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Identification and determination of butyltin compounds in water by ion trap gas chromatography–mass spectrometry after conversion to methyl or hydride derivatives

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Abstract

Capillary column gas chromatography with ion trap mass spectrometric detection has been shown to be a powerful technique for the determination of trace and ultratrace quantities of tributyltin and its degradation products (di- and monosubstituted analogues) in water. Butyltins were extracted into hexane in the presence of tropolone (0.2%, w/v) followed by either Grignard methylation or $NaBH_4$ reduction to corresponding butyltinhydrides to produce species of sufficient volatility. The wide linear dynamic range (over three orders of magnitude) and pg sensitivity obtained for the ion trap mass spectrometer operating in electron impact (EI) mode has demonstrated the ability of this GC–MS configuration to provide routinely trace and ultratrace analyses of organotins. Two derivatization routes are compared, in combination with GC–MS using classical electron impact or chemical ionization (CI). Hydride derivatization offers reduced labour effort and for most cases easier interpretation of observed spectra. Grignard methylation provides lower detection limits when using EI ionization and superior stability of standard calibration solutions. CI detection mode using CI reagent gases methane, isobutane, acetonitrile a methanol was studied. Methanol and acetonitrile CI provide simple mass spectra, yielding complementary spectral information to EI. The reported values of detection limits for acetonitrile CI are comparable to those using EI ionization mode. The acetonitrile CI mass spectra are characterized by the formation of $[M_{(FRAGMENT)} + 42]^+$ ions.

1. Introduction

Organotin compounds have been used over the last decades in increasingly large amounts as wood preservatives, agrochemicals and poly(vinyl chloride) stabilizers. The use of organotins in industry rose from ca. $5 \cdot 10^6$ kg worldwide in 1965 to $35 \cdot 10^6$ kg in 1980 [1]. In the Czech Republic the produced quantity of formulations based on tributyltin derivatives is estimated to $5 \cdot 10^5$ kg annually. The growing concern about the fate of organotin in the environment created a need for the development of faster, more sensitive and more accurate methods for speciation analysis of organotin compounds in environmental samples. The toxicity of organotin compounds is species dependent so a viable analytical method should allow the determination of the target compound without the interference from other organotin species. It should also

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provide sufficient sensitivity: $\langle 1$ ng/l for water and $\langle 1$ ng/g for dry solid material [2].

Analytical techniques for the determination of trace amounts of organotin compounds in environmental samples have been reviewed in several papers [2,3]. Most organotins are present in the environment in the form of ionic species such as R_3Sn^+, R_2Sn^{2+} and RSn^{3+}. Gas chromatography (GC) is usually preferred to high-performance liquid chromatography as a separation technique due to its higher resolving power and the availability of more sensitive and selective detectors. Complexation and solvent extraction followed by a derivatization technique based on Grignard alkylation or hydride generation with sodium borohydride reagent are in common use to convert ionic organotin compounds to more volatile species. Recently an alkylation technique using sodium tetraethylborate was reported [4]. Sample preparation via Grignard derivatization is a tedious and time-consuming procedure using a very reactive reagent of limited stability. Hydride generation is much faster and can be performed in presence of a protic solvent. However, organotin hydrides produced exhibit limited stability and fresh standard solutions must be prepared for every calibration.

Several detection techniques have been applied in combination with GC: flame photometric detection [5], atomic absorption spectrometry [6], atomic emission detection [3] and mass spectrometry (MS) [3]. Reported MS electron impact spectra of organotin compounds [7] exhibit extensive fragmentation corresponding to cleavage of carbon–tin and carbon–carbon bonds and an absence of molecular ion signal. Chemical ionization (CI) frequently provides a valuable structural information concerning the molecular ion. This information helps to identify unknown components of samples. Ion trap MS detectors allow to use routinely various reagent gases in CI, promising more selective and sensitive analyses of organometallic species.

The present study reports the evaluation of Grignard methylation and hydride derivatization techniques in combination with GC–ion-trap MS for speciation of different butyltin compounds in water solutions. MS detection with different ionization techniques has been used for structural identification and quantification. Comparison has been made between hydride and Grignard alkylation derivatization techniques. Various reagent gases for chemical ionization MS have been investigated for the ultratrace analysis of butyltin compounds.

