The Analyst

Effect of hydrogen bromide doping on capillary gas chromatographic analysis of tributyltin and triphenyltin halides

Kazuko Mizuishi*[a], Masahiro Takeuchi[a] and Toshiyuki Hobo[b]

[a] *The Tokyo Metropolitan Research Laboratory of Public Health, Hyakunincho 3-chome, Shinjuku-ku, Tokyo, 169-0073, Japan*
[b] *Department of Industrial Chemistry, Tokyo Metropolitan University, Minamiohsawa, Hachiohji, Tokyo, 192-0364, Japan*

Tributyltin (TBuT) and triphenyltin (TPhT) compounds have been used as effective antifoulants in the marine environment. Trace levels of the trisubstituted tin halides (chloride and bromide) were separated unsatisfactorily on a capillary GC column (without any treatment). The halides, especially TPhT halides, are very polar, and when injected onto a GC column, most are adsorbed on the active sites on the column surface and do not elute smoothly from the column. In this paper, an apolar capillary GC column with flame photometric detection was used to investigate the direct GC analysis of TBuT and TPhT halides. Spiking of the column used was carried out by doping 1 μl of dilute methanolic HBr solution into the GC system prior to the injection of a standard or sample solution. Under the acidic conditions of doping, the peaks of TBuT and TPhT appeared. HBr doping was effective and showed excellent results; sharper and more symmetrical peaks and larger peak areas could be obtained by increasing the HBr concentration. Using a DB-1 capillary column and doping with HBr, trace levels of TBuT and TPhT halides were determined efficiently. Tripentyltin halide was used as an internal standard. Calibration graphs for TBuT and TPhT halides were linear in the range 0.1–0.6 μg ml^{-1}. Chlorides and bromides showed almost identical results. The mechanism of halide elution and peak sharpening by acid doping and the resulting halogen exchange reaction during GC analysis is considered from a chromatographic viewpoint.

Keywords: *Capillary gas chromatography; tributyltin halide; triphenyltin halide; tripentyltin halide; hydrogen bromide doping; halogen exchange; flame photometric detection*

Gas chromatographic trace analysis of organometallic halides, which are highly polar compounds, is problematic, and derivatization methods have been generally used for their analysis.[1] Organotin compounds have been employed in industry as catalysts, biocides, stabilizing agents in poly(vinyl chloride), *etc*. The large amounts of these materials used in industry contribute to environmental pollution.[2–6] Tributyltin (TBuT) and triphenyltin (TPhT) species are very effective active agents in antifouling coatings for ships and fishing nets and are used worldwide in the marine environment. In general, these compounds are extracted from environmental samples with acidic organic solvents as the halide form (chloride and bromide). They are generally highly polar, or rather cationic compounds. It is unusual for the halides to be analyzed directly by gas chromatography (GC) even though they have adequate volatility. This is because, particularly for trace analysis, most organotin halides injected into GC systems do not elute smoothly because of their high adsorptive activity. Most analytical GC techniques for the determination of TBuT and TPhT halides use derivatization methods: *e.g*., alkylation with Grignard reagents (RMgX),[7–17] ethylation with sodium tetraethylborate [$NaB(C_2H_5)_4$] and hydride formation (reduction) with sodium tetrahydroborate ($NaBH_4$).[18–27] These derivatization methods increase the analysis time and may affect the result of the determination adversely with respect to the accuracy and precision.

We have studied direct GC for organotin halides and have developed a GC method using a packed column pre-treated with a hydrogen halide such as hydrogen chloride (HCl) or hydrogen bromide (HBr) for the analysis of TBuT chloride (TBuTCl) and TPhT chloride (TPhTCl).[28,29] One other GC method for organotin compounds using a packed column and carrier gas doping with hydrogen halides has also been reported.[30] A small amount of hydrogen halide introduced into the GC system was very effective in eluting such cationic organotin compounds from the packed column.

