

STRUCTURAL ANALYSIS OF ORGANOMETALLIC COMPOUNDS WITH SOFT IONIZATION MASS SPECTROMETRY

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The analysis of organometallic compounds with mass spectrometry has some special features in comparison with organic and bioorganic compounds. The first step is the choice of a suitable ionization technique, where the electrospray ionization is certainly the best possibility for most classes of organometallic compounds and metal complexes. Some ionization mechanisms of organometallic compounds are comparable to organic molecules, such as protonation/deprotonation, and adduct formation with sodium or potassium ions; however, in many cases, different mechanisms and their combinations complicate the spectra interpretation. Organometallics frequently undergo various types of adduct and polymerization reactions that result in significantly higher masses observed in the spectra in comparison to molecular weights of studied compounds. Metal elements typically have more natural isotopes than common organic elements, which cause characteristic wide distributions of isotopic peaks; for example, tin has ten natural isotopes. The isotopic pattern can be used for the identification of the type and number of metal elements in particular ions. The ionization and fragmentation behavior also depend on the type of metal atom; therefore, our discussion of mass spectra interpretation is divided according to the different type of organometallic compounds. Among various types of mass spectrometers available on the market, trap-based analyzers (linear or spherical ion-traps, Orbitrap) are suitable to study complex fragmentation pathways of organometallic ions and their adducts, whereas high-resolution and high-mass accuracy analyzers (time-of-flight-based analyzers, or Fourier transform-based analyzers—Orbitrap or ion cyclotron resonance mass spectrometers) provide accurate masses applicable for the determination of the elemental composition of individual ions. © 2010 Wiley Periodicals, Inc., Mass Spec Rev 30:1013–1036, 2011

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I. INTRODUCTION

Organometallic compounds are defined as molecules that consist of an organic part, with one or more metal elements incorporated into their structure. In general, organometallic compounds

consist of at least one covalent bond between carbon and metal atoms (Mehrotra & Singh, 2004). If the metallic character of non-metallic elements, such as boron, silicon, arsenic, selenium, and tellurium, is also taken into consideration, then this definition might be extended to the statement that organometallic compounds contain a carbon atom bonded to elements that are more electropositive than carbon itself (Pruchnik, 1990). Moreover, so-called metal complexes that contain the central metal surrounded by ligands bounded to this metal ion by a coordination covalent bond (donor–acceptor) can be considered as well (Garnovskii, Vasilchenko, & Garnovskii, 2003). These complexes are often formed by the metal complexation with amino acids, sugars, and drugs (Alvarez, Vartanian, & Brodbelt, 1997; Vaisar et al., 2005; Fournier et al., 2008). Their gas-phase ion-molecule reactions are often studied (Gatlin & Tureček, 1997; Lemr, Holčápek, & Jandera, 2000; Asmis & Sauer, 2007; Di Marco et al., 2007; MacAleese & Maitre, 2007; Mo et al., 2007; Tureček, 2007; Burgert & Schnockel, 2008; Jirásko et al., 2008; Polfer & Oomens, 2009). The most famous metal complexes are even naturally occurring, such as chlorophyll (Mg), hemoglobin (Fe), and myoglobin (Fe), and their presence in living organisms is indispensable (Wöhrle & Pomogailo, 2003). Nevertheless, metal complexes or gas-phase reactions are not the main subject of this review, and will be not further discussed.

The first organometallic compound, tetramethyldiarsine (Cacodyl), was prepared by Louis Claude Cadet in 1760 (Mehrotra & Singh, 2004). Although many other compounds were synthesized later, the remarkable growth of organometallic chemistry was started during the second half of the 20th century. Due to many applications in the catalytical, agricultural, and pharmaceutical industries, organometallics have significantly contributed to the scientific progress (Halpern, 2001), as proved by four Nobel prizes for chemistry awarded in 1912 (Victor Grignard and Paul Sabatier), 1963 (K. Ziegler and G. Natta), 1973 (G. Wilkinson and E. O. Fischer), and 2005 (Y. Chauvin, R. Grubbs, and R. Schrock) (<http://nobelprize.org>). The most important properties of these compounds become apparent, their participation in many stoichiometric and catalytical reactions (e.g., cross-coupling reactions) are used to implement different chemical groups into the molecular structure. Mainly transition-metal complexes, but also organometallics with bismuth, antimony, tin, and other metals, are used for this purpose (Rao et al., 2002; Hocek, 2003; Netherton & Fu, 2004; Yasuie et al., 2005). Organotin compounds are also used as stabilizers of rigid polyvinyl chloride against photochemical and thermal transformations (Kizlink, 1996). It is also worth mentioning the applications in photocatalytical and asymmetrical reactions (Noyori, 2002; Yasuie et al., 2005).

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Concerning biological applications, early studies even reveal an anticancer activity of some organometallics. However, many of them are usually perceived as being too toxic, and their applications for medicinal purposes are accepted only in fields where no viable therapy is available, such as organotin and organoantimony compounds (Norman, 1997; Gielen, 2002). On the other hand, the relatively low toxicity of organogermanium (Kaplan et al., 2004), organoruthenium compounds (Allardyce et al., 2005; Jaouen, Beck, & McGlinchey, 2006), various metallocenes (Ti, Nb, Mo, V) (Allardyce et al., 2005; Vinklársek et al., 2006), and also organic complexes with important essential transition-metals (Cu, Co) suggests their suitability in a variety of medical applications (Osinsky et al., 2004; Wang & Guo, 2006).

In addition to antitumor properties, some organometallic compounds exhibit activity against various types of bacteria. The biological studies proved that organotin compounds inhibit the growth of *Trypanosoma equiperdum*, causes sleeping-sickness (Susperregui et al., 1999); organorhodium and organoruthenium compounds have been found active against the malaria (*SanchezDelgado et al., 1996*); and leishmania can be cured with organoantimony compounds (Norman, 1997). Most organometallic compounds have an artificial character; however, few natural occurring organometallics can be found, too. Most widely known is cobalamin and methyl cobalamin (Jaouen, Beck, & McGlinchey, 2006).

Nowadays, a huge number of new organometallic compounds is synthesized annually; their biological properties are studied and require reliable analytical techniques for structure verification of new compounds and to monitor the reaction course of synthetic reactions. Established spectroscopic techniques for this purpose are mainly X-ray crystallography, nuclear magnetic resonance, and mass spectrometry (MS), which is strongly dependent on the type of ionization technique. In older works, the use of conventional electron (EI) and chemical ionization (CI) coupled with double-focusing magnetic sector or quadrupole analyzers (Bruce & Thomas, 1968; Hunt, Torian, & Russell, 1972; Efraty, Huang, & Weston, 1975; Gielen & Jurkschat, 1983) was quite common; nowadays, EI is almost completely replaced by soft ionization techniques, such as fast atom bombardment (FAB), matrix-assisted laser/desorption ionization (MALDI), and atmospheric pressure ionization techniques, especially electrospray ionization (ESI) is suitable for most classes of organometallic compounds including polar and ionic compounds. A survey of published articles with soft-ionization techniques, together with mass analyzer, is listed in Table 1.

The growing interest in the use of ESI to characterize organometallic species has emerged from the possibility to analyze highly diluted solutions and soft conditions for the ionization process (Colton, Dagostino, & Traeger, 1995; Henderson et al., 1998; Henderson, Nicholson, & McCaffrey, 1998; Stewart, 1999; Traeger, 2000; Henderson & McIndoe, 2005). ESI-MS allows the acquisition of mass spectra directly from the sample solution due to transferring ions from the liquid-phase to the gas-phase; therefore, it enables an easy coupling with high-performance liquid chromatography (HPLC) (Rosenberg, 2003). ESI-MS is ideally suited for the analysis of polar and ionic organometallic compounds, the characterization of their hydrolysis mechanisms (Henderson & Taylor, 1996; Lintschinger, Schramel, & Kettrup, 1998; Wei & Miller, 2001), their biological studies (e.g., metal interactions with biomolecules) (Yan et al., 2005), and even to screen short-lived reactive intermediates

involved in organometallic catalytic reactions (Plattner, 2001; Chen, 2003; Moreno-Manas et al., 2003; Guo et al., 2005; Pla-Quintana & Roglans, 2005; Chevrin et al., 2007; Santos, 2008). The soft character of ESI permits one to analyze organometallic complexes with weakly bound ligands (Bhaskar et al., 2005), and the possibility of cold-spray ionization techniques is offered for very labile compounds (Henderson & McIndoe, 2005). Mass spectra are relatively poor in fragment ions, which can be supported with in-source dissociation or tandem MS experiments (Traeger, 2000). Mass spectra of some non-polar organometallics can be measured with atmospheric pressure chemical ionization (APCI) or atmospheric pressure photoionization (APPI), as illustrated by several works (Ogo, Makihara, & Watanabe, 1999; Dorcier, Dyson, & McIndoe, 2003; Meurer et al., 2003; Rosenberg, 2003). MALDI is a method of choice to characterize polymeric species or dendrimers that contain metal elements because of the presence of mainly singly charged molecular adducts with a minimum fragmentation and the high-mass range accessible with a time-of-flight analyzer (Ferri et al., 1998; Xu et al., 2000; Arevalo et al., 2001; Royo & Brintzinger, 2002; Schumann et al., 2006). This technique is also suitable for mass spectrometric measurements of insoluble or low-soluble organometallic compounds (Wyatt, Stein, & Brenton, 2008).

II. INTERPRETATION OF MASS SPECTRA OF ORGANOMETALLIC COMPOUNDS

A. Basic Ionization Mechanisms of Organometallic Compounds

The character of organometallic ions observed in mass spectra depends on many factors, such as the type of ionization, polarity mode, values of applied voltages, solvents, and behavior of studied compounds.

The most important ionization mechanisms are summarized in the following text and in Table 2. One of the most common mechanisms of ion formation observed in the full-scan positive-ion mass spectra is the formation of sodium and potassium adducts ($[M + Na]^+$, $[M + K]^+$, $[2M + Na]^+$, $[2M + K]^+$), which are usually used to determine molecular weights (Henderson, Nicholson, & McCaffrey, 1998; Traeger, 2000; Kolářová et al., 2004). In general, the different metallation ($[M + Ag]^+$, $[M + Li]^+$, etc.) of organometallics can be observed, depending on particular ions present or added to the solution. Similarly, ammonium adducts $[M + NH_4]^+$ or $[2^*M + NH_4]^+$ are described for some organometallics (Dinger & Henderson, 1998, 1999; Pla-Quintana & Roglans, 2005). When ionic contaminants such as trimethyl- or triethyl-ammonium ions are present in the sample (from the synthesis) or mass spectrometer (from previous MS or HPLC/MS experiments), the ions $[M + (CH_3)_3NH]^+$ or $[M + (C_2H_5)_3NH]^+$ can be formed (Ang et al., 2006; Kilpin, Henderson, & Nicholson, 2007). Protonated molecules are also important for some organometallics that contain an appropriate ligand with a high proton affinity (Traeger, 2000), and even double-charged ions $[M + 2H]^{2+}$ are observed in case of a compound with possible double-protonation.