2. Experimental

2.1. Materials

Bis-(tributyltin)oxide (97% purity) and tributyltin naphthenate (94% purity) were obtained from Bochemie (Bohumín, Czech Republic). Samples of tri-*n*-butyltinchloride (Bu_3SnCl), di-*n*-butyltindichloride (Bu_2SnCl_2), *n*-butyltintrichloride ($BuSnCl_3$), di-*n*-butyldimethyltin (Bu_2SnMe_2) and tetra-*n*-butyltin (Bu_4Sn) were a kind gift from Department of Inorganic Chemistry of the University Pardubice (Czech Republic). All samples exhibited a chromatographic purity $\geq 95\%$. Tri-*n*-butylmethyltin (Bu_3SnMe, bp 126°C/1.6 kPa) was prepared by the methylation of Bu_3SnCl. Tropolone (2-hydroxy-2,4,6-cycloheptatrienone, 98%) was from Aldrich, sodium tetrahydroborate (for synthesis) was supplied by Sojuzchimexport (USSR). The Grignard reagent methyl magnesium iodide (MeMgI, 2 mol/l solution in diethylether) was prepared in our laboratory by the dropwise addition of 0.4 mole of methyliodide (Merck, Germany) dissolved in 100 ml of dry diethylether to 0.4 mole of magnesium metal (Lachema, Brno, Czech Republic) and 100 ml of dry diethylether in a nitrogen atmosphere. All solvents used were analytical-grade quality and were distilled in a glass still before use. All other chemicals used in this study were the highest purity materials available from commercial sources and were used without any purification.

2.2. Apparatus

The ion trap MAGNUM GC–MS benchtop system (Finnigan MAT, USA) utilized Varian 1075 injector in splitless mode (held at 250°C,

split valve was closed from 0.01 to 0.51 min after injection, split ratio was 30: 1) and DB-5 ms capillary column (JW Scientific, USA) 30 m × 0.25 mm with a 0.25 μm film thickness. The carrier gas (He 99.996%) velocity was 33.1 cm/s (at 60°C). The GC oven was maintained at 60°C for 1 min, increased at 8°C/min to 100°C and at 15°C/min to a maximum of 250°C. Samples were introduced as 1 μl aliquots with Hamilton 10 μl syringe using "solvent flush hot needle" technique [8]. The transfer line was held at 280°C and ion trap manifold at 200°C. The ion trap was tuned using default software settings (Magnum 2.4, Finnigan MAT) to obtain suitable mass calibrations, filament emission current, multiplier voltage and AGC (Automatic Gain Control) settings. The GC–MS ion abundance test [9] using *p*-fluorobromobenzene and decafluorotriphenylphosphine was performed daily to check the GC–MS system performance. For chemical ionization (CI) filament emission current was set at 10 μA and a target value of AGC was set to 60% of the value obtained for electron impact ionization. Ion trap parameters setting for CI operation using methane (99.9995% Linde-Technoplyn, Prague), isobutane (puriss, Fluka) acetonitrile (Lichrosolv, Merck) and methanol (analytical-grade, Lachema, Brno, Czech Republic) is summarized in Table 1.

2.3. Sample extraction

Synthetic samples were prepared by spiking 200 ml of distilled water with the calculated volume of the solution of the organotin compound in absolute ethanol. Water samples taken from the Vltava river (Řež near Prague, May 1994) were transported to the laboratory in 2.5 l glass bottles. A volume of 200 ml water was immediately taken for analysis after separation of suspended material by sedimentation for 2 h.

To a 200 ml sample 20 ml acetate buffer (prepared by mixing equivalent volumes of 5.4 *M* acetic acid and 3.4 *M* NaOH) was added and the sample was extracted twice with 10 ml of 0.2% (w/v) tropolone solution in hexane [13] (shaking for 3 min, phase separation 7 min.) Extracts were dried over anhydrous sodium sulphate and their volume was reduced to 1 or 2 ml.

2.4. Derivatization

The Grignard methylation procedure [10] was performed by mixing 1 ml of dry hexane extract with 1 ml 2 *M* MeMgI. Every 10 min the reaction mixture was shaken by hand and after 50 min 3 ml hexane was added followed by addition of 3 ml of 2 *M* H_2SO_4 to destroy the excess of Grignard reagent. After separation the organic layers were evaporated to 1 ml under a gentle stream of nitrogen.

Hydride derivatization procedure [11] was performed by addition 1 ml of freshly prepared solution of $NaBH_4$ (0.25 g $NaBH_4$ in 10 ml of absolute ethanol) to 2 ml of hexane extract. After 15 min 5 ml of H_2O was added, the mixture was shaken thoroughly for 3 min and 1 ml of organic layer was than transferred to another vial.

Table 1
Operation parameters of CI ionization for different reagents

	Methane	Isobutane	Acetonitrile	Methanol
Maximum ioniz. time (μs)	1500	1500	1500	1500
Maximum reaction time (ms)	30	50	100	30
Ionization level (amu)	5.4	20	15.4	10.0
Reaction level (amu)	13.4	40.0	35.0	25.0
Reagent ion eject level (amu)	45	65	85	60
Reagent ion eject adjust (%)	100	100	100	100
Reagent reaction time (μs)	2400	15000	5400	5600

2.5. Preparation of calibration standards

Solutions of alkyltin compounds for calibration were prepared by stepwise dilution of the stock solution prepared from 0.5–1 mg of substance and hexane. Samples for analysis were prepared by mixing 1 ml volumes of internal standard solution (cyclododecane 1 μg/ml in hexane) and analyte solution. In this way samples in concentration range 1 ng/ml to 70 μg/ml were prepared containing cyclododecane in the same concentration 0.5 μg/ml.

