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## Characterization of Organo-Tin and Organo-Mercury Compounds with Electrospray Mass Spectrometry

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CHARACTERIZATION OF ORGANO-TIN AND ORGANO-MERCURY  
COMPOUNDS WITH ELECTROSPRAY MASS SPECTROMETRY

by

Kan Zhu

A Thesis  
Submitted to the  
Faculty of The Graduate College  
in partial fulfillment of the  
requirements for the  
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Department of Chemistry

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Kan Zhu

# CHARACTERIZATION OF ORGANO-TIN AND ORGANO-MERCURY COMPOUNDS WITH ELECTROSPRAY MASS SPECTROMETRY

Kan Zhu, M.A.

Western Michigan University, 2001

Metal-containing compounds are often found as pollutants in the environment. Obtaining speciation information about these compounds is important to understanding toxicity and bioaccumulation. Electrospray Mass Spectrometry (ES-MS) is a technique that has the potential to provide rapid and direct speciation information of solution phase metal compounds. The ionization behavior of chemical species is related to their electron affinities. The higher the electron affinity, the easier it will be reduced during the ionization process. Additionally, solvent with different polarity and surface tension will also affect the ionization and reduction products. Organo-tin compounds with more alkyl groups will be ionized more efficiently, but will be reduced more easily. The type of alkyl groups does not have significant effect. All mono-organo-tin compounds showed same spectrum and so it is with tri-organo-tin compounds. The spectra for organo-mercury compounds were different than for tin compounds in that they were characteristic of the alkylated metal ion native to the analytical solution. The spectral pattern observed represent the mass of mercury isotope plus the mass of the organo group. Other than solvent, anion may also have an effect on ionization.

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## INTRODUCTION

### Introduction to Organo-tin Compounds

Since the first preparation and investigation of ethylzinc iodide and diethylzinc led by Frankland in 1853, organometallic compounds have been widely studied and contributed significantly both to chemical theory and practice.

Organometallic compounds are defined as those compounds having a bond between a metal atom and a carbon atom. Most organometallic compounds resemble organic rather than inorganic compounds in their physical properties. Many exist at ordinary temperatures as low melting crystals, liquids or gases. Commonly they are soluble in weakly polar organic solvents. Organo-tin and organo-mercury compounds have tin-carbon and mercury-carbon bond respectively. They are highly toxic pollutants with wide industrial applications.

Organo-tin compounds have two unique characteristics. The first is the strong affinity of the tin atom to a donor ligand atom such as sulfur, oxygen and nitrogen. So tin forms a variety of organometallic derivatives that may be divided into three main types: (1) The tetraalkyls and -aryls; (2) compounds of the type  $R_{4-x}SnX_x$  where  $X$ =halide,  $NR_2$ , H, OH, OR, etc.; and (3) tin(II) compounds. The second unique characteristic is their physiological affects. Trialkyltin compounds can inhibit oxidative phosphorylation and deactivate some phosphatases, so they are widely used as fungicides, pesticides, marine antifoulants and rodents repellants. Dialkyltin

compounds are likely to combine with dithiol groupings in enzymes necessary for the production of mitochondrial adenosine triphosphate. However they are considerably less toxic, which is particularly important since they are used to stabilize poly(vinyl chloride). The annual world consumption of organo-tin compounds was 55,000 tons in 1988, among which  $R_3SnX$  was about 10,000 tons and the other  $R_2SnX_2$  and  $RSnX_3$  were about 45,000 tons. Of all consumption of organo-tin compounds, stabilizers for PVC are about 60% and next one, biocidal agent, is about 30% [1-10].

The toxicity of organo-tin compounds to mammalian animals varies considerably with the number of organic groups bonded to tin. Compounds having three tin-carbon bonds show the highest toxicity. Toxicity is also closely related to the nature of the organic groups attached to tin. Triethyltin compounds are the most toxic and trioctyltin is basically non-toxic when given orally by mouth to rats.  $R_3SnX$  compounds are easily decomposed to nontoxic inorganic tin compounds through photochemical reactions, but organo-tin compounds used as antifouling paints for ships are able to reach a depth without light and the decomposition of these compounds becomes very slow. Food chain accumulation and bioconcentration of organo-tin compounds have been demonstrated in many non-target organisms, such as fish. This makes organo-tin compounds particularly toxic to fish, so they are regulated in Europe, United States and Japan [1, 7].

### Introduction to Organo-mercury Compounds

Mercury containing compounds are also widely used. Metallic mercury is used to produce chlorine gas and caustic soda and is also used in thermometers,

dental fillings, and batteries. Phenylmercuric acetate has been used as a pesticide, herbicide, fungicide, disinfectant and a preservative in cosmetics. Trace levels of mercury containing compounds are found in the ocean, the atmosphere, even in Antarctica and the Arctic [3, 11]. Mercury is a highly toxic heavy metal because of its affinity to form tight coordinate bonds with sulphhydryl groups diffusely disrupting enzyme systems in multiple organs such as brain, kidney and lung. Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and a developing fetus. Effects on brain functioning may result in irritability, shyness, tremors, changes in vision or hearing, and memory problems. Mercury's harmful effects may be passed from the mother to the developing fetus [12].

The toxicity of mercury is closely related to its chemical form.

Methylmercury and metal vapors are more harmful than other forms, because more of the mercury in these forms reaches the brain. Hg(I) salts are relatively non toxic compared to Hg(II) salts because of their lower solubility in body fluids, but the activity of certain bacteria, molds and enzymes in the soil or sediment can produce methylated mercury from elemental or inorganic mercury. The alkylated mercury compounds are potentially more toxic than inorganic mercury forms. Monomethyl and dimethyl mercury are particularly neurotoxic. The lipophilic nature of these compounds allow them to be concentrated in higher trophic levels and the effects of this biomagnification is a serious problem. For example, one microgram methylmercury will cause severe adverse effects (weight reduction and poor spawning) on nonmarine fish in 30 days. The secondary effect results from

methylmercury induced perturbations in protein and carbohydrate metabolism and disruptions in redox energy related processes.

The symptoms of mercury poisoning, which, like lead poisoning are hard to diagnose in its early stages, include loss of muscle control and blurred vision, leading ultimately to paralysis and kidney failure. Because the body has a neutral mechanism for eliminating mercury, mercury is not a great threat as a low-level cumulative poison. A very serious incidence of mercury poisoning occurred in Japan among fishermen and their families who three times a day ate fish from Minamata Bay, which was receiving a mercury-laden effluent from a plastics factory. Other mercury poisonings have occurred when people or their farm animals ate seed grain treated with mercury-containing fungicides [13].

#### Current Analytical Methods on Organo-tin and Organo-mercury Compounds

In order to understand the whole picture of the toxicity and environmental biogeochemistry and to assess the health hazards and bioavailability of tin and mercury containing compounds, it is important to know the amounts and kinds of these species, forms or phases present in a material, i.e. the oxidation states of central ion and the binding ligands bound to tin or mercury. The process is defined as speciation.

Many methods have been developed to identify organo-tin and organo-mercury compounds. GC/MS is one of the more frequently used methods, but it requires treatment of the sample with sodium borohydride or with a Grignard reagent to yield a volatile derivative. This is a tedious and time-consuming process. Most

other methods are based on a separation such as liquid chromatography, gas chromatography, electrophoresis or super critical fluid chromatography, followed by tin or mercury selective detectors such as atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or ICP-mass spectrometry [1-2, 5, 14-17]. All of these methods provide good sensitivity but specific binding ligands are usually identified and quantified by measuring retention times and peak areas compared with those of available standards. In real samples, the presence of complicated sample matrices may shift the retention times of the proper chromatographic peaks. Sometimes, there are no standards available. Additionally, there is the possibility of chemical conversion occurring during the separation process that can give erroneous results. According to previous research in our group,  $\text{Hg}^+$  was reduced to  $\text{Hg}^0$  when analyzed using high performance liquid chromatography. This interference can lead to inaccuracies in quantification and give erroneous results for speciation.

It would be advantageous to develop new speciation techniques for determination of organo-tin and organo-mercury compounds. Electrospray is one of the possible ideal techniques because it is able to directly transfer a wide range of ions from solution phase to gas phase and provide a complete picture of the cationic and anionic composition in a solution. Then the separation step can be eliminated. The potential advantages include: (a) simultaneous detection of all compounds in a sample, (b) analysis time for a sample is decreased compared to HPLC analysis, (c) no mobile phase or chromatographic column used, (d) chemical conversion of the analyte of interest is unlikely since ions formed in the gas phase will not experience

the complex chemical environment of the mobile phase and column stationary phase used for HPLC analysis. So a sample can be analyzed in less than 1 minute with electrospray mass spectrometry compared to an analysis time that can exceed 10 minutes, per sample. Instrumentation can also be simplified. The cost and time of analysis are both decreased.

Horlick et al. has successfully obtained the spectrum of trimethyltin with ES-MS[3]. Siu, et al. also determined tributyltin in a reference standard PACS-1 with Ion spray MS/MS[17]. But a systematic study of organo-tin and organo-mercury compounds with ES-MS has not been published yet. Our work has focused on the effects of solvent, alkyl group, anion and charge in the electrospray ionization process. Understanding the ionization process will help develop direct analysis of organo-tin and organo-mercury compounds with ES-MS, further understand the ionization theory of electrospray and establish basis for both qualitative and quantitative analysis for these compounds.



## EXPERIMENT

### The Electrospray Mass Spectrometer

The diagram of the electrospray source and the interface used to transfer ions into the mass spectrometer (Sciex Elan) is shown in Figure 1. The Kratos ES ionization source consists of a syringe pump (Sage Instruments, Model 237-1), a glass sample syringe (100  $\mu$ L), and an ES tip. The ES tip is a silica capillary (140  $\mu$ m outer diameter, 74  $\mu$ m inner diameter) extended out the stainless steel needle for about 1 mm. The other end of the 40 cm silica capillary is connected to the glass sample syringe with standard fittings. The syringe pump was set at 10  $\mu$ L/min to deliver sample solution. The distance of the silica tubing to the endplate is about 5 mm.

The stainless steel needle is biased at a positive 3.5 to 4.2 kV. Higher than 4.2 kV will cause a discharge between the needle and the endplate. The bias voltage was supplied by a Kratos Analytical Instruments ES power supply. The needle is surrounded by a cylinder, to which a positive potential as high as 2-3 kV is applied. Down the path are the endplate and skimmer. The endplate replaces the normal sampling cone used in ICP-MS measurements and serves as a sampling component. The diameter of the cone is 1 mm and to the whole endplate about 400 V was applied.

