International Journal of Mass Spectrometry 289 (2010) 162–166

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Ion identification in EI mass spectra of tetraalkyltins using chemometric approach based on isotope pattern

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ARTICLE INFO

Article history:
Received 10 August 2009
Received in revised form 5 November 2009
Accepted 9 November 2009
Available online 11 November 2009

Keywords:
EI mass spectra
Isotope pattern
Ion identification
Chemometrics
Tetraalkyltins

ABSTRACT

Analysis of EI mass spectra of R_4Sn organotins series (R = Me, Et, Pr, *iso*-Pr, Bu, *iso*-Bu) performed in this work by means of alternative chemometric procedure BCA (band composition analysis) based on isotope profiles, confirmed the presence of almost all ions identified earlier in these spectra using other methods, like standard interpretation procedure or tandem mass spectrometry. BCA successfully determined ions in both simple and complex band of the spectra, which are often complicated by the effect of signal overlapping or presence of signals having incorrect intensities. Some interesting fragmentation trends for organotins having *n*- or *iso*- structure of R substituents were disclosed.

1. Introduction

Numerous chemometric methods and procedures in low-resolution electron ionization mass spectrometry (EI-MS) used for routine identification of compounds by library searching [1] or interpretation of mass spectra of unknowns [2,3] work well for EI mass spectra of typical organic compounds (i.e., containing such elements as C, H, O, N, S). Unfortunately, they appeared to be ineffective in case of mass spectra of organometallics, which contain multi-isotopic metals, such as Sn, Pt, and Mo. A very modest representation of such spectra in popular databases (e.g., among ca. 200,000 spectra collected in NIST [4] only about 3000 belong to organometallics) practically does not allow for successful identification of organometallics by means of library search. Moreover, EI of such compounds produces numerous fragmentation ions which give extremely complex spectra. They indicate broad isotope patterns (bands) from ions containing multi-isotopic metals, which are often additionally complicated by signal overlapping [5] of two or more neighboring bands of ions having similar masses. For all those reasons identification of ions in organometallic mass spectra and their consequent interpretation are known to be tedious and time-consuming tasks.

Chemometric methods using isotope patterns and computer assistance seem to be a very promising way to analyze mass spectra, since such patterns are information-rich and practically independent of spectrometer type and ionization technique. There are several papers in which isotope patterns were applied for elemental analysis of typical organic compounds [6,7]. Rockwood et al. [8,9] elaborated a couple of algorithms to calculate isotopic distributions potentially useful for elucidation of fragmentation pathways, elemental composition, and chemical structure of high molecular weight compounds.

In the case of organometallic mass spectra, isotope patterns have been applied by various authors mainly to solve particular problems encountered during their interpretation. Meija and Caruso [10] described an isotope pattern reconstruction (IPR) algorithm helpful in deconvolution of isobaric interferences in ICP-MS spectra of Se organometallic compounds. Bhat [11] published program generating isotope profiles for interpretation of novel multinuclear cluster carbonyls and aryls containing metal atoms such as Fe, Ru, Os, W, Mo, Te, and Se. In his paper however, only the results for one particular compound, i.e., $Fe_2Os_3Te_2(CO)_{17}$, are shown. Moraes et al. [12] and Gorączko and Szymura [13] presented the original chemometric methods for the identification and subsequent elimination of interferences from (M-*n*H) dehydrogenation ions in low-resolution spectra of selected organometallic compounds containing Hg, Pb, Ge, Se, Zn and Cd multi-isotopic metals. Recently Szymura and Lamkiewicz [14] elaborated a chemometric procedure called band composition analysis (BCA) for the deconvolution of mass spectra of organometallics, which is based on isotope pro-

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doi:10.1016/j.ijms.2009.11.003

files. Generally, all authors cited above tested their methods on a few randomly chosen compounds rather than on their series indicating common structural features. The latter type of studies can be helpful in developing computer-assisted procedures for automatic elucidation of chemical structures of unknown compounds [3], especially organometallics or identification of substructures from given experimental mass spectra [1].