Standard solutions of tin hydrides were prepared by derivatization from the solutions of Bu_2SnCl_2 and $(Bu_3Sn)_2O$ as described above. By the mixing of 1 ml of organic solution of tin hydride with 1 ml of internal standard solution samples of butyltin hydrides in the concentration range 20 ng/ml to 50 μg/ml containing 0.5 μg/ml cyclododecane were prepared.

2.6. Quantification

Peak areas were used for quantitative calculation. Peaks in the chromatograms were assigned to individual organotin compounds on the basis of retention time and successful fits to reference library mass spectra. Magnum 2.4 software was used to build a routine for peak identification, integration and quantitation. A statistical software package ADSTAT (Trilobyte, Pardubice, Czech Republic) was used to calculate and evaluate the parameters of calibration curves. All presented results represent an average value from minimum triplicate measurements. The values of detection limit were calculated as an amount of injected sample that gives a detector signal equal to triple the noise level. Calculation was performed from the measurements where signal (S) to the noise level (N) $S/N \leq 20$.

3. Results and discussion

3.1. Detection of organotin compounds

With the GC conditions used in this study a baseline separation was easily achieved both for alkyltin compounds and alkyltin hydrides. Table 2 summarizes the retention data of compounds under the study. An internal standard quantification strategy was employed to minimize the response variation. From cyclododecane, *n*-tridecane and benzylnaphthalene tested, cyclododecane was selected as internal standard that provides a fragmentation pattern in MS spectra convenient for all data acquisition methods used in this study.

Table 2
Retention data of organotins

Compound	Retention time t_{Ri} (min:s)	Relative retention r_G^a
$BuSnMe_3$	4:35	0.72
Bu_2SnMe_2	8:59	1.41
Bu_3SnMe	11:52	1.85
Bu_4Sn	13:54	2.17
Bu_2SnH_2	7:33	1.18
Bu_3SnH	11:35	1.81

[a] Unadjusted relative retention $r_G = t_{Ri}/t_{R(st)}$ relative to *n*-decane ($t_{R(st)} = 6:24$)

Full scale monitoring with electron impact ionization produces MS spectra of butyltin compounds characterized by clusters of isotope ion at each fragment as seen in Fig. 1 for Bu_3SnH and Bu_3SnMe species. The isotope pattern created by ten tin isotopes contributions is particularly useful for recognition of any organotin compound occurring in a sample. Butyltin compounds can be identified using the comparison of their ion trap mass spectra with the standard MS spectra from the reference NIST library (National Institute of Standards and Technology Mass Spectrometry Library, Edition 1990). Excellent NIST library matches were obtained even at the concentration level corresponding to 5 pg of Bu_3SnMe injected.

The molecular ion $[M]^{+\cdot}$ was not observed for any of butyltin compounds studied and the characteristic fragmentation pattern is dominated by successive cleavage of alkyl groups from $[M]^{+\cdot}$ with preferential cleavage of the largest alkyl group accompanied by the formation of $[M - R + 1]^+$ ions as usually observed [12,14].