The imposed electric field of the needle will penetrate the liquid at the capillary tip. In the positive ion mode, positive ions in the liquid will drift toward the

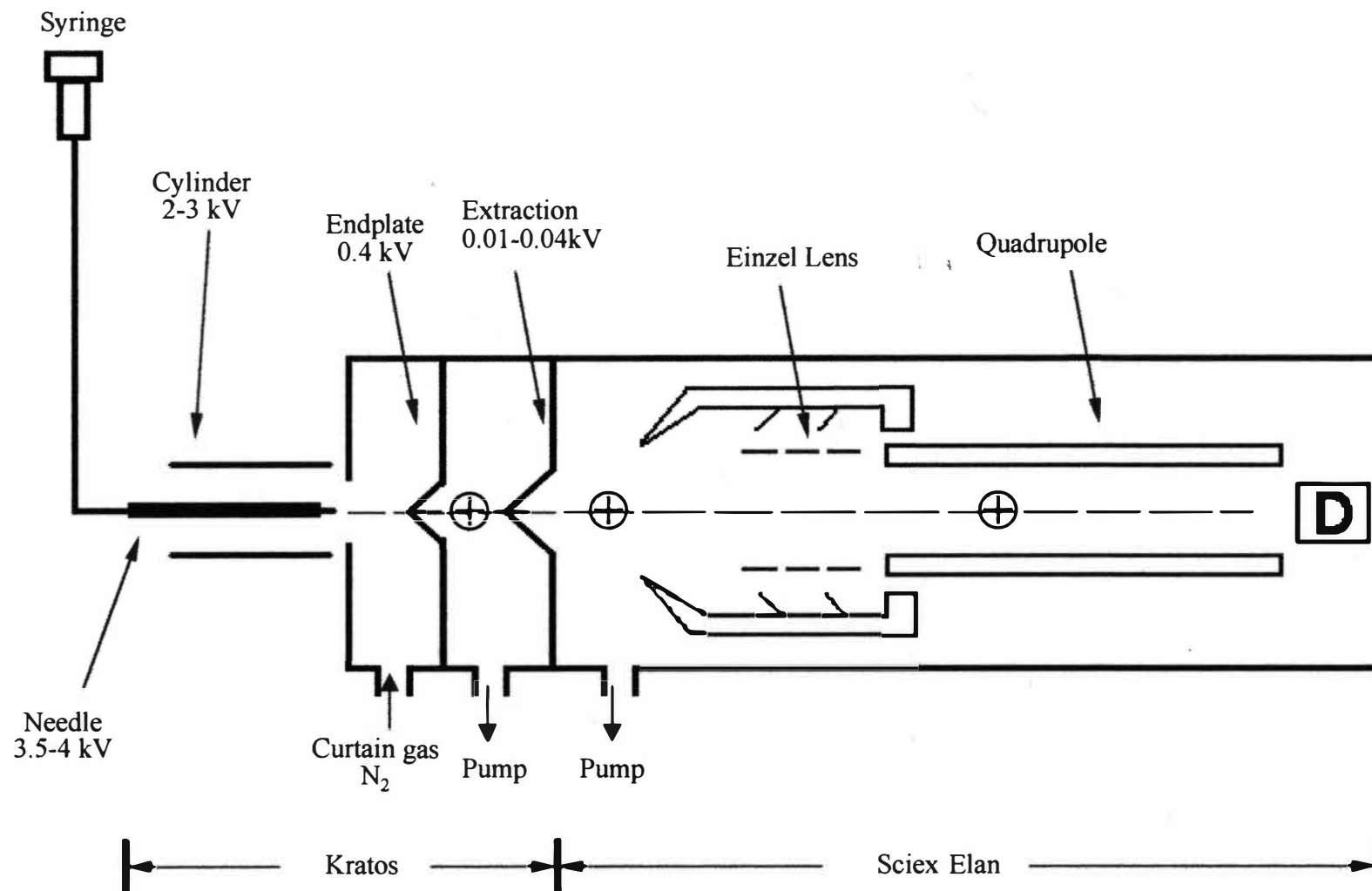


Figure 1. Schematic Diagram of Electrospray Mass Spectrometer.  
Representation is not drawn to scale.

liquid surface and negative ions drift away from it. The surface is then drawn downfield and a liquid cone (Taylor cone) forms. At a sufficiently high field, the cone is unstable and liquid droplets with positive charges on surfaces are produced. These droplets will be stable when the surface tension equals the repulsion of the charges on surface. In the endplate chamber,  $N_2$  heated to  $75^\circ\text{C}$  is introduced. The warm nitrogen helps the solvent molecules evaporate from the droplets, increasing the repulsion. If the ratio of charge to radius exceeds the Rayleigh limit, the droplet will split into smaller droplets. This process repeats and the resulting droplets ultimately lead to gas-phase ions.

The ions formed are accelerated and fly through the extraction cone. The diameter of the cone is 1 mm. The ions then pass into quadrupole mass analyzer and are detected. The chamber between the endplate and the extraction cone is pumped down to 1 torr with a mechanical pump. Downstream is another chamber pumped down to  $10^{-5}$  torr with a cryogenic pump.

### Effects of Experimental Parameters on Signal

Since the potentials applied to the needle, cylinder, endplate and extraction cone will determine the electric field between them. Changes of these potentials will greatly affect the spectrum of samples. Horlick et al and Kobarle et al [18-23] have published several papers on studying metal ions with ES-MS. However a study of the relation of needle, cylinder, endplate and extraction cone potentials with signal is worthwhile. It is important for us to understand our interface and optimize

experimental conditions for later study on organo-tin and organo-mercury compounds.

Since most of our attention was focused on the ionization process of positive ions, only the positive ion mode was used in our experiments. In positive ion mode, positive voltage is applied to needle, cylinder, endplate and extraction skimmer, so only positive ions can be accelerated to mass analyzer and detected. Additionally, scan mode and time resolved modes were also used to collect data. In scan mode, a certain range of  $m/z$  is scanned, so it is used to collect spectrum. While in time resolved mode, the intensity of the interested peak was continuously monitored for 30 seconds and the averaged result was released, so it was used to obtain the intensity at the specific  $m/z$  ratio.

To characterize the ES interface,  $10^{-3}$  M solution of nickle(II) chloride in methanol was selected as sample solution. All the data were collected in time-resolved mode.

The effect of needle potential on signal is shown in Figure 2. The potential window investigated ranged from 2.0 kV to 4.0 kV. There was no signal at potentials lower than 2.0 kV. When the potential is higher than 4.0 kV, arcing occurs between the needle and the endplate. Figure 2 indicates that the intensity increases with an increase of needle potential. Thus the onset potential for the solution is a little higher than 2.0 kV. At the onset potential, the Taylor cone is unstable and sample is emitted from the Taylor cone tip. The liquid filament splits into smaller positively charged droplets and the Electrospray ionization process is initiated. When the needle potential increases, the electric field between needle and endplate increases, and the

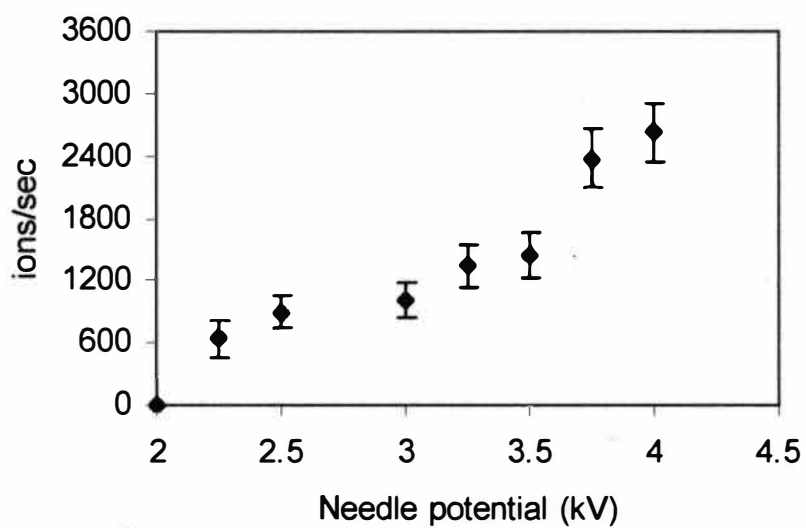


Figure 2. The Effect of Needle Potential on Signal.

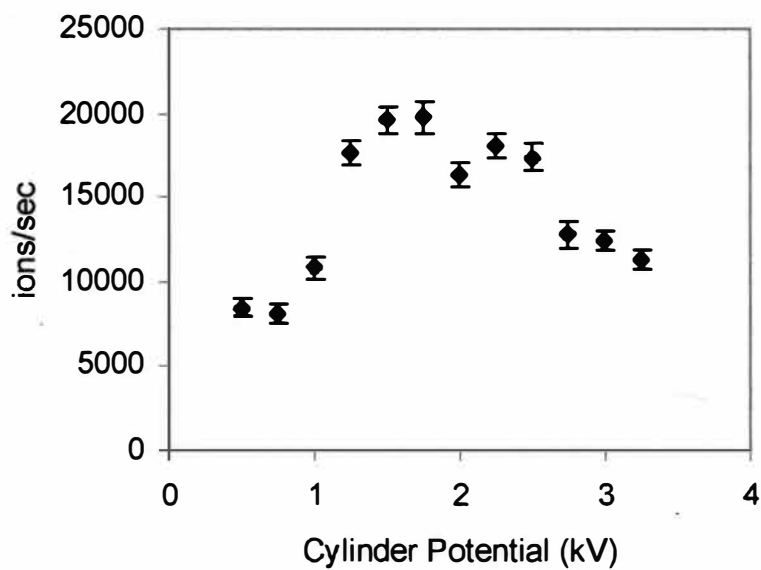


Figure 3. The Effect of Cylinder Potential on Signal.

central cone no longer exists. Instead droplet emission occurs from a crown of four to six short liquid tips formed at the rim of the capillary. Thus the ionization rate increases and results in higher intensity. Needle potential is one of the key parameters that will affect the final results. Since different solvents have different surface tensions, it is expected that higher surface tensions will require higher onset needle potentials.

