ELECTROSPRAY MASS SPECTROMETRY OF BORANE SALTS: MAXIMUM RESULTS WITH MINIMAL EFFORT

Cornelis E.C.A. Hop,* Dovas A. Saulys, Adam N. Bridges,
Donald F. Gaines and R. Bakhtiar+

Department of Chemistry, University of Wisconsin-Madison,1101 University Avenue,
Madison, WI 53706, USA

Abstract

Data are presented to show that electrospray ionization mass spectrometry can be used on a routine basis to analyze a wide variety of borane salts (e.g. $[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]$, $[(Ph)_3PMe][B_{11}H_{14}]$, $Na[B_{10}H_{13}]$, $Na_2[B_{12}H_{11}SH]$ and $[(Et)_4N][B_{12}H_{10}(SCN)_2]$). The ESI mass spectrum provides the molecular weight of the anion as well as the cation and the isotope pattern of the signals reveals the number of boron atoms in the anion. In addition, the detection limit for analysis of borane salts via electrospray is less than 1 microgram.ml^{-1}.

Introduction

Anionic boron hydride clusters (borane anions) constitute a substantial group containing some of the most reactive as well as some of the most stable boron hydride cluster species. Many of the more reactive borane anions are important precursors for the syntheses of larger homo- and heteroatom cluster species.[1] Because of their ionic properties, borane anion salts have not been successfully analyzed by electron impact or chemical ionization mass spectrometry. Liquid secondary ion mass spectrometry is not feasible in most cases because borane anions generally appear in the mass range dominated by the matrix, and many borane anions are expected to react with typically used matrices. We have recently found that electrospray ionization (ESI)[2] is very useful for mass spectral analysis of borane anion salts.[3,4] ESI is a mild, solvent-based ionization technique, which does not generally give rise to solvent signals. In addition, this ionization technique is very sensitive.

---

* Dedicated to Professor S.G. Shore in recognition of his outstanding contributions to boron chemistry.

+ Permanent address: Merck Research Laboratories, P.O. Box 2000, Rahway, NJ 07065

Our initial investigations have shown[3] that acetonitrile solutions of well known borane salts, such as $(Me)_4N][B_3H_8]$, $Cs[B_3H_8]$, $Cs_2[B_{10}H_{10}]$ and $Na_2[B_{12}H_{12}]$ give rise to ESI mass spectra that characterize both the anion and the cation. In the negative ion mode all signals correspond to anionic clusters of ions (henceforth called cluster ions) having the general formula $\{[\text{cation}^{m+}]_x[\text{anion}^{n-}]_y\}^{(ny-mx)-}$. In contrast, ESI mass spectra of methanol solutions of $B_3H_8^-$ salts do not exhibit cluster ions containing B_3 units, but only $B(OCH_3)_4^-$ cluster ions,[4] indicative of an electrochemical reaction in the electrospray needle.[5] We report herein ESI mass spectral data to illustrate applications of this extremely valuable technique for identification of a wide variety of borane salts, including several that are quite air sensitive. We also provide an example to show the sensitivity of the ESI technique in mass spectral analysis.

Experimental

Mass Spectrometry: A VG AutoSpec triple sector (EBE) mass spectrometer, equipped with the Mark II electrospray source,[6] was used to obtain all regular ESI mass spectra. The Mark II ESI source has (1) an all-steel needle, (2) a pepper-pot style counter electrode, (3) a larger orifice for the sampling cone, (4) increased pumping capacity and (5) a hexapole focusing unit to improve sensitivity and ease of use. All experiments were performed in the negative ion mode and with a

---

Table 1. List of borane salts examined, including references for their synthesis.