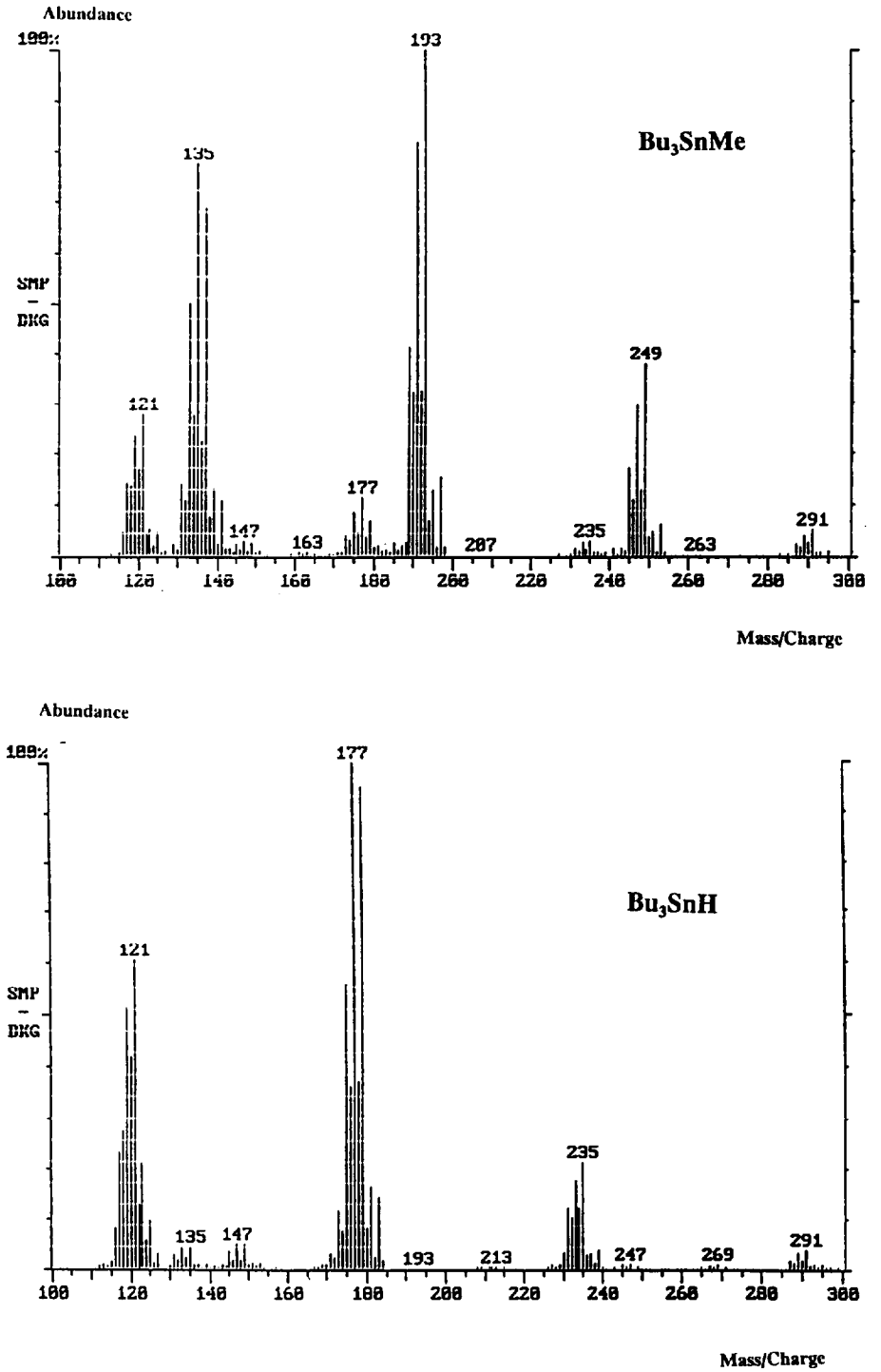

Fig. 1. Full scan EI spectra with background subtraction of Bu_3SnMe and Bu_3SnH.

Table 3 presents the characteristics of MS spectra of compounds under study.

3.2. Determination of butylmethyltin compounds

Two data acquisition procedures of detector operation were used for quantitative analyses of alkyltin compounds with electron impact ionization. Method 1: at ultratrace level (up to 50 pg of substance injected) using MS operation range 100–250 amu, background mass value 95 amu and the ions selected for quantitation as follows: $Bu_3SnMe = 193$, $Bu_2SnMe_2 = 149 + 151$, cyclododecane (internal standard) = 111. Method 2: at trace level (10 pg to 30 ng of substance injected) with mass range 50–350 amu, background mass value 50 amu and the ions selected for quantitation as follows: $Bu_3SnMe = 245 + 247 + 249$, $Bu_2SnMe_2 = 203 + 205 + 207$, cyclododecane = 83 + 111. Method 1 was optimized to produce a maximum signal to noise ratio of monitored ions. The mass range scanned and the background mass value chosen suppress the contribution of hydrocarbon background to the detector response in the range bellow 100 amu. All ions of m/z lower than background mass value 95 are ejected from the ion trap before AGC procedure determines the optimum ionization time for the scan. Method 2 is suited to produce full scale spectra for identification of tributyltin degradation products in a broad concentration range. Excellent linearity was observed over 3 orders of magnitude (correlation coefficient $r \geq 0.998$, number of points $n = 12$, intercept value statistically not different from zero) up to concentration 30 μg/ml both for Bu_3SnMe and Bu_2SnMe_2. However, for injected amount exceeding 10 ng of substance distortion of MS spectra was observed similar to reported by Reader and Pelletier [14] due to a overload-

Table 3
Comparison of theoretical and observed masses for major ions in EI ionization mode[a]

