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Preliminary Studies on Identification of Inorganic Species in
Complex Mixtures by Electrospray Mass Spectrometry in the
Counter Ion Mode

by

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MS Thesis submitted to Iowa State University

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Date Transmitted: November 8, 1999

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

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Preliminary Studies on Identification of Inorganic Species in Complex Mixtures by
Electrospray Mass Spectrometry
in the Counter Ion Mode

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Electrospray mass spectrometry (ES-MS) has shown to be a powerful technique in identifying inorganic complexes in solutions coupled with information obtained from elemental analysis using ICP-MS. One major hindrance in this identification process using direct infusion ES-MS is matrix problem. Solutions containing $>0.1\%$ HCl suppresses most of the mass peaks due to alkali and alkaline earth metal chloro complexes of the forms MCl_2^- and MCl_3^- , but does not seem to affect zinc or copper chloro complexes as much. Peaks due to metal-EDTA complexes (MY_x^-), such as FeY^- , are also affected by excess chloride ions present in the solution. This is not the case for solutions containing excess nitrate ions; peaks due to metal nitrate ions $[M(NO_3)_x]^-$ can still be observed in solutions containing 1% HNO_3 . In solutions containing both HCl and HNO_3 , the formation of metal nitrate ions dominates over the chloro complexes. In some cases, complexes containing mixture anions, of the form $[M(Cl)_x(NO_3)_y]^-$ can be observed.

CHAPTER 1.

GENERAL INTRODUCTION

Electrospray ionization has had and continues to have a profound effect on the field of mass spectrometry. New opportunities for both applications and fundamental research have been created due to several unique aspects of electrospray. One aspect is that electrospray has been successful for the production of gaseous ions from highly polar and non-volatile species. Its capability to produce a variety of ions that are otherwise difficult to obtain in the gas-phase makes this a popular technique.

Historical Perspective

Although the electrospray phenomenon was reported three hundred years ago by Bose¹, the formation of gas phase ions from a solution in a capillary held at high voltage was first described by Dole² in the late 1960s. Since then, the efforts of Fenn and Yamashita³ simultaneously with Aleksandrov⁴ led to the development of Electrospray-Mass Spectrometry (ES-MS).

Initially, ES-MS was primarily used for analysis of organic compounds and biomolecules, but is now showing great potential in the studies of metal ions and inorganic species. Colton⁵⁻⁸, one of the pioneers in this field, examined labile and non-labile inorganic and organometallic complexes. Recently, qualitative and quantitative studies of complexed and uncomplexed inorganic species are being examined by some researchers⁹⁻¹⁶ particularly Horlick, Larsen, and Corr. One of the first demonstrations of an electrochemical reaction between an analyte and solvent by ES-MS was shown by Hop et al.¹⁷. Kinetic and

thermodynamic studies¹⁸⁻²¹ of inorganic species and metal-ligand clusters have also been reported.

Principle of Electrospray-Mass Spectrometry

Basically, electrospray is an electrostatic spraying process where the solution flowing through a capillary is subjected to a high potential. This causes the formation of sprayed charged droplets (Fig.1) whose polarity will depend on the potential applied to the capillary tip. A positively biased capillary tip will produce positively charged droplets and vice versa for negatively charged tip. The typical flow rates of the solution through the capillary are usually 1-10 $\mu\text{L}/\text{min}$. A modification of the electrospray called ionspray was used by Henion et al.²²⁻²³. Ionspray is considered to be a concentric nebulizer combined with electrospray. One of the advantages of using ionspray is that a higher flow rate around 200 $\mu\text{L}/\text{min}$ can be used.

There are three main steps to the electrospray mechanism: production of charged droplets, shrinkage of the charged electrospray droplets, and formation of gas phase ions

Production of charged droplets:

The high voltage applied to the capillary tip, around 3-6 kV, imposes an electric field at the tip and also in the solution of the capillary²⁴. This imposed field causes the separation of the positive and negative ions to eliminate the imposed field. The polarity of the charged droplet will depend on the potential applied to the capillary tip. If a negative voltage is applied, the negative ions will migrate to the surface or meniscus of the solution (Fig.1). Due to the excess charge, the meniscus elongates downfield and forms a cone shaped structure called a "Taylor cone". The Taylor cone is unstable and forms a weak filament with a radius of a few

Figure 1. Illustration of the electrospray process.

micrometers. This filament finally breaks down into smaller droplets with excess charges on their surfaces. In the case of electrospray, droplets are formed mainly due to the voltage applied, but for an ionspray (a pneumatically assisted ES), a nebulizer gas flowing around the needle assist in droplet formation.

Shrinkage of charged droplets:

As the droplets progress downfield, solvent evaporation takes place leading to the increase of the charge to volume ratio of the droplets. This process takes place successively until it reaches the Rayleigh limit²⁵ where the charge on the droplets becomes

sufficient enough to overcome the surface tension²⁶. As a result, Rayleigh fission takes place causing the parent droplet to disintegrate into smaller daughter ions which carry typically 15% charge and 2% of the volume of the parent droplet. The daughter ions continue to undergo Rayleigh fission with continual solvent evaporation leading to smaller and smaller droplets.

Production of gas phase ions:

The mechanism by which ions transfer from the liquid phase to the gas phase is still not fully understood but there have been two theories proposed. They are single ion droplet theory (SIDT) and ion evaporation theory (IET). SIDT was first proposed by Dole² and more extensively explained by Rollgen²⁷. SIDT states that after several fission steps, extremely small droplets containing a single ion is formed which then transfers from a liquid to a gas phase. IET was first proposed by Iribarne and Thomson²⁸, stating that there is a competition between Rayleigh fission and evaporative emission of very small highly charged droplets. At a certain point the emission process prevails over Rayleigh fission. These highly charged droplets could also contain charged paired electrolytes.