$Cs[B_3H_8]$	1	$[(Ph)_3PMe][B_{11}H_{14}]$	5
$[(Me)_4N][B_3H_8]$	1	$[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]$	6
$[(n\text{-}Bu)_4N][B_3H_8]$	1	$Na_2[B_{12}H_{12}]$	7
$Cs_2[B_{10}H_{10}]$	2	$Na_2[B_{12}H_{11}SH]$	8
$Na[B_{10}H_{13}]$	3	$Na_2[^{10}B_{12}H_{11}SH]$	9
$[C_{14}H_{19}N_2][B_{10}H_{13}]$	4	$[(Et)_4N][B_{12}H_{10}(SCN)_2]$	10

(1) W.J. Dewkett, M. Grace, and H. Beall, *Inorg. Syn.* **1974**, *15*, 115. (2) M.F. Hawthorne and R.L. Pilling, *Inorg. Syn.* **1967**, *9*, 16. (3) M.F. Hawthorne, A.R. Pitochelli, R.D. Strahm, and J.J. Miller, *J. Am. Chem. Soc.* **1960**, *82*, 1825. (4) T. Onak, G. Rosendo, G. Siwapinyoyos, R. Kubo, L. Kiauw. *Inorg. Chem.* **1979**, *18*, 2943. (5) T.D. Getman, J.A. Krause, and S.G. Shore, *Inorg. Chem.* **1988**, *27*, 2938. (6) A.N. Bridges, R.K. Hayashi, and D.F. Gaines, *Inorg. Chem.* **1994**, *33*, 1243. (7) E.I. Du Pont De Nemours and Co., Wilmington, Del. (8) W.F. Bauer, Idaho National Engineering Laboratory, Idaho Falls, ID. (9) Boron Biologicals, Inc., Raleigh, NC. (10) D.F. Gaines and J.H. Morris, unpublished results.

resolution of 1,250 (5% valley definition) to obtain maximum signal strength. The sampling cone voltage was kept low for all experiments, because at higher sampling cone voltages fragmentation of relatively weakly bound species, such as our cluster ions, can occur. (For more details see refs. 3 and 4.) The samples were dissolved (200 $ng.ul^{-1}$) in acetonitrile or tetrahydrofuran (THF) and the flow rate was 15 $ul.min^{-1}$. Nitrogen was used as both the nebulizer gas (16 $l.hr^{-1}$) and the bath gas (400 $l.hr^{-1}$; 40 C). A Sciex API III Plus triple quadrupole mass spectrometer was used to obtain MS/MS mass spectra for cluster ions from $[(Ph)_3PMe][B_{11}H_{14}]$. The sample was dissolved (300 $ng.ul^{-1}$) in acetonitrile and the flow rate was 2.5 $ul.min^{-1}$. Nitrogen was used as the nebulizer gas and the curtain gas; Ar was the collision gas. (For more details see ref. 7.)

Materials: Anhydrous acetonitrile in a Sure/Seal™ bottle was purchased from Aldrich. THF was distilled from sodium under nitrogen. The list of borane salts examined, including references for their synthesis, is presented in Table 1. Details about the ESI mass spectra of acetonitrile solutions of $(Me)_4N][B_3H_8]$, $Cs[B_3H_8]$, $[(n\text{-}Bu)_4N][B_3H_8]$, $Cs_2[B_{10}H_{10}]$ and $Na_2[B_{12}H_{12}]$ have been presented in ref. 3.

Results and Discussion

The ESI mass spectrum of an acetonitrile solution of $[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]$ is presented in Figure 1. The spectrum is dominated by the signal centered at m/z 217,[8] which corresponds to the intact $B_{11}H_{13}\text{-}C_6H_{13}^-$ anion. The inset in figure 1 shows an expansion of the region around m/z 217; the observed isotope pattern for this ion matches the pattern calculated for the $B_{11}H_{13}\text{-}C_6H_{13}^-$ anion. All other signals in the mass spectrum correspond to cluster ions having the general formula $\{[(Ph)_3PMe]_x[B_{11}H_{13}\text{-}C_6H_{13}]_{x+1}\}^-$. For example, the signal centered at m/z 711 [8] corresponds to $\{[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]_2\}^-$. Thus, a wealth of information is available from the ESI mass spectrum: (1) the signal at the lowest m/z value (m/z 217) provides the molecular weight of the anion, (2) the isotope pattern of the signal reveals how many boron atoms are present in the anion and (3) the separation between the two signals at the lowest m/z values (m/z 217 and 711) provides the molecular weight of the anion plus cation. Thus the nature of both the anion and the cation are confirmed.

