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Identification of Metal Cations, Metal Complexes, and Anions by Electrospray Mass Spectrometry in the Negative Ion Mode

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Pneumatically assisted electrospray mass spectrometry (ES-MS) is used in the negative ion mode for aqueous metal (M) solutions in an excess of hydrochloric or nitric acid, where the major anion $X = Cl^-$ or NO_3^-. A collision energy of ∼20 eV removes anion−solvent clusters for most elements and leaves negative complex ions of the general form $(M^{n+}X_{n+1})^-$. Complexation with anions prevents charge reduction reactions at least to $n = 3$, even in cases where the third ionization energy of M greatly exceeds the first ionization energy of the solvent. These negative ions thus preserve the charge state of the metal cation from the solution and allow identification of both cations and anions in a single set of electrospray conditions. Cations such as Fe^{3+} or Cu^{2+} that have a lower oxidation state in solution produce a distribution of negative ions, each with a single negative charge overall; e.g., an Fe^{3+} solution produces both $Fe^{III}X_4^-$ and $Fe^{II}X_3^-$. This distribution of Fe^{III} and Fe^{II} species is attributed to electrochemical reduction of Fe^{3+} at the negatively charged ES needle. "Native" anions such as perrhenate or molybdate produce singly charged analogues such as ReO_4^- or $HMoO_4^-$. Metal−EDTA complexes are seen as $M^{III}Y^-$ or $M^{II}HY^-$. The sensitivity for these "native" anions is suppressed by competition with the excess chloride or nitrate used to produce the metal-containing complex ions.

There is a general need for analytical methodology that can identify a wide range of components in solution: organic and inorganic ions, complexes, and complexing agents. For such mixtures, no single general method is completely suitable. Atomic spectroscopy is very selective for the elements present but is generally not sensitive to their oxidation state or chemical form, unless it is combined with chromatographic separations. When such separations are used, the species can be identified only on the basis of their retention time and the unique elements they contain, and only the total element in a compound corresponding to an unknown peak can be quantified. Some species are inherently unstable when retained on a column or when isolated from other forms of the same element. Ion chromatography is widely used for the determination of inorganic anions, but again the anions are generally identified only on the basis of their retention time. Detection methods that provide molecular information are also required.

Electrospray mass spectrometry (ES-MS) shows substantial promise along these lines. The "ionization" process in ES-MS can be very "soft" in that the ions are originally present as such in the sample solution and are merely liberated from the solvent. The main application of ES-MS is the determination of biological and pharmaceutical compounds, but there is growing interest in ES-MS for inorganic analysis. This latter area has recently been reviewed by Stewart[1] and has evolved along three main avenues: structural studies of pure compounds,[2] identification of unknown inorganic and organometallic species containing particular elements of environmental or toxicological interest,[3−7] and basic studies of the spectra produced for small inorganic ions, mostly metals. This latter area has been studied by Kebarle,[8,9] Douglas,[10] Agnes and Horlick,[11,12] Siu,[13,14] Sharp,[15] and Caruso[16] and is of primary interest to the present work.

Nearly all the work cited above has been performed using positive ions. Many doubly and triply charged metal cations produced in positive ion mode react with solvent. Such processes

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are activated by collisions in the extraction process and are called charge reduction reactions,[1,17] e.g.,

$$M(H_2O)_m{}^{3+} \rightarrow MOH(H_2O)_{m-2}{}^{2+} + H_3O^+ \qquad (1)$$

As solvent molecules are removed, the ion solvation sphere becomes smaller. At some point, the ion−solvent complex becomes too small to delocalize the high positive charge. Reaction with solvated water (or other molecules) is favorable thermodynamically because of the high third ionization energies of most elements. Although the original oxidation state of the metal remains intact, such reactions can produce ions not in the original solution. Thus, it is difficult to see free 3+ and some 2+ metal cations in the gas phase unless they are complexed (e.g., with crown ethers)[18] or very gentle collision conditions are used so that solvent molecules are not removed during the droplet desolvation process. If solvent clusters are retained, a distribution of solvated ions with various values of m are usually formed, which makes the spectra complicated.

The present work describes a general procedure for measuring both cations and anions using negative ions. It extends the basic idea of an earlier paper on the measurement of both anionic Cr(VI) and cationic Cr(III).[19] In an excess of nitrate or chloride, many cations attach anions to make negative ions of the general form $MX_n{}^-$. Collision conditions strong enough to remove solvent clusters can be used without inducing internal chemical reactions in these $MX_n{}^-$ ions. The oxidation state of the M atom is consistent with that expected from the solution chemistry of the element of interest, as long as the element M is not converted to a different ion by electrochemical reduction at the ES needle. Negative ions from other anions are also seen such as $ReO_4{}^-$ and MY^-, where H_4Y = EDTA. In this mode, it is therefore straightforward to identify both anions and cations together under a single set of spray conditions and ion extraction voltages.

Negative ions are much less commonly used than positive ions in biomedical applications of ES-MS, partly because corona discharge begins at lower voltages in negative ion mode. Similarly, relatively little work has been published on electrospray MS of inorganic ions in the negative ion mode. Stewart and Horlick[20] briefly mentioned the observation of $LaCl_4{}^-$ ions in a study devoted primarily to positive ions from lanthanides. The $MX_n{}^-$ ions described below are related to the MX^+ ions reported by Horlick[17] and Siu.[13,14] Operating conditions based on intermediate collision energies that do not dissociate such MX^+ ions have sometimes been referred to as the “counterion mode”. To retain a net positive charge, only one or two anions can be attached to the cation, so these positive “counterions” often still contain solvent and remain prone to charge reduction reactions.