Compound [M]	Fragment	Expected ion	Calculated mass	Observed mass
Bu_3SnMe	BuSnMe	$[M - 114]^+$	192	193
[306]	MeSn	$[M - 171]^+$	135	135
	Bu_2SnMe	$[M - 57]^+$	249	249
Bu_2Sn	Me_2Me_2Sn	$[M - 114]^+$	150	151
[264]	MeSn	$[M - 129]^+$	135	135
	$BuSnMe_2$	$[M - 57]^+$	207	207
	BuSnMe	$[M - 72]^+$	192	193
$BuSnMe_3$	Me_3Sn	$[M - 57]^+$	165	165
[222]	Me_2Sn	$[M - 72]^+$	150	151
	MeSn	$[M - 87]^+$	135	135
	$BuSnMe_2$	$[M - 15]^+$	207	207
Bu_4Sn	Bu_2Sn	$[M - 114]^+$	234	235
[348]	BuSn	$[M - 171]^+$	177	177
	Bu_3Sn	$[M - 57]^+$	291	291
Bu_3SnH	Bu_2SnH	$[M - 57]^+$	235	235
[292]	BuSnH	$[M - 114]^+$	178	179
Bu_2SnH_2	BuSn	$[M - 59]^+$	177	177
[236]	Sn	$[M - 116]^+$	120	120

[a] Masses are calculated for the ^{120}Sn isotope. Fragment ions are presented in decreasing intensity order.

ing of the ion trap with analyte leading to loss of linear response. Detection limit calculated for S/N = 3 was 0.9 pg for Bu_3SnMe and 1.2 pg for Bu_2SnMe_2 (METHOD 1 acquisition). The calibration data obtained were used to evaluate derivatization yields of Grignard methylation reaction of Bu_3SnMe. An average value of derivatization yields of Bu_3SnMe at 200 ng/ml to 10 μg/ml concentration level (5 measurements) was found 93.6%. This value corresponds well with literature data [3]. Reaction efficiency of methylation appears to give higher recoveries than using the bulkier molecules or reagents with longer aliphatic chain.

3.3. Determination of butyltin hydrides

From aqueous solutions the butyltin species were separated by extraction into hexane and organic extract was directly subjected to reaction with $NaBH_4$ to produce the corresponding hydrides. Excellent linearity was obtained for 0.1–30 μg/ml ($r > 0.999$, for $n = 7$) for both compounds studied. Detector response of ions with m/z 177 + 179 was monitored for Bu_3SnH and for Bu_2SnH_2 ions 118 + 120 were selected (cyclododecane 83 + 111). The calibration solutions were prepared not by the dilution of stock solution of the substance but by derivatization of corresponding solutions of Bu_2SnCl_2 and $(Bu_3SnO)_2$. The detection limit was 24 pg and 17 pg for Bu_3SnH and Bu_2SnH_2, respectively.

The solutions of butylhydrides were tested and found to be stable for two weeks when stored in glass vials in a refrigerator at 4°C. Reproducibility of the derivatization step was determined by replicate analysis of Bu_3SnCl and $(Bu_3SnO)_2$ hexane solutions. RSD value 8.1 and 8.8% respectively was found ($n = 4$). These figures are higher when compared with 3% value reported [11] but they are quite acceptable for this type of trace analysis.

3.4. Precision and accuracy

The precision of determination of butyltin compounds expressed as relative standard deviation (RSD) was calculated from replicate measurements ($n = 5$) at concentrations covering the whole linear dynamic range of the method. Both methylation and hydride derivatization exhibit RSD value in the range 5–20%. The higher value corresponds to concentration near the determination limit (S/N = 10). To estimate the accuracy of the method samples spiked with known amount of analyte were analyzed. The difference between recovery values observed and 100% was less than precision of the analysis and it is believed that accurate results have been achieved.

3.5. Application to water sample

To test practical utility of the procedures both hydride derivatization and methylation was used to analyze samples from the Vltava river. No background concentration of organotin compounds was detected. In a series of experiments the sample was spiked at 1 μg/ml to 30 μg/ml level with Bu_2SnCl_2 and $(Bu_3Sn)_2O$ and analyzed. No matrix interference disturbing the determination was observed. Recovery data obtained did not notably differ from those obtained in experiments with distilled water solutions.

3.6. Chemical ionization

CI experiment has been performed to provide complementary spectroscopic information to EI spectra of organotins for identification purposes and to study the ways to increase signal to noise level for organotin compounds. The ion trap offers the flexibility to switch from EI to positive CI mode instantly with no system venting, recalibration or hardware changes even in the same analysis. Four reagent gases were of particular interest: methane, isobutane acetonitrile and methanol. Methane and isobutane are widely used classical proton transfer ionizing reagents usually producing recognizable ion due to protonated molecule. Methanol and acetonitrile are reagents that promise a selective gas phase reaction with organometallic compounds.