The effect of cylinder potential on signal is shown on Figure 3. It suggests that the potential applied on cylinder has little effect between 1.25 and 2.5 kV. Lower or higher potential tend to decrease the intensity. When a high needle potential is applied, it usually requires higher cylinder potential. Otherwise, it is easy to cause a discharge. In some electrospray ionization interfaces [18, 19], the cylinder is not included. Droplets produced directly enter a chamber similar to the endplate chamber. The cylinder helps to prevent arcing and reshapes the electric field around the needle, and will affects the ionization process and the intensity of signal.

Solution droplets are desolvated and ionized in the endplate chamber. Heated nitrogen gas keeps the chamber at 75°C. The cone serves as the sampling cone and the ions formed will be accelerated and enter the chamber downstream. Variation of the endplate potential will influence the potential difference between the endplate and the extraction cone. The ions from the endplate chamber will collide with gas molecules or ions in the chamber between the endplate and the extraction cone when they are accelerated. Thus the change in potential difference will result in the change of collision energy. If the collision energy is high enough, the ions will be fragmented

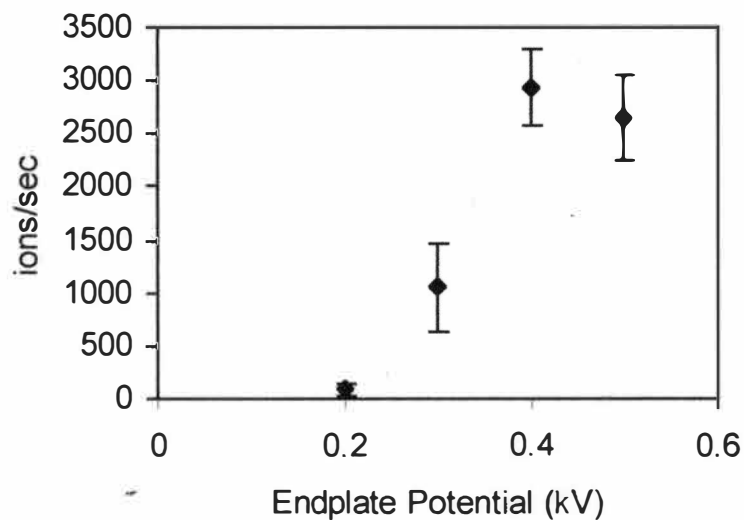


Figure 4. The Effect of Endplate Potential on Signal.

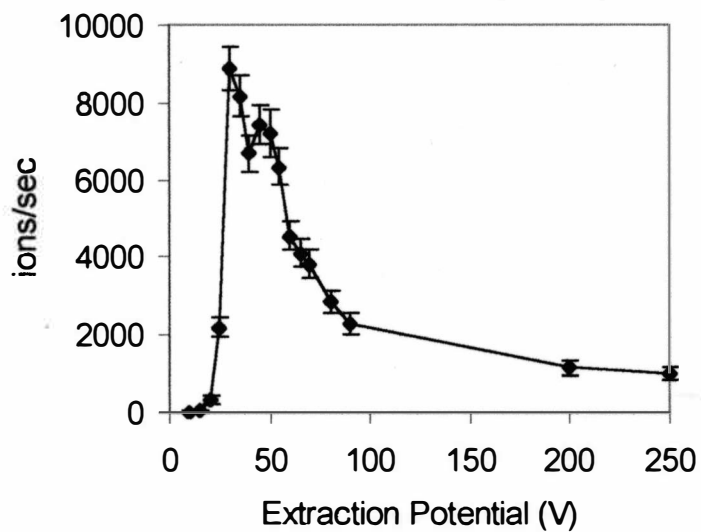


Figure 5. The Effect of Extraction Potential on Signal.

and the spectrum will change. Figure 4 shows the effects of endplate potential on signal. With the increase of endplate potential, the signal increases and then tends to level off. As we can see, the standard deviation dramatically increases.

The change of the extraction potential will also change the collision energy. In addition, it may also affect the ion transmission. Its effect is different from endplate as seen by comparing Figure 4 and Figure 5. In Figure 5, there is an optimum potential. The signal is very sensitive to the variation of the extraction potential. At about 40 V, the highest intensity was obtained. Later experiments were carried out at experimental conditions listed in Table 1.

Table 1  
Typical Operating Conditions in ES-MS Experiment

Parameter	Value
Needle Potential	3.75 kV
Cylinder Potential	1.5 kV
Endplate Potential	0.4 kV
Extraction Potential	40 V
Sample flow rate	10 $\mu$ l/min
Curtain gas	Nitrogen
Curtain gas flow rate	100 ml/min
Curtain gas temperature	75 $^{\circ}$ C



## Chemicals

All analytes and reagents were used without further purification.

Metal salts: (ACS grade)  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{NiCl}_2$  obtained from J.T.Baker Chemical Co., Phillipsburg, NJ.  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$  from Fisher Scientific.  $\text{SnCl}_2$  from Fisher Scientific (ACS grade).  $\text{SnCl}_4$  from J.T.Baker Chemical Co. Used without additional purification.

Organo-tin compounds:  $\text{CH}_3\text{SnCl}_3$ ,  $(\text{CH}_3)_3\text{SnCl}$ ,  $(n\text{-C}_4\text{H}_9)\text{SnCl}_3$ ,  $(n\text{-C}_4\text{H}_9)_3\text{SnCl}$ ,  $(\text{C}_6\text{H}_5)\text{SnCl}_3$  obtained from Strem Chemicals, Newburyport, MA.

Organo-mercury compounds:  $\text{CH}_3\text{HgCl}$  from Strem Chemicals,  $(\text{CH}_3\text{CH}_2)\text{HgCl}$  Alfa, Johnson Matthey, Ward Hill, MA;  $\text{C}_6\text{H}_5\text{HgCl}$  from Aldrich Chemical Company, Milwaukee, WI;  $\text{C}_6\text{H}_5\text{HgAc}$  from Columbia Organic Chemical Co. Inc, Columbia, SC.

Solvents: HPLC grade  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CN}$ ,  $\text{H}_2\text{O}$  from Fisher Scientific.

Since organo-tin compounds are water or moisture sensitive, all organo-tin solutions were prepared in glove box purged with  $\text{N}_2$  gas and then transferred out for ES-MS experiments.

## RESULTS AND DISCUSSION

### The Ionization Characteristics of Group II Metal Ions

Electrospray (ES) is a well-known soft ionization source widely used for the analysis of peptides, and in nucleic acid. It is able to produce multiply charged ions with the same molecular form in the solution phase. But its application in elemental analysis, especially metal salts, has also been investigated to some extent. These studies are closely related to the characteristics and mechanism of the ionization processes.

To further understand the ionization aspects of our interface, group II metal salts (  $\text{Mg}(\text{NO}_3)_2$  ,  $\text{Ca}(\text{NO}_3)_2$  ,  $\text{Sr}(\text{NO}_3)_2$  ,  $\text{Ba}(\text{NO}_3)_2$  ) were selected for investigation. Solutions of each at  $10^{-3}\text{M}$  in methanol solution was studied unless otherwise specified. The gas phase ions produced by our interface is extremely interested. The spectra of these ions are shown in Figure 6, Figure 7, Figure 8 and Figure 9 respectively.  $5 \times 10^{-4}\text{M}$   $\text{NiCl}_2$  was introduced as an internal standard to account for intensity variation due to the fluctuation of interface. ES-MS intensely varied from day to day, but the relative sensitivities within a mass spectrum were very reproducible. Mixtures of methanol/ $\text{H}_2\text{O}$  and acetonitrile/ $\text{H}_2\text{O}$  were investigated to study the solvent effects on ionization and signal.

The spectrum of  $10^{-3}\text{M}$   $\text{Mg}(\text{NO}_3)_2$  in MeOH was shown in Figure 6.  $\text{Mg}^{2+}$ , which is the solution cation species of  $\text{Mg}(\text{NO}_3)_2$  , was totally reduced to  $\text{Mg}^+$  and

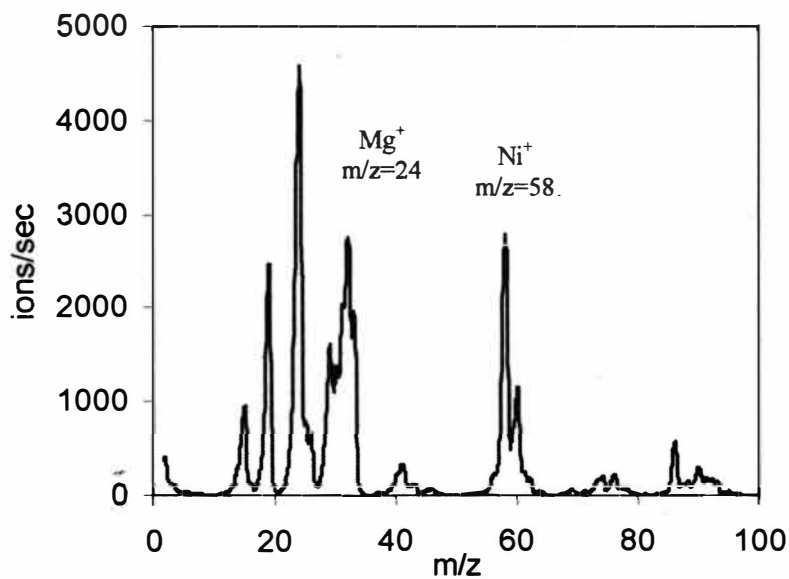


Figure 6. ESMS Spectrum of  $10^{-3}$  M  $\text{Mg}(\text{NO}_3)_2$  in MeOH With  $\text{NiCl}_2$  as Internal Standard.

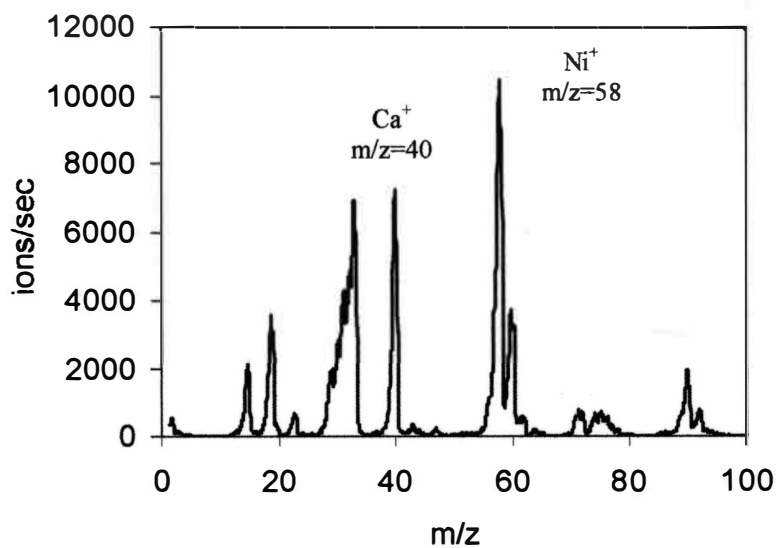


Figure 7. ESMS Spectrum of  $10^{-3}$  M  $\text{Ca}(\text{NO}_3)_2$  in MeOH With  $\text{NiCl}_2$  as Internal Standard.