Wang and Cole[21] described the use of $(M_nX_{n-1})^+$ and $(M_nX_{n+1})^-$ ions for fundamental study of the ES process. The abundances of various positive cluster ions provide information about the relative importance of solvation energy vs gas-phase stability and the charged residue model vs the ion evaporation model for the final stages of ion production in ES. Their experiments differ from ours in several important ways. Their solutions are salts in which the metal and anions are present in stoichiometric amounts; our solutions are acids with a large excess of anion X^-. They reported results only for alkali metals; we do so for alkaline earth and transition metals as well. They saw much higher levels of cluster ions with two or more metal atoms. Finally, the whole focus of Wang and Cole’s study was to deduce basic information about the ES process; ours is to investigate the potential analytical value of such ions. Another paper by Cole[22] shows that neutral organic molecules can be observed as Cl^- adduct ions in ES-MS, with the Cl^- coming from a chlorinated organic solvent. Negative ions of the general form $MX_n{}^-$ have also been formed directly from solids by fast atom bombardment, secondary ion MS,[23] or laser desorption.[24]

Several papers deal with ES-MS of inorganic species that are already anions in the sample. Agnes and Horlick[12] described initial observations of negative ions from solution anions. Barnett and Horlick[25] described the measurement of solution anions such as Cl^- and $ClO_4{}^-$, and $HCrO_4{}^-$ and $HSO_4{}^-$ from chromate[26] and sulfate[27] solutions. Colton and Traeger[2] briefly described the observation of the large cluster anion $[Mo_{18}S_2O_{62}]^{4-}$ Sheppard and Henion[28] used $NiHY^-$ to quantify EDTA, and Sharp et al.[15] reported observation of EDTA and citrate complex ions.

Most previous inorganic ES-MS experiments have been performed in organic solutions, particularly methanol or acetonitrile. The present work employs 50% methanol−water and is thus suitable for analysis of samples that are already aqueous solutions by simple dilution. Mixed aqueous−organic solvents can yield mixed-solvent clusters $M(H_2O)_x(MeOH)_y{}^{n+}$, which complicate the spectrum greatly and are highly prone to charge reduction. Such problems are minimized by using $MX_n{}^-$ negative ions with collision conditions strong enough to remove solvent molecules.

EXPERIMENTAL SECTION

Samples and Sample Preparation. Concentrated aqueous HNO_3 and HCl were obtained from Ultrex. Aliquots of these concentrated acids and acidic stock solutions of the elements of interest (Spex Certipure) were mixed and then diluted with 50% methanol/deionized water (18 MΩ, Barnstead Nanopure) to a final composition of 0.01, 0.1, or 1% acid in 50% water/methanol. The large excess of Cl^- or $NO_3{}^-$ anion in the acid served as the “reagent ion” to help drive production of the $MX_n{}^-$ anions desired. Methanol was used to enhance droplet production and desolvation.

ES Conditions. Pneumatically assisted electrospray, sometimes called “ion spray”,[29] was employed. Operating parameters are listed in Table 1. Droplets were produced by both the applied

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Table 1. Experimental Conditions

sample flow rate	17 μL min^{-1}
nebulizer gas	N_2, 40 psi
curtain gas	Ultrapure carrier grade nitrogen, 80 psi
ionization needle voltage (ISV)	-3.5 to -4.5 kV
ES current	4$-$5 μA
interface plate voltage (V_{IN})	-400 to -500 V
orifice plate voltage (V_{OR})	-130 to -110 V
rf-only quadrupole voltage (V_{rf})	20 V more positive than V_{OR}
mass analyzer quadrupole voltage (V_{RI})	-115 to -90 V
CEM detector voltage	$+2.6$ to $+4.0$ kV
operating pressure of quadrupole chamber	3.0×10^{-5} Torr

voltage and the nitrogen nebulizer gas. The voltage difference between the ES needle and the interface plate was 3100 V. This voltage difference was the highest value that could be employed consistently without severe corona discharge, which is a general problem in ES-MS with negative ions.

Ion Extraction Conditions. A single-quadrupole device (model API1, PE Sciex, Thornhill, ON, Canada) was used. The ions are extracted through a curtain gas interface.[1,8,17,29] Behind the sampling orifice the ions travel through a free jet expansion into rf-only quadrupole rods. The extent of solvation and fragmentation observed is selected mainly by adjusting the voltage difference between the orifice plate and the rf-only rods. In the present work, a potential difference of 20 V is used to remove solvent clusters from most elements and provide a reasonable yield of MX_n^- ions for analysis. This voltage difference is lower than the 65 V used in our first ES-MS paper on Cr speciation;[19] the higher voltage difference used there probably enhanced chemical reactions that produced species such as $CrOCl_2^-$.