In this paper, we have investigated the use of capillary GC analysis for three organotin compounds [TBuT, TPhT and TPenT (tripentyltin used as an internal standard)] as their halides (chloride and bromide) with an apolar capillary column and HBr doping prior to injection of standard and sample solutions. HBr doping was effective and showed excellent results for analysis of the halides. Using a DB-1 capillary column and doping with HBr, three organotin halides were determined efficiently. The adsorption and desorption mechanism of the organotin halides and the resulting on-column halogen exchange reaction from chlorides to bromides in the GC system due to HBr doping is discussed.

This approach could be applicable to the determination of TBuT and TPhT in environmental samples. The determination of TBuT and TPhT in fish (sea bass) is presented as an example.

Experimental

Materials

TBuTCl, TPhTCl, TPenTCl, TBuTBr and TPhTBr were purchased from Tokyo Kasei (Tokyo, Japan) or Aldrich (Milwaukee, WI, USA). Stock solutions of 1 mg ml^{-1} were prepared by dilution with hexane after dissolving the organotin halide in a small amount of ethyl acetate. TPenT was used as internal standard to correct for injection volume. A stock solution of TPenTBr was prepared by shaking the chloride stock solution with an equal volume of 0.1 M aqueous HBr. The internal standard solution was prepared by diluting the TPenT stock solution with hexane to give a concentration of 1 μg ml^{-1}. Mixed standard solutions from 0.1 to 0.6 μg ml^{-1} were prepared by mixing each stock solution and diluting with hexane, in which the concentration of internal standard was 0.1 μg ml^{-1}.

HBr (25%) solution in acetic acid was obtained from Wako (Osaka, Japan). Methanolic HBr solutions for doping (0.1–3

mM) were prepared by diluting the 25% HBr solution with methanol. All other reagents were of analytical-reagent grade.

For the validation of the method, a fish tissue CRM, *viz.*, NIES No. 11, was supplied by the National Institute of Environmental Studies of Japan (NIES, Ibaraki, Japan) with a certified content for TBuT and an indicative value for TPhT.

Apparatus

GC was performed on a Hewlett-Packard (Avondale, PA, USA) 5890 series II gas chromatograph equipped with a flame photometric detector (FPD) with a 611.6 nm filter. The GC column used was a fused-silica capillary column (15 m × 0.25 mm id) coated with DB-1 (0.1 μm film thickness) (J & W Scientific, Rancho Cordova, CA, USA). Injections were made in the splitless injection mode (1 min split time) with an inlet pressure of 70 kPa using helium as the carrier gas. A temperature program was employed in which the column temperature was initially held at 40 °C for 1 min, then increased at 15 °C min^{-1} to a final temperature of 240 °C. The injector temperature was held constant at 250 °C. GC–MS was performed on a VG TRIO-1 quadrupole mass spectrometer (VG Organic, Cheshire, UK) interfaced by a direct transfer line to a Hewlett-Packard 5890A II gas chromatograph under the same conditions as for GC, with the conditions shown in Table 1 for MS. All mass spectra were measured in the electron impact ionization (EI) mode. Injection was performed manually.

Doping of HBr and injection of sample solution

Doping of HBr into the GC system was performed by injecting 1 μl of a 0.1–3.0 mM methanolic HBr solution in the splitless mode onto the GC column held at 40 °C immediately before the injection of a sample solution. About 1 min after this injection, when most of the HBr molecules should have entered the capillary, a standard or sample solution was injected also in the splitless mode and the GC analysis was started.

Practical doping for the analysis of sample solutions

A fresh capillary column was pre-treated by injecting 1 μl portions of 1 mM methanolic HBr solution onto the GC column at 40 °C 2–3 times at 1 min intervals after which the GC temperature program described above was initiated. In a practical analysis, 1 μl of 0.5 mM methanolic HBr solution was doped at 40 °C, and then, after about 1 min, a 1 μl aliquot of the sample or standard solution was injected onto the column and analyzed.