An interesting subject for such studies is tin organic compounds, since their mass spectra indicate extremely broad and distinctive isotope patterns from 10 natural tin isotopes, as well as particularly intensive effects of signal overlapping. An extensive investigation of EI mass spectra of various organotins performed by Gielen et al. [15–18] by means of standard interpretation procedure (SIP) [19] led to the identification of fragment ions and determination of fragmentation pathways for those compounds. In case of mass spectra of R_4Sn derivatives (R = Me, Et, Pr, Bu, Ph), besides R_3Sn^+, R_2SnH^+, $RSnH_2^+$ and SnH^+ ions formed in main fragmentation pathways, the evidence of R_2Sn^+, RSn^+, SnH_3^+ and Sn^+ ions originated from alternative fragmentations has also been reported [15,17]. The presence of all those ions in mass spectra of R_4Sn derivatives has recently been confirmed by Lawson and Ostah [20,21] and Meija et al. [22], who used techniques of tandem mass spectrometry and isotope dilution GC/ICP-MS, respectively.

Organotin compounds containing C–Sn covalent bonds are remarkably various in their biological, chemical and physical properties [23,24]. Among them tetraorganotins are generally very stable non-toxic compounds that do not have any large-scale commercial use, however, they can be metabolized to toxic triorganotins. R_4Sn are also important intermediates in the production of less alkylated derivatives, that have a significant impact in the environmental as widely used biocides, anti-fouling paints, PVC stabilizers and catalysts [23]. Since analysis of organotins in the environment demands very selective, sensitive instrumental techniques and MS is particularly well suited to it, so any improvements or new approaches simplifying interpretation of their mass spectra are highly desirable for practical reasons.

The main goal of this study was to identify ions in mass spectra of R_4Sn organotins series (R = Me, Et, Pr, *iso*-Pr, Bu, *iso*-Bu) by means of an alternative chemometric approach based on a recently published novel procedure called band composition analysis (BCA) [14]. It uses isotope patterns for deconvolution of mass spectra containing complex bands (i.e., arising from more than one ion), which are typical features in mass spectra of organotins. Throughout this paper the terms “pattern” and “band” are sometimes used interchangeably.

2. Mass spectra

The subject of the present study was low-resolution EI mass spectra of R_4Sn organotins (R = Me, Et, *n*-Pr, *iso*-Pr, *n*-Bu, *iso*-Bu) taken from NIST Library [4]. For comparison purposes the spectrum of *n*-tetrabutyltin recorded by the authors in AMD-402 mass spectrometer via the direct insertion probe for a sample (93% purity) manufactured by Sigma–Aldrich (Poland) was also included in this study and labeled as n-Bu_4Sn^E.

3. Chemometric procedure used for identification of ions

For identification of ions in all spectra in this work, the latest version (v.2.2.) of BCA chemometric method [14] has been applied. It generates theoretical multi-isotopic bands T of ions using natural isotopic abundances [25]. Then method combines them to obtain a model band M, which is finally compared with the experimental band E. All of these operations realized with computer assistance can be performed for bands containing main signal which intensity exceeds 5%. Such modeling yields three parameters characterizing the experimental band: theoretical variance (s^2_{theor}) which estimates fit between the bands E and T, factor (α, in percentages) which estimates matching between the bands E and M and contribution (x) of a given ion from theoretical band in experimental band.

If $s^2_{\text{theor}} < 20$, the experimental band originates from a single ion and is called simple. In cases where $s^2_{\text{theor}} > 20$, it arises from two or more ions whose signals overlap and is then deemed a complex. For $\alpha > 90\%$ the fit may be considered meaning the proposed theoretical ions are responsible for the appearance of the complex band in the mass spectrum studied. For $\alpha < 90\%$ a whole modeling procedure is repeated using different sets of theoretical ions. If still $\alpha < 90\%$ and $s^2_{\text{theor}} > 20$, the differences of signal intensities E–M must be analyzed individually to determine the reasons for all observed discrepancies.