RESULTS AND DISCUSSION

Background Spectra. The major ions from 1% HNO_3 or 1% HCl in 50% MeOH/H_2O are shown in Figure 1. For HNO_3 (Figure 1a), the main peaks are NO_3^- ($m/z = 62$), O_2^- and/or CH_3OH^- ($m/z = 32$), and cluster ions involving nitrate, all with overall charge of -1. The signal distribution for the various peaks is NO_3^- > $H(NO_3)_2^-$ > $H_2(NO_3)_3^-$. The situation is somewhat different for 1% HCl in 50% MeOH/H_2O (Figure 1b). As expected, Cl^- is the main peak, but the clusters $H_nCl_m^-$ are much less abundant than the corresponding species for nitric acid. For either nitric or hydrochloric acid, solvent clusters $X(H_2O)_n^-$ or $X(MeOH)_n^-$ are not prominent at the 20 eV collision energy chosen.

These spectra differ from those usually generated in other applications of ES-MS in that the analyte ions are not the most abundant ions. Instead, ions characteristic of the major anions in the acid solvent dominate the spectra. These mass spectra of NO_3^-, Cl^-, and their cluster ions are quite similar to those observed in drift tubes and chemical ionization reaction cells meant to simulate ion$-$molecule reactions in certain regions of the Earth's atmosphere.[30] This similarity is not surprising since the curtain gas is nitrogen and water vapor is added from the sample.

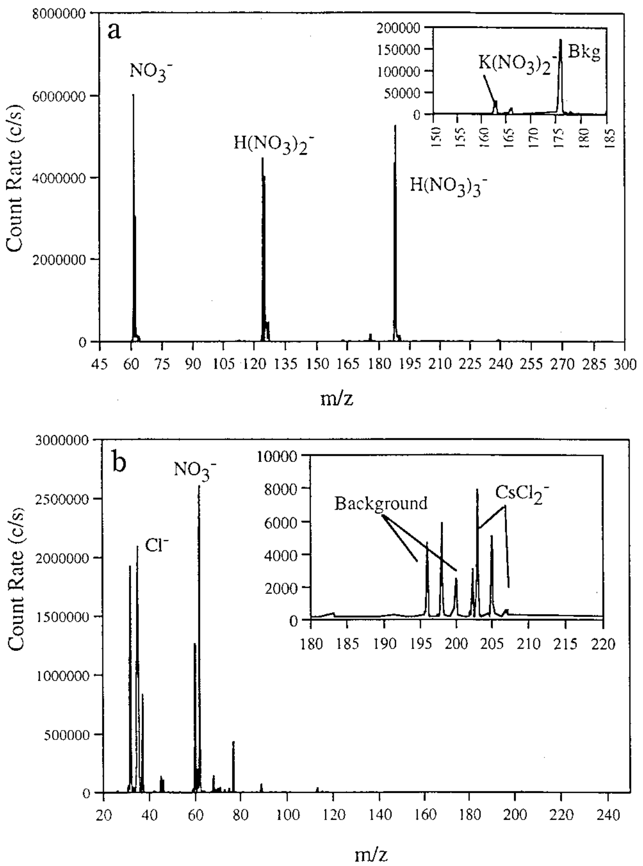

Figure 1. Mass spectra of (a) 20 ppm K in 1% HNO_3 and (b) 20 ppm Cs in 1% HCl.

Figure 1b also illustrates several problems. First, the peak at $m/z = 32$ indicates the source is on the verge of corona discharge, as does the high ES current (4$-$5 μA, Table 1). Second, nitrate and metal complex anions with nitrate are observed even when there is no nitrate in the sample. This nitrate memory can only be removed by replacing the sample capillary and cleaning the interface plate thoroughly. The nitrate ions then return permanently as soon as a nitrate solution is sprayed. This memory effect is much less severe for Cl^- solutions but is still significant.

Anions from previous samples also appear as weak peaks, particularly carboxylate ions $RCOO^-$ from previous measurements of carboxylic acid solutions with this device. Examples are malonate ($m/z = 103$) and maleate ($m/z = 115$). These anions also produce some clusters such as $RCOOH(NO_3)^-$. Unlike atomic ion sources, organic ions are not dissociated in ES-MS under "mild" collision conditions, which presents opportunities for measuring them as well as problems from overlap interferences.

All these ions are superimposed on a background that averages to ~500$-$1000 counts s^{-1}. This background is apparently a small peak at most m/z values. As noted by Sharp et al.,[15] the background is much lower than that observed in positive ion mode.

M^{n+}(aq) Cations Produce MX_{n+1}^- Counteranions. Spectra have been measured for a variety of cations in HNO_3, HCl, and mixtures of the two acids. Representative spectra are shown to illustrate the ions observed. Some of these figures are also used to illustrate other points later in the text.