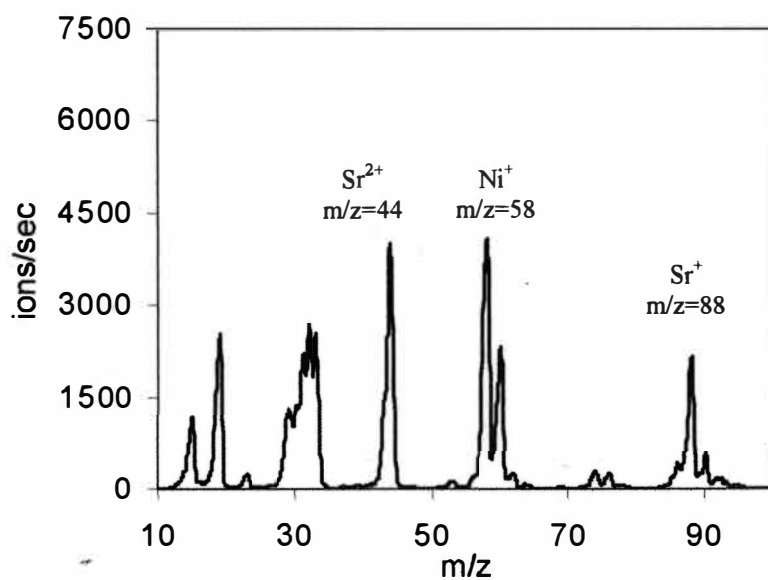


Figure 8. ESMS Spectrum of  $10^{-3}$  M  $\text{Sr}(\text{NO}_3)_2$  in MeOH With  $\text{NiCl}_2$  as Internal Standard.

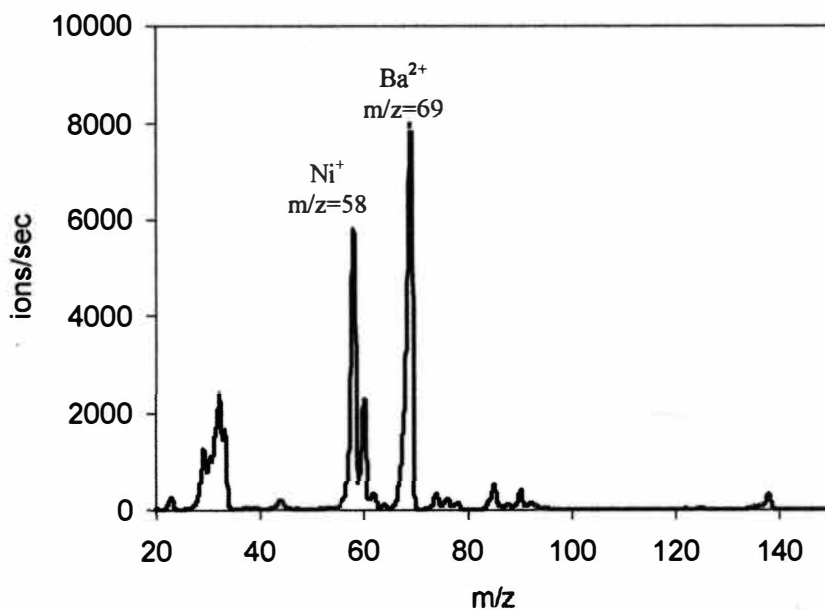


Figure 9. ESMS Spectrum of  $10^{-3}$  M  $\text{Ba}(\text{NO}_3)_2$  in MeOH With  $\text{NiCl}_2$  as Internal Standard.

exhibited peak at 24 amu. No clustered form, such as  $\text{Mg}(\text{MeOH})_n^{2+}$ . No 2+ form should be observed at 12 amu if  $\text{Mg}^{2+}$  ion existed. A peak at 15 amu arises from  $\text{CH}_3^+$ , while  $\text{H}(\text{MeOH})^+$  accounts for the peak at 33 amu. The peak at 19 is also from solvent, possibly from  $\text{H}_3\text{O}^+$ . Internal standard  $\text{Ni}^{2+}$  was also totally reduced to the +1 ion and exhibited maximum at 58 and 60, which are principle isotopes of nickel.

$\text{Ca}^{2+}$  ion exhibited similar results in Figure 7. All 2+ calcium ions were reduced to 1+ and appeared at 40. Furthermore no clustered ions were observed. Lower in the periodic table, the next element of the Group II column is Sr. Its spectrum in  $\text{MeOH}$  is shown in Figure 8. A large portion of  $\text{Sr}^{2+}$  which is the native form of  $\text{Sr}^{2+}$  in solution remained unreduced, although there were still significant amounts of  $\text{Sr}^+$  presented at 88 amu, the principle isotope of Sr. The  $\text{Ba}(\text{NO}_3)_2$  spectrum is seen in Figure 9. Almost all of  $\text{Ba}^{2+}$  remained as 2+ ion. Only a small amount was reduced to 1+ and appeared at 138 amu, the same as its major isotope mass.

The results of group II metal ions are summarized in Table 2. From Mg to Ba, the tendency of group II ions to be reduced is decreased. The tendency is similar to that observed by Agnes and Horlick [19]. In their work these ions were seen as clustered ions, such as  $\text{Sr}(\text{MeOH})_2^{2+}$ ,  $\text{Sr}(\text{MeOH})_1^{2+}$  and  $\text{Sr}(\text{MeO})_1^+$ .

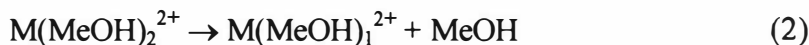
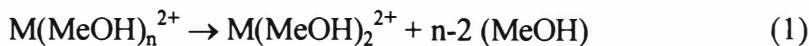
In methanol, magnesium and calcium ions are totally reduced, no +2 oxidation state is obtained. The ratio of +2/+1 for Sr is 4 and dramatically increased to 90 for Ba. The same trend remained for these ions in 5%  $\text{H}_2\text{O}$ +95% acetonitrile. Part of the  $\text{Ca}^{2+}$  remained in the +2 form. The ratio of +2/+1 is also changed. For the group II metals, the second ionization potential decreased from Mg (15.035 eV) to Ba

Table 2  
Ionization Results of Group II Metal Salts

Solvent	Element	Mg	Ca	Sr	Ba
MeOH	Oxidation State Observed	+1	+1	+1,+2	+2
	Ratio: +2/+1	0	0	4	90
5%H <sub>2</sub> O+95%ACN	Oxidation State Observed	+1	+1,+2	+1,+2	+1,+2
	Ratio: +2/+1	0	4	10	20
	1 <sup>st</sup> Ionization potential(eV)	7.646	6.113	5.695	5.212
	2 <sup>nd</sup> Ionization Potential(eV)	15.035	11.871	11.030	10.004

(10.004 eV). The higher the ionization potential of an element or ion, the easier the element or ion will be reduced. The reduction of these ions should have close relation with their ionization potential or electron affinity. But in solution, ions are not bare. They are solvated and surrounded by solvent molecules. The solvation sphere plays an important role in reduction. To reduce the central metal ion, an electron donor must transfer an electron through the solvation sphere to the central ion. According to Marcus theory [24], the theoretical rate constant for the electron transfer reaction is exponentially proportional to the reciprocal of the distance between the electron donor and the electron acceptor. Since both the electron donor and the electron acceptor are solvated in solution, the intramolecular electron transfer rate is negligible. The reduction may occur through intermolecular electron transfer. Horlick

has suggested the following mechanism [19].



Like in solution, central ions are stabilized by solvent molecules even in the gas phase. The loosely bounded solvent molecules around the central ion will be removed or evaporate in the endplate chamber. This process is described by Equation (1), where  $n$  is the number of solvent molecules around the central ion and  $M$  designates the central metal ion, which may be  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ . Further declustering of group II metal ions will be different. According to Table 1, only the +1 oxidation state was observed for magnesium and no clustered ions were formed, so  $\text{Mg}^{2+}$  may be reduced through steps (4) through (7). The intensity ratio of  $I(\text{H}(\text{MeOH})^+)/I(\text{Ni}^+)$  decreased from Mg (0.97), Ca (0.74), Sr (0.67) to Ba (0.41) proved that this pathway is dominant for  $\text{Mg}^{2+}$ . The wide peak around 32 and 33 suggested that step (7) competes with step (4) and produced  $\text{MeOH}^+$ .  $\text{Ca}^{2+}$  took the same pathway as  $\text{Mg}^{2+}$  during its reduction. However for  $\text{Sr}^{2+}$ , some remained as  $2+$ . Its lower 2<sup>nd</sup> ionization potential helps energetically the removal of solvent molecules as designated in equation (2) and (3). For  $\text{Ba}^{2+}$ , most of its +2 oxidation state remained since it was favored in energy to follow step (2) and (3) instead of breaking O-H bond in  $M(\text{MeOH})_2^{2+}$ . The spectra of  $10^{-3}\text{M}$   $\text{Cu}(\text{NO}_3)_2$  and  $\text{Zn}(\text{NO}_3)_2$  in methanol are shown in Figure 10 and Figure 11. They all reduced to the +1 ion and

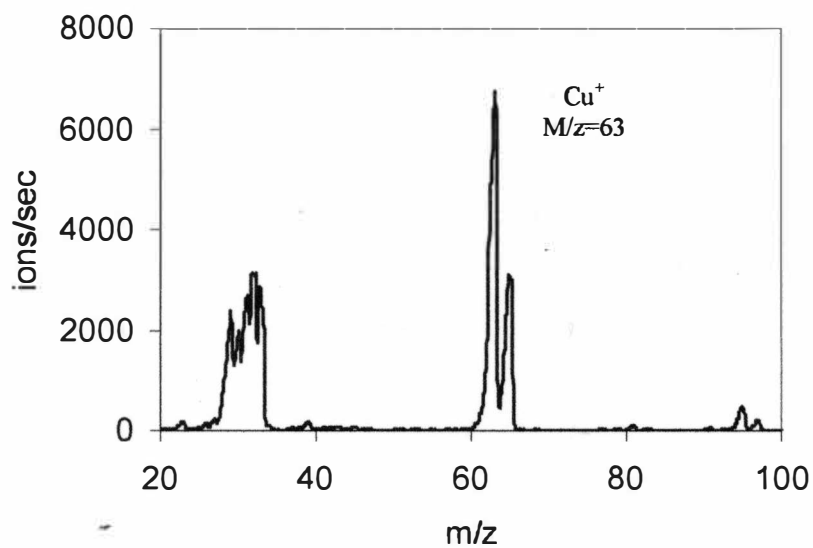


Figure 10. ESMS Spectrum of  $10^{-3}$  M  $\text{Cu}(\text{NO}_3)_2$  in Methanol.

