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In situ ethylation–purge and programmed-temperature-vaporizer cold trapping–gas chromatography–mass spectrometry as an automated technique for the determination of methyl- and butyltin compounds in aqueous samples

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Abstract

A new method for the determination of methyl- and butyltin compounds in aqueous samples is presented. The organotin species are derivatized in situ with sodium tetraethylborate ($NaBEt_4$) in an 800-ml sample, purged on-line with helium and cryofocused at −40°C in the Tenax-filled glass insert of a modified split/splitless injector. The injector is equipped with a liquid nitrogen cooling and a heating wire which serves for programmed-temperature vaporization. After thermal desorption the peralkylated tin species are refocussed on the capillary GC column at 10°C followed by GC separation and mass spectrometric detection in the full scan mode. All steps are computer-controlled so that once the derivatizing reagent is added, the analysis is performed automatically. The concentration of $NaBEt_4$, the reaction time, the purge flow-rate and the purge time were optimized. The preconcentration of sample volumes of 800 ml led to detection limits in the range of 1–2 ng Sn/l. Due to the compound specific information of the full scan mass spectra, the presented method is a powerful tool for the speciation of alkyltin compounds in aqueous samples.

Keywords: Sample handling; Purge-and-trap methods; Organotin compounds

1. Introduction

In spite of the growing understanding and awareness of the ecotoxicological importance of organotin compounds they are still used worldwide in large amounts [1]. The undiminished interest in organotin speciation analysis is reflected in the large number of analytical methods published in recent years and reviewed in [2–5]. Most of them are based on the use of hyphenated techniques using liquid or gas chromatography and sensitive element specific detection like atomic absorption spectrometry (AAS), atomic emission spectrometry (AES), flame photometric detection (FPD) or inductively coupled plasma mass spectrometry (ICP-MS). The respective methods use different analyte isolation, derivatization, preconcentration and sample introduction procedures, depending on the chromatographic system and the detection method.

Gas chromatography (GC) requires more or less volatile compounds and therefore three-, two- and monosubstituted organotin compounds are derivatized, mostly by hydride generation, Grignard alkyla-

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tion or ethylation with sodium tetraethylborate ($NaBEt_4$). Grignard alkylation needs water free solvents whereas hydride generation and ethylation with $NaBEt_4$ can be performed in aqueous solution and thus are used for in situ derivatization of aqueous samples. With regard to interferences and stability of the analytes ethylation is advantageous over hydride generation [6,7]. Once derivatized, the analytes can be subjected to different isolation and preconcentration procedures, e.g., solvent extraction [8], purge-and-trap methods [9] or solid-phase microextraction [10,11], followed by suitable sample introduction methods.

The aim of our work was to combine a suitable derivatization, isolation, preconcentration and sample introduction procedure with a GC–MS coupling for the determination of methyl- and butyltin compounds in aqueous samples. Besides AES, MS is the only compound-specific method of detection used in organic trace analysis. Especially ion trap MS allows the positive identification of organotin compounds by their full scan mass spectra [12] and should therefore allow the identification of unknown organotin compounds not only by boiling point calculation [13,14].

For the reasons mentioned above we chose the in situ ethylation with $NaBEt_4$ as derivatization method. A purge-and-trap method combines isolation and preconcentration of the analytes in a single step which is easy to automate. Ceulemans et al. used a capillary cold-trap to preconcentrate methylated tin, lead and mercury compounds followed by thermal desorption and GC–AES determination [9]. Due to the high sensitivity of the AES, sample volumes of 10 ml were enough to reach sufficiently low detection limits. With regard to the lower sensitivity of the GC–MS and the following need of a higher preconcentration capacity, we modified a split/splitless injector to receive a cold trap–thermal desorption system similar to a programmed temperature vaporizer. In this study the automated experimental set-up and the optimization of critical system parameters are described.

2. Experimental

2.1. Apparatus

Fig. 1 shows a schematic diagram of the ethylation–purge-and-PTV cold trapping–GC–MS setup. A 1-l glass bottle with a gas dispersion tube served as reaction and purge vessel which was connected with a six-port/two-way motor valve (Valco Europe, Switzerland) via a nafion drying tube (type MD-050-24F, Omnifit, UK). A heating wire (12 V, Conrad Electronic, Germany) was wound around the drying tube in order to compensate for the cooling effect of the compressed air which was used as drying gas. When the motor valve is in the ‘desorption position’ a needle valve reduces the helium flow to a flow-rate suitable for GC separation.

