^+$. Evidently, formation of $(CuCl_2)Cu^+$ is not favored, because this ion was not observed. The observation of the oxidized and reduced copper chloride species demonstrates that a wide variety of processes is occurring; it may be that these species are formed as reduced products of the reactions leading to the highly oxidized cations mentioned in Sec. 3.1.3. MS/MS of $(CuCl_2)_2Cu^+$ resulted in the elimination of CuCl to produce $(CuCl_2)CuCl^+$ (Scheme 4).



Scheme 4. MS/MS fragmentations of reduced cations, observed in the ion trap.

3.2. Secondary anions

The anionic species observed were the same using all three instruments, with some minor exceptions. The polyatomic secondary ions can be thought of as clusters of CuCl and/or $CuCl_2$, which are made anionic through the attachment of Cl^- (Table 2). Hence, all the sputtered anion species contain Cu(+1) and/or Cu(+2). Willett et al. [22] has reported the formation of tin sulfide anions that are similar to the CuCl clusters in that they have mixed oxidation states. Generally, the abundance of the secondary ions decreases with increasing mass, which is clearly indicated in the spectra collected using the ToF-SIMS instrument (Fig. 3). The excellent dynamic range and high mass sensitivity of the ToF instrument allow for the facile detection of ions up to m/z 538 ($Cu_4Cl_8^-$) and beyond. In addition, Cl^- is by far the most abundant ion in the ToF-SIMS spectrum, being much more abundant than that recorded using either the quadrupole or the ion trap. We believe that this latter observation originates from two factors. First, the secondary ion lens of the ToF instrument is capable of collecting secondary ions having a broad range of kinetic energies, which leads to enhanced abundance of atomic ions compared to the quadrupole. Second,

Table 2
Interpretation of secondary anions sputtered from $CuCl_2$, using the quadrupole, ToF, and ion trap SIMS

	Reduced	Partially reduced, mixed oxidation states	Redox neutral
$n + m$	$(CuCl)_nCl^-$	$(CuCl)_n(CuCl_2)_mCl^-$	$(CuCl_2)_nCl^-$
0	Cl^-, (35)	Not applicable	Cl^-, (35)
1	$(CuCl)_1Cl^-$ (135)	Not applicable	$(CuCl_2)_1Cl^-$ (170)
2	$(CuCl)_2Cl^-$ (233)	$(CuCl)_1(CuCl_2)_1Cl^-$ (268)	$(CuCl_2)_2Cl^-$ (303)
3	$(CuCl)_3Cl^-$ (333)	$(CuCl)_2(CuCl_2)_1Cl^-$ (368)	
3		$(CuCl)_1(CuCl_2)_2Cl^-$ (403)	
4		$(CuCl)_2(CuCl_2)_2Cl^-$ (503)	
4		$(CuCl)_1(CuCl_2)_3Cl^-$ (538)	

Abundances are reported to one significant figure. Values in parentheses correspond to the mass of the principal isotopic ion.