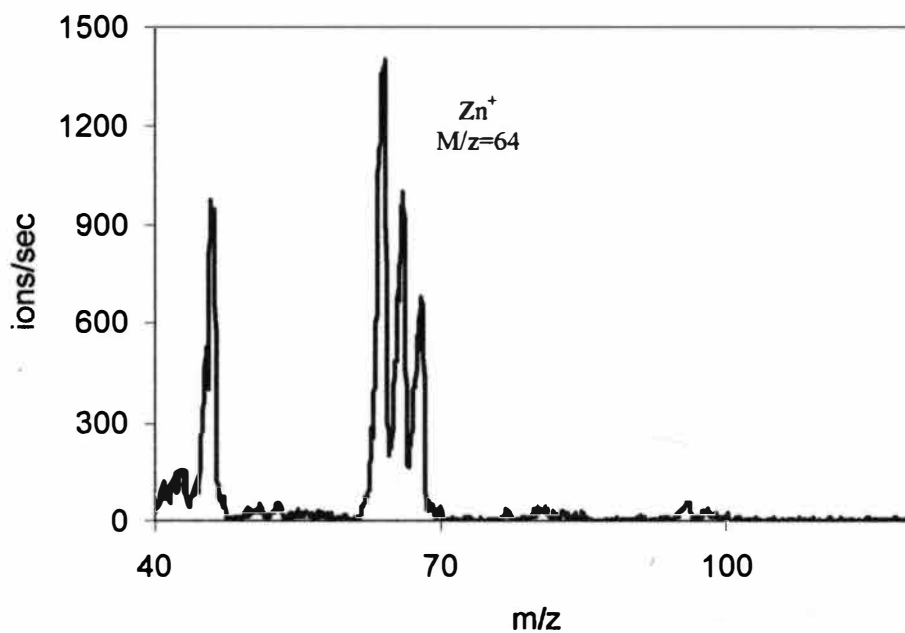


Figure 11. ESMS Spectrum of  $10^{-3}$  M  $\text{Zn}(\text{NO}_3)_2$  in Methanol.



exhibit maximum at about 65 amu and 62 amu. No solvent molecule clustered metal ion peaks were seen. This is due to the high second ionization potential, which is much higher than that of Group II metals. It was no surprise to see reduced peaks for both of them.

Since no clustered peaks were observed, these results are similar with high CID (collision induced dissociation). This suggests that our interface had high collision energy and was very harsh.

### Solvent Effect

In the ionization process, the surface tension of the solvent is an important factor. The higher the surface tension is, the higher the on-set potential that is required. It is also expected that the polarity and other characteristics of solvent will also affect the signal and the reduction pattern.

To study the effect of solvent, mixtures of H<sub>2</sub>O/ACN and of H<sub>2</sub>O/MeOH were investigated. The intensity ratio of +2 to +1 of Group II metal ions varied with the change of the water percentage. The result for H<sub>2</sub>O/ACN mixture is summarized in Table 3, and that of H<sub>2</sub>O/MeOH mixture is summarized in Table 4. Variation of the percentage of water will result in varied polarity and surface tension.

The intensity of these ions were collected on time resolved mode for 30 s. All experimental conditions were the same. The polarity index (the index introduced by Synder was used to evaluate the polarity of solvent. The higher the polarity index, the more polar the solvent. Polar and ionic compounds have higher dissociation ability in more polar solvents) was calculated from equation 8, where P is the polarity index of

Table 3

I(+2)/I(+1) of Group II Metal Ions in the Mixture of Water and Acetonitrile

	Polarity Index	Surface Tension (mN/m) 20 °C	Mg +2/+1	Ca +2/+1	Sr +2/+1	Ba +2/+1
5%H <sub>2</sub> O + 95%ACN	6	25.37	0.1	3.9	11.8	301
25%H <sub>2</sub> O + 75%ACN	6.9	28.34	0.1	4.6	27.9	394
50%H <sub>2</sub> O + 50%ACN	8	33.15	0	3.5	28.4	342
75%H <sub>2</sub> O + 25%ACN	9.1	40.87	0	2	22.1	222

Table 4

I(+2)/I(+1) of Group II Metal Ions in the Mixture of Water and Methanol

	Polarity Index	Surface Tension (mN/m) 20 °C	Mg +2/+1	Ca +2/+1	Sr +2/+1	Ba +2/+1
100% MeOH	5.1	22.61	0	0	4	90
5%H <sub>2</sub> O + 95%MeOH	5.4	25.20	0	0.3	4.8	91.2
25%H <sub>2</sub> O + 75%MeOH	6.4	29.46	0	0.1	2.5	44.4

the mixture of solvent A and B.  $P_i$  and  $X_i$  are polarity index and volume percentage of solvent i respectively [25].

$$P = P_A X_A + P_B X_B \quad (8)$$

Surface tension value of acetonitrile and methanol in water from CRC handbook were shown in Table 5. No equations are available. For the specific mixtures in solvent effect experiments, a regression equation was obtained based on data in Table 5 for each mixture group. Equations (9) and (10) were regression equations for acetonitrile in water and methanol in water. Their correlation

Table 5

Surface Tension of Acetonitrile and Methanol in Water at 20 °C

Acetonitrile in water at 20 °C		MeOH in water at 20 °C	
%(w/w)	r	%(w/w)	r
1.13	69.02	7.5	60.9
3.35	63.03	10	59.04
11.77	47.61	25	46.38
20.2	39.06	50	35.31
37.58	31.84	60	32.95
61.33	30.02	80	27.26
81.22	29.02	90	25.36

From CRC Handbook of Chemistry and Physics, 73th edition.

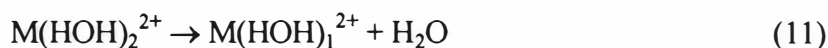
coefficients,  $R^2$ , values are 0.9791 and 0.9932 respectively.  $x$  is the volume percentage of methanol or acetonitrile, while  $r$  is the surface tension in mN/m.

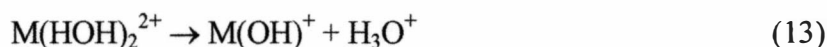
$$r = -10.279 \ln(x) + 72.04 \quad (9)$$

$$r = -14.842 \ln(x) + 92.59 \quad (10)$$

The surface tension for the specific mixtures in our experiments were calculated from equations (9) and (10).

Water has very high surface tension and polarity compared to methanol and acetonitrile. The increase of water percentage in the mixture resulted in higher surface tension and higher polarity. In the electrospray ionization process, solvent with higher surface tension requires higher onset potential to initiate the emission of smaller charged droplets or ions and then to initiate ionization process. While the increase of polarity of the solvent will cause stronger solvation of central ion. The bond energy of H-OH is 61 KJ/mol higher than H-OCH<sub>3</sub>. Thus compared with methanol, water is advantageous energetically to take steps (11) and (12) rather than (13). This means the tendency of reduction will decrease with an increase of water percentage in the mixture. The ratio of +2 oxidation state intensity to +1 oxidation state intensity also tends to increase. In Figure 10 and Figure 11 the +2/+1 ratio decreases at high water percentage. Higher surface tension will require higher onset potential. Since all the experiments were conducted at same needle, cylinder, endplate and extraction potentials, the experimental conditions for one solvent might result in the best signal for one but not for the other. It seems higher surface tension is advantageous to charge reduction. Two different effects result in a highest +2/+1 ratio in Group II metal ions.





### Organo-tin Compounds

Emanuele Magi [1] have developed LC particle beam mass spectrometry to determine tributyltin in marine environments. Treatment of organo-tin compounds with sodium borohydride or with Grignard reagent yields a volatile derivative which were analyzed by GC/MS were also studied. Jay J. Corr [2] studied tributyltin using elemental and molecular dual mode analysis by ionspray mass spectrometry.

K.W.M.Siu et al [17] published their work on quantitation of tributyltin with ionspray mass spectrometry. For most other works, separation techniques are used first with subsequent elemental analysis. To develop methods that can get solution phase information directly, electrospray mass spectrometry was one of the techniques that need systematic investigation.

The compounds selected are organo-tin with different types and different number of alkyl groups such as methyltin trichloride, n-butyltin trichloride, phenyltin trichloride and organo-tin all with three alkyl groups but different types.