Instrumentation

An electrospray interface for ES-MS is shown in Figure 2. The sample flows through a fused silica capillary, which is connected to a stainless steel capillary. This stainless steel capillary acts as the electrospray needle. The electrospray tip is located about 3 cm away from the interface or front plate and 1.2 cm to the right of the orifice. The orifice plate is around 0.75 cm away from the interface plate. The orifice diameter of the sampling plate is 0.1mm. The orifice plate is used to control the solvent declustering in the jet expansion. Nitrogen or argon gas is introduced into the region between the interface and orifice plate as

the curtain gas. The curtain gas has two purposes²⁹. First, it minimizes the entrance of solvent and the other unwanted neutral molecules into the mass spectrometer. The second reason is to provide a source of neutrals for collision induced dissociation (CID). Nitrogen is usually the chosen curtain gas due to its low tendency of forming clusters with electrosprayed ions. Electric discharges are also more effectively suppressed using this gas of higher dielectric strength such as nitrogen rather than argon.

Figure 2. Schematic of a Perkin-Elmer Sciex API 1 system.

Principles of Ion cluster Formation

For the extent of ion collisions taking place, the critical parameters are the voltages applied to the electrospray tip, interface plate, orifice plate, RF only rods, quadrupole, ion extractor lens and the curtain gas flow rate.

There are essentially two modes of operation:

- 1) A "bare metal ion" mode where ions are stripped or declustered down to their elemental or molecular form by increasing the potential difference between the orifice plate and only quadrupole rods. This extensive fragmentation condition is termed as a 'harsh condition'.
- 2) The "ion cluster mode" where a 'gentle condition' is applied to obtain ion-solvent clusters.

Mass spectra of ion clusters, partially declustered ions and bare metal ions can be obtained by varying the potential difference (ΔV) between interface plate and sampling plate. A larger potential difference offers a larger collision energy resulting in an increase in fragmentation of the metal clusters.

During the electrospray process, two different reactions could take place. They are:

- 1) Ligand loss reaction
- 2) Charge reduction reaction

*Example*³⁰:

From the above scheme, step 1 shows a ligand loss reaction. In this case, the overall charge of the metal ion cluster remains the same after losing a water ligand. Eventually, there will be a point where the solvent is stripped down to a minimum number such that the metal centered complex is no longer stable. At this point, charge reduction takes place which is shown in

step 2. Single ligand loss usually gives way to charge reduction at low ligand number.

Therefore, the $M^{2+}(H_2O)_n$ would eventually form MOH^+ and H_3O^+ at low n (H_2O molecules).

Usually, the charge reduced species are formed when the ionization energy (I.E.) of a metal ion, M^{n+} , is larger than the ionization energy of the ligand¹⁵. As a result, the type of ligand used during the electrospray process would also influence the charge reduction process.

Usually, the dominant electrospray process is charge reduction to singly charged ions. Doubly or triply charged ions, such as $M^{2+}(H_2O)_n$, can be obtained for M^+ of relatively low ionization energy. Example of this type of species are magnesium, calcium, and barium. Changing ligands may also change the stabilization of M^{2+} towards charge reduction. Replacement of H_2O by dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) increases the stabilization of $M^{2+}(L)_n$. In contrast, ammonia increases the tendency towards charge reduction. Therefore, elements that produce M^{2+} hydrates are not observed as the ammoniated species.

Thesis Objectives and Organization

The emphasis of this thesis is the use of ES-MS in the negative ion mode to identify inorganic species in complex mixtures. There is an environmental, toxicological and biological importance in being able to identify species in samples whether present in a large quantity or in trace levels. Even if the measurements are not quantitative, a rapid qualitative means for sample analysis would still be useful. Due to electrospray's characteristic of being a soft ionization technique, the chemical nature of the species can be preserved. This makes electrospray more a viable process when compared to other "harsher" techniques. Another advantage of electrospray is that this technique requires little time and volume for analysis.

The first part of the paper discusses the major complexes identified for metal ions present in solutions containing excess nitrate and chloride anion. The latter part of the paper is focused on the effect of change in pH and solution composition on the mass spectra of metal-EDTA complexes. Chapter 3 presents a general conclusion and ideas for future research.

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CHAPTER 2

PRELIMINARY STUDIES ON IDENTIFICATION OF INORGANIC SPECIES IN
COMPLEX MIXTURES BY ELECTROSPRAY MASS SPECTROMETRY
IN THE COUNTER ION MODE

A paper ready to be submitted to *Analytical Chemistry*

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Abstract

Electrospray mass spectrometry (ES-MS) has shown to be a powerful technique in identifying inorganic complexes in solutions coupled with information obtained from elemental analysis using ICP-MS. Solutions containing $>0.1\%$ HCl suppresses most of the mass peaks due to alkali and alkaline earth metal chloro complexes of the forms MCl_2^- and MCl_3^- , but does not seem to affect zinc or copper chloro complexes as much. Peaks due to metal-EDTA complexes (MY_x^-), such as FeY^- , are also affected by excess chloride ions present in the solution. This is not the case for solutions containing excess nitrate ions; peaks due to metal nitrate ions $[M(NO_3)_x]^-$ can still be observed in solutions containing 1% HNO_3 . In solutions containing both HCl and HNO_3 , the formation of metal nitrate ions dominates over the chloro complexes. In some cases, complexes containing different anions, of the form $[MCl_x(NO_3)_y]^-$, can be observed.