3.7. Methane and isobutane CI

Table 4 summarizes the characteristic ion fragments of methane CI spectra for organotin

Table 4
Characteristic ions in methane CI spectra of butyltin compounds[a]

Compound [M]	Fragment	Expected ion	Calculated mass	Observed mass
Bu_3SnMe	Bu_2SnMe	$[M-57]^+$	249	249
[306]	Bu_3Sn	$[M-15]^+$	291	291
	BuSnMe	$[M-114]^+$	192	193
Bu_2SnMe_2	$BuSnMe_2$	$[M-57]^+$	207	207
[264]	Bu_2SnMe	$[M-15]^+$	249	249
Bu_4Sn	Bu_3Sn	$[M-57]^+$	291	291
[348]	Bu_2Sn	$[M-114]^+$	234	235
Bu_3SnH	Bu_2SnH	$[M-57]^+$	235	235
[292]	BuSnH	$[M-114]^+$	178	179
	Bu_3SnH	$[M-1]^+$	291	291
Bu_2SnH_2	$BuSnH_2$	$[M-57]^+$	179	179
[236]	Bu_2SnH	$[M-1]^+$	235	235

[a] Masses are calculated for the ^{120}Sn isotope. Fragment ions are presented in decreasing intensity order.

compounds under study. The molecular peak was not observed for any butyltin compound similarly as observed by Greaves and Unger [13] in quadrupole mass spectrometric study. Methane CI spectra observed are similar to EI spectra as seen in Fig. 2, the intensity of lower m/z fragments is decreased and high m/z fragments are more intense. The isotopic ion pattern is not deformed by the formation of $[M-R+H]^+$ ions. The sensitivity of the method is lower when compared to EI. Detection limit of about 30 pg was calculated for butyltin species (compared to ~1 pg in EI).

CI spectra using isobutane exhibit very similar features as methane CI MS spectra but sharp decrease of the sensitivity of detection was observed for butylmethyltins and butyltinhydrides. Therefore, methane and isobutane CI brings no advantage for ion trap mass spectrometric detection of organotins.

3.8. Acetonitrile CI

Acetonitrile CI spectra of organotin compounds are characterized by selective adduct formation as demonstrated for Bu_3SnMe in Fig. 3. Table 5 presents the characteristic ions observed for butyltins. The fragmentation pattern is suppressed and $[M_{(FRAGMENT)}+42]^+$ ions are produced. The formation of adducts is not influenced by the change of MS manifold temperature in the range 150–200°C. Relatively simple acetonitrile CI spectra provide useful information on the $[M+42]^+$ ion. Simplicity of the spectra results in high sensitivity of the method. The sensitivity is equivalent to that of the EI mode for methylbutyltins and Bu_3SnH. For Bu_3SnH lower value of detection limit was found than in EI ionization mode. The best signal to noise level ratio was found at selective monitoring of the abundance of ions at m/z 288 + 290 and 274 + 276 for methylbutyltins and butyltinhydrides, respectively. The method exhibits a good linear dynamic range at 1 pg to 10 ng of injected substance.

3.9. Methanol CI

Methanol stimulates preferential cleavage of methyl groups in Bu_2SnMe_2 (Fig. 4) in a similar way as it was observed for acetonitrile CI spectra. The most intense ion in methanol CI spectra