4. Exemplary ion identification in mass spectrum of Et_4Sn

Mass spectrum of tetraethyltin [4] was chosen as an example for a detailed presentation of how BCA works during ion identification. This spectrum (Fig. 1) can be divided into six bands: B1–B5, originating from fragment ions, and B0, assigned to the molecular ion Et_4Sn^+. Both B0 and B4 were not considered in the analysis owing to the very low intensity (<5%) of their signals. According to the criterion that $s^2_{\text{theor}} < 20$, B1 (at *m*/*z* 199–213) and B2 (at *m*/*z* 171–184) are simple bands arising from Et_3Sn^+ and Et_2SnH^+ single ions, respectively.

Comparison of the pattern of the next experimental band B3 from the analyzed spectrum with that of $EtSn^+$ representing its main ion reveals substantial differences between the signals occurring in 145–147 and 150–151 *m*/*z* regions (Fig. 2a). This points to the fact that signals of additional ion contribute towards the pattern of B3 band. The largest positive difference between E and M visible at 150 *m*/*z* suggests the presence of $EtSnH^+$. Subsequent modeling of B3 applying $EtSn^+$ and $EtSnH^+$ ions shows that the obtained value of fit factor equal to 12.01% (Fig. 2b) does not satisfy the essential BCA criterion $\alpha > 90\%$. It is worth noting that at 145–148 and 151 *m*/*z* the intensities of E signals are always lower than those of M, and they do not correspond to the intensities resulting from combination of Sn, C and H isotopic profiles. To explain the observed discrepancies a consecutive modeling step was performed with modified set of ions ($EtSn^+$, $EtSnH^+$ and $EtSnH_2^+$). Also during this modeling, the intensities of E signals in the positions mentioned above have been subjected to changes. Finally, the best fit, $\alpha = 99.38\%$ (Fig. 2c) was reached for the $EtSn^+$ and $EtSnH_2^+$ pair of ions, after the intensities of 145 and 151 *m*/*z* signals were increased from 2.70% to 21.90% and from 7.84% to 79.60%, respectively. Such results of modeling prove that these two signals present in the B3 band of experimen-

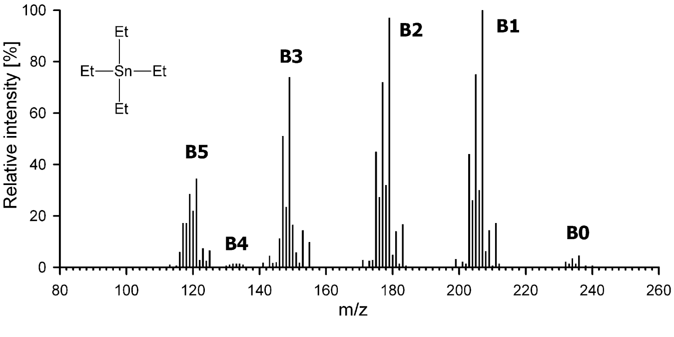

Fig. 1. Mass spectrum of tetraethyltin ($C_8H_{20}Sn$) from NIST database [4] showing the division on bands B0–B5.