The ESI mass spectrum of an acetonitrile solution of $[(Ph)_3PMe][B_{11}H_{14}]$ (Figure 2) displays characteristics similar to those of $[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]$. The spectrum is dominated by signals centered at m/z 133,[8] $B_{11}H_{14}^-$, and signals corresponding to $\{[(Ph)_3PMe]_x[B_{11}H_{14}]_{x+1}\}^-$ anions are visible as well. The variation in intensity among the latter signals is noteworthy; for example, the signal due to $\{[(Ph)_3PMe]_3[B_{11}H_{14}]_4\}^-$, m/z 1363,[8] is about twice as intense as that due to $\{[(Ph)_3PMe]_2[B_{11}H_{14}]_3\}^-$, m/z 953.[8] If ion cluster formation were entirely a concentration effect, the intensities of the cluster ions should decrease with increasing mass. Thus, the

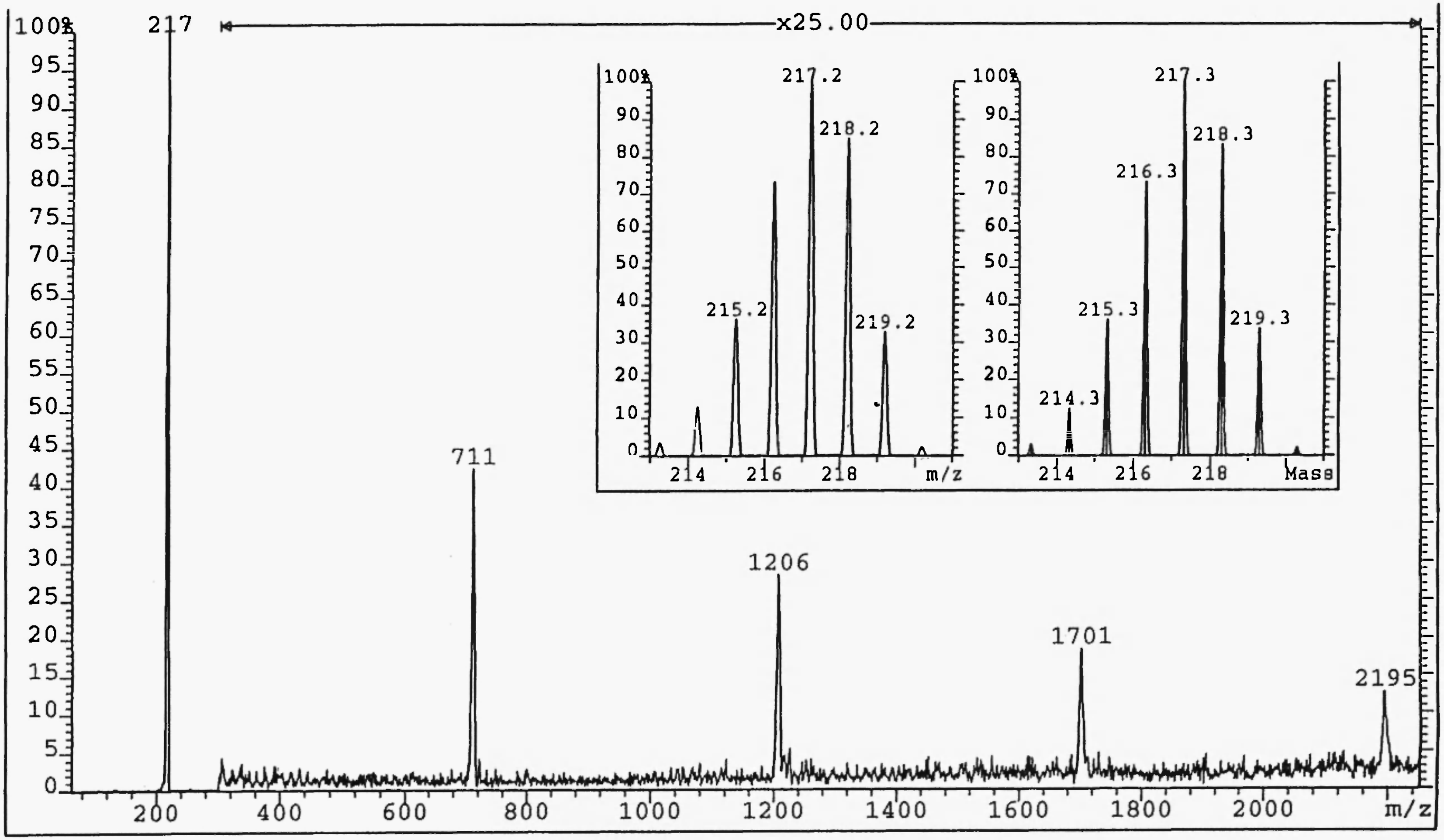

Figure 1. The negative mode ESI mass spectrum of $[(Ph)_3PMe][B_{11}H_{13}\text{-}C_6H_{13}]$ in acetonitrile. Inset: experimental vs. theoretical isotope pattern of the $B_{11}H_{13}C_6H_{13}^{-}$ ion.

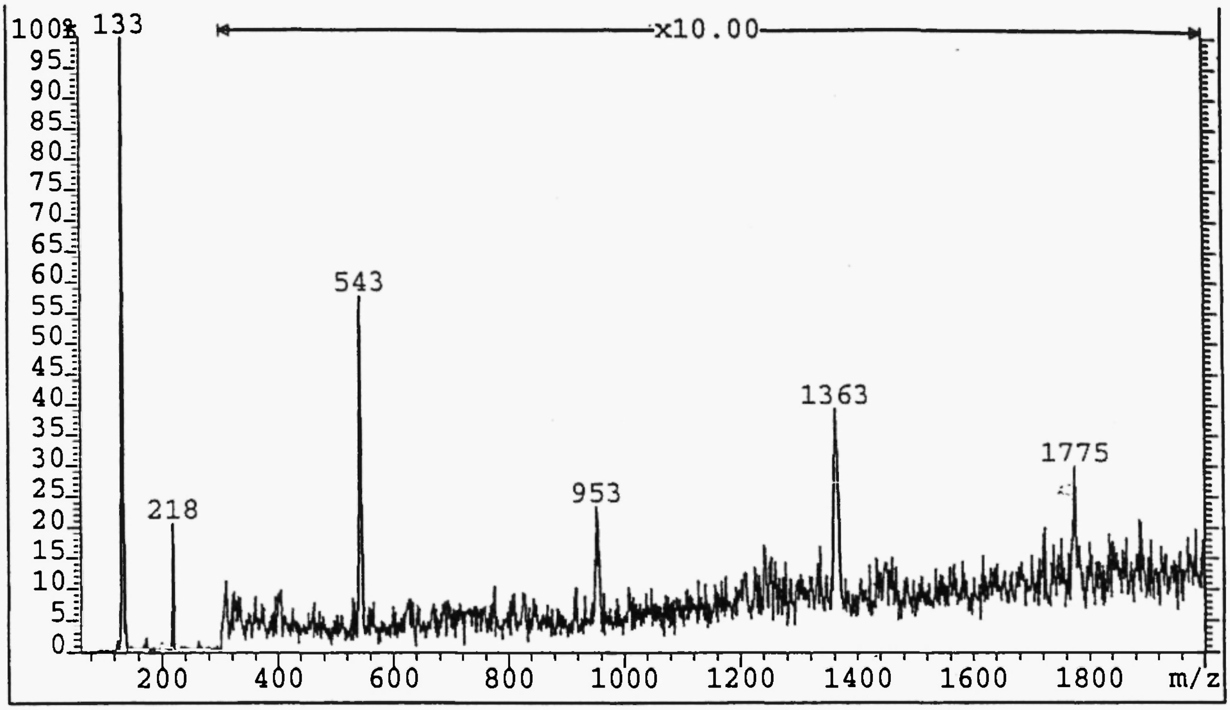

Figure 2. The negative mode ESI mass spectrum of [$(Ph)_3PMe$][$B_{11}H_{14}$] in acetonitrile.