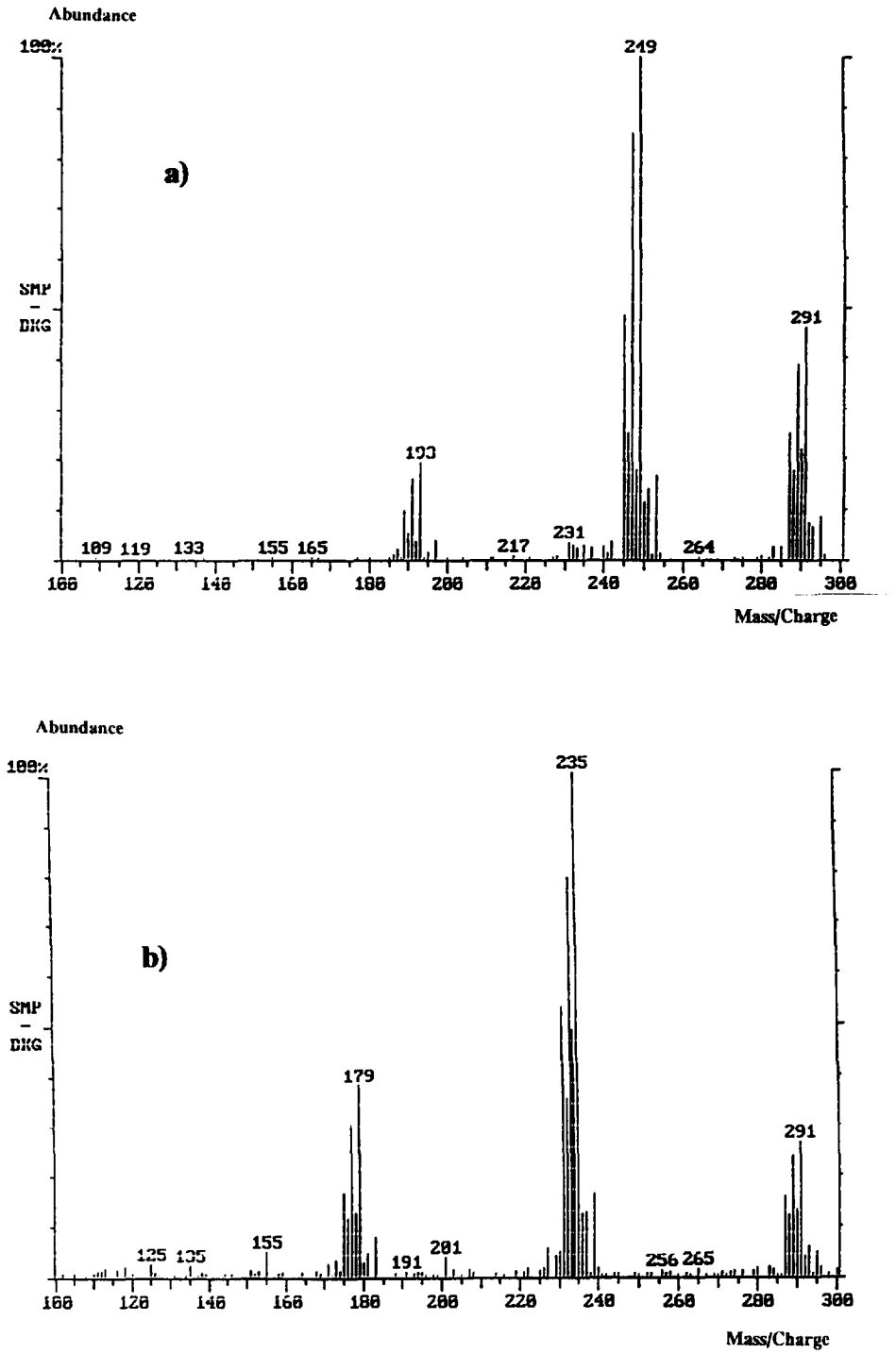

Fig. 2. Mass spectra of (a) Bu_3SnMe and (b) Bu_3SnH obtained using positive CI with methane as reagent gas and background subtraction.

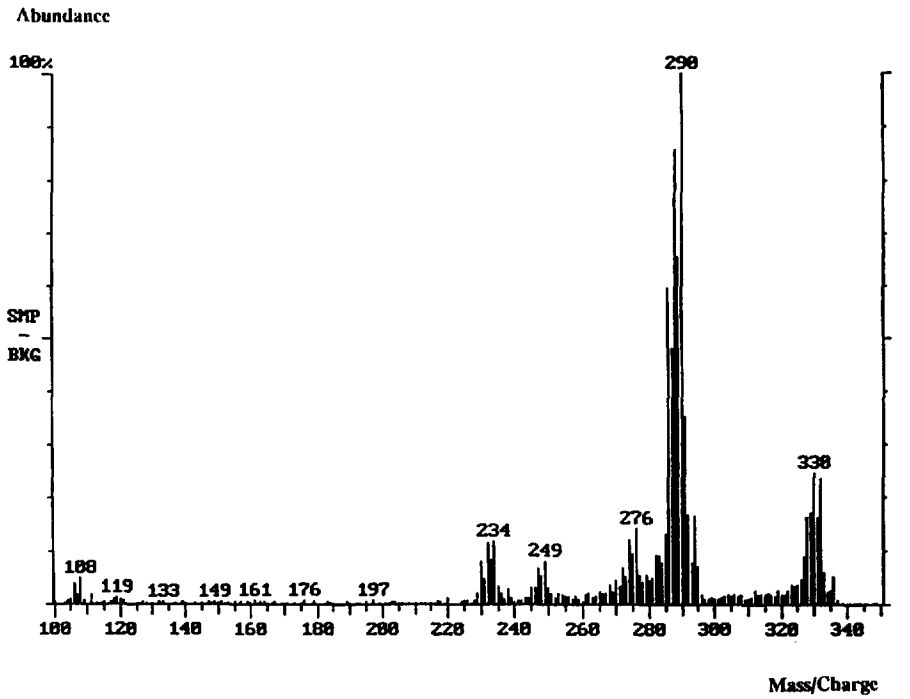

Fig. 3. Mass spectrum of Bu_3SnMe obtained using positive CI with acetonitrile as reagent gas and background subtraction.

of alkyltin hydrides is $[M - H]^+$. This phenomenon can serve as a unique identification tool of unknown compounds. Table 6 presents the characteristic ions observed in methanol CI spectra of organotins. The optimum values of signal to noise level were found for monitoring ions at

Table 5
Characteristic ions in acetonitrile CI spectra of butyltin compounds[a]

Compound [M]	Expected ion	Calculated mass	Observed mass
Bu_3SnMe	$[M - Bu + 42]^+$	291	290
[306]	$[M - Me + 42]^+$	333	331
Bu_2SnMe_2	$[M - Me + 42]^+$	291	290
[264]	$[M - Bu + 42]^+$	249	248
Bu_4Sn	$[M - Bu + 42]^+$	333	332
[348]	$[M - 2Bu + 42]^+$	276	276
	$[M - Bu]^+$	291	291
Bu_3SnH	$[M - Bu + 42]^+$	277	276
[292]	$[M + 42]^+$	334	330
	$[M - H]^+$	291	291
Bu_2SnH_2	$[M + 42]^+$	278	276
[236]	$[M - Bu + 42]^+$	221	220

[a] Masses are calculated for the ^{120}Sn isotope. Fragment ions are presented in decreasing intensity order.