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Introduction

In environmental and biological sciences, the toxicology of the elements is dependent on their chemical speciation. For example, organotin compounds have a wide range of chemical and toxicological properties. Tributyltin used as a biotin is responsible for the degradation of edible aquatic resources whereas triphenyltin is used as a pesticide¹. Therefore, one must not only know the presence of tin but also its chemical form and/or oxidation state. Identifying the chemical forms of elements and their complexes in the presence of various anions, organic compounds, and complexing agents is important in cases such as clean-up of waste sites that contain numerous unknown materials. Once the contents of wastes are identified, disposal becomes less tedious. A quick qualitative analysis or survey to identify unknown samples would be valuable.

In such cases electrospray mass spectrometry (ES-MS) shows great promise for obtaining such information, as the solution information tends to be preserved rather than being destroyed. To do speciation work, some other techniques need to be coupled to a chromatographic method. At times speciation can be done using electrospray without resorting to chromatography²⁻⁴. Low collision energy is applied so that the solvent can be eliminated, but at the same time the metal-ligand clusters can be obtained for identification.

In this work, the viability of ES-MS as a technique for such identification is demonstrated. Also assessed is the extent to which this technique could be used for practical purposes. The experiments performed are preliminary in nature and focus mainly in identifying inorganic species. Although more work is being done, studies in the negative ion mode are much less popular than those in positive ion mode. Recently, Horlick and coworkers^{2, 5-7} have investigated inorganic anions ranging from complexes to mixed systems. These included

elemental, speciation and quantitation works such as determination of chromium (III) and (VI) and quantitation of halides. Counter ion mode ES-MS was also used by Gwizdala et al.⁴ to perform quantitation work for chromium (III) and (VI) solutions. One major problem in working in this mode is corona discharge which takes place due to electrons emerging from the sharp edges of the electrospray capillary needle held at a high negative voltage relative to the counter electrode⁸. One way to counteract this problem is to add O₂ or SF₆ gas, which act as electron scavengers to suppress electric discharge⁹. This can also be accomplished by using solvents containing components with higher electron affinities⁹. Some other methods are using a sharper capillary tip¹⁰ or a cylindrical capacitor configuration¹¹.

Even with this drawback, there are advantages in using negative ion mode over positive ion mode. First, there is less background noise in negative ion spectra than in the positive ion spectra. Second, cations, anions, and metal complexes can be identified in the same spectra. Converting between positive and negative modes become more time consuming because one has to switch to negative ion mode to observe anions or negatively charged complexing agents. When trying to strip away solvent in positive ion mode, there is a large possibility to get charge reduction. As a result, it is difficult to maintain initial charge state for M³⁺ or even M²⁺. This can be prevented in the negative mode by stabilizing the metal ions by making counter ions.

Experimental Section

Instrumentation

Mass spectrometry experiments were performed on a Perkin-Elmer Sciex API 1. Voltages were optimized on a daily basis to maximize the intensity of the species of interest. All spectral scans were collected by adding 10 consecutive scans together at a 10 ms dwell time

for each 0.1 amu. A syringe pump (74900 series, Cole-Parmer Instrument Co.) was used to transport solutions from a 1mL syringe (Hamilton Co.) through a 100 μ m i.d. fused silica capillary (Polymicro Technologies Inc.) to the ion source. The sample flow rate used was 17 μ L/min. Collision energy of 10- 20 eV is obtained from the voltage difference between the orifice plate and RF only rods (Fig.1). The optimized ES-MS conditions for the experiments are listed in Table 1. The collision energy applied determines the type of spectra obtained. Applying a high collisional energy, also known as a “harsh condition,” causes species to be stripped off solvent and undergo fragmentation. When a low collision energy is applied (“gentle condition”), species retains its solvent clusters. A collision energy of 10 – 20 eV is large enough to remove most of solvated ions but stops short of causing extensive fragmentation.

Table 1. Experimental operating conditions.

Sample flow rate	17 μ L/min
Nebulizer gas	Nitrogen, 40 psi
Curtain gas	Ultra pure carrier grade nitrogen, 80 psi. 60 ⁰ C
Ionization needle voltage (ISV)	-3.5 to - 4.5 kV
Interface plate voltage (V_{IN})	-400 to -500 V
Orifice plate voltage (V_{OR})	-130 to -110 V
RF only quadrupole voltage (V_{RF})	-120 to -100 V
Mass analyzer quadrupole voltage (V_{RI})	-115 to -90 V
CEM detector voltage	+2.6 to 4.0 kV
Operating pressure of quadrupole chamber	3.0x10 ⁻⁵ torr

Chemicals and reagents

Most metal solutions were prepared by diluting aliquots of 1000ppm aqueous ICP standard solutions (PlasmaChem Corp.) with 50% methanol/water solvents. Since most ICP standards contain 1% or 2% HNO_3 , nitrate free solutions were prepared by dissolving the ACS grade salts in distilled deionized water to form stock solutions. Aliquots of the stock solution were then diluted with a 50% methanol/water. The required percentage of Ultrex II ultrapure HCl (v/v) and/or Ultrex II ultra pure HNO_3 (v/v) was then added to the prepared metal solutions. EDTA stock solution was prepared from ACS grade disodium ethylenediamine tetraacetate salt (Fisher Scientific). The methanol/water solvent mixture was prepared using HPLC grade methanol (Fisher Scientific) and water deionized to a resistance of 18 $\text{M}\Omega$ with a Barnsted Nanopure-II system (Newton, MA).

A Cole-Parmer Digi-Sense (model 5985-80) pH meter was used for pH measurements. The probe was standardized by pH 4, 7 or 10 buffer solutions depending on the range studied. The pH of the metal-EDTA solutions was adjusted by adding NH_4OH (Malinckrodt) or Ultrex II ultra pure HNO_3 to the aqueous solvent. The concentration was then brought to the desired level by adding methanol/water solvent to these solutions. These pH values are only estimates as the actual pH of a solution in a mixed aqueous/organic solvent is difficult to determine.