Analytical procedure

The preparation procedure for the fish sample is shown in Fig. 1. TBuT and TPhT were extracted with three 50 ml portions of hexane–diethyl ether (3 + 1, v/v) as the corresponding chlorides in the presence of HCl, methanol and ethyl acetate. The combined extract was concentrated to about 5 ml and then subjected to column chromatography using 3 g of Florisil (lower layer) and 2 g of anhydrous sodium sulfate (upper layer). Preparation of the column was as follows: Florisil (3 g) or anhydrous sodium sulfate (2 g) was suspended in hexane–diethyl ether (3 + 1, v/v) and packed into a glass column (30 × 1.0 cm id). The concentrate was poured into the column and then washed successively with 40 ml of hexane–diethyl ether (3 + 1, v/v) and 50 ml of hexane–acetone (3 + 1, v/v). The compounds of interest were eluted with 40 ml of hexane–diethyl ether–acetic acid (75 + 25 + 1, v/v/v) and the eluate was concentrated to less than 2 ml. To the concentrated solution was added 0.2 ng of TPenTCl (internal standard) and the solution was then made up to 2 ml with hexane. To this solution 1 ml of 1.0 M NaOH–5% NaCl (1 + 1) solution was added and the mixture was centrifuged. The upper organic layer was subjected to GC–FPD. The procedure did not include any derivatization steps; this resulted in a reduction in sample preparation time and also a reduction in the loss of the analytes.

Table 1 Mass spectrometric conditions

Ionization voltage (EI)	70 eV
Mass spectrometric resolution	1000
Ion current	150 μA
Scan range	*m/z* 50–500
Ion source temperature	200 °C
Interface temperature	250 °C

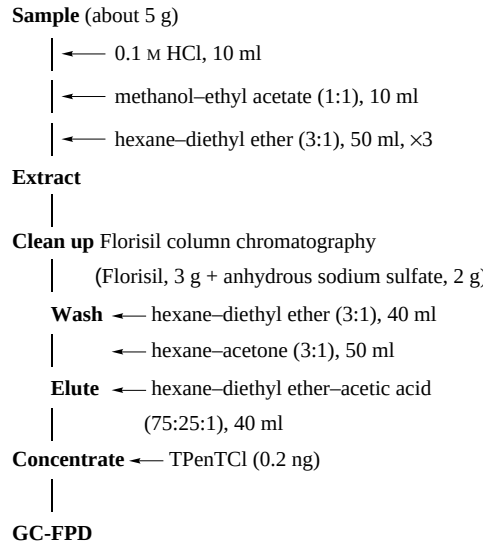


Fig. 1 Sample preparation procedure for TBuT and TPhT in fish.

Results and discussion

Organotin halides are easily formed in acidic solution and are usually extracted from a complex sample matrix for analytical purposes. Since organotin halides have an inclination to interact with many materials in the GC system and cannot be separated satisfactorily, alkylation (Grignard) or hydride ($NaBH_4$) derivatizations have been used for trace analysis by GC.[7–27] We have studied a direct GC analysis for organotin halides and have developed a packed column GC method for TBuTCl and TPhTCl.[28,29] The column was pre-treated with HCl or HBr to deactivate many of the active materials in a packed GC column such as silanol groups and metal oxides. A packed column has many active sites; hence, acids are required to some extent for its deactivation.

It is evident that ordinary capillary columns are largely deactivated and have very few active sites compared with packed columns. Nevertheless, organotin halides readily react with OH groups and other reactive sites in the column. It is also difficult to analyze TBuT and TPhT halides directly and precisely by capillary GC. Derivatization methods, such as those described above, are usually required. Attempts were made to use capillary GC for the analysis of halides of TBuT and TPhT by applying a doping technique.