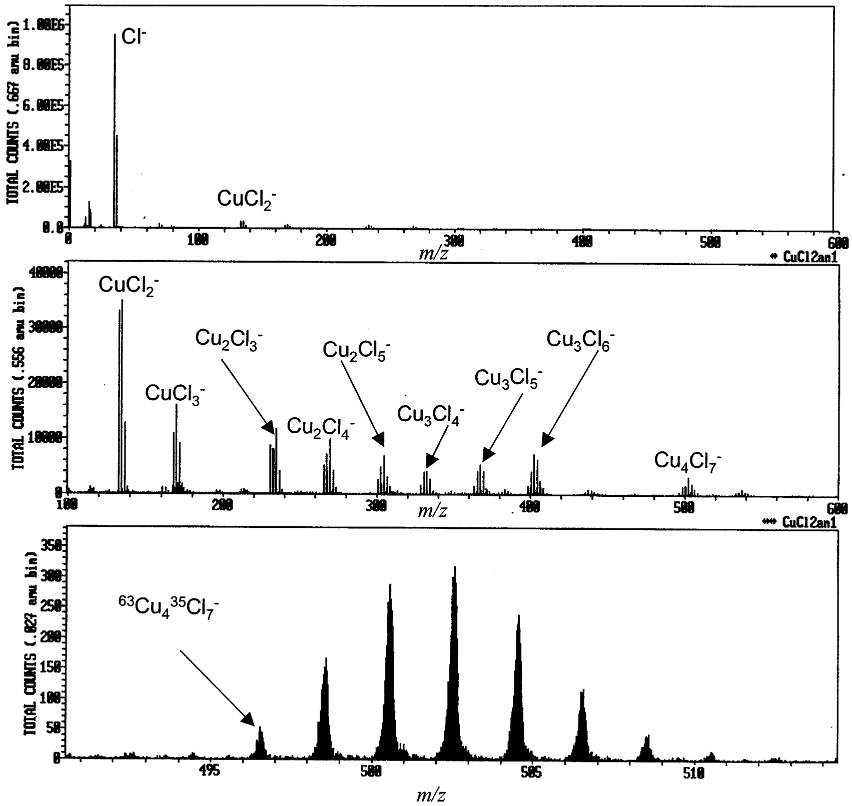


Fig. 3. Anion spectrum of $CuCl_2$, acquired using the ToF-SIMS instrument. Top, full spectrum, full scale. Middle, m/z 100–600, y axis expanded 25×. Bottom, $Cu_4Cl_7^-$ isotopic ions, y axis expanded 3000× (original magnification).

the ToF employs a Ga^+ primary projectile, which is less efficient at generating polyatomic (or molecular) secondary ions compared with the ReO_4^- projectile employed in both the quadrupole and ion trap instruments in this study [1b].

The ToF-SIMS spectra collected for $CuCl_2$ and CuCl were practically identical; the only significant difference was that the CuCl spectra contained a group of isotopic ions at m/z 145, 147, 149, which were identified as $CaCl_3^-$. The origin of the Ca contamination has not been identified. Indium contamination could also be observed on some of the spectra in which indium foil was employed as a sample mounting medium. This was evidenced by an abundant $InCl_4^-$, with lower abundance ions that corresponded to $InCl_2^-$, $InCl_3^-$, $In_2Cl_7^-$, and $In_2Cl_8^-$. The $CuCl_{(1,2)}$ particles could not be mounted in indium foil without generating these ions. We believe that the indium is transported onto the surface of the $CuCl_{(1,2)}$, either through the gas phase in vacuum, or by diffusion across the surface or through the bulk matrix of the Cu salts. To circumvent this problem, indium foil was abandoned as a mounting medium. Instead the $CuCl_{(1,2)}$ particles were placed on gold coated silicon, and held in place using a fine tungsten mesh.

The anion analyses acquired for $CuCl_2$ using the quadrupole SIMS contained a lower abundance of Cl^- and also a lower abundance of the high mass clusters; otherwise, the spectra were similar to those collected using the ToF-SIMS (Fig. 4). The spectra collected for CuCl were very similar to those collected for the $CuCl_2$; however, some quantitative differences were observed. The abundance of the Cu(+2)-bearing ions $CuCl_3^-$ and higher mass clusters