First,  $10^{-3}\text{M}$   $\text{SnCl}_2$  and  $\text{SnCl}_4$  methanol solution was studied. Comparing the results with alkylated tin compounds will give us an idea of the effects of alkyl groups. According to the previous results on Group II metal ions and some transition metal salts,  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ , both be reduced to +1 oxidation state, since they must have very high corresponding ionization potential compared to the second ionization potential of Group II element. The forth ionization potential of Sn ( $I_{IV} = 40.734 \text{ eV}$ ,

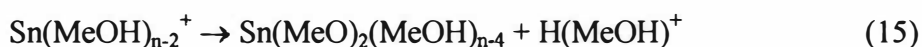
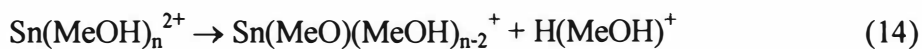
$I_{II} = 14.632$  eV). Surprisingly, the signal of the expected reduced form,  $\text{Sn}^+$ , the original form of which is  $\text{Sn}^{2+}$  or  $\text{Sn}^{4+}$ , is not significant. While in the mixture of 5% water and 95% acetonitrile they both show peaks at 60 amu and 30 amu which means they kept their original form in solution instead of being reduced to +1 oxidation state. It seems that solvent can greatly affect the ionization and reduction of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ . The surface tension and polarity index of 5%  $\text{H}_2\text{O}$ +95% ACN are 25.37 mN/m and 6 respectively, similar to 22.61 mN/m and 5.1 of methanol. So the polarity

Table 6  
Bond Strengths of Solvent Molecules

Bond	H-OH	H-OCH <sub>3</sub>	CH <sub>3</sub> -CN
Bond Strength (kJ/mol)	$498 \pm 4$	$436.8 \pm 4$	$518.4 \pm 2.9$

index and surface tension may not be the reason for the different behavior of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  in these two solvents. The difference should come from the difference in chemistry. According to Table 6, it is much easier to break the H-OCH<sub>3</sub> bond than to break the H-OH and CH<sub>3</sub>-CN bonding. In methanol,  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  may take steps like (14) and (15) and produce neutral species  $\text{Sn}(\text{MeO})_2(\text{MeOH})_i$  and  $\text{Sn}(\text{MeO})_4(\text{MeOH})_j$  where i and j represent the number of solvent molecule bound with tin ions. In mass spectrometry, these neutral species can not be observed. Thus in the spectra of  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  in methanol solution, only solvent peaks were observed. They are consistent with the explanation. For acetonitrile and water solvated  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$ , the solvated

ions may take steps like equation (1) till all the solvent molecules were stripped, which is energetically more advantageous. Consequently  $\text{Sn}^{2+}$  and  $\text{Sn}^{4+}$  remained their original solution form and their +2 and +4 oxidation state were observed in Figure 12 and Figure 13 respectively. The isotope peaks were compressed because of the multiple charges on these two ions. This is another example of solvent effect on the ionization process.



#### Effect of Alkyl Groups on the Ionization Process

The organo-tin compounds investigated varied in both the alkyl group and the number of alkyl groups.  $\text{CH}_3\text{SnCl}_3$  only has a short alkyl chain on its cation; (n- $\text{C}_4\text{H}_9$ ) $\text{SnCl}_3$  has a longer chain, while  $\text{C}_6\text{H}_5\text{SnCl}_3$  has an aromatic ring. They varied in bond energy, structure and polarity.

All the organo-tin compounds studied were  $10^{-3}\text{M}$  methanol solutions and experiments were all conducted at same ionization conditions. The mixtures of water and acetonitrile were not selected as solvents because these organo-tin compounds are moisture sensitive. The ES-MS spectra of these compounds are shown from Figure 14 through Figure 18. Figure 14, Figure 16 and Figure 18 are very similar. They all have two main groups of peaks. One group is from 116 amu to 124 amu and the intensity of these peaks are proportional to the abundance of Sn isotopes ( $\text{Sn}^{116}$ :  $\text{Sn}^{118}$ :  $\text{Sn}^{120} = 14.53 : 24.22 : 32.59$ ). This proves that  $\text{Sn}^+$  was produced in ionization

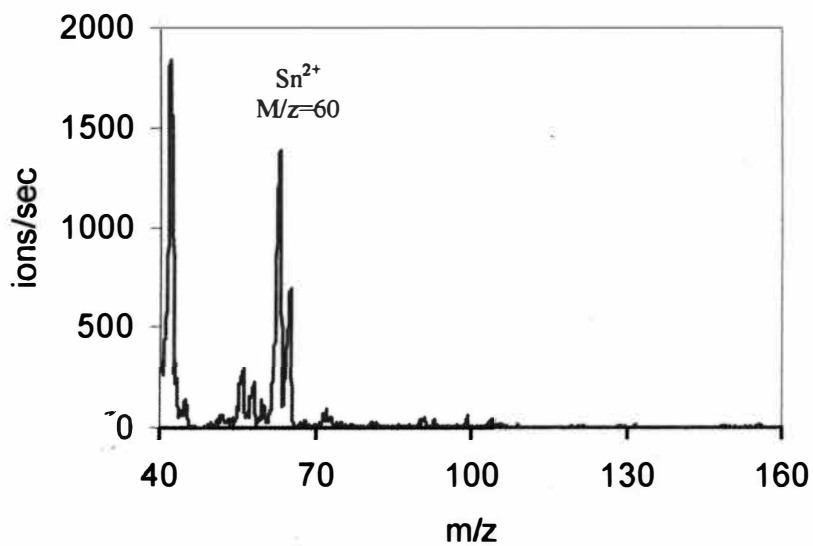


Figure 12. ESMS Spectrum of  $10^{-3}$  M  $\text{SnCl}_2$  in 5%  $\text{H}_2\text{O}$  + 95% Acetonitrile.

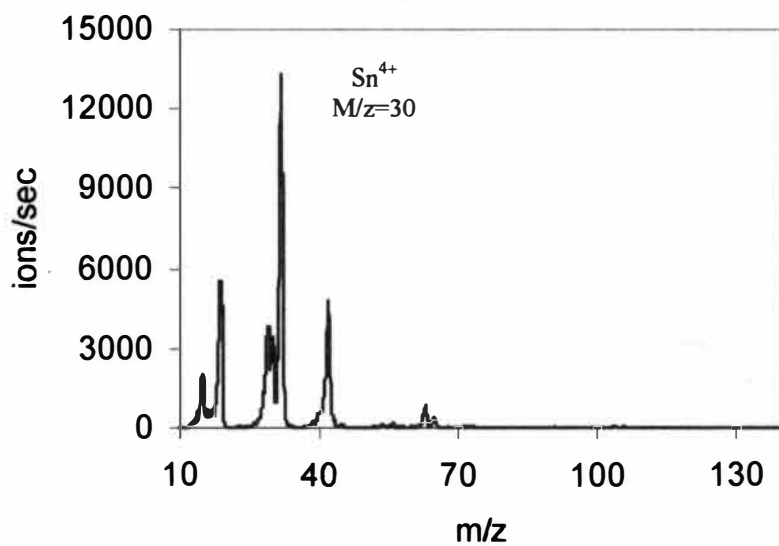


Figure 13. ESMS Spectrum of  $10^{-3}$  M  $\text{SnCl}_4$  in 5%  $\text{H}_2\text{O}$  + 95% Acetonitrile.



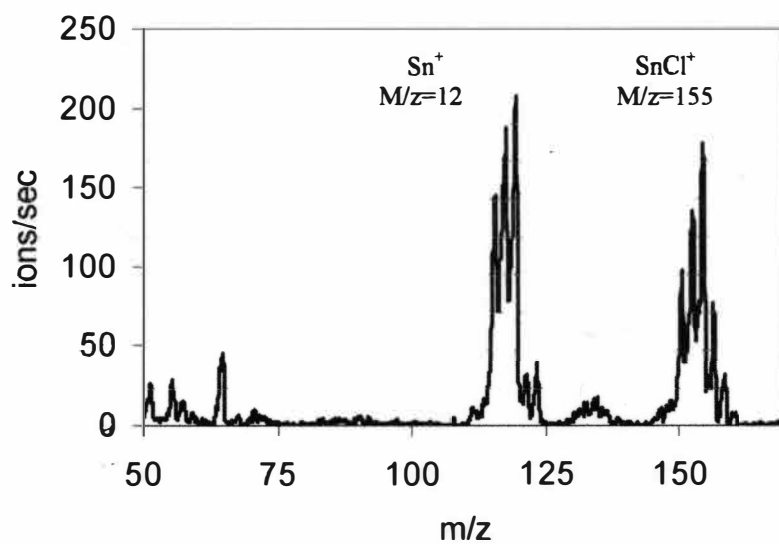


Figure 14. ESMS Spectrum of  $10^{-3}$  M  $\text{CH}_3\text{SnCl}_3$  in Methanol.

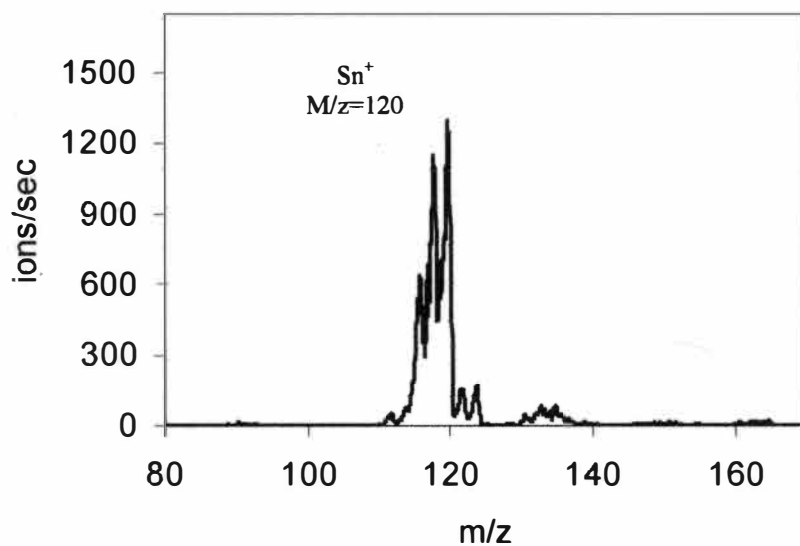


Figure 15. ESMS Spectrum of  $10^{-3}$  M  $(\text{CH}_3)_3\text{SnCl}$  in Methanol.

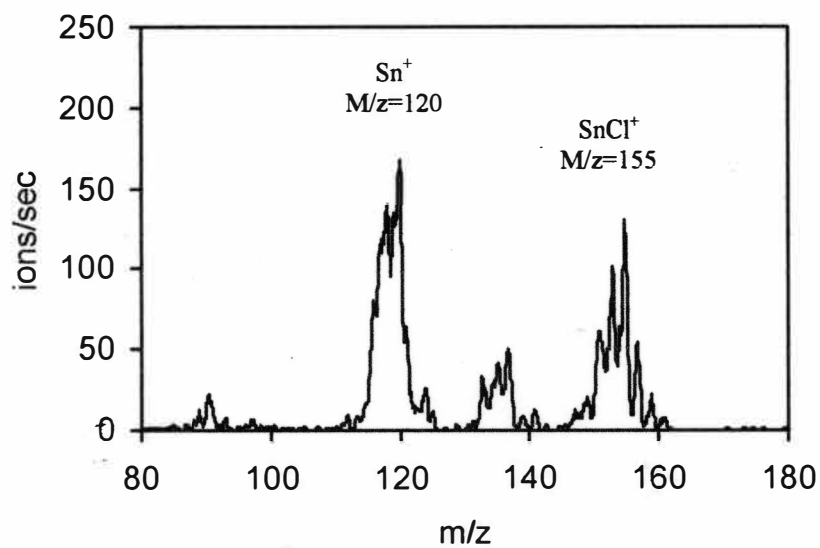


Figure 16. ESMS Spectrum of  $10^{-3}$  M (n-Butyl) $\text{SnCl}_3$  in Methanol.