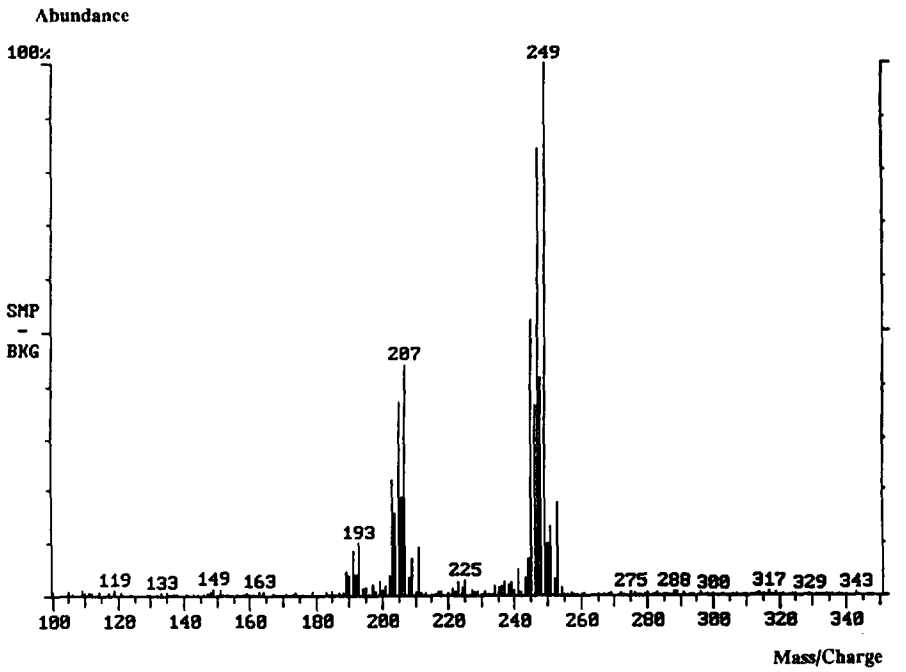

Fig. 4. Mass spectrum of Bu_2SnMe_2 obtained using positive CI with methanol as reagent gas and background subtraction.

m/z 247 + 249 for butylmethyltins, 291 for Bu_3SnH and 231 + 233 + 235 for Bu_2SnH_2. Calibration graphs exhibit very good linear dynamic range at 1 pg–10 ng level of injected substance. Values of detection limits achieved with different ionization techniques are compared in Table 7.

Table 6
Characteristic ions in methanol CI spectra of butyltin compounds[a]

Compound [M]	Observed ion	Observed mass
Bu_3SnMe	$[M - Bu]^+$	249
[306]	$[M - Me]^+$	291
Bu_2SnMe_2	$[M - Me]^+$	249
[264]	$[M - Bu]^+$	207
Bu_3SnH	$[M - H]^+$	291
[292]	$[M - Bu]^+$	235
Bu_2SnH_2	$[M - H]^+$	235
[236]		

[a] Masses are calculated for the ^{120}Sn isotope. Fragment ions are presented in decreasing intensity order.

For butyltinhydrides methanol CI ionization exhibits comparable detectability to EI mode and provides an information on molecular weight of the analyte.

4. Conclusion

With the analytical method described in this paper, the presence of trace and ultratrace amounts of butyltin species either individually or

Table 7
Detection limits[a] (in pg) of organotin for various detection techniques

Compound	EI ionization	CI ionization Acetonitrile	CI ionization Methanol
Bu_3SnMe	0.9	1.3	14
Bu_2SnMe_2	1.2	1.9	18
Bu_3SnH	24	9	32
Bu_2SnH_2	17	7	24

[a] Presented as minimal detectable amounts of Sn for S/N = 3.

simultaneously present in dilute aqueous solutions can be determined quantitatively. Ion trap GC–MS lowers detection limits to the sub-pg level on routine basis. Hydride derivatization offers reduced labour effort and the increased sample throughput and for most cases easier interpretation of observed spectra. Grignard methylation provides lower detection limits when using classical EI ionization and superior stability of standard calibration solutions. The ion trap detector proved to be a sensitive and versatile device for routine use of chemical ionization with broad variety of reagents. This makes it possible to use selective reagents for organometallic species. Further study of CI ionization is in progress to assess its full potential especially in the field of biological and sediment matrices, where selective ionization of organotin species seems to bring very promising results.

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