

ANALYSIS OF METALS IN SOLUTION USING
ELECTROSPRAY IONIZATION MASS SPECTROMETRY

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Electrospray ionization-mass spectrometry (ES-MS) has gained most of its recent attention because of the ability to produce multiply charged ions from very large biomolecules making them amenable to analysis by most modern mass spectrometers. However, ES-MS is equally well suited for compounds of low or moderate molecular weight that are difficult to volatilize intact by other methods. Moreover, the early work of Fenn and co-workers (1,2) and recent reports by Kebarle and co-workers (3,4) attest to the applicability of ES-MS to the study of the gas-phase chemistry of multiply solvated or coordinated metal ions. The utility of ES-MS for the analysis of metals in solution derives in part from the facility with which the metal ions are solvated by or form complexes with the ES solvent or other reagents added to the solvent. Solvation and complexation can be a hindrance, however, in the analytical application of ES-MS to the analysis of metals in solution, especially solutions of metals in water.

The data presented here demonstrate that many of the problems in the ES-MS analysis of metals can be overcome by complexing the metals with crown ethers and/or extracting the metals from water into an organic phase using crown ethers. This procedure, in addition to transferring the metals to a solvent more amenable to the spraying process, concentrating the metals by reduction in solvent volume (thereby lowering detection limits), and providing the possibility of preferential metal complexation/extraction, usually results in the observation of a single metal-ligand complex of the same charge as the metal in solution when using the appropriate crown ether for the metal(s) of interest.

The data described in this paper were acquired on an ES/ion trap mass spectrometer combination that has been described previously (5). All reagents were obtained from commercial suppliers and used without further purification and all solvents used were HPLC grade. Methanol/water soluble metal salts were used to prepare standard solutions of the metals in water and methanol. Standard solutions of the crown ethers were prepared in toluene.

One of the major problems faced in the analytical application of ES-MS to metal analysis is the formation of metal-solvent adduct ions. These adducts complicate the spectra and spread the analyte signal out over several ionic species thereby raising detection limits. This problem is less severe for singly charged species such as the alkali metals, but for multiply charged species the problem can be quite pronounced. Another problem in the analysis of metals is the loss of charge state information. That is, the charge state of the metal in solution is not always preserved in the gas-phase. As Kebarle and co-workers (3,4) have pointed out, charge reduction of a particular metal ion depends on the relative ionization energies of the metal ions and ES solvents employed. The ES mass spectrum of UO_2^{2+} demonstrates this phenomenon. In this spectrum (not shown), UO_2^+ and other singly charged species are observed rather than UO_2^{2+} , which is the ionic species in solution.

The first of these problems, and possibly the second, can be largely overcome by complexing the metals in solution with a crown ether such as 12-crown-4 or dibenzo-18-crown-6 (see Figure 1). For example, the ES spectrum of Na^+ sprayed from methanol (Figure 2) is complicated by the presence of adduct ions containing both water and methanol. The ES spectrum in Figure 3, obtained from the same solution after addition of the complexing agent dibenzo-18-crown-6, contains only one peak, which corresponds to the Na-crown complex. It should be pointed out that the affinity of dibenzo-18-crown-6 for other metals ions, for example Ba^{2+} and Ca^{2+} , is much less than for Na^+ . Also, for these two particular multiply charged metal ions, 2:1 and 3:1 crown:metal complexes are observed in the ES spectrum rather than the 1:1 complex. However, formation of a 1:1 complex for most metals is probably possible since a large number of crown ethers have been synthesized that are selective for specific metal ions or sets of metal ions.

The selective nature of crowns for particular metal ions can be used to selectively extract metal ions from aqueous solutions into an organic solvent for analysis by ES-MS. The spectrum in Figure 4 was obtained from the toluene extract of a water/ HNO_3 solution containing each of the alkali metals using 12-crown-4 as the complexing agent. The peaks indicative of several of the metals present in the water solution, namely peaks from the Li-, Na-, and K-crown complexes, are observed. It should be pointed out that no signal from the metal ions could be observed when spraying the water/ HNO_3 solution. The spectrum obtained from the extract is complicated by the presence of H^+ , H_3O^+ , and MeOH_2^+ -crown complexes. However, this problem might be alleviated by adjustment of solution pH. More importantly, the Cs- and Rb-complexes are not observed since the affinity of 12-crown-4 for these ions is very low. Other crowns could be used to selectively extract these metal ions versus the other alkali metals in the mixture.

We have also begun to investigate the MS/MS behavior of the metal-crown complexes. Initial results indicate that certain of the 1:1 metal-crown complexes dissociate by loss of the neutral crown with the charge remaining with the metal. Results for complexes where the crown:metal ratio was greater than 1:1 show successive losses of the neutral crowns from the metal. Based on these results, it appears that MS/MS spectra of a series of metal-crown complexes using a single crown and/or a single metal with several different crowns might be used to determine the relative gas-phase affinities of selected metals and selected crowns. Also, the data from the MS/MS spectra might be used to determine successive metal ion-crown bond energies.

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