Alkali metals are singly charged in solution and produce ions of the general form MX_2^- or MXY^- (e.g., $K(NO_3)_2^-$ and $CsCl_2^-$

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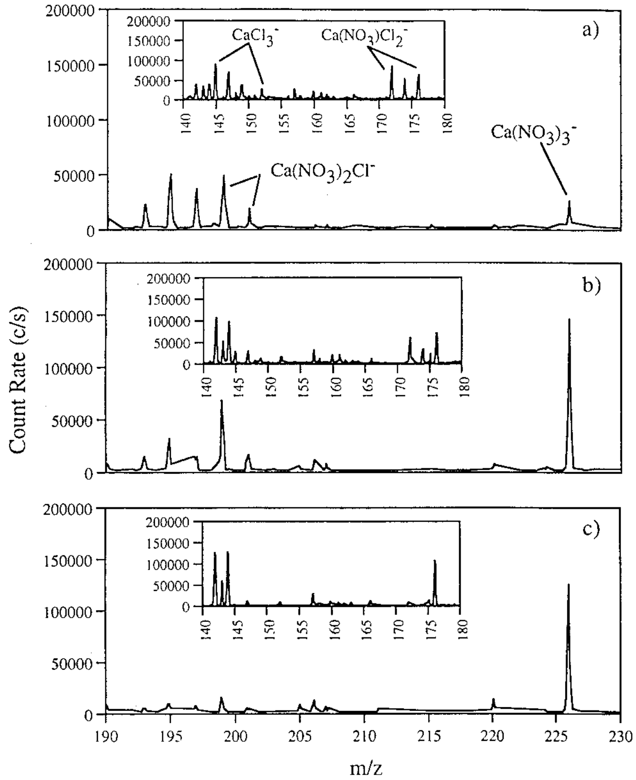

Figure 2. Mass spectra of 20 ppm Ca and 0.1% HCl in the presence of (a) 0.01, (b) 0.05, and (c) 0.1% HNO_3.

in Figure 1). Generally, the mixed species with different anions X^- and Y^- are simply referred to as MX_2^- for brevity in the subsequent discussion. The matrix anions X^- can be identified from the major peaks; e.g., the likely presence of Cl^- in $CsCl_2^-$ (Figure 1b) is indicated by the large background peaks at $m/z = 35$ and 37 from Cl^-. Once the counteranions X^- have been identified, the charge state of the M atom is deduced easily. In Figure 1, two X^- anions are needed to produce a counteranion with total charge -1, so the M atom has a charge of $+1$. The identities of M and X can also be deduced from the various isotope peaks of MX_2^-.

For alkali metals, $M(NO_3)_2^-$ ions tend to more abundant than MCl_2^-. The former is sometimes the major peak containing M^+ even when the solvent is actually HCl. The $M(NO_3)_2^-$ peaks basically bear the isotope signature of the metal, because of the low abundance of the minor isotopes of N and O. In mixed HNO_3 and HCl, the progression of signals for alkali metals is $M(NO_3)_2^- > M(NO_3)Cl^- > MCl_2^-$.

An interesting set of background ions is evident in Figure 1b at $m/z = 196$, 198, 200, and 202. The spacing between peaks and progression of intensities suggests a combination of Br and/or Cl isotopes with stoichiometry of either Cl_4 or Cl_2Br. This isotope pattern combined with the m/z values observed is consistent with the ion $FeCl_4^-$. The Fe atom does not greatly affect this isotope pattern, as Fe contributes primarily ^{56}Fe (91.7% natural abundance). Assignment of these ions was difficult at first because no Fe was added to the solution. The Fe^{3+} probably comes from dissolution of the stainless steel tube at the ES tip by the acids used.

On the basis of the above discussion, alkaline earth metals and other divalent metals M^{2+} would be expected to yield MX_3^- ions. Such species are illustrated for Ca^{2+} in Figure 2. Transition metals with only the 2+ oxidation state, such as Zn^{2+}, also yield only MX_3^- ions. Here the metal atom is clearly in the 2+ oxidation state and corresponds to the expected oxidation state in the solution.

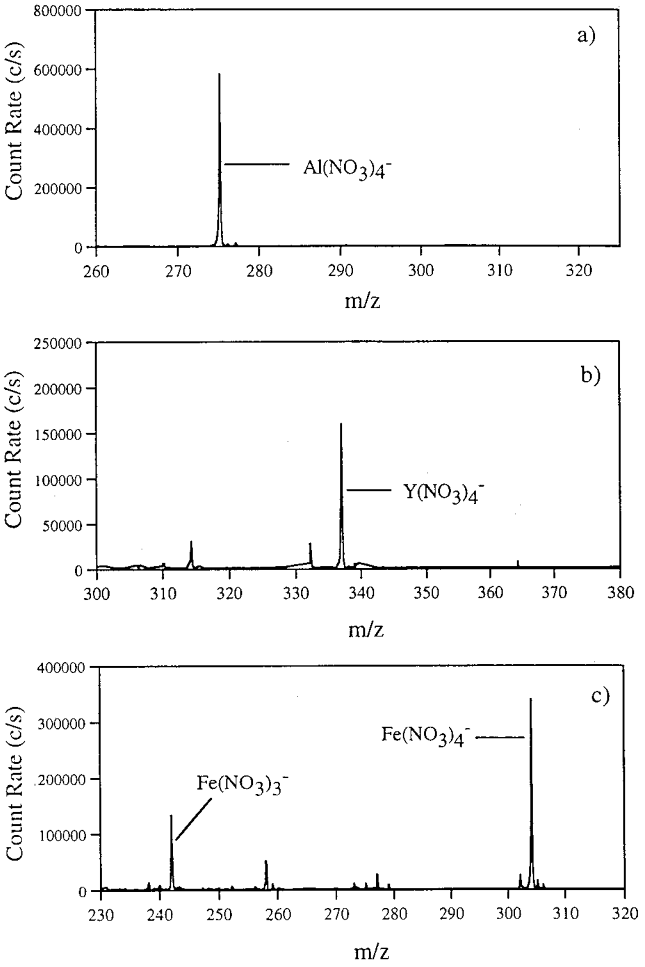

Figure 3. Mass spectra of (a) 20 ppm Al, (b) Y, and (c) Fe in 0.1% HNO_3.