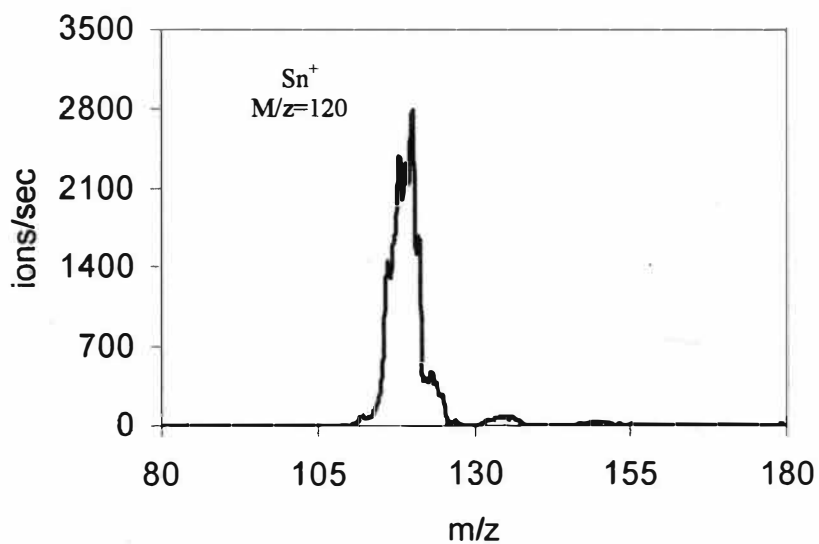


Figure 17. ESMS Spectrum of  $10^{-3}$  M  $\text{Bu}_3\text{SnCl}$  in Methanol.

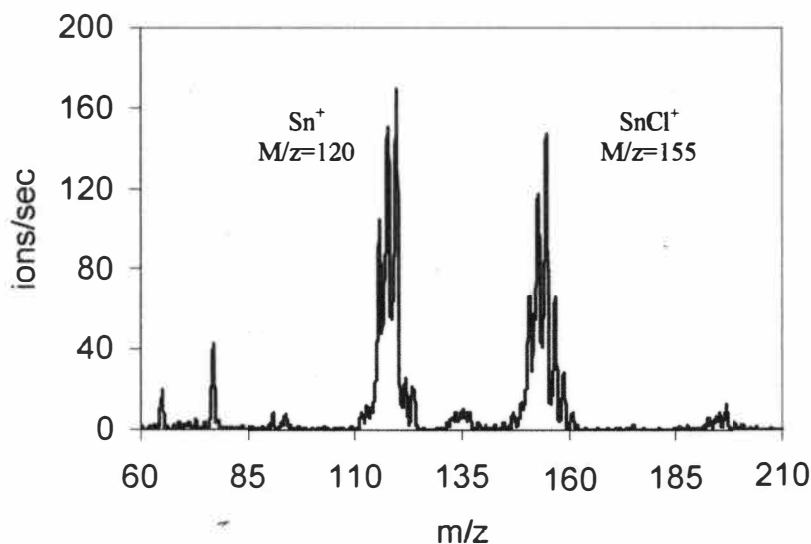


Figure 18. ESMS Spectrum of  $10^{-3}$  M  $C_6H_5SnCl_3$  in Methanol.

processes. The second group exhibited maximum at 35 amu higher than the previous group with a similar peak pattern. These peaks come from  $SnCl^+$ , an adduct of  $Sn^{2+}$  and  $Cl^-$ . The samples analyzed were  $RSnX_3$ , where the valence of Sn is 4. There are no expected  $RSn^{3+}$  peaks which should be present around 45 for  $CH_3Sn^{3+}$ , 59 for  $C_4H_9Sn^{3+}$  and 66 for  $C_6H_5Sn^{3+}$ . All monoorgano-tin compounds were fragmented and tin(IV) was reduced to +1 and +2 oxidation state. The solvent molecule clustered ions such as  $RSn(MeOH)_n^{3+}$ ,  $Sn(MeOH)_n^+$  and  $SnCl(MeOH)_n^+$  were also not seen. It seems that the alkyl groups bonded with tin(IV) do not affect the ionization processes, no matter what the length of the chain and the aromatic ring. The effect of the alkyl group is not too significant.

The results of  $10^{-3}$  M  $R_3SnX$  in methanol and with the same experimental conditions as before were different from  $RSnX_3$ . In their spectra shown in Figure 15 and Figure 17, only one main group peaks were observed. The peak intensity and

mass to charge ratio indicate they arise from  $\text{Sn}^+$ . Again, tin(IV) in trialkyltin chloride compounds were reduced and no clustered peaks were observed. Different alkyl group tin compounds exhibited similar results under experimental conditions. The  $\text{SnCl}^+$  peaks in  $\text{RSnX}_3$  were not present. Different number of alkyl groups and differences in cation charge do make differences in the ionization processes.

The difference should have close relationship to the structure and properties of these organo-tin compounds. Tin has low energy d-orbitals that can be used in bonding so its coordination number could be expanded above 4. Considered as Lewis acids, organo-tin compounds can form stable complexes with Lewis bases. The Lewis acid strengths of the organo-tin halides  $\text{R}_n\text{SnX}_{4-n}$  ( $n=1-3$ ) decreases as  $n$  increases. The compounds  $\text{R}_3\text{SnX}$  ( $\text{X}=\text{halides}$ ) usually give five-coordinate complexes  $\text{R}_3\text{SnXL}$  which are approximately trigonal bipyramidal, where  $\text{L}$  designates external ligand. The compounds  $\text{RSnX}_3$  usually form six-coordinate complexes  $\text{RSnX}_3\text{L}_2$  which are approximately octahedral. The halide atom has unshared electron pairs, and can serve as Lewis bases, resulting in intermolecular self-association to give dimers, oligomers, or polymers in solid phase. The nature of halide and the steric structure of  $\text{R}$ ,  $\text{X}$  and  $\text{L}$  will affect the self-association. Physical state will also affect self-association, with solid phase having the highest self-association and gas phase having the lowest. When tin is attacked by nucleophilic reagent, the reaction is greatly facilitated by the formation of coordinated intermediates which lower the energy of the transition state.

In  $\text{R}_n\text{SnX}_{4-n}$  methanol solution, organo-tin compounds are solvated. The lone electron pair on the oxygen atom tends to coordinate with the  $\text{Sn}$  atom. For  $\text{RSnCl}_3$ , there will be at least two  $\text{MeOH}$  molecules in the inner shell of the solvation sphere

and the 6 ligands around Sn form an octahedron, as shown in Figure 19(B). For  $R_3SnCl$ , there will be at least one MeOH molecule around Sn and a trigonal bipyrimide is formed, as shown in Figure 19(A). The electron acceptor strength of tin in these organo-tin compounds is proportional to the electronegativity of the substituents bonded to the tin. The stronger the electron attracting power of the substituents, the less the electron density around tin and the acceptor strength increases accordingly[19]. Consequently the  $RSnCl_3$  should have stronger electron acceptor strength and have stronger interaction with MeOH molecules.

Sn-Cl bond strength is also different in  $RSnCl_3$  and  $R_3SnCl$ . The unshared electron pairs of chlorine (in  $p_z$  orbital) may be donated to the empty d-orbitals of tin ( $d_{xz}$  and  $d_{yz}$  orbitals) and contribute to the decrease of the Sn-Cl bond length on

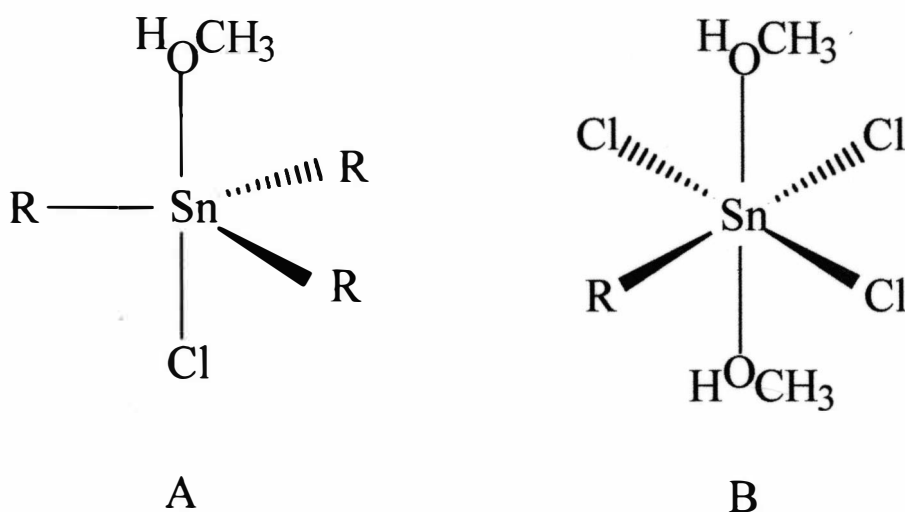


Figure 19. The Diagram of the Solvated Monoalkyltin Cation and Trialkyltin Cation in Methanol.  $R=CH_3$ ,  $n-C_4H_9$  and  $C_6H_5$ .

progressive chlorination of  $(\text{CH}_3)_4\text{Sn}$ . Increased  $p_\pi\text{-d}_\pi$  bonding and the increase of the electronegativity of the group  $\text{R}_n\text{SnCl}_{3-n}$  with increasing halogen substitution would both tend to decrease the polarity of the Sn-Cl bond. But the  $\pi$  bonding contribution is very weak and unable to counterbalance the electron withdrawal from tin by the inductive effect of the chlorine atoms. Actually the Sn-Cl bond polarity increases with increasing number of chlorine atoms. With the phenyltin chlorides, the overlapping of the  $\pi$ -electron system of the phenyl ring with the d-orbitals of tin and causes a decrease of the Sn-Cl bond polarity. While the Sn-C bonds are much less polar [7]. So in polar solvent like MeOH, the Sn-Cl bond may break more easily compared with Sn-C bond under the attack of MeOH or  $\text{MeO}^-$ . This kind of nucleophilic substitution is the most characteristic property of the organo-tin halides. At same condition, the Sn-Cl in  $\text{R}_3\text{SnCl}$  could be broken easier than that in  $\text{R}_2\text{SnCl}_2$ . So it is possible for  $\text{R}_2\text{SnCl}_2$  to keep Sn-Cl while  $\text{R}_3\text{SnCl}$  can not.