The injection system was a split/splitless injector (PAS-1, Gerstel, Germany) modified similar to a programmed temperature vaporizer. A heating wire (75 W, Horst, Germany) was wound around the body of the injector. The glass insert was filled with Tenax TA (Supelco, Deisenhofen, Germany) held in place with plugs of silanized glass wool (Baker, Germany). A cylinder shaped brass jacket (30 mm O.D.) connected to a liquid nitrogen reservoir served for cooling the body of the injector to -40°C. The electrically actuated motor valve, the split valve, the cooling valve, the drying gas valve and the injector heating were computer-controlled by self-made software. The analytes were separated using a GC equipped with a cryo option (Model GC 6000 Vega series 2, Carlo Erba, Italy) and detected by means of an ion trap mass spectrometer (ITD 800, Finnigan MAT, Germany) operating with electron impact ionisation (EI) in the full scan mode. The operating conditions of the purge-and-trap–GC–MS system are listed in Table 1.

2.2. Chemicals

Dimethyltin dichloride (>95%), trimethyltin chloride (97%), *n*-butyltin trichloride (>95%) and sodium tetraethylborate (>98%) were purchased from Strem (Kehl, Germany), di-*n*-butyltin dichloride (97%) and tri-*n*-butyltin chloride (97%) from Fluka (Deisenhofen, Germany). Acetic acid (99–100%) was obtained from Riedel-de Haen (Seelze, Germany), sodium acetate (99%) from Roth (Karlsruhe, Germany) and acetone (analytical-reagent grade) from Merck (Darmstadt, Germany)

$NaBEt_4$ was filled in 100-mg portions into 30-ml vials under argon atmosphere by means of a glove