Negative Ions $M^{III}X_4^-$ from M^{3+} Cations in Solution. The ion $FeCl_4^-$ (Figure 1b) was described above. Other M^{3+} ions such as Al^{3+} and Y^{3+} also produce the expected $M(NO_3)_4^-$ species (Figure 3a and b). In positive ion mode, these cations are highly prone to charge reduction reactions if the collision energy is increased enough to remove solvent, as noted previously.[1,8,17,20] They are readily observed as the complex anions MX_4^- with the 3+ charge on the cation stabilized by X^- anions rather than by delocalization over neutral solvent molecules.

Reduction of Cu^{2+} and Fe^{3+}. Some transition metals yield several negative ions with the M atom in different oxidation states. Iron has both 2+ and 3+ oxidation states in solution and is observed as a mixture of $Fe^{III}X_4^-$ and $Fe^{II}X_3(H_2O)_n^-$ species (Figure 3c). When the solution contains only Fe^{2+}, only $Fe^{II}X_3^-$ ions are seen. Copper and iron in these acidic solutions should be present primarily as Fe^{3+} and Cu^{2+}. For Cu, the corresponding ion CuX_3^- is indeed observed (Figure 4), along with similar signals from CuX_2^-.

We suggest the Cu^+ and Fe^{2+} are made primarily by electrolysis at the electrospray tip. The negative voltage applied to produce

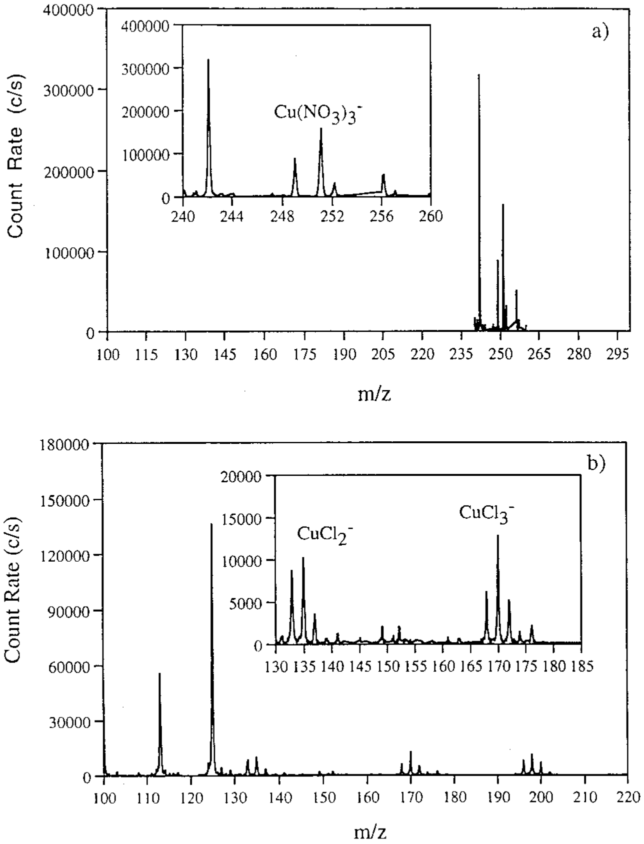

Figure 4. Mass spectra of 20 ppm Cu in 1% (a) HNO_3 and (b) HCl.

negative ions induces reduction reactions:

$$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq) \qquad E° = +0.161\ V \quad (vs\ SHE) \tag{2}$$

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq) \qquad E° = +0.771\ V \tag{3}$$

Some Cu^{2+} is thereby converted to Cu^+ in the solution, so both CuX_2^- and CuX_3^- are formed as the droplets evaporate. Likewise, some Fe^{3+} is converted to Fe^{2+} by electrolysis in the solution as well.

This reduction process only produces "new" ions for elements that have a stable lower oxidation state in solution. If other metal ions such as Zn^{2+} are reduced, Zn^0 metal is produced, which does not remain in the solution droplets and therefore does not appear in the spectrum. The only ions observed from Y and Al have the metal atom in the 3+ state (Figure 3). Yttrium and aluminum would also produce $M^{II}X_3^-$ ions if the reactions necessary occur in the gas phase, which corroborates our explanation that Fe^{2+} and Cu^+ species are seen mainly due to reduction of the Fe(III) and Cu(II) ions in the solution.

Zhou and Van Berkel[31,32] showed that the ES source can be considered as a controlled-current electrolytic cell. The maximum concentration of the electrolysis product can be estimated from Faraday's law:

$$i_{ES} = nAFv \tag{4}$$

where i_{ES} is the electrospray current (typically 4−5 μA), n is the number of electrons per mole of product in half-reaction, A is the solution concentration of product, F is the Faraday constant, and v is the solution flow rate (17 $\mu L\ min^{-1} = 2.8 \times 10^{-7}\ L\ s^{-1}$).