On the other hand, the most important ions observed in full-scan negative-ion mass spectra are deprotonated molecules $[M - H]^-$. Compounds that contain an ionic bond provide relatively simple spectra (Traeger, 2000; Fridrichová et al., 2009) with two complementary ions, depend on the polarity mode,

TABLE 1. The type of soft-ionization techniques together with mass analyzers used in organometallic analysis

Ion source	Mass analyzer	Metal present in organometallic compounds (references)
APCI	Q	<i>Fe</i> (Diehl & Karst, 2002) <i>Pt</i> (Mastrorilli et al., 2004)
APCI	QqQ	<i>Ge</i> (Takeuchi et al., 2006) <i>Si</i> (Takeuchi et al., 2006)
APCI	3D ion-trap	<i>Sn</i> (Bekri et al., 2006)
APCI	QqTOF	<i>Ti</i> (Meurer et al., 2003; Meurer et al., 2006)
ESI	Q	<i>Ag</i> (Rais et al., 2002) <i>As</i> (Pedersen & Francesconi, 2000) <i>Au</i> (Dinger & Henderson, 1998a, b; Dinger et al., 1998; Dinger & Henderson, 1999; Goss et al., 2003; Kilpin et al., 2007) <i>Cu</i> (Lipshutz et al., 1999) <i>Fe</i> (Alley & Henderson, 2001; Henderson & Alley, 2002) <i>Hg</i> (Nicholson & Whitley, 2004) <i>Ir</i> (Ozkar & Finke, 2004) <i>Pb</i> (Mester & Pawliszyn, 1999; Pham et al., 2007) <i>Pd</i> (Chevrin et al., 2007; Moreno-Manas et al., 2003; Pla-Quintana & Roglans, 2005) <i>Pt</i> (Mastrorilli et al., 2004) <i>Re</i> (Jiang et al., 2000) <i>Ru</i> (Wang et al., 2002; Yeo et al., 1999) <i>Sb</i> (Brown et al., 2006) <i>Sn</i> (Beckmann et al., 2002; Henderson & Taylor, 1996; Lawson et al., 1996; Yeo et al., 2001) <i>Te</i> (Beckmann et al., 2005)
ESI	QqQ	<i>As</i> (Florencio et al., 1997) <i>Co</i> (Alsberg et al., 2001) <i>Fe</i> (Bakhtiar & Kaifer, 1998; KaneMaguire et al., 1996; Murao et al., 2005; Quirke & Van Berkel, 2001; Tharamani et al., 2008) <i>Ge</i> (Lamb & Sweetman, 1996) <i>Ir</i> (Ogo et al., 1999) <i>Ge, Ni</i> (Goicoechea & Sevov, 2006b) <i>Mo</i> (Thompson et al., 2003) <i>Os</i> (Dyson et al., 2000) <i>Pb</i> (Aplin et al., 2002) <i>Ru</i> (Kriesel et al., 1998; Pelagatti et al., 2005) <i>Sb</i> (Lintschinger et al., 1998)

(Continued)

TABLE 1. (Continued)

		<i>W</i> (Thompson et al., 2003) <i>Zn</i> (Goicoechea & Sevov, 2006a)
ESI	3D ion-trap	<i>As</i> (Larsen et al., 2001) <i>B</i> (Dostál et al., 2007c) <i>Bi</i> (Dostál et al., 2006a; Dostál et al., 2007c; Dostál et al., 2009b; Fridrichová et al., 2009; Chovancová et al., 2009) <i>Co</i> (Arrais et al., 2006) <i>Cr</i> and <i>Fe</i> (Martinez-Alvarez et al., 2004) <i>Cr</i> and <i>Ru</i> (Moret et al., 2005) <i>Fe</i> and <i>Ru</i> (Paim et al., 2005) <i>Ge</i> (Jirásko et al., 2009; Wei et al., 2001) <i>Mo</i> (Gun et al., 2003) <i>Os</i> (Dorcier et al., 2005; Dorcier et al., 2008; Schmid et al., 2007) <i>Pb</i> (Casas et al., 2004) <i>Pd</i> (Macchioni et al., 2003) <i>Rh</i> (Dorcier et al., 2008) <i>Ru</i> (Ang et al., 2006; Dorcier et al., 2005; Dorcier et al., 2008; Schmid et al., 2007) <i>Se</i> (Zhou et al., 2007) <i>Sb</i> (Dostál et al., 2006a; Dostál et al., 2007a; Dostál et al., 2007c; Dostál et al., 2008; Dostál et al., 2009a; Dostál et al., 2009b; Fridrichová et al., 2009; Chovancová et al., 2009; Machuča et al., 2007) <i>Sn</i> (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2006d; Baul et al., 2007a; Baul et al., 2007b; Baul et al., 2008; Bouška et al., 2009; Dostál et al., 2006b; Dostál et al., 2007b; Holčapek et al., 2006; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2007; Jones-Lepp et al., 1999; Jones-Lepp et al., 2001; Kašná et al., 2008; Kolářová et al., 2004; Wei & Miller, 2001) <i>V</i> (Palačková et al., 2007; Vinklárek et al., 2006)
ESI	Q-trap	<i>Fe</i> (Seiwert & Karst, 2007) <i>As</i> (Schaeffer et al., 2006)
ESI	magnetic sector	<i>Bi</i> (Mlýnek & Dahl, 1997) <i>Si</i> and <i>Sn</i> (Beckmann et al., 1998)
		<i>heteromultimetallic</i> (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)

TABLE 1. (Continued)

ESI	TOF	<i>Ge</i> (Takeuchi et al., 2006) <i>Ru</i> (Mattsson et al., 2008) <i>Sb</i> (Zheng et al., 2001) <i>Si</i> (Takeuchi et al., 2006)
ESI	QqTOF	<i>Au</i> (Kilpin et al., 2007) <i>Co</i> (Gentili et al., 2008) <i>Fe</i> (Ding et al., 2003; Wu et al., 2008) <i>Ga</i> (Young et al., 2007) <i>Pd</i> (Evans et al., 2002) <i>Rh</i> (Jimenez et al., 2008) <i>Ru</i> (Crawford et al., 2006; Chisholm et al., 2007) <i>Te</i> (Kandasamy et al., 2003)
ESI	FT-ICR	<i>Pd</i> (Guo et al., 2005; Qian et al., 2006) <i>Pt</i> (Hartnell & Arnold, 2004) <i>Ru</i> (Mattsson et al., 2008) <i>Ru</i> and <i>Si</i> (Kriesel et al., 1998)
FAB	Q	<i>Ag</i> (Rais et al., 2002) <i>Au</i> (Ferrer et al., 2005) <i>Os</i> and <i>Si</i> (Wong et al., 2003) <i>Ru</i> and <i>Si</i> (Wong et al., 2003)
FAB	magnetic sector	<i>Al</i> (Majoumo-Mbe et al., 2005) <i>Au</i> (Lash et al., 2004) <i>Fe</i> (Osei-Twum et al., 2005) <i>Ge</i> (Lamb & Sweetman, 1996) <i>Pd</i> (Brady et al., 1995; Macchioni et al., 2003) <i>Pt</i> (Brady et al., 1995; Leininger et al., 1998) <i>Te</i> (Canseco-Melchor et al., 2001; Chauhan et al., 2002; Kandasamy et al., 2003)
FAB	TOF	<i>Fe</i> (Manzur et al., 2003) <i>Fe</i> and <i>Ru</i> (Štěpnička et al., 1997)
MALDI	TOF	<i>Ag</i> (Xu et al., 2000) <i>B</i> (Kappaun et al., 2006) <i>Fe</i> (Alonso et al., 2001; Wyatt et al., 2008) <i>Fe</i> and <i>Si</i> (Jain et al., 2005; Kohler et al., 2002; Ruiz et al., 1999) <i>Ni</i> and <i>Si</i> (Kohler et al., 2002) <i>Pd</i> (Sicard et al., 2004) <i>Pt</i> (Jang, 2005; Siemsen et al., 2001) <i>Rh</i> (Alvarez et al., 2007; Jimenez et al., 2008) <i>Ru</i> (Royo & Brintzinger, 2002; Salmain et al., 2004)

(Continued)

TABLE 1. (Continued)

		<i>Ru</i> and <i>Si</i> (Kriesel et al., 1998)
		<i>Sn</i> (Carraher & Lanz, 2003; Carraher & Morie, 2004; Carraher et al., 2007)
		<i>Sn</i> and <i>Si</i> (Schumann et al., 2006)
		<i>Ti</i> and <i>Si</i> (Arevalo et al., 2001)
MALDI	QqTOF	<i>Fe</i> (Osei-Twum et al., 2005)

[Cat]⁺ and [An][−], eventually doubly charged ions [Cat]²⁺ and [An]^{2−}. This approach is common also for organometallic compounds with a labile covalent bond usually between metal–halogen (Kolářová et al., 2004) or metal–oxygen (Baul et al., 2005b, 2008) present in some ligands or substituents. The labile covalent bond is also cleaved to yield two complementary ions, where the cationic part of the molecule (e.g., [LSnR₂]⁺, [SnR₃]⁺, [M – X]⁺) is detected in the positive-ion mode, and the anionic part ([L][−], [X][−]) in the negative-ion mode (Holčapek et al., 2006). Among others, the formation of fragment ions is often observed according to the type of ionization and the values of applied voltages. Moreover, some adducts with these fragments are observed in the spectra, such as [M + SnR₃]⁺, [M + SnR₃–H + Na(K)]⁺, and [M + L][−], [M + X][−]. Ions that undergo an oxidation-state change can be further observed in mass spectra of organometallics that contain an appropriate metal, for example; Fe (Ding et al., 2003). It is also noteworthy that some organometallics can undergo hydrolysis reactions because of the presence of polar bonds on the metal atom, and hydrolysis and solvent adducts might be observed in their mass spectra (Jirásko et al., 2007).

The various ionization mechanisms described above concern mainly ESI and APCI; only few mechanisms are found in articles that deal with FAB or MALDI of organometallics; for example, [M + Na]⁺, [M + H]⁺ for MALDI or [M]⁺, [M + H]⁺, [M – Cl]⁺, [M – Br]⁺, and various fragment and dissociation adducts for FAB.

B. Importance of Isotopic Distribution of Polyisotopic Elements

The wide distribution of isotopic peaks for most compounds is often observed in the spectra because of the greater number of isotopes of some elements (Sn, Ge, Se, Ni, Te, and others), which contributes to total isotopic distributions of studied ions (Goraczko & Szymura, 1999; Jirásko et al., 2007, 2008; Jirásko, Holčapek, & Rosenberg, 2009). Theoretical isotopic distributions for selected polyisotopic **p** and **d** elements that contain at least three isotopic peaks are shown in Figure 1. The complex isotopic distribution can sometimes complicate the spectra interpretation due to the presence of a high number of isotopic peaks. However, the main advantage of a complex isotopic distribution is the possibility to identify the presence and exact number of polyisotopic metals in individual ions by the comparison of experimental isotopic distributions with theoretical ones (Fig. 2). The complexity of isotopic pattern is enhanced with the increased number of

polyisotopic elements, and the isotopic envelope can convert even to the Gaussian character; for example, in case of a high number of tin atoms (Fig. 2D). Compounds that contain a high number of metals with two isotopes also markedly extend the isotopic pattern; for example, a multisilver complex (Rais et al., 2002). Other non-metal elements that affect the isotopic distribution are bromine, chlorine, sulfur, or a high number of carbons.

The determination of the number and type of polyisotopic elements can be done with low- and high-resolution mass analyzers. However, properly calibrated high-resolution mass analyzers offer accurate *m/z* values of all isotopic peaks, and can be subsequently used for elemental composition verification based on the calculation of mean mass-accuracy parameters. The ion overlaps that occur due to the wide isotopic distribution of polyisotopic complexes can be detected as well (Jirásko, Holčapek, & Rosenberg, 2009).