Results and Discussion

Blank spectra

Solutions containing metal ions present in HNO_3 and HCl were examined in this work. Figure 2 shows a spectrum of 1% HNO_3 present in a solution of 50% methanol/ water. The

major peaks observed were at m/z 62, 125, and 188 which corresponds to NO_3^- , $\text{HNO}_3.\text{NO}_3^-$, and $(\text{HNO}_3)_2.\text{NO}_3^-$, respectively. Some other background peaks observed due to this blank solution are at m/z 176 and 178. In the case of solutions containing HCl (Fig.3), the major background peaks observed were due to the chloride ion (Cl^-) isotopes at m/z 35 and 37. Background peaks can also be observed at m/z values of 196, 198, and 200. Although the isotope pattern resembles that of an ion containing a bromide and a chloride or FeCl_4^- , it is not definitely known what species gives rise to these peaks. It is possible that the iron could be released from the stainless steel needle and then complexes with the chloride ion present in the solution. The peak due to nitrate ion at m/z 62 could still be observed which is due to memory problem.

Alkali metals

Alkali metals would be expected to yield negative ions of the general form MX_2^- . Experiments were carried out with the addition of 1% HNO_3 to 20 ppm of metal solutions. The elements examined were Li, Na, K, Rb, and Cs. Mass spectra of the solutions show an intense peak at m/z 62, which indicates the presence of nitrate ion (NO_3^-), the prominent peak in all cases. This is expected since NO_3^- is the major anion in the solution. Also seen are peaks due to $\text{H}(\text{NO}_3)_2^-$ (m/z 125) and $(\text{HNO}_3)_n.\text{NO}_3^-$. The most prominent metal species peak observed is that of the metal nitrate ion, $(\text{M}(\text{NO}_3)_2^-)$, as shown in figures 4a-e.

In cases where 1% HCl is added to the metal solutions, an interesting trend is observed. First of all, the peaks for chloride ion (Cl^-) can be easily identified at m/z 35 and 37. A peak

from NO_3^- is also observed which tends to be a major memory problem. In spite of changing and rinsing the capillary extensively with methanol, there is still a severe memory effect from NO_3^- . Metal nitrate peaks are seen even in the absence of nitric acid in the solution. It is believed that this NO_3^- memory effect comes from solid nitrates deposited on the interface plate and orifice cone of the instrument rather than the capillary.

The mass spectrum of a solution of Cs in 1% HCl shows the presence of CsCl_2^- (Fig.5) and the absence of $\text{Cs}(\text{NO}_3)_2^-$. The observed peak pattern of CsCl_2^- matches the theoretical isotope pattern of CsCl_2 . As for solutions containing the metals Li, K, Na, and Rb, no chloro complexes are detected. Instead, metal nitrate ions are found which is due to the nitrate memory problem.

Different results are obtained when the concentration of HCl is reduced to 0.1 or 0.01%. Mass spectra of these solutions now show the presence of peaks due to metal-chloro complexes (MCl_2^-) (Fig.6). In some cases, metal complexes of the form MCINO_3^- can also be detected. Nitrate already present in the instrument can cause the formation of this type of species. Apparently, excess chloride ion in the 1% HCl solution suppresses the metal chloride peaks but the peaks due to metal-nitrate species do not seem to be affected to such an extent. The excess nitrate ions in the 1% HNO_3 solutions do not cause such a severe matrix effect, either.

In the presence of both 1% HCl and HNO_3 , the mass spectrum of 20 ppm Cs solution shows CsCl_2^- , CsClINO_3^- , and $\text{Cs}(\text{NO}_3)_2^-$ (Fig.7). If the mass spectrum of Cs present in 1% HNO_3 (Fig.4e) is compared to that of Cs present in HNO_3 and HCl (fig.7), the intensities of $\text{Cs}(\text{NO}_3)_2^-$ in both cases are similar. The mass spectrum of the solution containing a mixture of the acids shows a decrease in the intensity of CsCl_2^- . This is because one of the Cl^- ions is

displaced by the NO_3^- to form $\text{CsCl}(\text{NO}_3)^-$. This type of mixed anion complex is not observed for the other alkali metals in solutions of 1% HCl and HNO_3 , but only metal nitrates are observed for those solutions.

In the presence of 0.1% HCl and 0.01% HNO_3 , the mass spectral peaks identified for the alkali metals were in the form MCl_2^- , $\text{MCl}(\text{NO}_3)^-$, and $\text{M}(\text{NO}_3)_2^-$. With the increase of HNO_3 concentration from 0.01% to 0.1%, the peaks due to metal-chloride species decrease until a point when the peaks are hardly observable (Fig.8).

From the results obtained, it is seen that $\text{M}(\text{NO}_3)_2^-$ form more readily than MCl_2^- peaks. Therefore, with increase of HNO_3 concentration, more nitrate ions are available for displacing the chloride ions to form $\text{M}(\text{NO}_3)_2^-$. Chloride ions are also known to be a poor nucleophile for cations ¹².

The reason why CsCl_2^- can be observed in 1% HCl whereas the other alkali – chloro complexes can not be observed is not understood. Cole et al.¹³ observed the abundance of positive cluster ions increasing with increasing size of the alkali cation. The cluster ions are less solvated which increases their abundance in the offspring droplets during the fission process. As Cs^+ is larger than the other alkali ions, CsCl_2^- would be more abundant so possibly even with Cl^- suppression, the intensity of CsCl_2^- is high enough to be observed.