Experiments using a DB-1 capillary column (15 m × 0.25 mm id, 0.1 μm film thickness) and an FPD demonstrated that trace levels of TBuT and TPhT halides (chloride and bromide) could not be easily determined by injecting them directly into the chromatograph without any treatment or modification. Fig. 2A shows a chromatogram of TBuTCl and TPh Cl (0.1 ng each)

injected onto the column without doping. TPenTCl (internal standard) was also injected. Since organotin halides are very polar, most of them are adsorbed on the column and hence sufficient and quantitative peaks are not observed. TBuT and TPenT appeared as relatively small peaks, and TBuT merely gave a degradation peak as shown in Fig. 2A. No peak was observed for TPhT. A very similar result was observed for the bromides as shown in Fig. 2B. TBuTBr appeared as a leading small peak.

HBr doping

Doping was performed by injecting 1 μl of a dilute methanolic HBr solution into the gas chromatograph about 1 min before the injection of a standard solution. The HBr concentrations studied were 0.1, 0.3, 0.5, 1.0, 2.0 and 3.0 mM. Fig. 2C shows a chromatogram of TBuTCl, TPh Cl and TPenTCl (0.1 ng each) obtained by doping the GC column with a 0.1 mM methanolic HBr solution. With HBr doping, TBuTCl and TPenTCl appeared as relatively sharp peaks compared with no doping. The small degradation peak of TBuTCl became a single large peak with increasing HBr concentration. The TPhTCl peak scarcely appeared with HBr doping although the peak area increased with increasing HBr concentration. Fig. 2D shows chromatograms obtained by doping with 0.1, 0.5 and 1.0 mM HBr. The chromatograms have been merged for comparison and each peak has also been magnified. Doping with 0.1 mM HBr was not sufficient. All the peaks were small; the TBuT and TPenT peaks were asymmetrical and their peak widths were fairly broad. However, doping with 0.5 and 1.0 mM HBr gave sharp peaks as shown in Fig. 2D.

Fig. 3 shows the relationship between HBr concentration and the resulting peak width and peak area. The amount of each compound injected was 0.1 ng on-column. It can be seen that all peaks became sharper and their areas increased as the HBr concentration increased. By doping at concentrations higher than 0.5 mM, peak area and peak sharpness (width) remained almost constant; the results of 0.5 and 1 mM HBr doping were almost identical. The TPhTCl peak scarcely appeared with 0.1 and 0.3 mM HBr doping, but above 0.5 mM HBr the peak became larger and sharper (the peak width became narrow). On the other hand, with 3 mM HBr doping, some minor decomposition of the analytes sometimes occurred as shown in Fig. 4.

Fig. 5 shows the mass spectra of TBuTCl, TPhTCl and TPenTCl separated by GC with HBr doping. These spectra showed that only the bromides were present. A halogen exchange reaction from chloride to bromide readily occurs during the GC separation. The spectrum of each organotin bromide separated by GC with HBr doping also showed the presence of the bromide. The acidic conditions generated by HBr and the ease of formation of the bromides resulted in excellent separation of organotin chlorides. Furthermore, almost identical results were obtained for bromide and chloride standards as shown in Fig. 6 in which both chromatograms have been merged. Almost identical retention times, peak areas, peak heights and peak widths were observed.