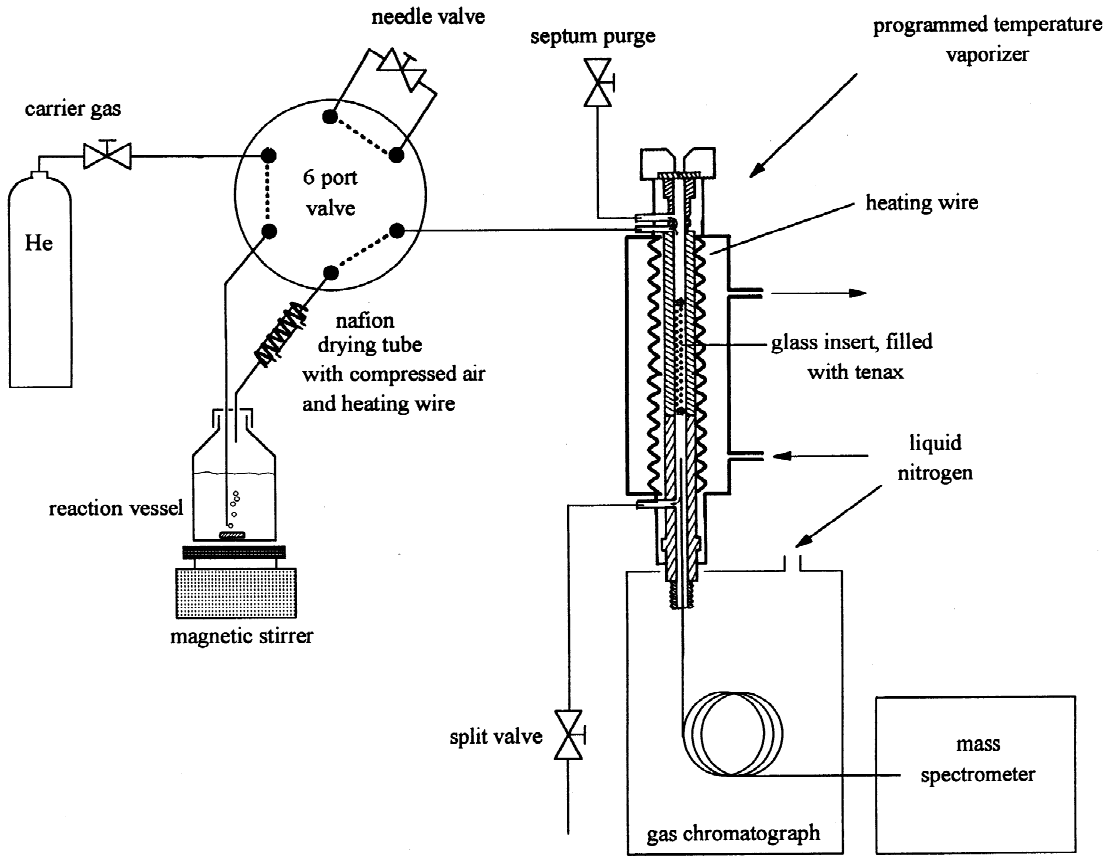

Fig. 1. Schematic diagram of the ethylation–purge and PTV cold trapping–GC–MS set-up.

box. The vials were stored at −18°C in the dark until use. Solutions of $NaBEt_4$ in double distilled water (1%) were prepared twice per week.

Stock solutions of the organotin compounds (1000 μg/ml each; as Sn) were prepared in acetone and stored at 4°C in the dark. A mixed standard solution (1 μg/ml per compound; as Sn) in acetone was prepared from the stock solutions once per week.

Table 1
Operating conditions of the purge and PTV cold trapping–GC–MS system

Operating conditions	
Purge flow-rate	650 ml/min
Purge time	5.0 min
Cryofocusing temperature	−40±2°C
Desorption temperature program	−40–275°C (90°C/min)
GC column	BPX5, 25 m×0.22 mm I.D., 1.0-μm (Resteck) DB-5MS, 30 m×0.25 mm I.D., 0.5-μm (J&W)
Oven program	10°C, 1.0 min 30°C/min 270°C 10.0 min
Column head pressure	70 kPa
Transfer line temperature	270°C

2.3. Analytical procedure

An 800-ml water sample was buffered with 1 *M* sodium acetate–acetic acid to pH 5.0. A 1-ml volume of 1% sodium tetraethylborate was reacted with the sample for 10 min. Thereafter the automated purge-and-trap–GC–MS analysis was started. In the first step, the drying gas valve and the cooling valve were opened and the injector was cooled with liquid nitrogen; the motor valve was in the desorption position so that the carrier gas passed through the needle valve which reduced the column head pressure to 70 kPa. The split valve was closed. When the injector temperature reached −40°C, the split valve was opened and the motor valve turned to the purge position. The peralkylated tin compounds were stripped from the aqueous solution with the helium flow, passed through the nafion drying tube for water removal and were cryofocused in the Tenax-filled glass insert of the injector. During the purge phase, the injector temperature was held between −42°C and −38°C. As the purge flow-rate was regulated via the split valve, the split ratio was regulated to maintain a similar column head pressure as during the desorption (and separation) phase. At the end of the purge time, the drying gas valve and the cooling and the split valves were closed, the motor valve turned to the desorption position and the injector temperature program was started. During the purge and the desorption phase, the GC oven was held at 10°C. At the end of the injector temperature program, the GC program and the MS acquisition were started automatically.

The optimization experiments were carried out with solutions of monomethyl-, dimethyl- and trimethyltin and monobutyl-, dibutyl- and tributyltin chlorides in 800 ml double distilled water at a concentration of 12.5 ng/l (as Sn) per compound.

3. Results and discussion

3.1. Injector and GC oven temperature

An initial injector temperature of −40°C proved to be low enough to trap the analytes in the Tenax-filled glass insert. The maximum injector heating rate of 90°C/min limited the choice of a desorption temperature program. With the chosen heating program (−40°C to 275°C at 90°C/min), the analytes were desorbed from the Tenax. The low heating rate and the resulting long desorption time caused severe peak broadening for the low boiling metal species when using a GC oven temperature program starting at 35°C. Therefore the GC oven was cooled with liquid nitrogen and the low boiling analytes could be refocussed on the column at an oven temperature of 10°C. Two capillary columns were tested: a BPX5 column, 25 m×0.22 mm I.D., 1.0-μm film thickness and a DB-5MS column, 30 m×0.25 mm I. D. with 0.5-μm film thickness. The peak shape and separation were good for both columns, the DB-5MS column showed a lower background signal.