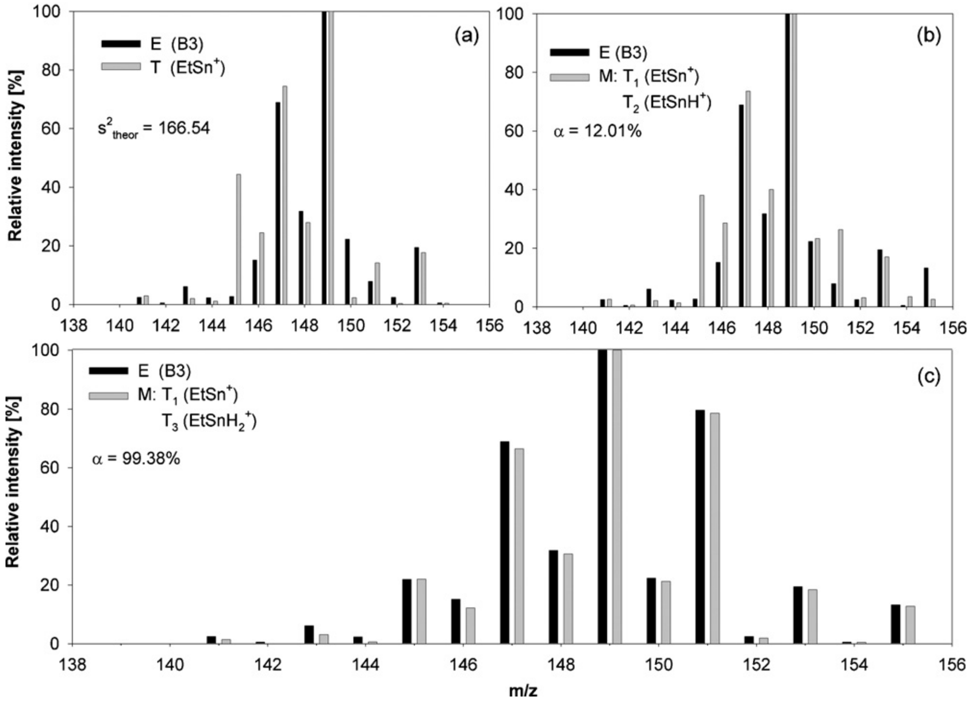

Fig. 2. Sequential steps showing the deconvolution of the B3 experimental complex band from Et_4Sn mass spectrum performed by means of BCA. (a) Comparison of experimental E and theoretical T signals for $EtSn^+$ ion. (b) Results of modeling obtained on assumption that E band originates from $EtSn^+$ and $EtSnH^+$ ions. (c) Results of final modeling that applies $EtSn^+$ and $EtSnH_2{}^+$ as proper set of ions contributing towards E band and introduces correction of the intensities from 2.70% to 21.90% and from 7.84% to 79.60% for experimental signals at 145 and 151 *m*/*z*, respectively.

tal spectrum taken from the database must have incorrect intensity values.

The last band of R_4Sn spectrum subjected to BCA procedure was B5. Comparison of E and T signal intensities for its main ion SnH^+ (column a and b in Table 1) reveals substantial differences visible in 116–120 and 122–125 *m*/*z* regions. This evidence together with a high value of $s^2{}_{theor} = 202.05$ suggest that B5 is a complex band originating from more than only SnH^+ ion. In subsequent modeling, an addition of Sn^+ ion results in obtaining the value of $\alpha = 96.95\%$ (column c in Table 1), which satisfies the essential BCA criterion for fitting E and M bands. However, the differences between E and M signals visible in 117–119 *m*/*z* (E < M) and 122–125 *m*/*z* (E > M) regions point to the fact that another ion, namely $SnH_3{}^+$ can also contribute towards the formation of B5. In fact, final modeling with model band M containing SnH^+, Sn^+ and $SnH_3{}^+$ ions (column d in Table 1) leads to a very good agreement between the signals of experimental and model bands in the whole range (112–127 *m*/*z*) of B5. In consequence, the obtained value of fit factor $\alpha = 99.83\%$ is exceptionally high.

Table 1
Results of ion identification in B5 band of Et_4Sn mass spectrum.

m/*z*	a E	b T: [SnH^+]	c M: T_1 [SnH^+] T_2 [Sn^+]	d M: T_1 [SnH^+] T_2 [Sn^+] T_3 [$SnH_3{}^+$]
		$s^2{}_{theor}$ 202.05	α 96.95%	 99.83%
112	1.01	0.00	1.11	1.10
113	3.19	2.98	2.98	2.78
114	1.01	0.00	0.75	0.74
115	2.03	1.99	2.38	2.52
116	17.39	1.04	17.71	17.52
117	49.86	44.58	53.39	50.52
118	49.86	23.57	51.36	49.68
119	82.61	74.35	84.20	83.17
120	63.77	26.37	63.74	63.84
121	100.00	100.00	100.00	100.00
122	8.12	0.00	5.31	7.66
123	21.45	14.21	14.21	22.28
124	7.25	0.00	6.64	6.60
125	19.13	17.77	17.77	17.86
126	0.00	0.00	0.00	0.00
127	1.01	0.00	0.00	1.60