Alkaline earth metals

Mass spectra of alkaline earth metals (Mg, Ca, Sr, Ba) in 1% HCl and HNO_3 show a similar trend as the alkali metals. The expected metal complexes to be observed are in the form MX_3^- . In the presence of HNO_3 , metal trinitrate complexes can be observed (Fig.9) whereas in the case of 0.1% HCl, metal-chloro complexes were detected. Spectra of

solutions containing 0.1% HCl and 0.01% HNO₃ show peaks in the forms MCl_3^- , $\text{MCl}_2\text{NO}_3^-$, $\text{M}(\text{NO}_3)_2\text{Cl}^-$ and $\text{M}(\text{NO}_3)_3^-$. With increase of HNO₃ concentration, intensity of the peaks due to MCl_3^- and $\text{MCl}_2\text{NO}_3^-$ decrease while that of $\text{M}(\text{NO}_3)_2\text{Cl}^-$ and $\text{M}(\text{NO}_3)_3^-$ increase (Fig.7) until a point where only $\text{M}(\text{NO}_3)_3^-$ peaks are observed.

Transition metals

Zinc

Zinc contains five isotopes at masses 64(48.6%), 66(27.6%), 67(4.1%), 68(18.8%), and 70(0.6%). Figure 11a shows the mass spectrum of a solution of 20ppm zinc present in 1% HNO₃. The peak pattern observed at m/z 250, 252, 253, 254, and 256 is indicative of $\text{Zn}(\text{NO}_3)_3^-$. This peak pattern correlates very well with the calculated peak pattern of $\text{Zn}(\text{NO}_3)_3^-$ which is shown in the inset of figure 11a.

Background overlap is encountered when examining Zn solution in 1% HCl. The peaks for ZnCl_3^- are obtained at m/z 171, 172, 173, 174, 175, 176, and 178 (Fig.11b). However, background peaks are observed at m/z 176 and 178. As a result, the intensity at m/z 176 and 178 are higher than that expected for just the ZnCl_3^- peaks. Therefore, there is a poor correlation between the theoretical (present in the inset of Fig.11b) and experimental isotope pattern for ZnCl_3^- . This background overlap has been a major hindrance in identification of species.

Similar to the cesium case, complexes containing a mixture of anions are seen for a 20ppm Zn solution in a mixture of 1% of both the acids. Peaks obtained at the mass range of 169-181 and 250-256 are identified as that of ZnCl_3^- and $\text{Zn}(\text{NO}_3)_3^-$, respectively. Peaks at m/z 196-208 and 222-232 are that of $\text{Zn}(\text{NO}_3)\text{Cl}_2^-$ and $\text{ZnCl}(\text{NO}_3)_2^-$, respectively.

As observed in figure 12, the peaks for the mixed anion zinc complex with two nitrates have a higher intensity than those with two chlorides. This again shows that nitrates are formed more favorably than chlorides.

Copper

Copper acts like zinc in the sense that the metal chloride peaks are not suppressed by 1% HCl. The major complex identified in the presence of 1% HNO₃ is Cu(NO₃)₃⁻ (Figure 13a), while in the presence of HCl, both CuCl₂⁻ and CuCl₃⁻ can be observed (Figure 13b). As can be observed from figure 13a, the ratio of peak intensity between m/z 249 and 251 is not what is expected for Cu(NO₃)₃⁻ (2:1). This is because there is also a peak formed by a cluster of nitrate ion at m/z 251 (HNO₃)₃.NO₃⁻ along with the peak for the copper nitrate complex.

Reduction of Cu(II) to Cu(I) is a common phenomenon in the electrospray process for the positive mode. However in the negative mode, if Cu(II) was to reduce to Cu(I) then similar observations would have been made for other transition metals. But higher oxidation state of other transition metal ions examined did not undergo such charge reduction. Therefore, maybe both Cu²⁺ and Cu⁺ are present in the solution. Electrochemical reduction could be another possible mechanism for formation of Cu(I) species¹⁴.

As for a solution containing 20 ppm Cu with 1% HCl and HNO₃, the mass spectrum shows a substantial decrease in intensity of the peaks due to copper chloro complexes while the intensity of copper nitrate peaks are unchanged (Fig.14). Again, this is because the nitrate ions displace the chloride ion to form metal nitrate ion. Therefore the intensity of the metal nitrate ion is expected to increase. The intensity of copper nitrate ion is unchanged maybe because the excess HCl and HNO₃ is starting to suppress the metal nitrate peaks.

From the results obtained, mass spectral peaks due to transition metal-chloro complexes are observed to be less susceptible to matrix effect due to the presence of 1% chloride or nitrate ions than the alkali or alkaline earth metal-chloro species. As will be discussed later on in the chapter, the extent to which peak intensities of complexes are suppressed by other electrolytes varies from species to species.

Mixture of cations

As was shown, identifying species present in solutions containing a single cation can be accomplished. But, real samples would consist of numerous cations, anions and complexing agents. The level of difficulty in analyzing these solutions would also be higher.

Shown in Figure 15 are mass spectra of solutions containing zinc, copper, and cesium. From the mass spectrum, the peaks obtained at m/z 249 and 251 are that of $\text{Cu}(\text{NO}_3)_3^-$. Peaks due to $\text{Cu}(\text{NO}_3)_2^-$ at m/z 188 and 190 can also be observed. The peaks at m/z 250, 252, 253, 254, and 256 are identified as $\text{Zn}(\text{NO}_3)_3^-$ whereas peak due to $\text{Cs}(\text{NO}_3)_2^-$ is observed at m/z 257.

Figure 16 shows the mass spectrum of a solution of the cations in 1% HCl. Some of the peaks due to ZnCl_3^- overlap with those from CuCl_3^- . The peaks for each species can be resolved by the method of deconvolution. The first peaks for CuCl_3^- and ZnCl_3^- occur at m/z 168 and 169, respectively. Therefore, the intensity of the other peaks for each species can be calculated based on the intensity of the first peak. Then the calculated intensity of the overlapping peak for each species can be added and finally compared to the observed peaks. Figure 17 shows the comparison between the calculated and experimental peak pattern. The calculated and experimental peaks closely match each other except for peaks at m/z 171 and

173. The intensity of the observed peaks are higher than the calculated values which could be due to higher background intensity or noise at those masses. Also shown in figure 16 are peaks observed due to $\text{Cs}(\text{NO}_3)_2^-$ and CsNO_3Cl^- which are formed due to NO_3^- present from earlier experiments.