C. Tandem Mass Spectra of Organometallic Compounds

Proposed structures of important ions can be confirmed with the additional fragmentation that is usually realized with collision-induced dissociation (CID). Tandem MS is divided into two groups according to the mechanism of the dissociation process (Henderson & McIndoe, 2005). When the selection of the precursor ion and the observation of product ions are carried out in different parts of the instrument, the technique is termed tandem MS in space (e.g., QqQ, QqTOF). The alternative approach is tandem MS in time (e.g., spherical and linear ion-traps, FT-ICR). Due to the possibility of a multistage mass spectra measurement, ion-trap analyzers are useful to characterize fragmentation paths (Larsen et al., 2001; Holčapek et al., 2006; Jirásko et al., 2007). The neutral losses typical for functional groups present in the organometallic compounds are summarized in Table 3. The presence of particular groups can be associated with the typical neutral losses, such as hydrogen halide for the presence of halogen, the loss of carbon dioxide for organometallic carboxylates, the loss of alkene or alkane in the presence of alkyl substituents on the metal atom or other ring structures, the loss of 28 (N₂) confirms the presence of an azo group in the molecule, etc. For organometallic compounds that contain two or more alkyl/aryl substituents, cleavages of these bonds that result in subsequent neutral losses of alkene and alkane for the alkyl substitution (Baul et al., 2005a, 2006a, 2008; Chalupa et al., 2006, 2008; Jirásko et al., 2007),

TABLE 2. Mechanisms of ion formation of organometallic compounds

Type of ion	Metal present in organometallic compounds (references)
[Cat] ⁺	<i>Ag</i> (Rais et al., 2002); <i>As</i> (Larsen et al., 2001); <i>Au</i> (Dinger et al., 1998); <i>Bi</i> (Dostál et al., 2007c; Fridrichová et al., 2009); <i>Cr</i> (Moret et al., 2005); <i>Ga</i> (Young et al., 2007); <i>Ir</i> (Ogo et al., 1999); <i>Pb</i> (Mester & Pawliszyn, 1999; Pham et al., 2007); <i>Pd</i> (Macchioni et al., 2003); <i>Pr</i> (Hartnell & Arnold, 2004; Mastroiilli et al., 2004); <i>Rh</i> (Dorcier et al., 2008; Jimenez et al., 2008); <i>Rh</i> and <i>Sb</i> (Brown et al., 2006); <i>Ru</i> (Dorcier et al., 2005; Dorcier et al., 2008; Yeo et al., 1999); <i>Ru</i> and <i>Fe</i> (Paim et al., 2005); <i>Os</i> (Dorcier et al., 2005; Dorcier et al., 2008); <i>Sb</i> (Dostál et al., 2007c; Fridrichová et al., 2009); <i>Sn</i> (Holčápek et al., 2006; Kašná et al., 2008); <i>V</i> (Palačková et al., 2007; Vinklárek et al., 2006); <i>heteromultimetallic</i> (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)
[M+H] ⁺	<i>As</i> (Florencio et al., 1997; Pedersen & Francesconi, 2000); <i>Au</i> (Dinger & Henderson, 1998a, b; Goss et al., 2003; Kilpin et al., 2007); <i>Bi</i> (Dostál et al., 2009b; Chovancová et al., 2009); <i>Co</i> (Alsberg et al., 2001); <i>Fe</i> (Henderson & Alley, 2002; KaneMaguire et al., 1996; Seiwert & Karst, 2007; Wu et al., 2008); <i>Ge</i> (Jirásko et al., 2009; Takeuchi et al., 2006; Wei et al., 2001); <i>Hg</i> (Nicholson & Whitley, 2004); <i>Pb</i> (Casas et al., 2004); <i>Pd</i> (Chevrin et al., 2007); <i>Ru</i> (Ang et al., 2006; Pelagatti et al., 2005; Yeo et al., 1999); <i>Sb</i> (Dostál et al., 2009a; Dostál et al., 2009b); <i>Se</i> (Zhou et al., 2007); <i>Si</i> (Takeuchi et al., 2006); <i>Sn</i> (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2008; Chalupa et al., 2006; Wei & Miller, 2001); <i>Sn</i> and <i>Si</i> (Beckmann et al., 1998); <i>Ti</i> (Meurer et al., 2003; Meurer et al., 2006); <i>heteromultimetallic</i> (Packheiser & Lang, 2007; Packheiser et al., 2008a; Packheiser et al., 2008b)
[M+Z] ⁺ Z=Na, K, Li, Ag	<i>As</i> (Florencio et al., 1997); <i>Au</i> (Goss et al., 2003; Kilpin et al., 2007); <i>Bi</i> (Dostál et al., 2009b; Chovancová et al., 2009); <i>Fe</i> (Alley & Henderson, 2001; Henderson & Alley, 2002; Pla-Quintana & Roglans, 2005); <i>Ge</i> (Jirásko et al., 2009); <i>Hg</i> (Nicholson & Whitley, 2004); <i>Pb</i> (Aplin et al., 2002; Casas et al., 2004); <i>Pd</i> (Chevrin et al., 2007; Pla-Quintana & Roglans, 2005); <i>Pr</i> (Hartnell & Arnold, 2004); <i>Ru</i> (Ang et al., 2006; Pelagatti et al., 2005); <i>Sb</i> (Dostál et al., 2008; Dostál et al., 2009b; Chovancová et al., 2009); <i>Se</i> (Zhou et al., 2007); <i>Sn</i> (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2007a; Baul et al., 2008; Dostál et al., 2006b; Dostál et al., 2007b; Chalupa et al., 2006; Jirásko et al., 2007; Kolářová et al., 2004); <i>Sn</i> and <i>Si</i> (Beckmann et al., 1998)
[2M+H] ⁺	<i>As</i> (Florencio et al., 1997); <i>Au</i> (Dinger & Henderson, 1998a, b; Goss et al., 2003; Kilpin et al., 2007); <i>Fe</i> (Henderson & Alley, 2002); <i>Ru</i> (Pelagatti et al., 2005)
[2M+Na] ⁺ or [2M+K] ⁺	<i>As</i> (Florencio et al., 1997); <i>Au</i> (Goss et al., 2003; Kilpin et al., 2007); <i>Fe</i> (Henderson & Alley, 2002); <i>Ru</i> (Pelagatti et al., 2005); <i>Sn</i> (Baul et al., 2005b; Baul et al., 2005c; Chalupa et al., 2006)
[M+R ₃ NH] ⁺ R=CH ₃ , Et	<i>Au</i> (Kilpin et al., 2007); <i>Ru</i> (Ang et al., 2006)
[M+NH ₄] ⁺	<i>Au</i> (Dinger & Henderson, 1998b, 1999); <i>Fe</i> and <i>Pd</i> (Pla-Quintana & Roglans, 2005)
[2M+NH ₄] ⁺	<i>Au</i> (Dinger & Henderson, 1999)
[M-X] ⁺ , X=halide, CF ₃ COO, CF ₃ SO ₃ or complex ligands	<i>Bi</i> (Dostál et al., 2006a); <i>Fe</i> (Henderson & Alley, 2002); <i>Os</i> (Dorcier et al., 2005; Dorcier et al., 2008); <i>Pb</i> (Aplin et al., 2002; Casas et al., 2004); <i>Rh</i> (Dorcier et al., 2005; Dorcier et al., 2008; Jimenez et al., 2008); <i>Ru</i> (Moret et al., 2005; Pelagatti et al., 2005); <i>Sb</i> (Dostál et al., 2006a; Dostál et al., 2007c; Dostál et al., 2008; Machuča et al., 2007); <i>Sn</i> (Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Baul et al., 2006c; Baul et al., 2008; Bekri et al., 2006; Henderson & Taylor, 1996; Chalupa et al., 2006; Jirásko et al., 2007; Kašná et al., 2008; Kolářová et al., 2004; Lawson et al., 1996; Wei & Miller, 2001)

TABLE 2. (Continued)

[2M-X] ⁺ , X=halide	<i>Ru</i> (Pelagatti et al., 2005)
[M+SnR ₃] ⁺ , R=CH ₃ , Et, Bu, Bz, Ph, C ₆ H ₇	<i>Sn</i> (Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2007a; Chalupa et al., 2006; Wei & Miller, 2001)
[M+SnR ₂ R'] ⁺ , R=CH ₃ , Bu, Ph; R'=C ₆ H ₁₂ N	<i>Sn</i> (Chalupa et al., 2008)
[M+Na-H+SnR ₃] ⁺ and [M+K-H+SnR ₃] ⁺	<i>Sn</i> (Baul et al., 2005b; Baul et al., 2005c)
[M] ⁺ or metal oxidation	<i>As</i> (Florencio et al., 1997); <i>Au</i> (Kilpin et al., 2007); <i>Fe</i> (Alley & Henderson, 2001; Diehl & Karst, 2002; Ding et al., 2003; KaneMaguire et al., 1996; Murao et al., 2005; Pla-Quintana & Roglans, 2005; Quirke & Van Berkel, 2001; Tharamani et al., 2008); <i>Te</i> (Kandasamy et al., 2003)
[M+2H] ²⁺	<i>Co</i> (Alsberg et al., 2001; Gentili et al., 2008)
[Cat] ²⁺	<i>Pt</i> (Hartnell & Arnold, 2004); <i>heteromultimetallic</i> (Packheiser et al., 2008a; Packheiser et al., 2008b)
[Cat] ⁿ⁺ , n=2 to 28	<i>Ru</i> and <i>Si</i> (Kriesel et al., 1998)
[An] ⁻	<i>B</i> (Dostál et al., 2007c; Kašná et al., 2008); <i>Mo</i> (Thompson et al., 2003); <i>Ni</i> (Goicoechea & Sevov, 2006b); <i>Re</i> (Jiang et al., 2000); <i>Ru</i> (Crawford et al., 2006); <i>W</i> (Thompson et al., 2003); <i>Zn</i> (Goicoechea & Sevov, 2006a)
[M+L] ⁻ , X=halide, CF ₃ SO ₃ , complex ligand	<i>Bi</i> (Dostál et al., 2006a); <i>Fe</i> (Henderson & Alley, 2002); <i>Sb</i> (Dostál et al., 2006a; Dostál et al., 2007a; Chovancová et al., 2009; Machuča et al., 2007); <i>Sn</i> (Baul et al., 2006a; Baul et al., 2007a; Wei & Miller, 2001)
[M-SnR ₂ R'] ⁻ , R=CH ₃ , Bu, Ph; R'=C ₆ H ₁₂ N	<i>Sn</i> (Chalupa et al., 2008)
[M-SnR ₃] ⁻ , R=CH ₃ , Et, Bu, Bz, Ph, C ₆ H ₇	<i>Sn</i> (Chalupa et al., 2006)
[M-H] ⁻	<i>As</i> (Florencio et al., 1997); <i>Cr</i> and <i>Fe</i> (Martinez-Alvarez et al., 2004); <i>Fe</i> (Alley & Henderson, 2001; Tharamani et al., 2008); <i>Ge</i> (Jirásko et al., 2009; Lamb & Sweetman, 1996; Wei et al., 2001); <i>Pt</i> (Mastroiilli et al., 2004); <i>Ru</i> (Pelagatti et al., 2005); <i>Sn</i> (Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006d; Baul et al., 2007a; Baul et al., 2007b; Jirásko et al., 2007)
[M+Na-2H] ⁻	<i>Sn</i> (Jirásko et al., 2007)
[2M+X] ⁻	<i>Fe</i> (Henderson & Alley, 2002); <i>Ru</i> (Pelagatti et al., 2005); <i>Sn</i> (Baul et al., 2006d)
[An] ²⁻	<i>Bi</i> (Mlýnek & Dahl, 1997); <i>Os</i> (Dyson et al., 2000); <i>Ru</i> (Crawford et al., 2006)
[M] ⁻	<i>As</i> (Florencio et al., 1997)
solvent adducts	<i>Fe</i> (Ding et al., 2003; KaneMaguire et al., 1996); <i>Fe</i> and <i>Ru</i> (Paim et al., 2005); <i>Ga</i> (Young et al., 2007); <i>Hg</i> (Nicholson & Whitley, 2004); <i>Mo</i> (Gun et al., 2003); <i>Pb</i> (Aplin et al., 2002); <i>Pd</i> (Guo et al., 2005); <i>Pt</i> (Mastroiilli et al., 2004); <i>Re</i> (Jiang et al., 2000); <i>Sb</i> (Lintschinger et al., 1998; Zheng et al., 2001); <i>Sn</i> (Henderson & Taylor, 1996; Jirásko et al., 2007; Jones-Lepp et al., 1999; Jones-Lepp et al., 2001; Lawson et al., 1996)
adducts with water, hydrolysis products	<i>Bi</i> (Dostál et al., 2006a); <i>Fe</i> (Ding et al., 2003); <i>Sb</i> (Dostál et al., 2006a; Dostál et al., 2007a; Dostál et al., 2008; Lintschinger et al., 1998; Machuča et al., 2007; Zheng et al., 2001); <i>Sn</i> (Baul et al., 2006d; Beckmann et al., 2002; Henderson & Taylor, 1996; Chalupa et al., 2006; Jirásko et al., 2007; Lawson et al., 1996; Wei & Miller, 2001)
[M-2H] ²⁻	<i>Fe</i> (Alley & Henderson, 2001)