5. Results and discussion

The results of ion identification for all bands in spectra of the R_4Sn series by means of BCA are summarized in Table 2. In case of molecular ion bands B0 for Me_4Sn, Et_4Sn and *iso*-Pr_4Sn spectra such identification was impossible due to very low (<5%) intensities of their main signals. Other spectra analyzed in this study show absence of bands from molecular ions, which is consistent with the literature [15,18]. Generally, B1 and B2 bands indicating simple character ($s^2{}_{theor} < 20$) originate from R_3Sn^+ and R_2SnH^+ or R_2Sn^+ ions, respectively. B3 and B5 being complex bands ($s^2{}_{theor} > 20$) consist of signals from two or three ions. In the case of Me, Pr, *iso*-Pr and *iso*-Bu tin derivatives, B4 arises mainly from CH_3Sn^+. Additional ions, i.e., CH_2Sn^+, $CHSn^+$ were found for Me_4Sn and $CH_3SnH_2{}^+$ ion for Pr_4Sn. The identification of ions in B4 bands of Et, Bu and Bu^E tin compounds cannot be done due to the low intensity (<5%) of their main signals.

For six bands of analyzed spectra, the obtained values of $s^2{}_{theor}$ or α (marked with grey background in Table 2) do not satisfy the essential BCA criteria due to the presence of incorrect signal intensities. To identify such troublesome effect a change of signal intensities appeared to be necessary during modeling. Such operation was mentioned in this work during exemplary modeling of B3 band from Et_4Sn spectrum.

In the present study on mass spectra of R_4Sn compounds by means of chemometric method we were able to identify all ions found earlier by Gielen's group [15,18] with two minor exceptions, i.e., our results show the lack of Me_2SnH^+ ion in the

Table 2
Results of ions identification in bands of low-resolution mass spectra of R_4Sn series by means of BCA.

R	Band Ion	B0 R_4Sn^+	B1 R_3Sn^+	B2 R_2SnH^+	R_2Sn^+	B3 $RSnH_2^+$	RSn^+	B4 $CH_3SnH_2^+$	CH_3Sn^+	CH_2Sn^+	$CHSn^+$	B5 SnH_3^+	SnH^+	Sn^+
Me	x	1.00	1.00	0.00	1.00			0.00	0.79	0.15	0.06	0.00	0.39	0.61
	s^2_{theor}	–	2.85	5.34		R = CH_3		–				–		
	α [%]	[a]	–	–				98.82				99.21		
Et	x	1.00	1.00	1.00	0.00	0.61	0.39	0.00	1.00	0.00	0.00	0.06	0.67	0.27
	s^2_{theor}	–	0.13	2.20		–		–				–		
	α [%]	[a]	–	–		99.38		[a]				99.83		
n-Pr	x	–	1.00	1.00	0.00	0.81	0.19	0.11	0.77	0.12	0.00	0.20	0.58	0.22
	s^2_{theor}	–	0.18	0.27		–		–				–		
	α [%]	–	–	–		96.01		89.31				99.27		
iso-Pr	x	1.00	1.00	1.00	0.00	0.67	0.33	0.00	1.00	0.00	0.00	0.00	0.68	0.32
	s^2_{theor}	–	2.49	3.30		–		17.33				–		
	α [%]	[a]	–	–		99.41		–				96.32		
n-Bu	x	–	1.00	1.00	0.00	0.82	0.18	0.00	1.00	0.00	0.00	0.25	0.58	0.17
	s^2_{theor}	–	0.14	0.25		–		–				–		
	α [%]	–	–	–		99.37		[a]				99.51		
n-Bu^E	x	–	1.00	1.00	0.00	0.80	0.20	0.00	1.00	0.00	0.00	0.24	0.58	0.18
	s^2_{theor}	–	11.96	7.25		–		–				–		
	α [%]	–	–	–		97.81		[a]				97.76		
iso-Bu	x	–	1.00	1.00	0.00	0.87	0.13	0.00	1.00	0.00	0.00	0.15	0.62	0.23
	s^2_{theor}	–	4.90	1.46		–		12.12				–		
	α [%]	–	–	–		93.36		–				98.86		

Grey background points at the results obtained for bands containing incorrect experimental signals.

[a] Intensity of main signal < 5%.

Me_4Sn spectrum and the presence of CH_2Sn^+ extra ion in band B4 (Table 2) of this spectrum. Results reported here are in very good agreement with those obtained recently by Lawson and Ostah [20,21].