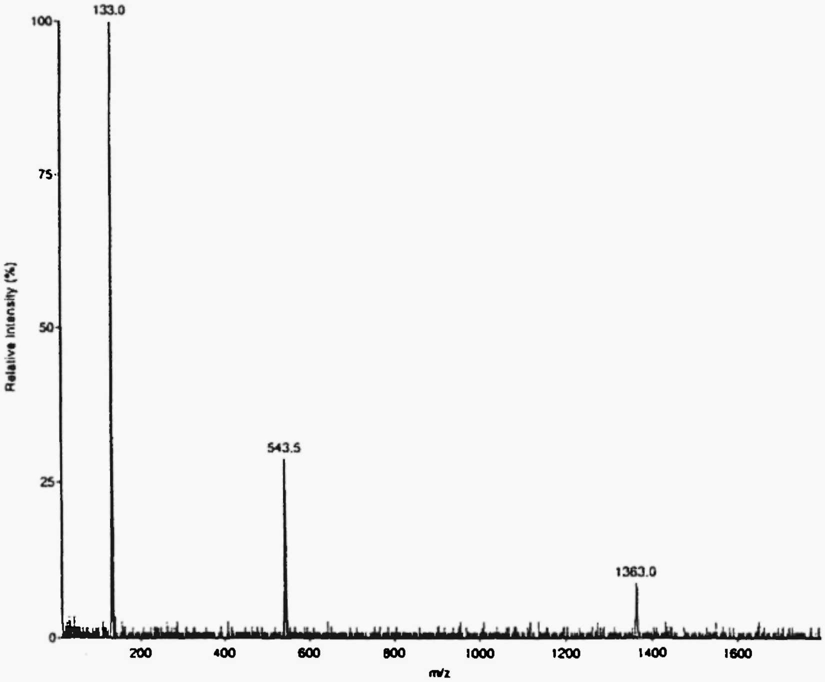

Figure 3. The negative mode ESI MS/MS mass spectrum of m/z 1775 from [$(Ph)_3PMe$][$B_{11}H_{14}$] with acetonitrile as solvent. See text for details.

observed intensity variation described above suggests that generation of certain cluster ions is favored, for indeterminate reasons, in our ESI source. A similar phenomenon is observed when MS/MS mass spectra are obtained by mass selecting a specific cluster ion and observing the fragments generated by collision with an inert target gas. For example, Figure 3 shows the MS/MS mass spectrum of $\{[(Ph)_3PMe]_4[B_{11}H_{14}]_5\}^-$, m/z 1775. In this experiment the fragment ions $\{[(Ph)_3PMe]_3[B_{11}H_{14}]_4\}^-$ (m/z 1363) and $\{[(Ph)_3PMe]_1[B_{11}H_{14}]_2\}^-$ (m/z 543) were produced, whereas $\{[(Ph)_3PMe]_2[B_{11}H_{14}]_3\}^-$ ions (m/z 953) were not observed. The stability (kinetic and/or thermodynamic) of the various cluster ions governs their intensity in regular and MS/MS mass spectra. The same effect was also observed in ESI and MS/MS mass spectra of $Cs[B_3H_8]$, $(Me)_4N][B_3H_8]$, $Cs_2[B_{10}H_{10}]$ and $Na_2[B_{12}H_{12}]$ (see ref. 3).

The negative mode ESI mass spectrum of $Na[B_{10}H_{13}]$, an air and water sensitive compound, is shown in Figure 4. The signal centered at m/z 121[8] is ascribed to $B_{10}H_{13}^-$ and most other signals in the spectrum can be assigned to cluster ions, $\{Na_x[B_{10}H_{13}]_{x+1}\}^-$. There is close agreement between the observed and calculated isotope patterns, as shown in the inset of the $\{Na[B_{10}H_{13}]_2\}^-$ signals, which confirms the identity of the ions. Note that each signal is accompanied by a small satellite peak at 16 Da higher mass, which likely corresponds to an uncharacterized oxidation product.