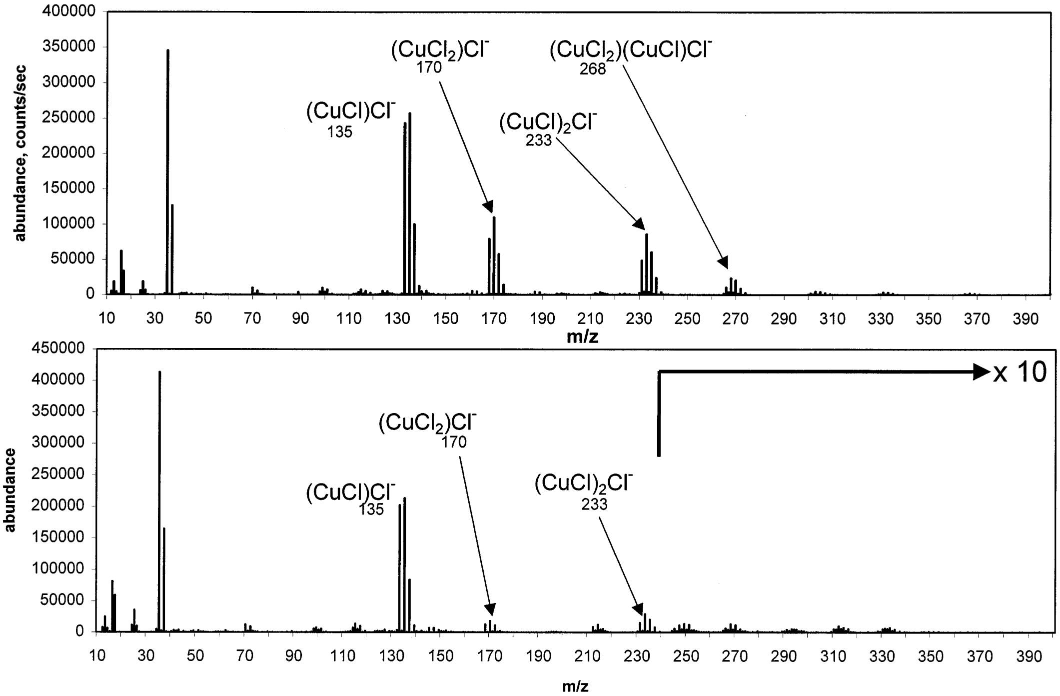


Fig. 4. Top, anion spectrum of $CuCl_2$, acquired using the quadrupole SIMS instrument. Bottom, anion spectrum of CuCl.

was markedly lower for CuCl than in the case of $CuCl_2$, which is consistent with the lower oxidation state of CuCl. This result indicates that surface oxidation state information may be acquired through careful use of the ReO_4^- projectile.

This result suggests that oxidation state information may be more readily obtainable using ReO_4^- than an atomic projectile. Generally, polyatomic projectiles such as ReO_4^- are more effective than monoatomic for generating intact molecular secondary ions most diagnostic for identification of surface species [1,23]. We speculate that ReO_4^- deposits its energy closer to the surface, which results in more efficient production of intact molecular species. If this explanation is correct, it implies that intact molecular species are not easily produced from the bulk. Certainly the bulk penetration of an atomic projectile is greater than that of ReO_4^-. It was noted that the secondary anion spectra acquired for $CuCl_{(1,2)}$ using the quadrupole could be markedly enhanced by exposing the surface of the sample to cyclohexylamine. We have previously studied cyclohexylamine on soil surfaces [24] and are familiar with its surface chemistry on inorganic substrates. We could not discern any change in the nature or relative abundances of the $CuCl_{(1,2)}$ secondary anions; however, the absolute abundances increased markedly. In the cation spectrum, the base peak corresponded to [cyclohexylamine + H]$^+$. We believe that the adsorbed amine facilitates anion desorption by providing a surface charge-balancing mechanism, *viz* the facile emission of abundant cations.

The anion spectra collected using the ion trap SIMS were again qualitatively similar to those recorded using the ToF and the quadrupole. Higher mass adduct ions were very low in abundance (Fig. 5), as the spectrum was dominated by abundant $CuCl_3^-$, with significant $CuCl_2^-$, and Cl^-. The higher mass anion clusters could be observed by ejecting the low mass ions from the trap and then irradiating the surface for a substantial time (~100 ms). However, even using this approach, the signal to noise of the secondary anions in the trap was usually poor.