Comparison of Bu_4Sn^E and Bu_4Sn spectra of the same compound obtained from two various sources (recorded by the authors and taken from the NIST database, respectively) shows that s^2_{theor} values for simple bands are significantly higher in the case of the former spectrum (Table 2). Such behavior is very likely caused by the presence of background in this spectrum. It is well known that most spectra are subjected to various procedures to improve their quality (e.g., background elimination), prior to their incorporation into popular databases.

It is finally worth noting that observation of the values of ion contributions (x) in complex bands B5 and B3 of all spectra studied revealed some interesting relationships. For B5, the contribution of Sn^+ ion decreases with the increase of hydrogen atoms number in organotin molecules (Fig. 3a), whereas in case of SnH_3^+, this tendency is the opposite (Fig. 3b). In Fig. 3a, it is also visible that the contribution of Sn^+ ion in case of organotins having a linear structure of alkyl groups *n*-R is lower than that for compounds containing branched alkyl groups *iso*-R. Such relationship for SnH_3^+ ion is again opposite (Fig. 3b). Analogous trends are visible for RSn^+ and $RSnH_2^+$ pair of ions in B3 complex band (Fig. 3c and d). All trends mentioned here suggest existence of the relationship between contribution of ions in experimental

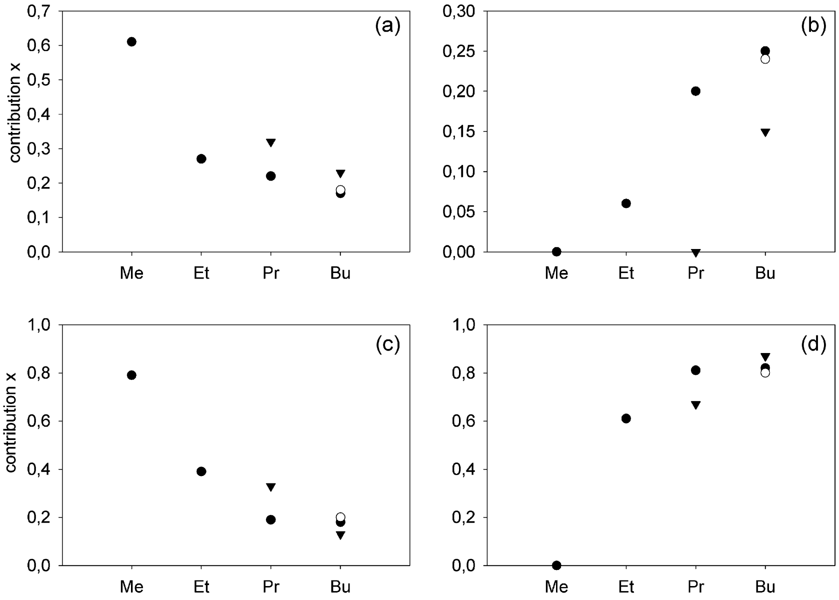

Fig. 3. Contributions of Sn^+ (a) and SnH_3^+ (b) ions in B5 band as well as RSn^+ (c) and $RSnH_2^+$(d) ions in B3 from EI mass spectra of R_4Sn organotin series vs. type of alkyl group R having linear (●—*n*) or branched (▼—*iso*) structure. Symbol ○ refers to the experimental mass spectrum *n*-Bu_4Sn^E recorded by the authors.

bands and type of alkyl group (*n*- or *iso*-) in symmetrical R_4Sn derivatives.

References

[1] S.E. Stein, Chemical substructure identification by mass spectral library searching, J. Am. Soc. Mass Spectrom. 6 (1995) 644–655.

[2] F.W. McLafferty, M.-Y. Zhang, D.A. Stauffer, S.Y. Loh, Comparison of algorithms and databases for matching unknown mass spectra, J. Am. Soc. Mass Spectrom. 9 (1998) 92–95.

[3] K. Varmuza, W. Werther, Mass spectral classifiers for supporting systematic structure elucidation, J. Chem. Inf. Comput. Sci. 36 (1996) 323–333.

[4] NIST/EPA/NIH Mass Spectral Library (National Institute of Standards and Technology and Advanced Chemistry Development, Inc.), Edition, 2002.

