

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

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ABSTRACT

Analysis of EI mass spectra of R_4Sn organotin 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.

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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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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*-tetraethyltin 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 $s^2_{theor} < 20$, the experimental band originates from a single ion and is called simple. In cases where $s^2_{theor} > 20$, 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 $s^2_{theor} > 20$, 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 $s^2_{theor} < 20$, 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 Et Sn^+ 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 Et SnH^+ . Subsequent modeling of B3 applying Et Sn^+ and Et SnH^+ 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 (Et Sn^+ , Et SnH^+ and Et SnH_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 Et Sn^+ and Et SnH_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-

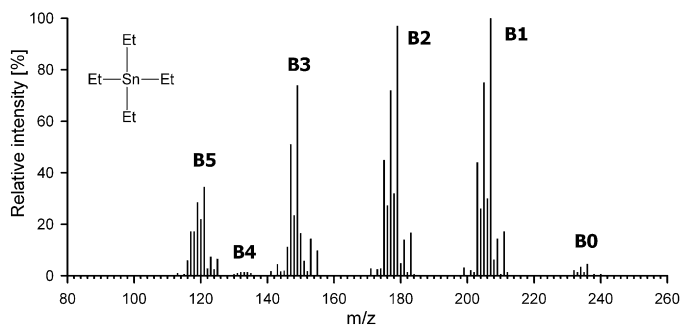


Fig. 1. Mass spectrum of tetraethyltin ($C_8H_{20}Sn$) from NIST database [4] showing the division on bands B0–B5.

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