Bu, butyl; Ph, phenyl; Bz, benzyl; Et, ethyl; L, ligand; Cat, cationic part; An, anionic part.

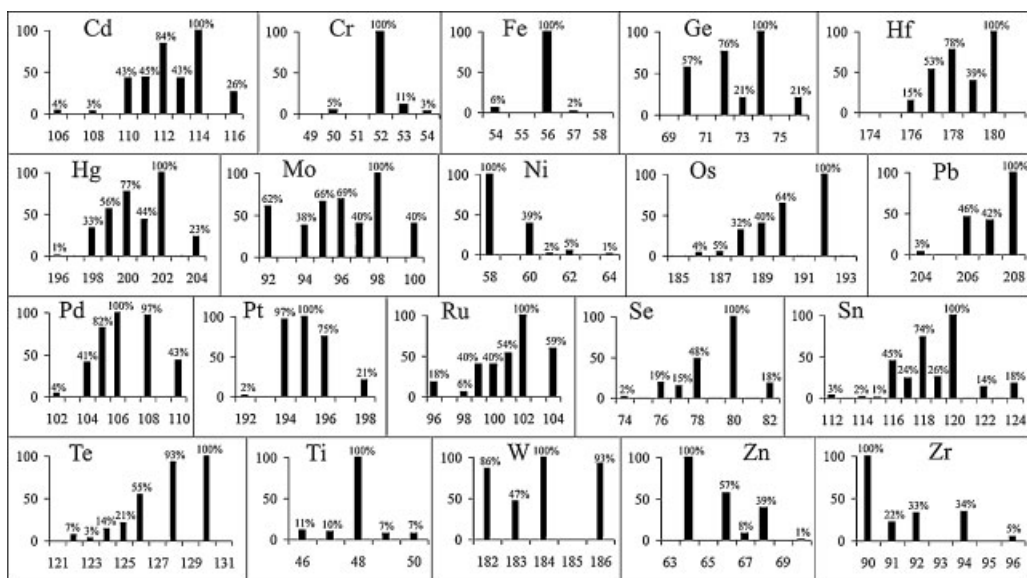


FIGURE 1. Isotopic distribution of polyisotopic p and d metal atoms.

cycloalkane and cykloalkene for cykloalkyl (Chalupa et al., 2006), C_6H_6 and C_6H_4 (Baul et al., 2006b; Chalupa et al., 2006, 2008) for the phenyl substitution or C_7H_8 , and C_7H_6 for the benzyl substitution (Baul et al., 2006c; Chalupa et al., 2006, 2008; Jirásko et al., 2007) are typical. In the case of the presence of some complex ligand on the metal atom, the neutral losses depend on the structures of particular ligands. Moreover, the formation of adducts inside the ion-trap is relatively common for organometallics due to their reactivity, for example, an addition of water ($\Delta m/z$ 18) or solvent (CH_3CN , $\Delta m/z$ 41) observed in the multistage mass spectra (Baul et al., 2005a; Henderson & McIndoe, 2005; Jirásko et al., 2007).

III. MASS SPECTROMETRY OF INDIVIDUAL ORGANOMETALLIC CLASSES

This chapter that describes the MS of individual organometallic compounds is divided into two groups according to the position of the metal in the periodic table; that is, the main-group and transition-metals. Organometallics, for which no important article on soft-ionization techniques has been found (organolanthanides, organoaluminum, organogallium, and organoindium compounds), are not included. Although the main emphasis is given to the MS of complex organometallic compounds, simple organometallics are also mentioned in special cases, such as alkyl and aryl derivatives of organotin, organomercury, organoarsenic,

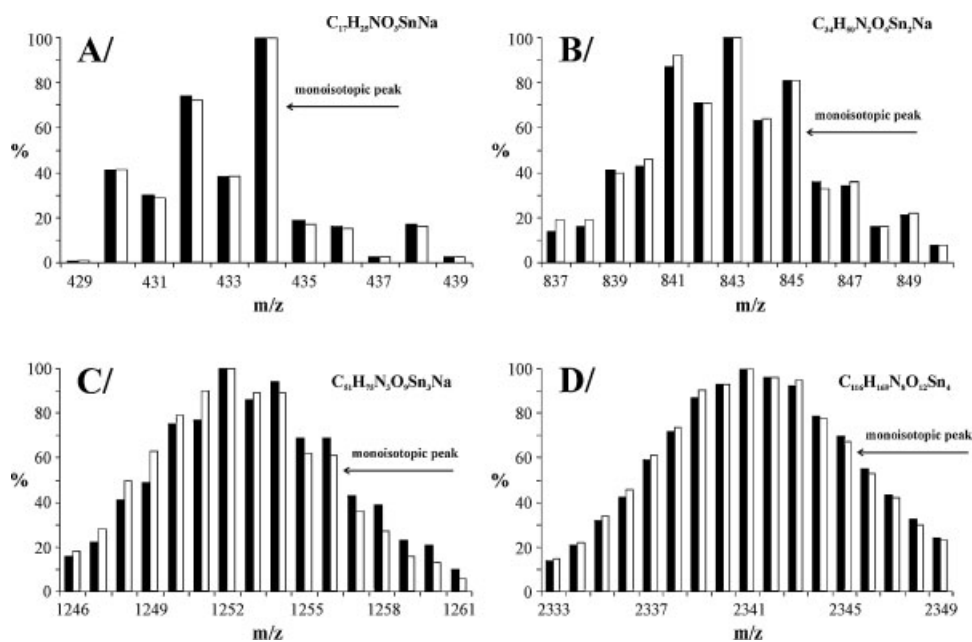


FIGURE 2. Comparison of experimental (white bars) and theoretical (black bars) isotopic abundances of ions with (A) one, (B) two, (C) three, and (D) four tin atoms (reproduced from Jirásko et al., 2007).

or organolead compounds. Metallocenes and their related compounds are also discussed.

A. Main-Group Organometallic Compounds

“Poor metals” (Al, Ga, In, Tl, Ge, Sn, Pb, Bi) but also so-called metalloids (B, Si, As, Sb, Te) can be present in the structure of main-group organometallics.

1. Simple Main-Group Organometallic Compounds

Due to the wide range of applications of organometallics, their long-time persistence in the environment with respect to their

water solubility, and the accumulation in the fat of living organisms is often observed. This serious problem is mainly related to organotin, organolead, organoarsenic, and organo-mercury compounds. These environmentally dangerous compounds are commonly observed at low concentration levels, so that the application of sensitive analytical technique is necessary to monitor their levels. The important point is the development of appropriate chromatographic methods. Gas chromatography combined with inductively coupled plasma time-of-flight mass spectrometry (ICP-MS) enables high sensitivity and resolution, but the time-consuming preparation of volatile derivatives is inevitable, and can influence the reproducibility, especially for

TABLE 3. Common neutral losses observed in CID mass spectra of organometallic compounds

Nominal mass shift [ΔDa]	Neutral loss	Functional group or substituent	References
2	H ₂	cyclization, oxidation	(Larsen et al., 2001)
15	CH ₃	methyl	(Larsen et al., 2001; Mester & Pawliszyn, 1999)
16	CH ₄	methyl	(Chalupa et al., 2006; Larsen et al., 2001; Pham et al., 2007)
18	H ₂ O	hydroxyl, carboxylate	(Baul et al., 2006d; Baul et al., 2007b; Florencio et al., 1997; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2009; Kolářová et al., 2004; Larsen et al., 2001; Wei et al., 2001; Wei & Miller, 2001)
28	C ₂ H ₄	ethyl	(Kolářová et al., 2004; Lamb & Sweetman, 1996)
	CO	carbonyl	(Baul et al., 2005a; Jirásko et al., 2007; Seiwert & Karst, 2007; Yeo et al., 1999)
	CO	carbene complexes	(Crawford et al., 2006; Jiang et al., 2000; KaneMaguire et al., 1996; Martinez-Alvarez et al., 2004; Mastroilli et al., 2004; Mlýnek & Dahl, 1997; Moret et al., 2005; Thompson et al., 2003)
	N ₂	azo group	(Baul et al., 2005b; Baul et al., 2006b)
29	C ₂ H ₅	ethyl	(Mester & Pawliszyn, 1999)
30	C ₂ H ₆	ethyl	(Chalupa et al., 2006; Mester & Pawliszyn, 1999; Mlýnek & Dahl, 1997; Pham et al., 2007)

(Continued)

TABLE 3. (Continued)

	H ₂ CO	methoxy	(Dostál et al., 2006a; Dostál et al., 2007c; Henderson & Alley, 2002; Kolářová et al., 2004; Larsen et al., 2001)
32	CH ₃ OH	solvent adducts, methoxy	(Florencio et al., 1997; Kolářová et al., 2004; Larsen et al., 2001)
36	HCl	chloride	(Dostál et al., 2006a; Dostál et al., 2007c; Chovancová et al., 2009; Kolářová et al., 2004)
42	CH ₂ CO	-	(Kilpin et al., 2007; Larsen et al., 2001)
	C ₃ H ₆	propyl	(Kolářová et al., 2004)
43	CH ₃ CN	solvent adducts	(Mastrorilli et al., 2004; Yeo et al., 1999)
44	CO ₂	carboxylate	(Baul et al., 2005a; Baul et al., 2005b; Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2007a; Baul et al., 2007b; Dostál et al., 2007b; Dostál et al., 2009a; Florencio et al., 1997; Chalupa et al., 2006; Chalupa et al., 2008; Jirásko et al., 2007; Jirásko et al., 2009; Larsen et al., 2001; Wei et al., 2001)
	CH ₂ CHOH	ethoxy	(Kolářová et al., 2004; Larsen et al., 2001)
45	(CH ₃) ₂ NH	dimethylamine	(Holčapek et al., 2006)
46	C ₂ H ₅ OH	ethoxy, solvent adducts	(Kolářová et al., 2004; Larsen et al., 2001)
	H ₂ O + CO	carboxylate	(Florencio et al., 1997)
56	C ₄ H ₈	butyl	(Baul et al., 2005a; Baul et al., 2006a; Beckmann et al., 1998; Dostál et al., 2006a; Dostál et al., 2007b; Dostál et al., 2007c; Dostál et al., 2008; Jirásko et al., 2007; Kolářová et al., 2004)
58	C ₄ H ₁₀	butyl	(Baul et al., 2006a; Baul et al., 2008; Beckmann et al., 2002; Chalupa et al., 2006)
60	CH ₃ COOH	-	(Baul et al., 2006a; Jirásko et al., 2007)
	C ₃ H ₇ OH	propyloxy	(Kolářová et al., 2004)
64	C ₅ H ₄	cyclopentadienyl	(Paim et al., 2005)
65	C ₅ H ₅	cyclopentadienyl	(KaneMaguire et al., 1996; Paim et al., 2005)