[5] J. Meija, Mathematical tools in analytical mass spectrometry, Anal. Bioanal. Chem. 385 (2006) 486–499.

[6] A. Tenhosaari, Computer-assisted composition analysis of the intensity ratios of isotope patterns of the molecular ion and daughter ions in low-resolution mass spectra, Org. Mass Spectra. 23 (1988) 236–239.

[7] M. Pelzing, C. Neusüß, M. Macht, Recent Applications in LC–MS, LCGC Europe 17 (2004) 38–39.

[8] A.L. Rockwood, S.L. van Orden, R.D. Smith, Rapid calculation of isotope distributions, Anal. Chem. 67 (1995) 2699–2704.

[9] A.L. Rockwood, J.R. van Orman, D.V. Dearden, Isotopic compositions and accurate masses of single isotopic peaks, J. Am. Soc. Mass Spectrom. 15 (2004) 12–21.

[10] J. Meija, J.A. Caruso, Deconvolution of isobaric interferences in mass spectra, J. Am. Soc. Mass Spectrom. 15 (2004) 654–658.

[11] R. Bhat, Isotope pattern simulation in the mass spectrum of multinuclear organometallic cluster, Comput. Chem. 21 (1997) 299–303.

[12] M.C.B. Moraes, J.G.A. Brito-Neto, V.F. Juliano, C.L. do Lago, Eliminating the interference of M-*n*H ions in isotope patterns from low-resolution mass spectra, Int. J. Mass Spectrom. 178 (1998) 129–141.

[13] A.J. Gorączko, J.A. Szymura, Dehydrogenation processes and molecular clusters in mass spectra of organometallic and coordination compounds, Comput. Chem. 24 (2000) 585–594.

[14] J.A. Szymura, J. Lamkiewicz, Band composition analysis: a new procedure for deconvolution of the mass spectra of organometallic compounds, J. Mass Spectrom. 38 (2003) 817–822.

[15] S. Boué, M. Gielen, J. Nasielski, Electron impact fragmentation of some mixed and symmetrical tetraalkyltins, Bull. Soc. Chim. Belges 77 (1968) 43–58.

[16] M. Gielen, G. Mayence, Organometallic compounds VII. Electron impact fragmentation of trialkyltin halides, J. Organomet. Chem. 12 (1968) 363–368.

[17] M. Gielen, J. Nasielski, Mass spectra of same aryltrimethyltins, Bull. Soc. Chim. Belges 77 (1968) 5–14.

[18] M. Gielen, M. DeClercq, Organometallic compounds XXXV. Physico-chemical properties of sterically hindered organotin compounds, J. Organomet. Chem. 47 (1973) 351–357.

[19] F.W. McLafferty, F. Tureček, Interpretation of Mass Spectra, 4th ed., University Science Books, Mill Valley, 1993.

[20] G. Lawson, N. Ostah, Comparison of the tandem mass spectrometry analysis of compounds of general structure $R_2R'SnPh$, $RR'SnPh_2$ with R_4Sn analogues, Appl. Organomet. Chem. 14 (2000) 874–881.

[21] G. Lawson, N. Ostah, Tandem mass spectral studies of the fragmentation pathways of organotin compounds of general formula R_3SnR', Appl. Organomet. Chem. 14 (2000) 383–388.

[22] J. Meija, G. Centineo, J.I. Garcia Alonso, A. Sanz-Medel, J.A. Caruso, Interpretation of butyltin mass spectra using isotope pattern reconstruction for the accurate measurement of isotope ratios from molecular clusters, J. Mass Spectrom. 40 (2005) 807–814.

[23] M. Hoch, Organotin compounds in the environment—an overview, Appl. Geochem. 16 (2001) 719–743.

[24] S.H.L. Thoonen, B.J. Deelman, G. Koten, Synthetic aspects of tetraorganotins and organotin(IV) halides, J. Organomet. Chem. 689 (2004) 2145–2157.

[25] J.R. De Laeter, K.G. Heumann, K.J.R. Rosman, Isotopic compositions of the elements 1989, J. Phys. Chem. Ref. Data. 20 (1991) 1327–1341.