For the 20 ppm Cu^{2+} and Fe^{3+} solutions (0.31 and 0.36 mM, respectively), assuming reduction of the metal ion is the only reaction, the concentrations of Cu^+ or Fe^{2+} produced would be 0.14 and 0.18 mM. Thus, roughly half of the original Cu^{2+} or Fe^{3+} could be reduced to Cu^+ or Fe^{2+}. These levels of Cu^+ and Fe^{2+} are consistent with but somewhat higher than those observed from the relative sensitivities seen in the mass spectra for CuX_2^-/CuX_3^- (Figure 4) and FeX_2^-/FeX_3^- (Figure 3). Perhaps metal ions in different oxidation states do not yield MX_n^- anions with the same efficiency, or some of the current goes to reduction of another component of the solution, such as H^+ or NO_3^-.

The effect of reduction reactions such as (2) and (3) on the relative abundances of ions observed in different oxidation states is expected to depend on total concentration of the metal, for the following reasons. The original concentration of reactant does not appear in eq 4. Suppose i_{ES} and v in eq 4 remain constant; the concentration A of product should also be constant. If samples containing lower levels of reducible analyte (e.g., Cu^{2+} or Fe^{3+}) are electrolyzed, product will be formed at the same concentration A until all the reactant is consumed, after which a different reaction will take over to support the ES current.[31,32] Therefore, the ratio of (product concentration)/(reactant concentration) will increase as reactant concentration decreases. For example, if the sample contains 20 ppm Fe^{3+} originally and 10 ppm is converted to Fe^{2+}, a solution of 10 ppm Fe^{3+} would be completely converted to Fe^{2+}, and the original Fe^{3+} in the sample would not be observed at all.

Mass Spectra of Simple Mixtures. The major analyte ions from a mixture of 20 ppm Zn, Cu, and Cs in 1% HNO_3 and HCl (i.e., three metal ions and two anions) are shown in Figure 5. The signal distribution for Cs ions is $Cs(NO_3)_2^- > CsCl_2^- > CsCl(NO_3)^-$. All these Cs ions contain Cs in the 1+ state.

For the ions containing Zn, the signal progression is $ZnCl_3^- > ZnCl_2(NO_3)^- > ZnCl(NO_3)_2^-$. There is very little $Zn(NO_3)_3^-$ in this spectrum, which is odd since $M(NO_3)_3^-$ ions are abundant for many other metals. We offer the following explanation. Chloride anions readily complex with Zn^{2+}; $ZnCl_3^-$ ($\beta_3 = 3.2$) and $ZnCl_4^{2-}$ ($\beta_4 = 1.6$) are known in solution.[33] Charged ES droplets in which the Zn is already bound in such complexes would dry to $ZnCl_3^-$, thus preventing the formation of mixed ions $ZnCl_x(NO_3)_y^-$ during the desolvation and ion extraction processes.

Copper forms weaker chloro complexes than Zn,[33] so various counteranions are seen, in the signal progression $CuNO_3Cl^- \sim CuCl_3^- > CuCl_2NO_3^- > CuCl(NO_3)_2^- \sim Cu(NO_3)_3^-$. Again there is a substantial peak for Cu(I) as $CuNO_3Cl^-$ but little $CuCl_2^-$. For all these ions, the pattern of isotope peaks from the juxtaposition of two Cu, five Zn, and two Cl isotopes agrees with the calculated distribution if corrections for overlap and occasional background peaks are included.

The main point of Figure 5 is that mixtures produce a variety of negative ions containing one metal atom and different anions. The likely anions X^- can be identified from their free X^- peaks.

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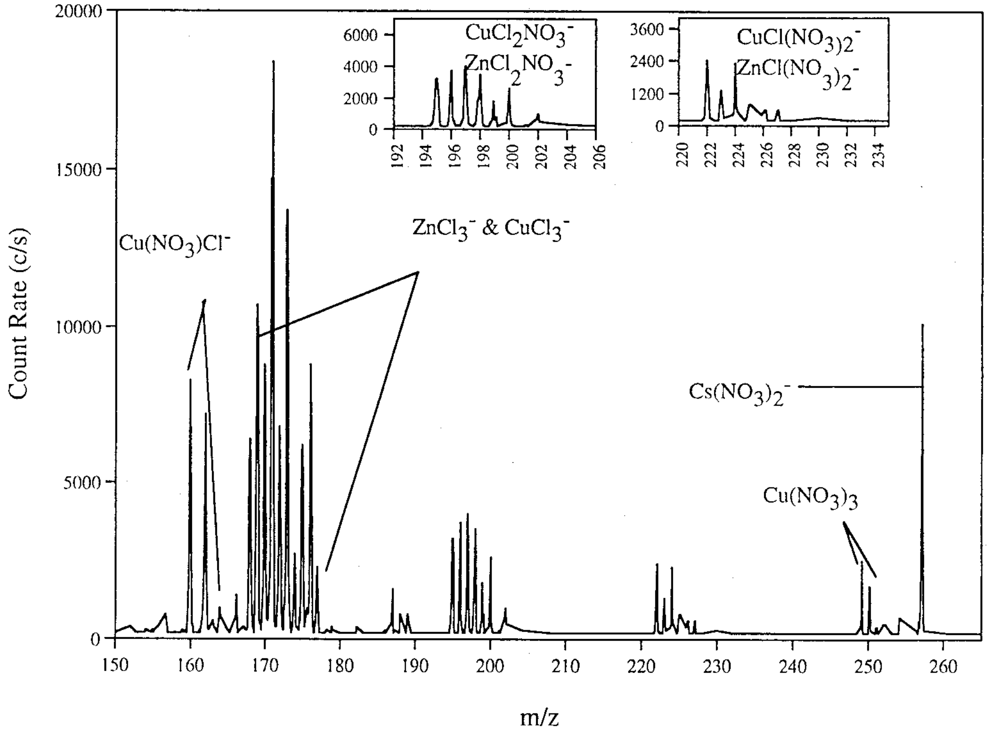

Figure 5. Mass spectrum showing peaks observed for a solution containing 20 ppm Cu, Zn, and Cs in 1% HCl and HNO_3.