Fig. 2 shows a chromatogram of 10 ng (per compound, as Sn) Me_3Sn^+, Me_2Sn^{2+}, $MeSn^{3+}$, $BuSn^{3+}$, Bu_2Sn^{2+} and Bu_3Sn^+ in 800 ml aqueous solution after ethylation; a full scan mass spectrum of Bu_3EtSn is included. The peak (A) at 4:40 min retention time stems from the derivatization agent and probably represents a boron compound resulting from the ethylation reaction or hydrolysis of $NaBEt_4$. The compounds eluting at 5:50 min (B) and at 10:09 min (C) are probably released from the Tenax material as they also appear in the blank.

3.2. Ethylation conditions

The effect of pH on the efficiency of $NaBEt_4$ in derivatizing alkylated tin, mercury and lead species was investigated in several studies [7,9,11]. In most of them the optimum pH ranges between 4 and 6 in acetate buffer medium. In order to restrict the parameters which had to be optimized, all experiments in this work were carried out with sodium acetate–acetic acid buffer at pH 5.0.

The remaining parameters which strongly influence the ethylation–purge-and-trap process, $NaBEt_4$ concentration, reaction time, purge flow-rate and purge time, were optimized in a conventional, systematic way whereas other authors preferred optimization by factorial experiments [7] or simplex algorithms [15].

We accepted the higher number of experiments (compared to the latter methods) to acquire detailed information about the influence of the parameters on the analytical procedure.

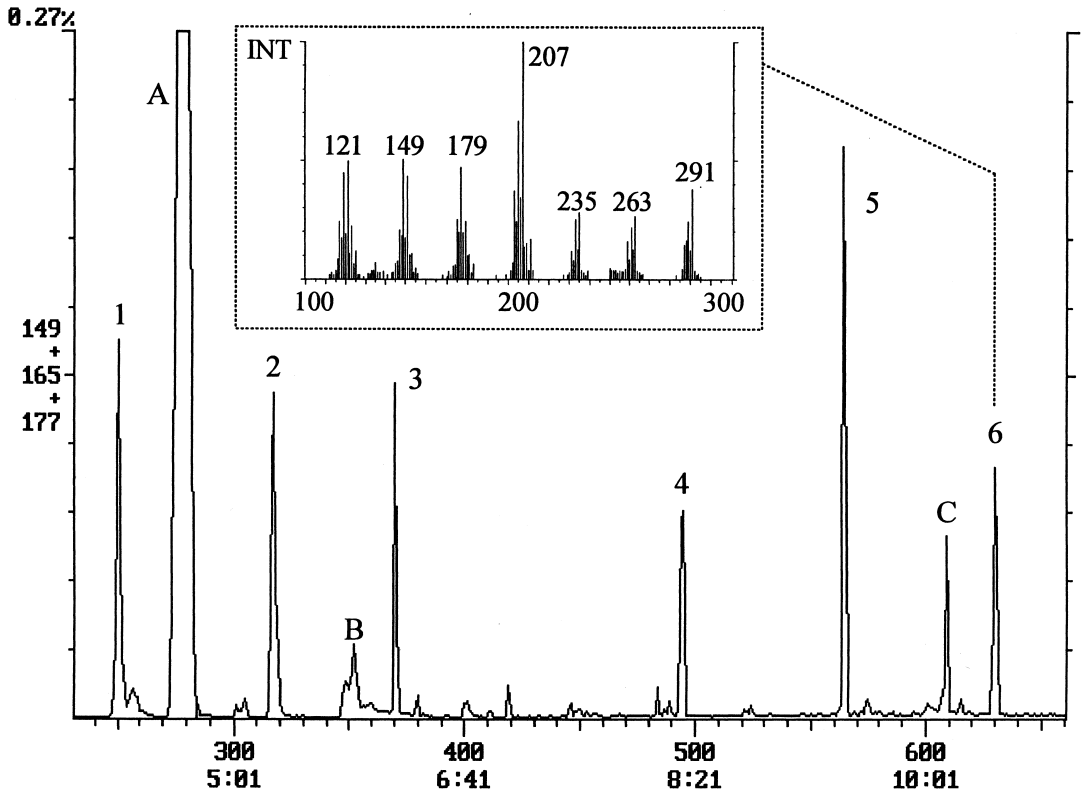

Fig. 2. Chromatogram of 10 ng (per compound, as Sn) Me_3Sn^+, Me_2Sn^{2+}, $MeSn^{3+}$, $BuSn^{3+}$, Bu_2Sn^{2+} and Bu_3Sn^+ in 800-ml aqueous solution after ethylation; monitored masses: m/z=149, 165, 177; mass spectrum of Bu_3EtSn.