The negative ion mode ESI mass spectrum of an acetonitrile solution of $Na_2[B_{12}H_{11}SH]$ is shown in Figure 5. Again, clustering is observed. As for $Na_2[B_{12}H_{12}]$, multiply charged cluster ions are generated. For example, m/z 306 corresponds to $\{Na_4[B_{12}H_{11}SH]_3\}^{2-}$. $B_{12}H_{11}SH^{2-}$ (m/z 87) is visible as well and the signal at m/z 141 is ascribed to $B_{12}H_{11}^-$, generated by in-source collision-induced fragmentation. (The intensity of fragment ions can be increased by increasing the sampling cone voltage.) The signal-to-noise ratio of m/z 197, $\{Na[B_{12}H_{11}SH]\}^-$, is about 200:1. As for all boron containing species, the signal-to-noise ratio is clearly limited by the presence of two boron isotopes, ^{10}B (19%) and ^{11}B (81%), which causes the $\{Na[B_{12}H_{11}SH]\}^-$ signal to be spread out over several masses. To avoid this problem in this case, ESI experiments were performed with $Na_2[^{10}B_{12}H_{11}SH]$. This compound is commercially available and it is one of the many ^{10}B labeled compounds used in boron neutron capture therapy.[9] At a concentration of 2.04 ng.ul^{-1} (9.71 x 10^{-6} mol.l^{-1}) the signal at m/z 187, $\{Na[^{10}B_{12}H_{11}SH]\}^-$, is still by far the most intense signal in the mass spectrum and the observed isotope pattern matches that obtained using a much higher concentration, e.g. 204 ng.ul^{-1}. Unfortunately, at low concentration several signals appear in the mass spectrum due to impurities in the acetonitrile, which is notoriously hard to purify.[10] Recently, it was shown that the detection limit by high-performance liquid chromatography is 0.5 ng.ul^{-1}.[11] Thus, in terms of sensitivity ESI mass spectrometry can