For $CuCl_2$, $CuCl_3^-$ [Cu(+2)] was more abundant

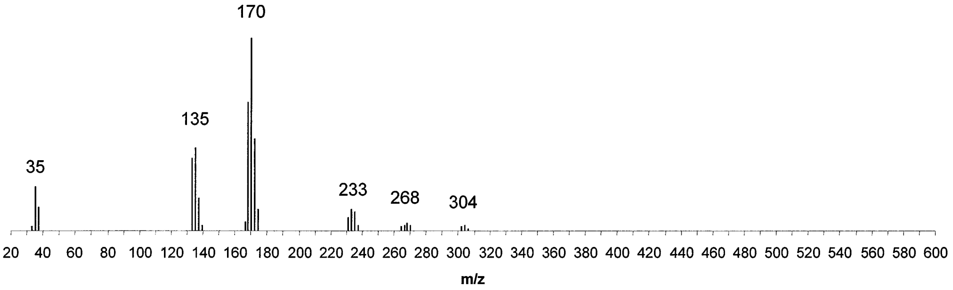


Fig. 5. Anion spectrum of $CuCl_2$, acquired using the ion trap SIMS instrument.

than $CuCl_2^-$ (Cu(+1)), which is consistent with the oxidation state of the metal in the starting salt. Other than this difference, the spectra recorded for the +1 and +2 salts were nearly identical.

MS/MS was performed on two of the ions to identify fragmentation pathways. $(CuCl)_2Cl^-$ predictably eliminated CuCl to form $(CuCl)Cl^-$ (Scheme 5). $CuCl_3^-$ could be fragmented to $CuCl_2^-$ (loss of Cl). We were unsuccessful in causing $CuCl_2^-$ to fragment, using either the ion trap or the triple quadrupole.

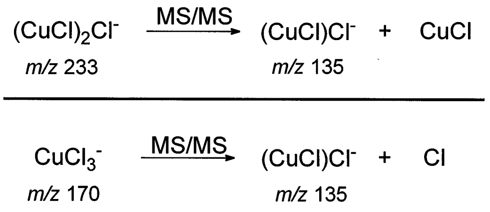
One species was observed in the ion trap analyses that was not observed using the other two instruments. A CuCl isotopic cluster was observed that had a principal isotopic ion at *m/z* 384. Modeling of the isotopic envelope suggested a composition of $Cu_3Cl_5O^-$; however, we do not know why this ion would be observed only in the ion trap SIMS experiments.

4. Conclusions

Distinctive clusters of isotopic anions can be readily observed by ion sputtering of both $CuCl_2$ and CuCl. The anion spectra contain species having Cu(+1), Cu(+2) and both oxidation states together. Ions having both oxidation states are observed irrespective of the oxidation state of the starting salt. However, the ReO_4^- primary projectile produces more abundant anions that are indicative of the oxidation state of the salt.

Cluster cations can be observed in the ion trap SIMS. Species contain Cu(+1), Cu(+2), and the more highly oxidized Cu(+3) and Cu(+4) are observed. These ions could not be observed using the other two instrument types. The reason for the abundant cluster cations observed in the ion trap is not clear. We speculate that the positively charged clusters are formed with a substantial amount of internal energy, which leads to kinetically fast decomposition reactions under high vacuum conditions. However, if the ions are thermalized through collisions with the He bath gas, their internal energies may be reduced below decomposition thresholds, and they may be observed as stable ions in the ion trap. The role of stabilizing collisions, occurring in the relatively high pressure environment of the ion trap (1×10^{-4} Torr He), has been reported previously [19].

The polyatomic ReO_4^- primary particle may also be contributing to the observation of the cation clusters. It could be argued that if this were the case, the clusters should be observed in the quadrupole, which is also equipped with the ReO_4^- primary. However, the quadrupole is known for a substantial drop-off in sensitivity with increasing mass, and the abundant clusters are observed at *m/z* 368 and 403, which are masses well beyond the range of efficient



Scheme 5. MS/MS fragmentations of anions, observed in the ion trap and in the triple quadrupole.

transmission for our quadrupole. Additional studies are needed to understand the origin, structure, and implications of the CuCl-bearing cations observed in the ion trap SIMS.

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