In this study, three of the four parameters were kept constant while one was varied. Each parameter was optimized in this way and then held at its optimum. When all optima had been found, the optimization was repeated varying one parameter while holding the others at their optima.

3.3. $NaBEt_4$ concentration

Fig. 3 illustrates the influence of the $NaBEt_4$ concentration on the peak areas of Et_2Me_2Sn, $BuEt_3Sn$ and Bu_2Et_2Sn. At a concentration of 3.75 mg/l, most of the analytes had already reached their maximum peak area, only $BuSn^{3+}$ required a concentration of 10 mg/l. The amount of $NaBEt_4$ had no influence on the Bu_2Et_2Sn signal, which is in agreement with observations of Martin and Donard [7]. In view of higher concentrations of the analytes and other compounds competing for the ethylation

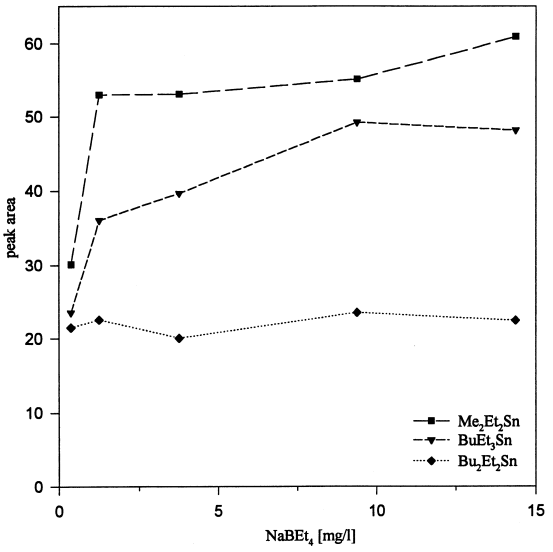

Fig. 3. Influence of the $NaBEt_4$ concentration on the peak areas of Et_2Me_2Sn, $BuEt_3Sn$ and Bu_2Et_2Sn.

reagent in real samples we used a $NaBEt_4$ concentration of 12.5 mg/l in subsequent experiments.

3.4. Reaction time

The reaction time of the ethylation reaction in simple solution does not seem to be very critical as variation between 2.6 and 12.5 min did not significantly change the peak areas of the analytes. However, with regard to possible matrix interferences in real samples, 10 min was chosen as reaction time.

3.5. Purge flow-rate

The effect of the purge flow-rate on the peak area of the analytes is demonstrated in Fig. 4. While the signals of Me_3EtSn, Bu_2Et_2Sn and Bu_3EtSn reached their maxima at a flow-rate of 650 ml/min and decreased at a higher flow-rate, the signals of Me_2Et_2Sn, $MeEt_3Sn$ and $BuEt_3Sn$ still increased when applying a flow-rate of 800 ml/min. The decrease of the Me_3EtSn signal at flow-rates higher than 650 ml/min indicates that the breakthrough volume of the cold trap was exceeded. For that reason a flow-rate of 650 ml/min was considered as optimum.

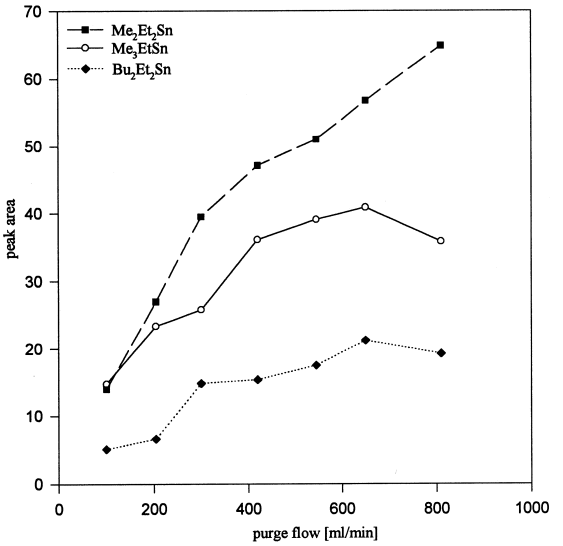

Fig. 4. Effect of the purge flow-rate on the peak area of Et_2Me_2Sn, $EtMe_3Sn$ and Bu_2Et_2Sn.