Mass spectra of the cation solution containing both 1% HCl and HNO_3 is shown in figure 18. Similar to the chloro mass spectra, there are overlap of peaks between $\text{CuCl}_2\text{NO}_3^-$ and $\text{ZnCl}_2\text{NO}_3^-$ as well as $\text{CuCl}(\text{NO}_3)_2^-$ and $\text{ZnCl}(\text{NO}_3)_2^-$ which can be deconvoluted and resolved.

Identification of unknown mixture

One other approach in elucidating sample components is by the usage of ES-MS in addition with other techniques such as ICP-MS. ICP-MS would provide information regarding the metal ions from which an idea about the metal complex present in the solution can be obtained. From the ES-MS data, these metal complexes can then be identified.

An unknown solution, made by a group member, was analyzed by a micromass platform ICP-MS. The major ions identified were Fe^+ , V^+ , Y^+ , Al^+ , Mg^+ , Li^+ , and Lu^+ (Fig. 19). From the ES-MS data, NO_3^- was easily identified at m/z 62. The different metal complexes identified were $\text{Fe}(\text{NO}_3)_4^-$, $\text{Li}(\text{NO}_3)_3^-$, $\text{Mg}(\text{NO}_3)_3^-$, $\text{Al}(\text{NO}_3)_4^-$, and $\text{Y}(\text{NO}_3)_4^-$ (Fig. 20). Also observed were clusters of Fe(II) nitrate ion with various number of water ligands. As observed, the highly charged 3+ states of the Fe, Al, and Y are stabilized through electrospray collisions by counter ions.

This approach of identifying inorganic complexes can be very advantageous. The

ES-MS spectra of complex solutions can be very complicated and at some point impossible to interpret. Complexes with multiple isotopes will contain numerous peaks and it would be difficult to ascertain whether a peak is due to the complex or just the background, especially if there is only trace level of the metal ion present. ICP-MS results would aid in identifying the correct metal ions present in the solution even those present in ppb levels. The anions in the solution can easily be identified from the ES-MS spectrum. With the information about the metal ions, their probable oxidation states and anions present in the solution, assignment of the peaks can be attempted by theoretically calculating the mass and isotope pattern of complexes (if they have more than one isotope) that might give rise to such peaks.

Matrix effect

As observed, analyte intensity in ES-MS is greatly dependent on the matrix composition of the solution. The extent of suppression of analyte signals depends on the type and concentration of electrolytes present in the solution. A minimum sample conductivity is necessary for the spraying process, but the sensitivity decreases if the solution conductivity is too high¹⁵. This is because the charged droplet emission current (ES current) is dependent on the presence of ionized electrolytes in the solvent to be sprayed. The ES current (I) is found to be related to the conductivity by the equation given below.

$$I = H\sigma^n \quad \text{----- (i)}$$

where H is a constant that depends on the experimental parameters such as dielectric constant and surface tension of the solvent, flow rate, and electric field at the tip, and n is between 0.2-0.4. Conductivity (σ) of electrolytes is a function of concentration and identity of electrolytes and thus is also a function of ES current.

Also, if $I_{(A^+,ms)}$ is the fraction of total current (I) due to gas phase ions generated by escape of analyte ions from the droplet, then

$$I_{(A^+,ms)} = pf \frac{k_A[A^+]}{(k_A[A^+] + k_E[E^+])} \text{ ----- (ii)}$$

where,

$[A^+]$ and $[E^+]$ are the respective electrolyte concentration in the droplets.

f is the fraction of droplet charge that gets converted into gas phase ions.

p is the sampling efficiency of the system.

k_A and k_E are rate constants expressing the rate of transfer of ions from droplets to gas phase.

When $[A^+] \gg [E^+]$,

The total current, which is proportional to intensity, is mainly due to $[A^+]$.

But when $[E^+] \gg [A^+]$,

$$I_{(A^+,ms)} = pf \frac{k_A[A^+]}{k_E[E^+]} \text{ -----(iii)}$$

Thus, when the electrolyte concentration increases, the intensity of the analyte decreases.

This model proposed by Tang and Kebarle is in an agreement with that proposed by Enke¹⁶. Applying a certain voltage creates droplets with a surface excess charge which are then converted into gas phase ions. The difference in the concentration of the cations and anions in the electrosprayed solution is called the concentration of excess charge ($[Q]$) which has a typical value of 0.1-0.2 equiv./L (for conditions used in these experiments). The rate of production of excess charge is dependent on both the flow rate and circuit current.

For a system,

$$[Q] = [A^-]_s + [E^-]_s \text{ -----(iv)}$$

where,

$[A^-]_s$ = concentration of analyte A^- on the surface of droplet.

$[E^-]_s$ = concentration of electrolytes in the solutions.

Therefore, if $[Q]$ remains fairly constant, increase of chloride concentration increases the surface concentration of electrolyte ($[E^-]_s$) and decreases surface concentration of the analyte. If intensity of the analyte observed in a mass spectrum is proportional to $[A^-]_s$, then a decrease in surface concentration of analyte would also result in a decrease of its intensity.