When the anion also contains several major isotopes, such as Cl^-, the spectra of mixtures quickly become complicated.

A Negative Ion with Two Metal Atoms: $Mn_2Cl_5^-$. So far, the only negative ions containing metal cations have had the general formula MX_n^-, i.e., only one metal atom per molecule. Large-scale formation of cluster ions with two or more metal atoms, while possibly interesting from a chemical standpoint, would cause a serious analytical problem, since the spectra are complicated enough with just the MX_n^- peaks. Ions analogous to $H_2X_3^-$ (Figure 1), with different metal atoms instead of protons, would be cause for concern.

For the ppm solutions of metals with excess anions studied so far, only one such $M_2X_n^-$ cluster ion has been observed, as shown in Figure 6. A mixture of Mn^{2+} and Zn^{2+} in 0.01% HCl yields the expected MX_3^- ions and small but significant peaks from $Mn_2Cl_5^-$. Since Mn is monoisotopic, these latter peaks have the characteristic isotope pattern of a Cl_5 species. The Mn atoms in this $Mn_2Cl_5^-$ ion are still in the 2+ oxidation state, so the original oxidation state of the Mn atoms remains consistent with that expected in the sample solution. The memory problem from nitrate is also apparent in Figure 6; nitrate peaks are of comparable abundance to the chloride peaks even though chloride is the only anion in this solution.

Matrix Effects on Counterions and "Native" Anions. Matrix effects are a substantial problem in ES-MS of either inorganic or biological ions. In general, the signal for analyte ions decreases as the concentration of matrix ions of the same polarity increases.[1,9,34,35] Enke[36] recently described the basic reasons for such suppression effects. The analyte ions used in the present work, however, contain the matrix anions X^-, so the MX_n^- signal could actually increase as $[X^-]$ increases, just from Le Chatelier's principle. For example, the formation of MX_n^- anions

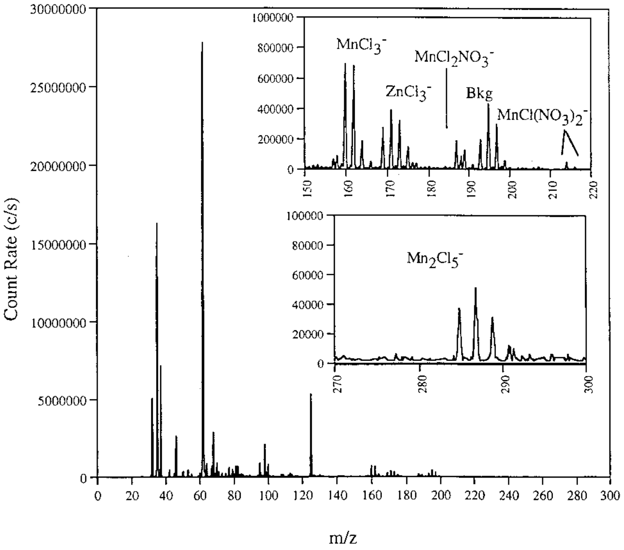

Figure 6. Mass spectrum of 10 ppm Mn and Zn in 0.01% HCl.

$$M^{2+} + 3X^- \rightarrow MX_3^- \qquad (5)$$

lies further to the right as $[X^-]$ increases if some free M^{2+} remains in excess X^-. Therefore, as $[X^-]$ increases, we expect a competition between suppression of all anion signals induced by the usual matrix interference and enhanced formation of MX_n^- ions.

This matrix effect is illustrated in Figure 2. For these three spectra, $[Cl^-]$ is 0.1% and $[NO_3^-]$ is increased from 0.01 (Figure 2a) to 0.1% (Figure 2b). The additional nitrate suppresses the

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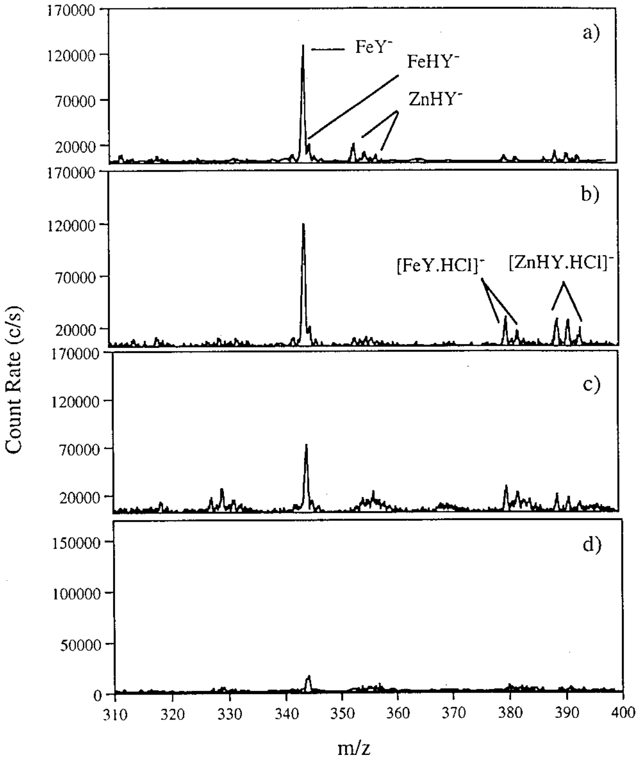