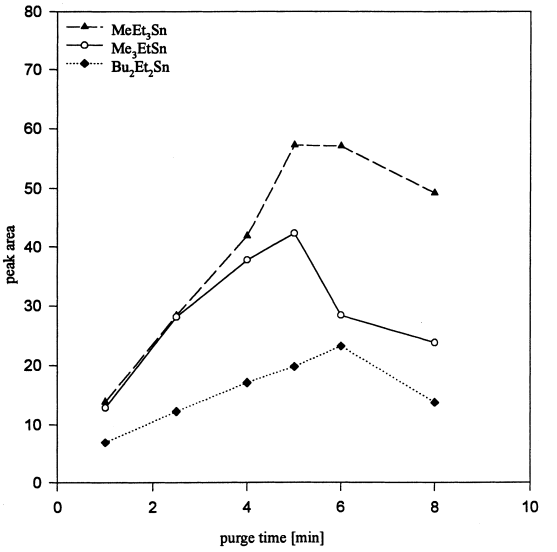

Fig. 5. Influence of the purge time on the peak areas of Et_3MeSn, $EtMe_3Sn$ and Bu_2Et_2Sn.

3.6. Purge time

Fig. 5 shows the variation of the purge time and the resulting peak areas of the analytes. Me_3EtSn and $MeEt_3Sn$ showed their highest peak areas at a purge time of 5.0 min, those of Me_2Et_2Sn, $BuEt_3Sn$, Bu_2Et_2Sn and Bu_3EtSn at 6.0 min. A part of the Me_3EtSn was stripped out of the trap after 6 min so the purge time was held at 5.0 min.

3.7. Influence of the buffer concentration

The influence of the sodium acetate–acetic acid buffer concentration on the peak area of the organotin species was studied. Me_3EtSn was not significantly influenced, but the $BuEt_3Sn$ peak area was increased up to the 1.5-fold after addition of 30 ml of 1 *M* sodium acetate–acetic acid. The peak areas of the other species were increased as well, but to a lesser extent. Therefore, 30 ml of 1 *M* buffer solution were added to each sample.

3.8. Limit of detection/quantification/reproducibility/linearity

The limits of detection (LODs, at a signal-to-noise ratio of 3:1) were determined with a sample volume

Table 2
Limits of detection ($S/N=3$, sample volume 800 ml), reproducibility and quantification masses

	LOD (ng/l as Sn)	R.S.D. ($n=7$) (%)	Quantification masses (m/z)
Me_3Sn^+	1.7	16.0	151, 165
Me_2Sn^{2+}	1.1	13.0	151, 193
$MeSn^{3+}$	0.6	10.7	165, 193
$BuSn^{3+}$	1.2	16.0	179, 235
Bu_2Sn^{2+}	1.3	15.6	179, 263
Bu_3Sn^+	2.2	10.0	179, 263

of 800 ml and are listed in Table 2. In the case of Me_3Sn^+ and Bu_2Sn^{2+} blank values, which were higher than the signal-to-noise ratio 3:1, were taken into account. The ethylated compounds were quantified by using two masses of two different fragments of the EI mass spectra, the masses are listed in Table 2. The fragment $BuEtSn^+$ with $m/z=207$ was not used because of the high background noise due to column bleeding.

The ion trap MS does not reach the absolute detection limits of element-specific detection methods like ICP-MS and AES, but as the whole analytes of an 800-ml sample are concentrated on the capillary GC column the relative sensitivity of the described method allows the determination of environmentally relevant concentrations. The relative standard deviation (R.S.D.) of seven replicate analyses at 12.5 ng/l (as Sn) ranged from 10% to 16% for the whole analytical procedure as shown in Table 2.

The calibration graphs were linear up to a concentration of 62.5 ng/l as Sn.

4. Conclusions

In situ ethylation–purge and PTV cold trapping–GC–MS is a suitable method for the speciation of methyl- and butyltin compounds in aqueous samples. Its main advantage is the efficient preconcentration step that makes compound specific detection at the low ng/l level via full scan mass spectra possible. Consequently reliable determination of the analytes and even the possibility of the identification of unknown organotin species are provided. Due to the computer-controlled automation the system is time saving and easy to handle.

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