TABLE 3. (Continued)

66	C ₅ H ₆	cyclopentadienyl	(Alley & Henderson, 2001; Seiwert & Karst, 2007; Wu et al., 2008)
76	C ₆ H ₄	phenyl	(Baul et al., 2006b; Chalupa et al., 2006; Chalupa et al., 2008)
77	C ₆ H ₅	phenyl	(Casas et al., 2004; Paim et al., 2005)
78	C ₆ H ₆	phenyl	(Baul et al., 2005c; Baul et al., 2006a; Baul et al., 2006b; Holčapek et al., 2006; Chalupa et al., 2006; Jirásko et al., 2007; Kolářová et al., 2004)
80	HBr	bromide	(Baul et al., 2005b)
84	C ₆ H ₁₂	cyclohexyl	(Chalupa et al., 2006)
90	C ₇ H ₆	benzyl	(Baul et al., 2006c; Chalupa et al., 2006; Jirásko et al., 2007)
92	C ₇ H ₈	benzyl	(Baul et al., 2006c; Chalupa et al., 2006; Jirásko et al., 2007)

natural samples (Prange & Jantzen, 1995; Jitaru, Infante, & Adams, 2004). Although the alternative approach for simple organometallic compounds separation is HPLC, where no derivatization is required, extraction and preconcentration steps are often necessary before the analysis (Harrington, Eigendorf, & Cullen, 1996; Ebdon, Hill, & Rivas, 1997; Mester & Pawliszyn, 1999; Gomez-Ariza et al., 2001; Forgacs & Cserhati, 2002). If no structural information is needed, then ICP-MS can be applied (Gonzalez-Toledo et al., 2003; Rosenberg, 2003). However, the most useful is ESI-MS (Jones-Lepp et al., 1999; Guo et al., 2005; Jones-Lepp & Momplaisir, 2005). The complicated situation is found for the HPLC of organotin compounds, and only few articles that deal with the HPLC separation of simple organotin compounds are found in the literature. Tin is very reactive to the oxygen, nitrogen, and sulfur present in analyzed matrices, stationary or mobile phases, which causes an irreversible adsorption and peak tailing of organotin compounds in normal- and reversed-phase systems.

Concerning simple organoarsenic compounds, ESI mass spectra (Florencio et al., 1997; Larsen et al., 2001; Schaeffer, Fodor, & Soeroes, 2006) are noted for several examples (e.g., arsenobetaine, tetramethylarsonium, dimethylarsenic acid). ESI yields a better specificity and sensitivity compared with preliminary experiments with APCI (Larsen et al., 2001). The presence of $[M + H]^+$, $[M + Na]^+$, and $[M]^+$ ions in the positive-ion mode, together with fragment and adduct ions, is observed, whereas $[M - H]^-$ and $[M]^-$ ions are typical for the negative-ion mode. Mass spectra of simple alkyl and aryl organotin derivatives as well as their organolead analogs depend on substituents. Usually, ESI is preferred for their ionization (Henderson, Nicholson, & McCaffrey, 1998; Jones-Lepp et al., 1999; Mester & Pawliszyn, 1999; Henderson & McIndoe, 2005), but the application of APCI (Bekri, Saint-Louis, & Pelletier, 2006) has been also published. When chlorine is bonded to the

metal atom, the cleavage of this polar bond to yield $[M - Cl]^+$ ion is predominantly observed (e.g., for R_3SnCl , R_2SnCl_2 , or R_3PbCl ; $R = CH_3$, C_2H_5 , C_4H_9 , C_6H_5) (Henderson & Taylor, 1996; Mester & Pawliszyn, 1999). Further, fragment ions formed from the loss of an alkyl or aryl substituent are found in their mass spectra ($[RPb]^+$, $[Pb]^+$, $[R_3SnH_2]^+$, etc.). In the negative-ion mode, the presence of a stable ion $[Ph_3Sn]^-$ is described for triphenyltin compounds in contrast to spectra of trialkyl derivatives, where $[R_3SnX_2]^-$ ($X = Cl, Br, I$) are rather common (Henderson & Taylor, 1996), as illustrated in Figure 3.

Reactive organotin compounds are predisposed to hydrolysis and solvent-adduct formation. The hydrolysis aggregates of a polymeric character $[(R_3Sn)_n(OH)_{n-1}]^+$ ($R = CH_3, Bu, Ph$) and adducts $[(R_3Sn)(ACN)]^+$ were investigated (Fig. 4) for triorganotin halide ACN/H_2O (1:1) solution (Henderson & Taylor, 1996). A similar behavior was reported for a methanol solution (Lawson et al., 1996), and solvent-adduct ions were also observed for simple organoantimony compounds (Lintschinger, Schramel, & Kettrup, 1998; Zheng, Takeda, & Furuta, 2001).

2. Organotin Compounds

Numerous interesting articles have been published on the MS of complex organotin compounds. Organotin complexes that contain so-called pincer ligands were studied with ESI-MS (Kolářová et al., 2004; Dostál et al., 2006b, 2007b; Holčapek et al., 2006; Bouška et al., 2009) with an ion-trap analyzer. Their spectra are strongly dependent on the character of other substituents and ligands, which are directly bonded to the tin atom. The basic process of ion formation of mono-, di-, and triorganotin complexes that hold at least one polar substituent (small inorganic ions, halogen- and oxygen-containing anionic species) or a weakly bonded ligand (azo dyes sulfonate and benzoate complexes) on the tin atom is the cleavage of this polar

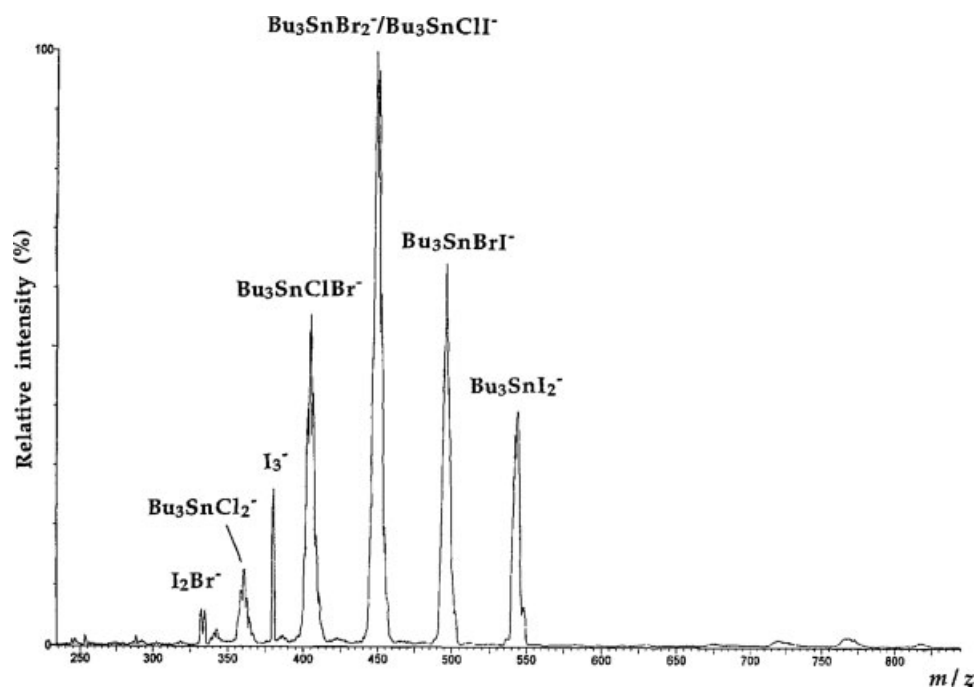


FIGURE 3. Negative-ion ESI mass spectrum of hydrolysis mixture of Bu_3SnCl in the solution with added NaCl , KBr , and KI (reproduced with permission from Henderson & Taylor, 1996).

bond to yield two complementary ions, positively charged and negatively charged parts, which are the base peaks in positive- or negative-ion ESI mass spectra for most compounds. The sum of the masses of those two parts corresponds to the MW. Negative-ion mass spectra of small inorganic ions are trivial (e.g., chloride, bromide, cyanide, etc.), but they provide valuable structure confirmation on the anionic parts of studied organotin compounds, which cannot be obtained from NMR spectra. The quadrupole analyzer is preferred for ions m/z lower than 100, because the sensitivity of an ion-trap is significantly decreased in the low-mass region because of the cut-off effect. The cationic

part includes usually a tin atom; therefore, the isotopic pattern can be useful for the spectra interpretation. Moreover, the fragment ions of the cationic part and sodium or potassium molecular adducts are often observed in the positive-ion full-scan mass spectra. When the polar bond on the tin atom is missing (tetraorganotin compounds), then the formation of molecular adducts with alkali metal ions is the most important process of ion formation. Monoorganotin derivatives that contain three chlorine atoms show a quite unexpected behavior. They might react in the gas-phase according to the equation $\text{M} + \text{M} \rightarrow \text{M}_{\text{dim}} + \text{SnCl}_4$ with $[\text{M}_{\text{dim}} - \text{Cl}]^+$ observed in the positive-ion full-scan mass

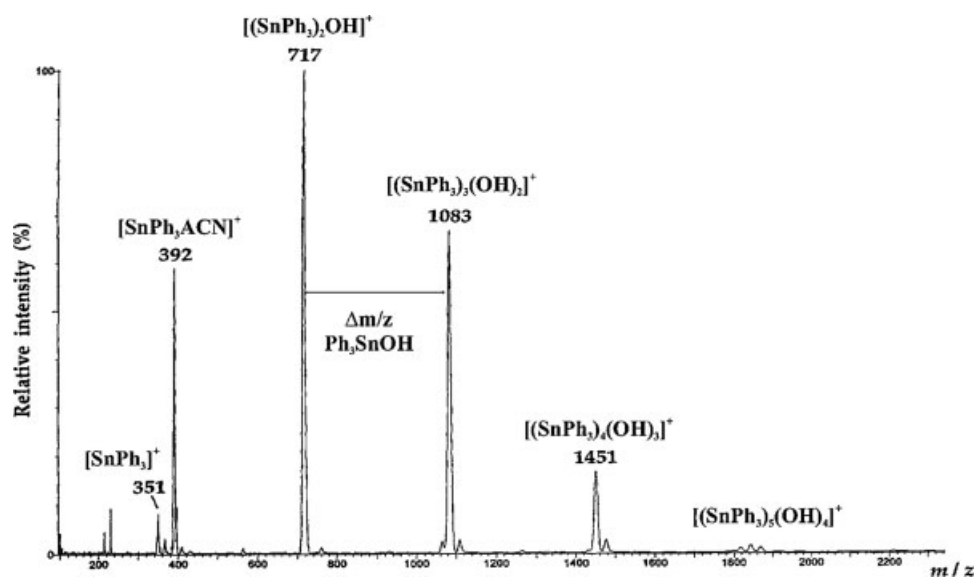


FIGURE 4. Positive-ion ESI mass spectrum of a hydrolysis mixture of Ph_3SnCl in 1:1 (v/v) $\text{H}_2\text{O}/\text{ACN}$ solution (reproduced with permission from Henderson & Taylor, 1996).