Figure 7. Mass spectra showing matrix effects caused by the effect of addition of (a) 0, (b) 0.1, (c) 0.5, and (d) 1% Cl^- to 0.3 mM Fe, Zn, and 0.6 mM EDTA solution at pH 6.5.

$CaCl_3^-$ peaks and those for Ca^{2+} with mixed chloro and nitrate counterions. The signal for $Ca(NO_3)_3^-$ increases at first and then decreases moderately as $[NO_3^-]$ increases.

Another such matrix effect is observed for KCl_2^-, the main ion from K^+, which is seen only when the HCl concentration is kept below 1%. At 1% HCl, the matrix suppression is so severe there is little in the spectrum other than NO_3^- memory and small memory peaks from carboxylate anions ($m/z = 103$ and 113). We could not find KCl_2^- from the 1% HCl solutions used in the early phases of this work because of this problem. There is apparently an optimum concentration of matrix anion for production of MX_n^- ions. This optimum $[X^-]$ may well differ for both different M^{n+} cations and X^- anions, depending on factors such as their ability to form complexes in the solution and on the competition for surface charge on the droplets.[36]

Species such as ReO_4^- and MoO_4^{2-} (seen as $HMoO_4^-$) that are already anions do not incorporate counterions during the ES process. Increasing the concentration of X^- merely suppresses the signal for these "native" anions. The suppression effect of the matrix anion on "native" anions is also illustrated by the spectra of Fe and Zn EDTA (H_4Y) complexes (Figure 7). The acidic media used above would protonate EDTA and prevent formation of complexes, so these experiments are done at pH 6.5 by neutralizing the hydrogen ion in HCl with NH_4OH. With no chloride, two major Fe peaks are seen, $Fe^{III}Y^-$ ($m/z = 344$ for ^{56}Fe) and $Fe^{II}HY^-$ ($m/z = 345$). These ions are seen in ~6:1 intensity ratio and probably represent the unassigned peaks reported by Sharp et al. in Figure 4c of ref 15. Note that the Fe^{3+} in FeY^- could have been reduced at the ES needle to Fe^{2+} with the EDTA complex still intact to yield $FeHY^-$ as the corresponding singly charged ion in the ES spectrum. The formation constant between Fe^{3+} and EDTA is $K_f = 1.3 \times 10^{25}$, much larger than that for Fe^{2+}–EDTA (2.1×10^{14}), yet the ES-MS peak for $Fe^{III}Y^-$ is only ~6 times more intense than that for $Fe^{II}HY^-$.

The Zn^{2+} in this solution appears as $Zn^{II}HY^-$, with a much lower yield than that for the Fe–EDTA complexes, for reasons that are unclear. These $M^{II}HY^-$ peaks are precisely the same as those seen for Ni^{2+} by Sheppard and Henion.[28] At 0.1% Cl^- (Figure 7b) the $ZnHY^-$ peaks are gone, while FeY^- and $FeHY^-$ remain substantial. Higher concentrations of Cl^- then suppress the Fe–EDTA peaks greatly.

Blank solutions of EDTA alone (added as the usual Na_2H_2Y salt) produce H_3Y^- and H_2Y^{2-}. The latter is the only doubly charged anion seen in this work so far. Thus, free complexing reagent can be observed as well. $Na(NO_3)_2^-$ is also prominent from the Na^+ added with the EDTA.

CONCLUSIONS

These initial studies indicate some potential for identifying metal cations and anions together by ES-MS in negative ion mode. A single set of collision voltages removes solvent clusters from a wide range of ions with little or no charge reduction. The major anions X^- can be discerned from the major peaks in the spectrum. This information is then combined with the m/z values and isotope patterns to identify both the metal cation and its oxidation state in the MX_n^- ions.

If the analytical objective is to assign the oxidation states of the metal ions in the original solution, then reduction of metal ions at the needle is a problem, especially since the ratio of reduction product to original analyte is expected to depend on concentration. It should be possible to prevent this reaction by adding an easily reduced substance to the sample that will occupy all the electrolysis current.[31,32,37,38] If the sample contains several components, the spectra are complicated. It would be helpful to have additional information concerning the identity of the metals, such as (a) high mass resolution and accurate mass measurements, or (b) an atomic mass spectrum provided by ICPMS or ES-MS in bare metal ion mode. The study of the structures of some of these ions by tandem MS or other means and determination of whether they are present as such in the solution or are made only during the ES and desolvation processes would be valuable. Reduction of the memory problem is also a concern. This general procedure can easily generate fairly intense beams (10^5–10^6 counts s^{-1} after mass analysis) of unique MX_n^- species that may be of fundamental interest in their own right. These and other experiments are underway in our laboratory.

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