Effect of HCl on metal – EDTA complexes

Apart from anions and cations, complexing agents may also be present in real samples. Being able to identify the complexing agent as well as its metal complex would be beneficial. Knowing the extent to which these complexing agents and its metal complexes are suppressed by matrix also becomes beneficial. The effect of addition of HCl to metal and EDTA solutions is discussed in this section. Mass spectra of Figures 21a-c show the changes in intensity of Fe-EDTA complex with the addition of HCl. EDTA (H_4Y) and Fe are both present in equal concentrations. The pH value of the solution is brought up to 6.5 by the addition of NH_4OH . At pH 6.5, the formation constants between Fe(III) and EDTA is fairly strong ($K = 1 \times 10^{20}$). Therefore, it is expected for most of the Fe ions to bind to EDTA leaving very little chance of Fe to form $FeCl_4^-$ or $FeCl_3^-$ in the presence of HCl. Experimental observations do show similar results as no peaks due to $FeCl_4^-$ or $FeCl_3^-$ are observed in the mass spectrum of Fe-EDTA solutions containing HCl. Also observed is the decrease of the intensity of FeY^- and $HFeY^-$ peaks with the increase of HCl concentration. When 1% HCl is added, FeY^- and $HFeY^-$ peaks are hardly noticeable.

Similar observations are made when solutions containing Zn, Fe, and EDTA are analyzed. The mass spectrum in Figure 22 shows a higher intensity for Fe-EDTA complex than Zn-EDTA species because Fe-EDTA species has a higher formation constant than Zn-EDTA. Also found was that the intensity of the FeY^- peak decreases at a faster rate with addition of HCl than that observed for the solution with no Zn present (Fig. 23). This is most probably because Zn increases the total concentration of electrolytes in the solution resulting in a more complex solution matrix.

The mass spectrum of a solution containing Fe, EDTA and 1% HCl at pH 1.00 is shown in Figure 24. At pH 1.00, most of the EDTA is present in the molecular form, H_4Y and a small fraction dissociated to H_3Y^- and so at m/z 291 and 145 peaks due to H_3Y^- and H_2Y^{2-} are observed. With less Y^{4-} , available to find Fe ions, this increases the chance of forming FeCl_4^- which is indicated by the peaks observed at a m/z range of 194-200. There is still formation of FeY^- shown by the peaks obtained at m/z 345.

Also obvious from the above results is that if the complex is already formed in the solution, then that complex will be seen in the mass spectrum. Since Fe^{+3} forms a very stable complex with Y^{4-} in solution, it will be observed in the spectrum even at pH 1.00. Similar result is obtained for rhenium solutions. Mass spectra of rhenium solutions in either 1% HCl or HNO_3 show major peaks at m/z 249 and 251 due to the perrhenate species, ReO_4^- (Fig. 25). This supports the solution chemistry of rhenium (VII) where rhenium forms a much more stable oxocomplex (ReO_4^-) rather than nitrates or chlorides¹⁷. The ReO_4^- ion does not form counterion with NO_3^- or Cl^- , in fact, other anions suppress the sensitivity for ReO_4^- .

Conclusions

The usage of ES-MS for identification of inorganic ions in solutions is demonstrated. Preliminary studies show that ES-MS has the potential to be particularly suitable for investigating simple solutions. If the ions can be observed, they can be identified even if quantification is difficult. Performing experiments in the counterion or negative ion mode does provide valuable information regarding the anions and metal species from the same spectrum. Problems such as the complexity of spectra and matrix effect are encountered when analyzing complex mixtures. With many unknown components, it becomes very difficult to differentiate the unknown component peaks from the background peaks especially when the unknown is present at trace levels. Peaks due to one species can also overlap peaks of another species when they have similar molecular weights and multiple isotopes. One approach that could be taken to resolve the peaks is to utilize an atomic MS technique, such as ICP-MS, to determine the metal ion present in the solution. With the identity of anions known from the ES-MS data, assumptions can be made and the peaks identified. The method of deconvolution can then be employed to validate the peaks.

From the results obtained, it could also be concluded that metal nitrate complexes formed are more stable during the electrospray process than the chloro complexes. Nitrate ion was also found to cause a severe memory problem. Although taking the instrument apart and cleaning the orifice cone and the interface eliminates most of the nitrate ion, it becomes very time consuming.

A complex sample mixture also causes severe suppression of the peaks of the analytes of interest. Concentration of $>0.1\%$ HCl suppresses most metal-chloro peaks of group I and II.

Zinc and copper chloro mass spectra peaks seem to be more tolerant of excess chloride ions in the solution than alkali or alkaline earth metals. Peaks due to metal nitrate ions can also be observed in the presence of 1% HCl and HNO₃.

Acknowledgments

This work was supported by funds from Ames Laboratory operated for the U.S. Department of Energy by Iowa State University under Contract Number W-7405-Eng-82. We thank Narong Prapairaksit and Zhiyang Du for preparing and analyzing the unknown sample A using the micromass platform ICP-MS.

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Figure 1. Schematic showing the collision pathway. a) capillary tube, b) ionization needle, c) gate valve, d) interface plate (IN), e) orifice plate (OR), f) RF only quadrupole rods (RO), g) quadrupole mass analyzer (R1) .

Figure 2. Mass spectrum of a solution of 1% HNO_3 and 50/50 methanol/water.

Figure 3. Mass spectrum of a solution containing 1% HCl and 50/50 methanol/water.

Figure 4. Mass spectra of 20 ppm a) Li, b) Na, and c) K in 1% HNO_3 .

Figure 4. Mass spectra of 20 ppm d) Rb and e) Cs in 1% HNO_3 .

Figure 5. Mass spectrum of 20 ppm Cs in 1% HCl.

Figure 6. Mass spectra showing the effect of addition of a) 0.01%, b) 0.1%, and c) 1% HCl to 20 ppm K.

Figure 7. Mass spectrum of 20 ppm Cs in 1% HCl and HNO₃.

Figure 8. Mass spectrum showing the addition of a) 0.01%, b) 0.5%, and c) 0.1% HNO₃ to a solution containing 0.1% HCl and 20 ppm K.