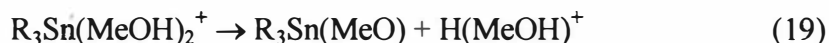
Since there are no free ions like  $\text{Sn}^+$ ,  $\text{SnCl}^+$ ,  $\text{R}_2\text{Sn}^{2+}$  and  $\text{R}_3\text{Sn}^+$  in organo-tin methanol solution, there must be a complicated ionization process. First the loosely bounded solvent molecules around the organo-tin molecule will evaporate or be removed till the inner shell molecules or atoms are exposed.  $\text{R}_2\text{SnCl}_2$  and  $\text{R}_3\text{SnCl}$  take the same process described by equation (16) and (17).



As shown in Figure 21,  $\text{R}_3\text{SnCl}(\text{MeOH})$  has trigonal bipyramidal structure and  $\text{R}_2\text{SnCl}_2(\text{MeOH})_2$  has octahedral structure. The cleavage of Sn-Cl bond is related to

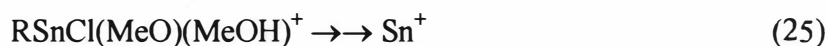
the nucleophilic attack of solvent molecule, which is a  $S_N2$  processes and requires the structure conversion. With Cl located at the apex of the trigonal bipyrimidal, it is easier to make the structure conversion and substitution. Also, Sn-Cl bond is more polar in  $R_3SnCl$  than that in  $RSnCl_3$ .  $R_3SnCl$  might break Sn-Cl bond before the reduction of Sn(IV).  $RSnCl_3$  might break two of the three Sn-Cl bonds and keep the third one, because there is a R-Sn bond opposite the Sn-Cl bond in the plane. This might be the reason for the higher intensity of  $R_3SnCl$  than that of  $RSnCl_3$ .

So for  $R_3SnCl$ , the Cl will be replaced by MeOH. And then the reduction results from the dissociation of MeOH and R-Sn bond. The mechanism might be described by equation (18) to equation (21). Equation (21) designates the process from  $R_3Sn^+$  to  $Sn^+$ . It is not that simple. It likely includes complicated processes about charge reduction and alkyl group elimination. The specific processes are not clear yet because of a lack of detailed data. According to previous discussions on the reduction of Group II metal ions, the reduction of Sn(IV) should take place through elimination of alkyl group and coordinated solvent molecules.



For  $RSnCl_3$ , two of the three chlorine atoms might be replaced and the last one left because of the unfavorable structure for substitution. Further ionization processes were represented by equation (22) to equation (25). Again the production

of  $\text{Sn}^+$  and  $\text{SnCl}^+$  is also complicated. A detailed description will depend on future experiments.



Compared with results on tributyltin presented by Magi et al with LC-PB-MS[1] and electron impact as ionization source, our results are similar to theirs at low mass to charge ratio. However their high end peaks, such as  $\text{C}_4\text{H}_9\text{Sn}^+$ , were not observed. Our results are also similar to Corr's [2] results of tributyltin with ion spray mass spectrometry at high declustering potential. This indicates that the interface or ionization condition we used was too harsh. All the organo-tin compounds were fragmented and declustered. Considering this point, we can only conclude that the length of the alkyl chain may have effects on the ionization process, but not significant. To distinguish their effects, the distance between the needle and the endplate should be decreased. The electric field between the endplate and the skimmer which is important to collision induced dissociation should also be decreased. Under softer conditions, the difference maybe determined.

In summary,  $\text{Sn}^{4+}$  is not ionizable in methanol. Monoalkyltin can be ionized, but tin is reduced and organo-tin cations are fragmented. Trialkyltin can be ionized more efficiently, but organo-tin cations are also fragmented and reduced. The results suggest that more alkyl groups will help ionization efficiency, but result in easier



reduction. Solvent plays a critical role in ionization process as it will affect both the intensity of the signal and the product of the ionization processes.

### Organo-Mercury Compounds

Pure metallic mercury is not as toxic as mercury vapor and soluble mercury compounds, which are highly poisonous. The mercury reaches man mainly in food. Bacteria can convert metallic mercury into methylmercury, a form in which it is highly poisonous. Mercury is concentrated up the food chain as bigger fish eat smaller fish that have eaten still smaller fish that contained mercury.

Harrington et al. [11] developed method based on HPLC(high performance liquid chromatography)/APCI(atmospheric pressure ionization mass spectrometry). In their experiments, organo-mercury compounds were first separated by HPLC and then detected by APCI MS. Solvent clustered organo-mercury cations were produced in APCI MS. Other works were also based on a separation technique, GC or LC, and an elemental detection technique, such as ICP-MS.

The organo-mercury compounds include  $\text{RHgX}$  and  $\text{R}_2\text{Hg}$ . All  $\text{RHgX}$  and  $\text{R}_2\text{Hg}$  compounds have linear bonds. In solution, solvation effects may contribute to nonlinearity. Organo-mercury compounds studied here include methylmercury chloride, phenylmercury chloride and phenylmercury acetate. Different solvents such as methanol and acetonitrile were used. The results were shown in Figure 20 and 21.

In Figure 20, there are well-defined peaks shown from 213 to 219 that are equal to specific mercury isotope plus the mass of methyl group. The intensities of those peaks are proportional to the abundance of mercury isotopes. This proves that

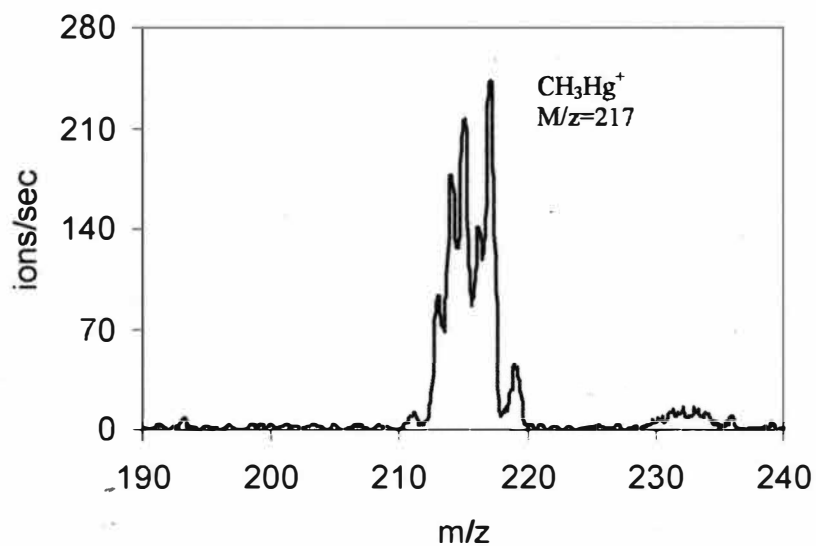


Figure 20. ESMS Spectrum of  $10^{-3}$  M  $\text{CH}_3\text{HgCl}$  in Methanol.

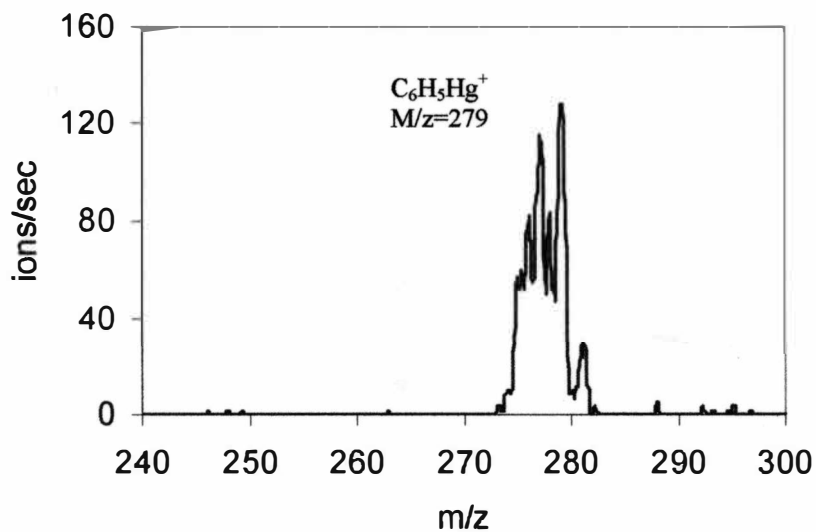


Figure 21. ESMS Spectrum of  $10^{-3}$  M  $\text{CH}_3\text{HgCl}$  in Methanol.

methylmercury remains intact during the electrospray ionization processes. No cluster and no reduction peaks were observed. This is better than the clustered results presented by Harrington et al [11]. The molecular form of methylmercury is directly detected, i.e. the ES-MS provide structural information on methylmercury. A solution of the same compound with acetonitrile as solvent gave no signal. It provided additional evidence of solvent effect on ionization processes.

The ionized product of phenylmercury acetate methanol solution was shown in Figure 21. Again, peaks are well defined with their intensities proportional to mercury isotope abundance. The  $m/z$  of those peaks were equal to the sum of the mass of phenyl group and the specific mass of mercury isotope. The whole cation remained intact. No clusters and no fragments were created. Methods based on this could provide structure information of organo-mercury compounds. In the spectrum of phenylmercury chloride, there were no peaks related to mercury observed. The difference in anion seems to affect the ionization processes, but to distinguish the effect, further experiments are required.

The results presented above show the advantages of application of ES on organo-mercury. Although direct quantitative analysis is still not available, ES-MS already showed powerful potential applications.

## CONCLUSION

According to results shown above, the following conclusions could be drawn. Organo-tin compounds with more alkyl groups will be ionized more efficiently, but will be reduced more easily. The type of alkyl groups does not have significant effect. Solvent plays a critical role in ionization process. It will affect both the intensity of signal and the product of the ionization processes. Anion might be important in the ionization process of organo-mercury compounds. Speciation of organo-mercury compounds with ESMS is possible.

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