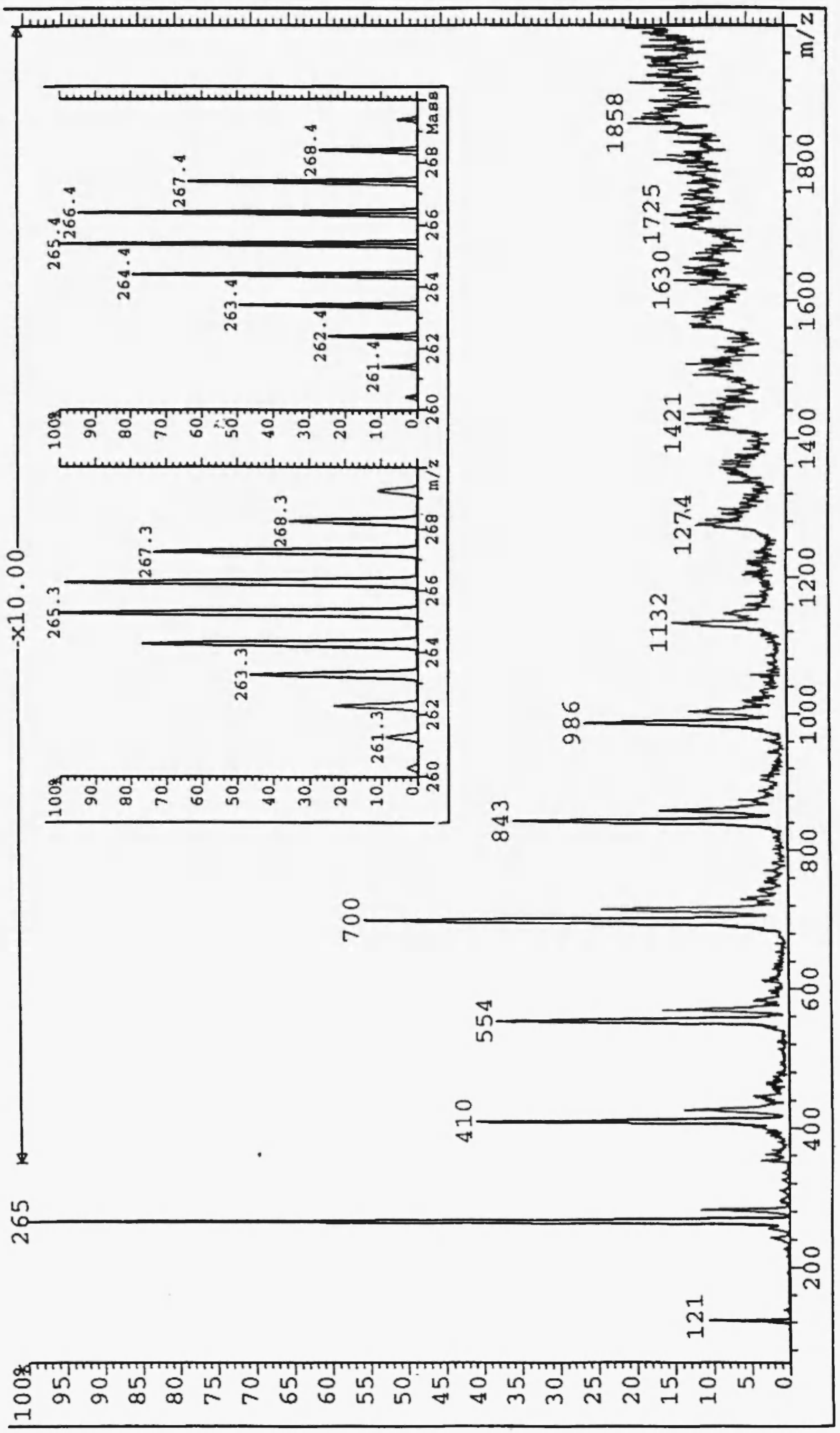

Figure 4. The negative mode ESI mass spectrum of $Na[B_{10}H_{13}]$ in THF. Inset: experimental vs. theoretical isotope pattern of $\{Na[B_{10}H_{13}]_2\}^-$.

compete with conventional analytical methods and it has the advantage that it provides specific molecular weight information.

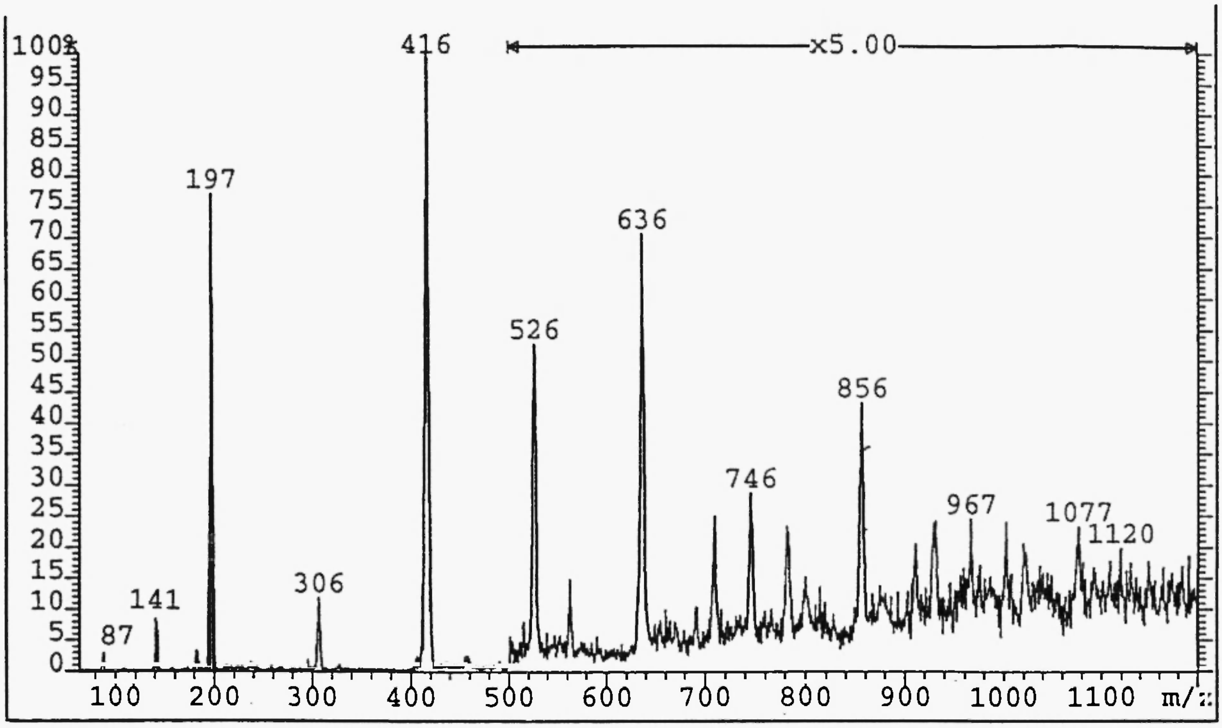

Figure 5. The negative ion mode ESI mass spectrum of $Na_2[B_{12}H_{11}SH]$ in acetonitrile.