Figure 9. Mass spectrum of 20ppm Ca present in a solution containing a) 1% HNO_3 , and b) 0.1% HCl .

Figure 10. Mass spectrum of a solution of 20 ppm Ca and 0.1% HCl in the presence of a) 0.01%, b) 0.05%, and c) 0.1% HNO_3 .

Figure 11. Mass spectrum of 20 ppm Zn in a) 1% HNO_3 and b) 1% HCl .

Figure 12. Mass spectrum showing major peaks from a solution containing 20 ppm Zn, 1% HCl and HNO₃.

Figure 13. Mass spectrum of 20 ppm Cu in 1% a) HNO_3 and b) HCl .

Figure 14. Mass spectrum of 20 ppm Cu in 1% HCl and HNO₃.

Figure 15. Mass spectrum of a mixture of 20 ppm Zn, Cs, and Cu in 1% HNO_3 . Inset shows peaks due to $\text{Cu}(\text{NO}_3)_3^-$ and $\text{Cs}(\text{NO}_3)_2^-$.

Figure 16. Mass spectrum of a mixture of 20ppm Cs, Zn, and Cu in 1% HCl. Insets show peaks due to CuCl_3^- , ZnCl_3^- and CsCl_2^- .

Figure 17. Comparison of the intensity of mass peaks obtained theoretically and experimentally at mass range 168 – 181.

Figure 18. Mass spectrum showing peaks observed for a solution containing 20 ppm Cu, Zn, and Cs in 1% HCl and HNO_3

Figure 19. ICP-MS spectrum of 20 fold dilution of unknown solution A.

Figure 20. Mass spectrum of unknown sample A diluted by 50% methanol. Figure 20 a and b shows the different mass ranges.

Figure 21. Mass spectrum showing the effect of addition of a) 0%, b) 0.1%, c) 0.5% and d) 1% Cl^- to 0.3 mM Fe and EDTA solution at $\text{pH } 6.5$.

Figure 22. Mass spectrum showing the effect of addition of a) 0%, b) 0.1%, c) 0.5% and d) 1% Cl^- to 0.3mM Fe, Zn and 0.6mM EDTA solution at pH 6.5.

Figure 23. Comparison of the decrease of peak intensity of FeY^- with the addition of Cl^- between a solution containing a) 0.3mM Fe and EDTA vs. b) 0.3mM Fe, Zn and 0.6mM EDTA.

Figure 24. Mass spectrum of 20ppm 0.3mM Fe, EDTA and 1% chloride at pH 1.00.

Figure 25. Mass spectrum of 20 ppm Re in 1% HNO₃.

CHAPTER 3

GENERAL CONCLUSIONS

Suppression of mass spectral peaks due to matrix problem is a major hurdle to overcome during identification work. So far, preliminary studies have been done in investigating solutions containing various percentages of nitric and hydrochloric acid. Since other anions would also be present in real samples, also needed to be examined is how the extent of suppression of metal complexes by Cl^- compares with suppression by other anions such as PO_4^{3-} or SO_4^{2-} . If suppression of other anions is as severe as that of the chloride ion, then it would be virtually impossible to analyze unknown samples containing large amount of such anions by direct infusion electrospray mass spectrometry. It seems like a separation step is needed to separate these matrix anions from the metal complexes prior to putting the solution through the electrospray. However, separation of inorganic complexes can be difficult and has not been studied thoroughly as LC separation of bioorganic compounds.

Both zinc and copper chloro complexes have been observed to be more tolerant to higher amount of chloride ion present in a solution compared to the group I and II metal chloro complexes. Other transition metals including the lanthanide complexes need to be examined more intensively to see how they fare against other transition metal complexes.

So far, only preliminary work has been done in identifying inorganic species in solutions using both ICP-MS and ES-MS. The solution contained a number of metals but only one major anion, NO_3^- . Therefore, complex solutions containing a number of anions and metals can be examined to see if identification is still feasible. This identification work can be continued on into investigating real samples.

ACKNOWLEDGMENTS

I would like to start by thanking my major professor, Dr. R. S. Houk. Dr. Houk is an excellent instructor and I am privileged to have been able to take classes from him. I am also proud for being able to work for the “inventor” of ICP-MS; although I hardly worked with an ICP-MS myself.

I would like to thank my undergraduate professors especially those in the chemistry and mathematics department. Special thanks to Dr. Huitink for her continual support, and giving me a chance to get a taste of research which led me to come to graduate school.

Special thanks to my high school chemistry teacher, Sagir Siddiqui, who was a superb teacher and the reason I got into chemistry. He will be greatly missed.

I have enjoyed working with the Houk group members, both past and present. Everyone helped each other out when needed just like a “Great Big Family”. I want to especially thank Steve Johnson and Al Gwizdala for sharing a lab and teaching me all about Mattilda – our baby. Thanks to Andrew Pris and Katie Fowler for helping me with my research work. Thanks to Dave Aeschlimann, Maan Amad, Zhiyang Du, Jay Leach, Mike Minnich, Narong Prapairaksit, and Jin Wang for their valuable discussions.

I want to thank all my friends including Jen, Laurie, and Chris, for all their help and driving me frequently to and from the Airport. Special thanks to Maria for helping me cope with living in Ames. Thanks to Vanda for spending so much time doing the computational work for me.

I want to thank my family for their continual support especially during my tough times. Thanks to my mom for her inspirational talks. Thanks sis for bearing with all the frequent

phone calls I made way past your bedtime. Thanks to my brothers for making me think logically when I started going astray.

Lastly, I want to thank my dad without whose hard work I would not have come this far. This one is for you dad.

This work was supported by funds from Ames Laboratory operated for the U.S. Department of Energy by Iowa State University under Contract Number W-7405-Eng-82. The U. S. government has assigned the document number IS-T 1886 to this report.