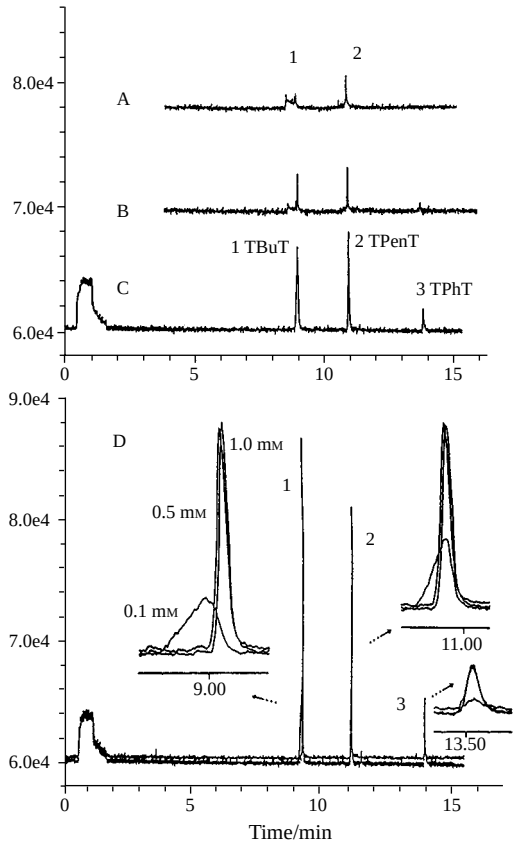


Fig. 2 Gas chromatograms of an organotin halide solution at 0.1 μg ml^{-1} level by use of a DB-1 capillary column, 15 m × 0.25 mm id, 0.1 μm film thickness, without and with HBr doping: A, without doping, TBuTCl, TPenTCl (IS) and TPhTCl; B, without doping, TBuTBr, TPenTBr (IS) and TPhTBr; C, 0.1 mM HBr doping, TBuTCl, TPenTCl (IS) and TPhTCl; D, 0.1 mM, 0.5 mM and 1.0 mM HBr doping were merged; 1, TBuT; 2, TPenT (IS); 3, TPhT; ⋯→, peak magnified.

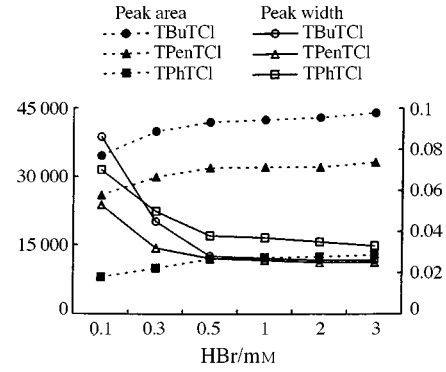


Fig. 3 Effect of methanolic HBr concentration on peak widths and areas of TBuTCl, TPenTCl (IS) and TPhTCl. Experimental conditions: HBr doping, 0.1, 0.3, 0.5, 1.0, 2.0 and 3.0 mM; analyte concentration, 0.1 μg ml^{-1}; injection volume, 1 μl.

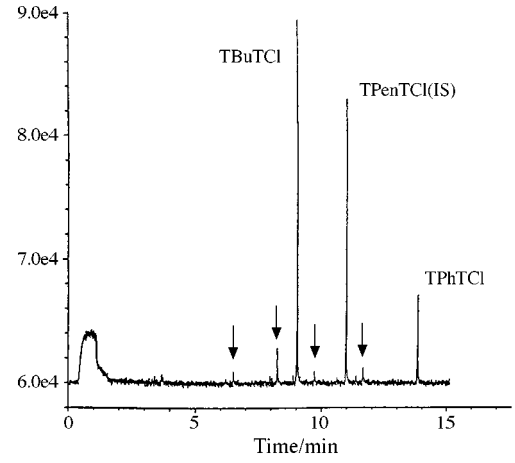


Fig. 4 Gas chromatogram of an organotin chloride solution [TBuTCl, TPenTCl (IS) and TPhTCl] at 0.1 μg ml^{-1} by use of a DB-1 capillary column with 3 mM HBr doping: →, decomposition compound.