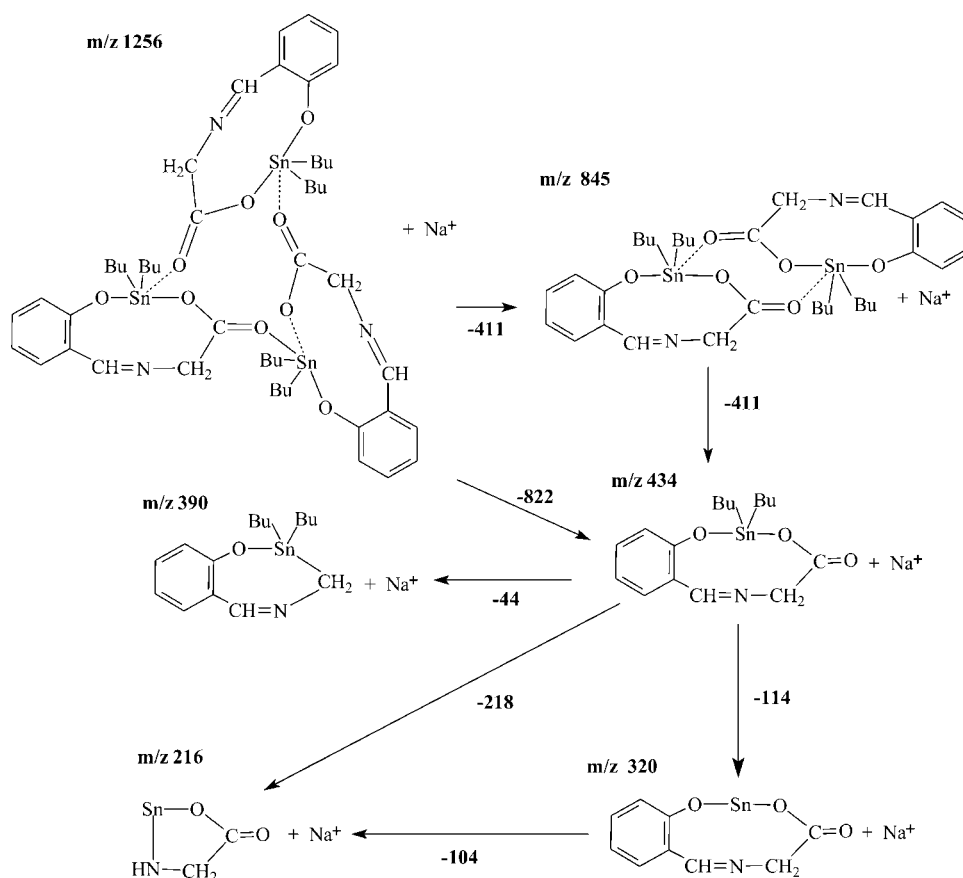


FIGURE 5. Suggested fragmentation pattern of the $[M + Na]^+$ ion at m/z 1,256 for trimeric organotin carboxylate (reproduced from Jirásko et al., 2007).

spectra (M_{dim} corresponds to the dimeric molecule $2M - SnCl_4$). Tandem mass spectra of organotin compounds with pincer ligands are related to substituents. Alkene losses are observed for *tert*-butyl and isopropyl substituents, whereas alcohol or aldehyde losses are preferred for methyl and ethyl substitution of a pincer ligand. Other neutral losses are Sn, C_6H_6 , C_6H_4 , etc. (Kolářová et al., 2004).

Similar ions are described also for other organotin compounds, such as trialkyl-, triphenyl-, dialkyl-, and diaryl-organotin complexes with carboxylated and hydroxylated ligands (Baul et al., 2005a,b,c, 2006a,b,c,d, 2007a,b, 2008; Beckmann et al., 2005; Jirásko et al., 2007). The formation of adduct ions $[M + SnR_3]^+$ and $[M + SnR_3 - H + Na(K)]^+$ is sometimes observed in addition to previous mechanisms. The simplest spectra exhibit compounds with the ionic bond that typically contain only two important ions, depending on the polarity mode, $[Cat]^+$ and $[An]^-$.

On the other hand, ESI mass spectra of organometallic compounds that contain more tin atoms with non-covalent bonds are rather complex and difficult to interpret, because these bonds are cleaved easily during the ionization process, and hence the corresponding ions of non-covalently bonded complexes are missing completely or they have low relative abundances in the full-scan ESI mass spectra. Therefore, the applied voltages on ion optics have to be reduced to minimize any undesirable fragmentation. Proposed structures of important complex ions are confirmed with MS^n analysis. Non-covalent bonds are much

weaker compared to covalent bonds; hence, the fragmentation of non-covalent bonds is strongly preferred. When all non-covalent bonds are broken, then the fragmentation continues with covalent bonds; for example, the fragmentation of a sodium adduct of trimeric organotin carboxylate at m/z 1,256 in Figure 5 (Jirásko et al., 2007). Unlike common organic molecules, multitin organometallic compounds have wide isotopic distributions, so that the isolation width for MS/MS experiments must be wider (8–12 m/z). The same situation applies to other polyisotopic metals (Goraczko & Szymura, 1999).

The formation of unusual solvent and hydrolysis adduct ions is also observed for more complex organotin compounds. The ESI-MS is often used for their mass spectrometric characterization (Beckmann et al., 2002; Jirásko et al., 2007). Various adduct ions with water are produced with ion-molecule reactions in an ion-trap analyzer. Unusual adduct ions with water can be confirmed with isotopically labeled standards (Fig. 6). This approach has been applied to study the hydrolysis of triorganotin chloride with a *C,N*-chelating ligand (Holčapek et al., 2006). Non-labeled, and three isotopically labeled, compounds (D6, D10, D16) have been treated with aqueous NaOH. Hydrolysis reaction products were the same for phenyl, methyl, and *n*-butyl substitution, but differ for a *tert*-butyl substituent probably because of steric reasons. Further, hydrolysis products of tribenzyltin substituted-phenoxyacetate compounds have been investigated in aqueous acetonitrile solution with the measurement of ESI-MS (MS^n) in both polarity modes (Wei & Miller,

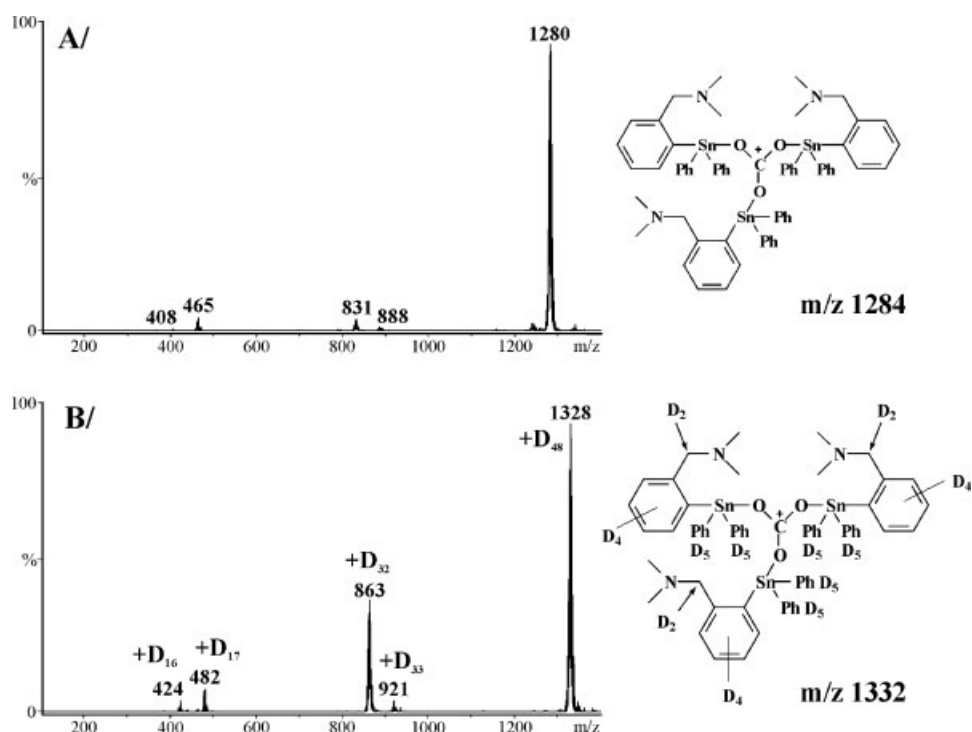


FIGURE 6. Positive-ion full-scan ESI mass spectra of the hydrolysis product of (A) [(2-dimethylamino-methyl)phenyl]diphenyltin(IV) chloride, and (B) its deuterated analog (reproduced with permission from Holčápek et al., 2006).

2001). No effect on the formation of hydrolysis products was observed for isomers that differ in the position of the substitution group on the phenyl group of tribenzyltin nitrophenoxycetates, and similar spectra were observed for all compounds. In general, the hydrolysis and solvent-adduct formation is caused mainly by the presence of a polar bond, such as between metal and halogen, and it is no wonder that the hydrolysis of diorganotin (Beckmann et al., 2002; Jirásko et al., 2007) and monoorganotin (Kolářová et al., 2004; Bouška et al., 2009) compounds occurs. Hydrolysis adduct ions with a polymeric character of OSnR_2 ($\text{R} = \text{Bu}$ or Oct) unit were observed for tetrameric diorganotin compounds (Jirásko et al., 2007) in positive-ion ESI-MS. To fully characterize these adducts, four solvents (acetonitrile, methanol, ethanol, and 2-propanol) were used for adduct characterization. In addition to the polymeric character, the spectra measured in alcoholic solvents contained solvent adducts. Similar types of ions were formed for all compounds and solvents, but with different masses due to the shifts of masses of individual solvents. In case of acetonitrile, only adducts with OSnR_2 were observed in the spectra contrary to alcoholic solvents. There is no doubt that ESI is the most suitable technique for study hydrolysis and solvent organotin adducts.

On the other hand, MALDI provides better results for high-molecular weight organotin polymers and dendrimers. Oligomeric and polymeric products of the polycondensation reaction system formed from medically important drugs (norfloxacin, ticarcillin) with diorganotin dihalides were characterized with MALDI-MS, and their mass spectra revealed multiple units of higher masses (Carraher & Lanz, 2003; Carraher & Morie, 2004). MALDI-MS does not require the polymer to be in the solution, and poorly soluble tin-containing condensation polymers

were characterized with a focus on fragment analysis (Carraher et al., 2007).