Summary

Electrospray mass spectrometry is a valuable technique for analysis of borane salts, and has been shown to be applicable to borane salts that are very moisture and/or air sensitive. For analysis dilute solutions of the borane salts are prepared in an appropriate, inert solvent (e.g. acetonitrile or THF) and electrosprayed into the mass spectrometer. The ESI mass spectral data are available in a matter of minutes, and provide the molecular weight of the anion and the cation, while the isotope pattern of the cluster ion envelope signals reveals the number of boron atoms in the anion. The sensitivity is an added advantage of this analytical technique. For example, the detection limit for $Na_2[^{10}B_{12}H_{11}SH]$ is substantially less than 2.04 $ng.ul^{-1}$

Acknowledgments

The authors thank the University of Wisconsin Graduate Research Foundation and the National Science Foundation (grants CHE-9304546, CHE-9305922 and DMR-9121074) for financial support. The authors are also grateful to Dr. W.F. Bauer for donating $Na_2[B_{12}H_{11}SH]$.

Supplementary Material

Mass spectra of all compounds, including expansions of particular regions to observe isotope patterns, can be obtained from the authors upon request.

References

1. (a) E.L. Muetterties, Ed., *Boron Hydride Chemistry*; Academic Press: New York, 1975. (b) R.N. Grimes, Ed., Metal *Interactions with Boron Clusters*; Plenum Press: New York, 1982. (c) J.F. Liebman, A. Greenberg and R.E. Williams, Eds., *Advances in Boron and the Boranes*; VCH Publishers, Inc.: New York and Weinheim, 1988.
2. See e.g. (a) J.B. Fenn, M. Mann, C.K. Meng, S.F. Wong and C.M. Whitehouse, *Science*, **1989**, *246*, 64. (b) R.D. Smith, J.A. Loo, C.G. Emonds, C.J. Baringa and H.R. Udseth, *Anal. Chem.* **1990**, *62*, 882. (c) R.D. Smith, J.A. Loo, R.R. Ogorzalek-Loo, M. Busman and H.R. Udseth, *Mass Spectrom. Rev.* **1991**, *10*, 359.
3. C.E.C.A. Hop, D.A. Saulys and D.F. Gaines, *Inorg. Chem.* **1995**, *34*, 1977.
4. C.E.C.A. Hop, D.A. Saulys and D.F. Gaines, *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 869.
5. (a) G.J. van Berkel, S.A. McLuckey and G.L. Glish, *Anal. Chem.* **1991**, *63*, 1098. (b) G.J. van Berkel, S.A. Mcluckey and G.L. Glish, *Anal. Chem.* **1992**, *64*, 1586. (c) X. Xu, S.P. Nolan and R.B. Cole, *Anal. Chem.* **1994**, *66*, 119. (d) A. Dupont, J.-P. Gisselbrecht, E. Leize, L. Wagner and A. van Dorsselaer, *Tetrahedron Lett.* **1994**, *35*, 6083.
6. (a) A.R. Woolfitt, J. Pugh and P.A. Bott, *Proceedings of the 42nd ASMS Conference on Mass Spectrometry and Allied Topics*, Chicago, IL, May 29-June 3, 1994; p 759. (b) K. Eckart and J. Spiess, *J. Am. Soc. Mass Spectrom.* **1995**, *6*, 912.
7. R. Feng, Y. Konishi and A.W. Bell, *J. Am. Soc. Mass Spectrom.* **1991**, *2*, 387.
8. For brevity, all the cluster ions are identified by their average m/z values, rather than their m/z distribution.
9. See e.g. (a) M.F. Hawthorne *Pure Appl. Chem.* **1991**, *63*, 327 and references therein. (b) M.F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 950 and references therein.
10. J.J. Kirkland, *J. Chromatogr. A* **1995**, *715*, 199.
11. P. Saini, K. Abu-Izza and D.R. Lu, *J. Chromatogr. B* **1995**, *665*, 155.