3. Organolead Compounds

Concerning organolead compounds, the generation of sodium and potassium molecular adducts was observed in ESI-MS of various organolead carboxylates. Due to the presence of carboxylic group bonded through oxygen to the lead atom, the ions $[\text{M} - \text{RCOO}]^+$ were observed in their spectra. The existence of facile ligand equilibration was deduced based on the formation of solvent (acetonitrile) and pyridine adducts for several different aryllead(IV) carboxylates (Aplin, Buston, & Moloney, 2002). Similar spectra were observed for other complexes formed by $\text{Pb}(\text{C}_6\text{H}_5)_2(\text{OAc})_2$ with salicylaldehyde, 2-ketobutyric acid, pyridine-2-carbaldehyde, 2-acetylpyridine, and 2-benzoylpyridine thiosemicarbazones, which were studied in detail with CID, ESI, and an ion-trap analyzer. Sodium adducts $[\text{M} + \text{Na}]^+$ were observed for compounds that contain a carboxylic group, whereas the production of abundant protonated molecules was recorded when no carboxylic group was present (Casas et al., 2004). Recently, simple organolead compounds (Ph_3PbCl , Ph_2PbI_2 , Ph_2PbBr_2 , and Me_3PbOAc) were treated with $[\text{Pt}_2(\text{l-S})_2(\text{PPh}_3)_4]^+$ to yield solutions that contain positive ions $[\text{Pt}_2(\text{l-S})_2(\text{PPh}_3)_4\text{PbR}_3]^+$ ($\text{R}_3 = \text{Ph}_3$, Ph_2I , Ph_2Br , Me_3) in ESI mass spectra, and their fragmentation behavior was studied (Pham et al., 2007). The initial loss of PPh_3 was observed in all cases. Furthermore, the loss of PbPh_2 occurred for $\text{R} = \text{Ph}$ compared with $\text{R} = \text{Me}$, for which the elimination of ethane followed by a loss of CH_4 . The simplification of the isotope envelope can be also mentioned for the loss of isotopically rich Pb.

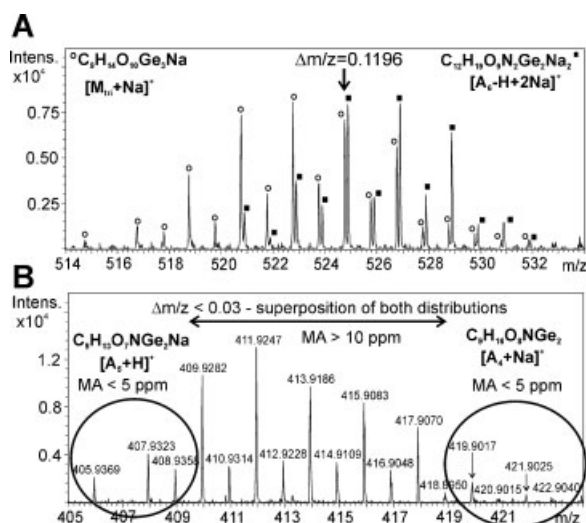


FIGURE 7. Details of full-scan positive-ion ESI mass spectra of a mixture of Ge-132 with alanine: (A) two resolved ions without the superposition of both isotopic distributions, and (B) two non-resolved ions with the superposition of both isotopic distributions (reproduced from Jirásko, Holčápek, & Rosenberg, 2009).

4. Organogermanium Compounds

Only a few articles of MS of organogermanium compounds can be found in the literature, and most of them are devoted to the analysis of so called Ge-132 (germanium sesquioxide) (Lamb & Sweetman, 1996; Wei, Chen, & Miller, 2001; Jirásko, Holčápek, & Rosenberg, 2009). ESI with an ion-trap analyzer was used for Ge-132 characterization. A wide range of complex polymeric ions were formed inside an ion-trap, and their fragmentation behavior was explained by MSⁿ measurements. Moreover, Ge-132 mixtures with different amino acids were measured, with an emphasis on the determination of the elemental composition and the theoretical isotopic pattern of product ions (Jirásko, Holčápek, & Rosenberg, 2009). The hybrid analyzer QqTOF was used, and information from both polarity modes was subsequently used to elucidate some structural aspects, and the proposal of reaction mechanisms that lead to the adduct formation. A new approach to identify potential overlap of ion signals with wide isotopic patterns was described based on the use of accurate masses of overlaid and non-overlaid isotopes at the borders of isotopic envelopes (7).

5. Organoarsenic, Organoantimony, and Organobismuth Compounds

MS of organoarsenic compounds is mostly concerned with the environmental analysis of simple arsenic species. Only arsenic-containing carbohydrates (arsenosugars) measured with ESI with a single quadrupole analyzer are more complex. The typical fragment ion at *m/z* 237 and protonated molecules were observed (Pedersen & Francesconi, 2000). ESI was also successfully applied to the analysis of rhodium and iridium distibine complexes (Brown et al., 2006) and homolog [Ni₁₀(EMe)₂(CO)₁₈]²⁻ dianions (E = P, As, Sb, Bi) (Mlýnek & Dahl, 1997). It is noteworthy that complexes with pincer ligands, similar to above-mentioned organotin compounds, can be also found with

antimony or bismuth. A similar mechanism of labile-bond cleavage to yield [M – X]⁺ in positive-ion and [X][–] in negative-ion spectra is observed (Dostál et al., 2006a, 2007b,c, 2008, 2009a,b; Machuča et al., 2007; Chovancová et al., 2009; Fridrichová et al., 2009). The main difference among the spectra of these three organometallics is the isotopic pattern that arises from the isotopic contribution of individual metals. The most important mechanism for ion formation in negative-ion mass spectra is an anion addition [M + X][–] that confirm the molecular weight. Organoantimony compounds are prone to hydrolysis in contrast to organometallics with Bi—as evident from their positive-ion mass spectra (Dostál et al., 2006a, 2007c).

6. Organoboron Compounds

Organoboron compounds often occur in the form of a polyhedral anion [CB₁₁H₁₂][–] or its thiaborane analog [SB₉H₁₂][–], which are usually counterparts of other organometallic cations (Alvarez et al., 2007; Dostál et al., 2007c; Kašná et al., 2008). Although the boron has only two isotopes ¹⁰B (24%) and ¹¹B (100%), a wide isotopic distribution is observed in their ESI and FAB mass spectra due to the presence of a high number of boron atoms. Further, MALDI was used for accurate mass determination of organoboron quinolinolates (Kappaun et al., 2006). The fragment ions [M – C₆H₅]⁺, together with molecular adducts [M + Na]⁺, were observed in their mass spectra.

7. Organoselenium and Organotellurium Compounds

ESI product-ion mass spectra of mercaptoethanol pre-column derivatization of a novel antitumor organoselenium heterocycle (Zhou et al., 2007) showed [M + H]⁺ and [M + Na]⁺ ions. Diphenacyltellurium dibromide and some other tellurium complexes were characterized with FAB (Canseco-Melchor et al., 2001; Chauhan et al., 2002) ionization, where the most intense peaks corresponded to fragment ions that have the characteristic isotopic distribution pattern of tellurium. The reaction products of tetraorganoditelluroxanes with water traces were revealed with ESI because of the mononuclear cation [(*p*-MeOC₆H₄)₂TeOH]⁺ observed in its solution spectra (Beckmann et al., 2005). In addition, cationic tellurium intermediates were monitored with ESI/MS/MS (Santos, 2008).

8. Organosilicon Compounds

The presence of other metalloids (Weinmann et al., 1999), main-group metal (Beckmann et al., 1998; Constantine, Cardin, & Bollen, 2000; Schumann et al., 2006), transition-metal (Ruiz et al., 1999; Arevalo et al., 2001; Wong, Wong, & Lu, 2003; Jain, Lalancette, & Sheridan, 2005), or lanthanoids (Al-Juaid et al., 1999) is typical for silicon organometallics. Complexes of low-molecular weights were mostly measured with EI MS (Al-Juaid et al., 1999; Weinmann et al., 1999; Constantine, Cardin, & Bollen, 2000), whereas the method of choice to measure polymers and dendrimers is MALDI-TOF. The observation of monocharged molecular adducts with a high-resolution isotopic pattern and a minimum of fragment ions establishes the chemical formula of different species, determines the abundance of all components, and the molecular weights and the mean ring size or chain length of samples (Kohler, Schell, & Weber, 2002) as for

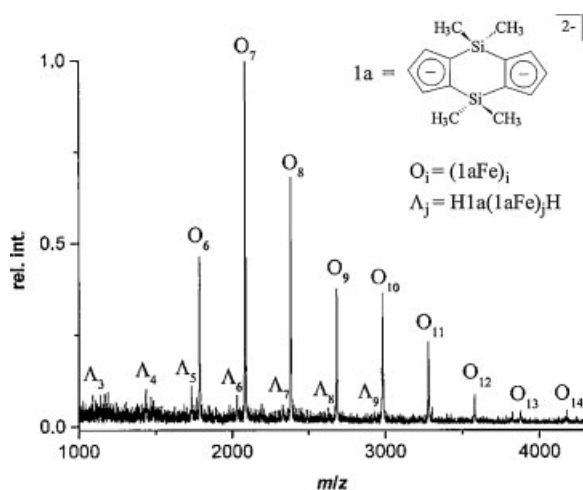


FIGURE 8. MALDI-TOF mass spectrum of products obtained from the reaction of $1aLi_2$ with $[FeCl_2(thf)_{1.5}]$ (reproduced with permission from Kohler, Schell, & Weber, 2002).

polymeric ion distribution of doubly silyl-bridged metallocenes in Figure 8. Concerning dendrimer characterization, the metalation (Na, K, Ag) of novel first-generation silicon-centered tin dendrimers was used in their MALDI spectra to verify no branching defect, and that all synthetic steps proceeded efficiently without the steric hindrance and competitive reactions (Schumann et al., 2006). Similarly, ESI spectra provided evidence for the first- and second-generation carbosilane dendrimers capped with C_5H_5Ru by a complete resolution of individual isotopic distributions of observed charge states (Kriesel et al., 1998). On the contrary, MALDI spectra of fourth-generation titanium–silicon-centered dendrimers contained no molecular ions, and only first- and second-generations were confirmed based on $[M + Na]^+$, $[M + K]^+$, and $[M + H]^+$ ions (Arevalo et al., 2001).

B. Transition-Metal Organometallic Compounds

In contrast to main-group metals, transition-metals are mostly in the form of metal complexes (Henderson & Evans, 1999; Di Marco et al., 2007) and metallocenes; not so many real organometallics that contain the covalent bond between carbon and metal is described.

1. Metallocenes and Related Compounds

Metallocenes can be defined as compounds in which two cyclopentadienyl ligands (Cp) are coordinationally bounded to the metal center with the oxidation state II in a so-called “sandwich” structure. Ferrocene (Cp_2Fe) and its related compounds are one of the most well-known metallocenes, and ESI is usually used for their mass spectrometric characterization. The easy oxidation of ferrocene results in a $[Cp_2Fe]^+$ positively charged ion in ESI-MS. This oxidation can be promoted by the reaction with the chemical oxidant followed by an increase of signal intensity (Henderson & McIndoe, 2005). The direct coupling of mass spectrometric techniques with electrochemical detectors is often used to monitor redox processes (Traeger, 2000; Henderson & McIndoe, 2005). No protonated molecules are generated for ferrocenes in contrast to

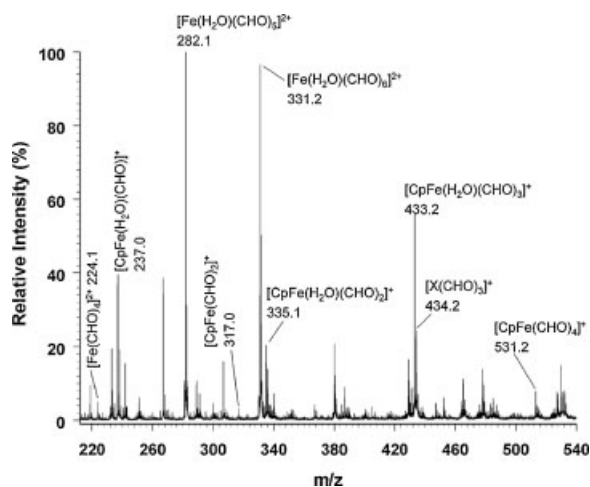


FIGURE 9. Full-scan positive-ion ESI mass spectrum obtained after the photolysis of $[CpFebz]^+$ and cyclohexene oxide (CHO) in 1,2-dichloroethane (reproduced with permission from Ding et al., 2003).

ferrocene derivatives that contain other elements (S, P, N, O), in which the formation of $[M + H]^+$, $[M + Na]^+$, and $[M + K]^+$ ions is common (Henderson & Alley, 2002). Redox properties of metallocenes often result in an interesting photochemical behavior, as illustrated in the study of $[CpFebz]^+$ with positive-ion ESI in a solution (Ding et al., 2003); Figure 9 represents the mass spectrum obtained after the photolysis of $[CpFebz]^+$ and cyclohexene oxide in 1,2-dichloroethane.

The negative-ion measurement can be useful for ferrocene-derived acids to provide deprotonated molecules (Alley & Henderson, 2001). Although typical fragment ions for the ferrocene skeleton correspond to the loss of one Cp ligand $[M - Cp]^+$, other fragments associated with the structure of ferrocene can be found as well (KaneMaguire, Kanitz, & Sheil, 1996). Recently, the monitoring of the metal-ion interaction with ferrocene derivatives was performed with ESI (Tharamani et al., 2008). Ferrocenes can be used as derivatization agents (Seiwert & Karst, 2008), because the derivatization improves the sensitivity of HPLC/MS determination. The simultaneous HPLC/ESI-MS/MS determination of free and disulfide-bound thiols in urine was developed with the sequential derivatization with two ferrocene-based maleimide reagents (Seiwert & Karst, 2007). The ferrocene derivatization was also used to determine of 1-hydroxyvitamin D_3 in rat plasma (Muraio et al., 2005). ESI/MS/MS spectra of ferrocene carbamate esters of saturated alkyl primary, secondary, and tertiary alcohols distinguished straight-chain primary alcohol derivatives from tertiary alcohol derivatives (Quirke & Van Berkel, 2001). Ferrocenyl esters were also investigated based on the rapid HPLC separation coupled with APCI ionization (Diehl & Karst, 2002). The application of MALDI or FAB ionization was also reported (Savage et al., 2005, 2006).

In addition to iron, other central metals can be present in metallocenes. Polyisotopic titanocene intermediates of the Tebbe olefination reaction (Meurer et al., 2006) and Petasis olefination reaction (Meurer et al., 2003) were characterized with APCI-MS/MS. MALDI-TOF MS in combination with reversed-phase HPLC was used to screen the reaction between ruthenocene derivative with hen egg white lysozyme (Salmain et al., 2004), and the application of ESI was published for ruthenocenes

(Henderson & McIndoe, 2005; Yeo et al., 1999) and vanadocenes (Vinklársek et al., 2006; Palačková et al., 2007).

When only one cyclopentadienyl or arene planar ligand is coordinatively bonded to the metal center, the wide family of so-called “half-sandwich” compounds can be prepared. Due to the common presence of a polar bond on the metal atom, ESI is mostly used for their mass spectrometric analysis. The formation of an $[M - Cl]^+$ ion is typical for structures with chlorine bonded to the central metal (Pelagatti et al., 2005; Schmid et al., 2007). ESI-MS is applicable for the mass spectrometric analysis of ruthenium and osmium arene complexes (Wang et al., 2002; Dorcier et al., 2005; Ang et al., 2006; Schmid et al., 2007; Mattsson et al., 2008), the analysis of dinuclear iridium with a μ -hydride complex (Ogo, Makihara, & Watanabe, 1999), the study of Ru(II)-catalyzed asymmetric transfer hydrogenation of acetophenone (Pelagatti et al., 2005), and the characterization of products formed from the reaction of “half-sandwich” (Ru, Rh, Os) complexes with DNA bases (Dorcier et al., 2008). Moreover, the combination of ESI-MS with infrared spectroscopy monitored thermal and photochemical reactions of cyclopentadienyl compounds with molybdenum or tungsten (Thompson, Jones, & Baird, 2003), and the electrochemical reduction of the complex $[Cp_2Mo_2O_5]$ was studied with an on-line electrochemical flow cell followed by ESI-MS (Gun et al., 2003).

2. Transition-Metal Organometallic Compounds That Contain a Covalent Carbon-Metal Bond

The organometallics, including precious metals (Ag, Au, Ru, Rh, Pd, Os, Ir, Pt), represent this class of compounds, and their mass spectra can be found in the literature. ESI-MS is the dominant technique for their characterization. The suitability of ESI can be demonstrated with the example of low-resolution mass spectra of auracyclic complexes; their reaction products show a strong signal of $[M + H]^+$, $[M + Na]^+$, or $[M + NH_4]^+$ ions accompanied by their dimeric analogs which are usually resistant towards cone voltage-induced fragmentation (Dinger & Henderson, 1998a,b, 1999; Goss et al., 2003; Kilpin, Henderson, & Nicholson, 2007). Low-resolution ESI-MS was also used to analyze of rhombic dodecahedral silver-alkynyl cages

$[Ag_{14}(C=C^tBu)_{12}X][BF_4]$ ($X = Cl, Br, F$), and to reveal that chloride and bromide complexes are very stable in solution contrary to fluoride analogs (Rais et al., 2002). Nevertheless, high-resolution ESI mass spectra offer the possibility of elemental composition determination—as illustrated with organopalladium (Evans et al., 2002) and organoplatinum compounds (Hartnell & Arnold, 2004). An appropriate mass analyzer can be useful to suggest a fragmentation mechanism as for ESI-FTICR-MS measurements of organopalladium ions with deuterium-labeling experiments (Qian et al., 2006). Concerning other ionization techniques, the solution aggregation of the dinuclear palladium(I) complex was observed in FAB mass spectra, and, together with ESI spectra, confirmed the stability of polynuclear aggregates (Macchioni et al., 2003). FAB-MS was further used for organoplatinum dendrimers (Leininger, Stang, & Huang, 1998); and σ -acetylide complexes of ruthenium- and osmium-containing alkynylsilane ligands (Wong, Wong, & Lu, 2003). MALDI ionization disclosed the presence of an oligomeric organometallic species that contained silver (Xu et al., 2000), palladium (Sicard et al., 2004), platinum (Siemsen et al., 2001), or rhodium (Hahn et al., 1999).

Some other transition-metal organometallic complexes were characterized with MS in addition to precious-metal complexes. An example is the HPLC/ESI-MS analysis of cobalamin or substituted derivatives performed either simultaneously with other water-soluble vitamins (Gentili et al., 2008) or independently (Alsberg et al., 2001). It was found that the intensity of the two most important ions $[M + H]^+$ and $[M + 2H]^{2+}$ depends on the solvent composition.

3. Heteropolymetallic Complexes

Many heteropolymetallic compounds contain transition-metals. These complexes are often ionic or ionizable already in the solution, therefore ESI-MS is a valuable tool in their analysis, as illustrated on the following examples. The most abundant ion in the spectra of heterotrimetallic complexes $Ru(Cp)(dppf)SnX_3$ as well as their heterobimetallic precursors $Ru(Cp)(dppf)X$ ($dppf =$ diphenylphosphine ferrocene, $X = Cl, Br$) corresponds to the positively charged ion at m/z 721, $[Ru(Cp)(dppf)]^+$ (Paim et al., 2005). The formation of the characteristic isotopic

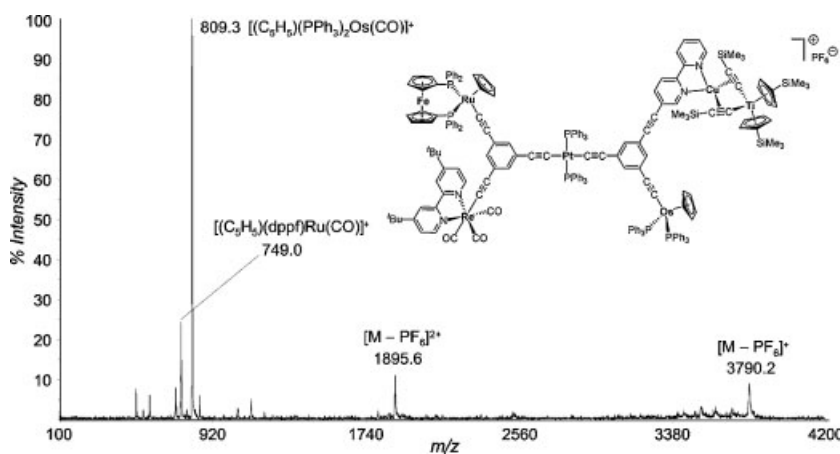


FIGURE 10. Full-scan positive-ion ESI mass spectrum of heteropentametallic complex shown in this figure (reproduced with permission from Packheiser et al., 2008b).

envelope from the superposition of all isotopes of particular metals plays an important role in the spectra interpretation. This fact is also evident for polymetallic carbene complexes (Martinez-Alvarez et al., 2004; Moret et al., 2005), nickel-centered clusters of nine germanium (Goicoechea & Sevov, 2006), or heteroatomic *closo*-clusters $[E_9Zn-Ph]^{3-}$ (E = Si, Ge, Sn, or Pb) (Goicoechea & Sevov, 2006). Furthermore, ESI-TOF MS of a unique series of heteromultinuclear transition-metal complexes with up to seven other different metal atoms (Ti, Fe, Ru, Os, Re, Pt, and Cu) and silicon was performed (Packheiser & Lang, 2007; Packheiser et al., 2008a,b), as illustrated in Figure 10. Ions that correspond to the loss of anionic part $[M - PF_6]^+$ were used for the molecular weight determination. These complexes that contain seven different metal atoms in their structures are probably the most complex organometallic species with reported ESI mass spectra in the literature.

IV. CONCLUSIONS

This review highlights the great potential of different mass spectrometric techniques in the structure characterization of complex organometallic compounds. The wide range of ionization techniques and mass analyzers have been developed and applied to organometallics. The most successful ionization technique in this field is electrospray ionization, which is applicable for organometallic compounds from medium polarity to ionic species that include non-covalent complexes and labile compounds. Conventional electron ionization might be a suitable alternative for certain types of organometallics with low polarity and good volatility. Although the use of other ionization techniques is less frequent that fact does not disqualify their use in particular applications. Typical ionization and fragmentation mechanisms are described for particular groups of organometallics with a discussion of some illustrative examples. Polyisotopic metal atoms offer an additional advantage for spectra interpretation, because their wide isotopic distributions can be theoretically calculated for individual ions and correlated with experimental results to confirm a proposed interpretation. Finally, the role of multistage tandem MS and accurate mass measurements performed with high-resolution mass analyzers is discussed.

V. NOMENCLATURE

An	anionic part
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
Bu	butyl
Bz	benzyl
Cat	cationic part
CI	chemical ionization
CID	collision-induced dissociation
Cp	cyklopentadienyl
EI	electron ionization
ESI	electrospray ionization
Et	ethyl
FAB	fast atom bombardment
FT-ICR	Fourier-transform ion cyclotron resonance
HPLC	high-performance liquid chromatography

HPLC/MS	high-performance liquid chromatography/mass spectrometry
L	ligand
MALDI	matrix-assisted laser desorption/ionization
Me	methyl
MS	mass spectrometry
MS/MS	tandem mass spectrometry
MS ⁿ	multistage mass spectrometry
MW	molecular weight
Ph	phenyl
QqTOF	quadrupole–quadrupole-time-of-flight
R	alkyl or aryl
TOF	time-of-flight
X	halide or simple negatively charged ligands

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