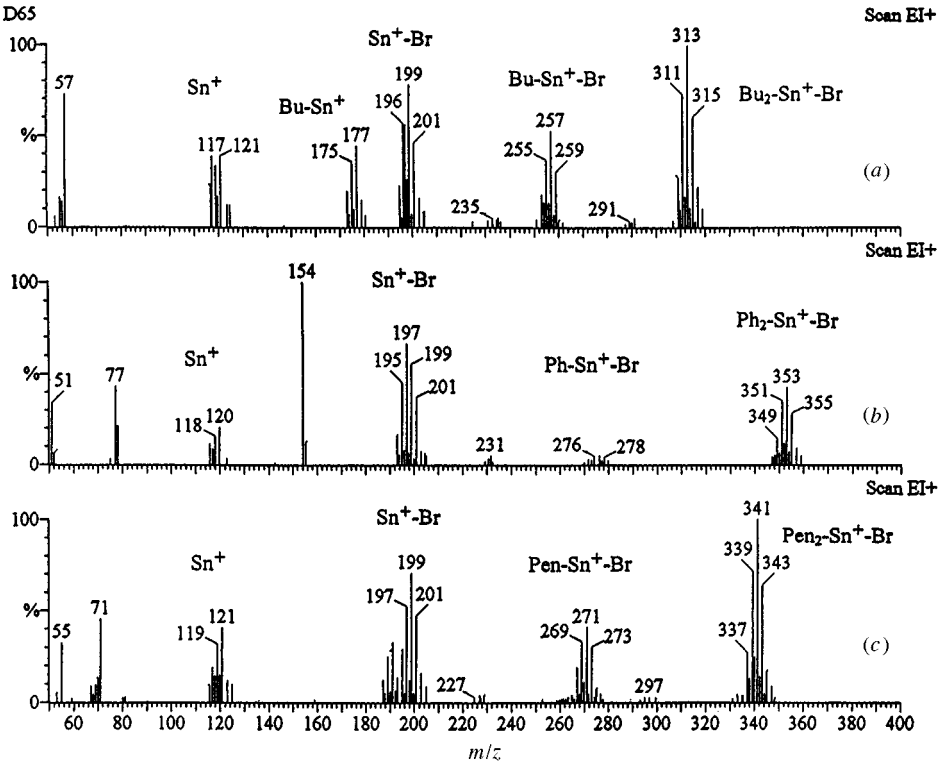


Fig. 5 EI-MS spectra of TBuTCl (*a*), TPhTCl (*b*) and TPenTCl (*c*) separated by a DB-1 capillary column under HBr doping. Bu, butyl; Ph, phenyl; Pen, pentyl.

It is clear that HBr doping is effective for the direct GC analysis of organotin halides. It has also been shown that trisubstituted organotin halides can be analyzed directly by capillary GC by doping with dilute methanolic HBr solution.

Elution mechanism of TBuT and TPhT halides under the conditions of hydrogen halide doping

TBuTCl injected onto the GC column without doping appeared as a small degradation peak as shown in Fig. 2A. TBuTBr also showed a small peak although it was slightly larger than that of the chloride (Fig. 2B). TPhT did not appear at all.

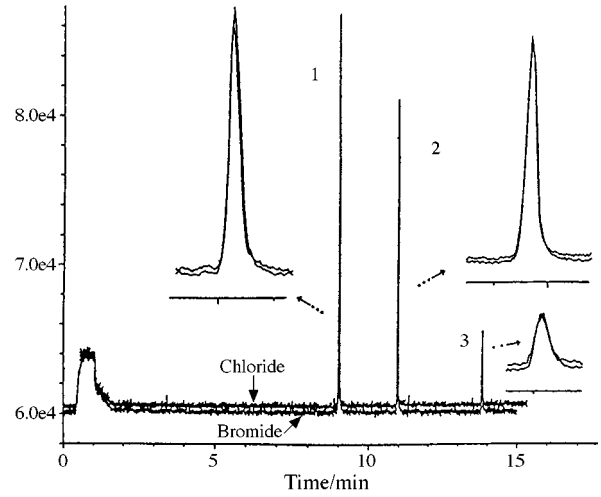
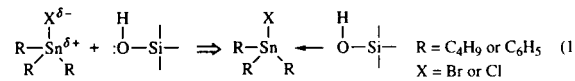


Fig. 6 Gas chromatograms of an organotin chloride solution [TBuTCl, TPenTCl (IS) and TPhTCl] and an organotin bromide solution [TBuTBr, TPenTBr (IS) and TPhTBr] at 0.1 μg ml^{-1} by use of a DB-1 capillary column with 0.5 mM HBr doping. Chromatograms of chlorides and bromides were merged: ⋯↪ peak magnified; 1, TBuT; 2, TPenT (IS); 3, TPhT.

The behavior of organotin halides on a capillary column in the absence or presence of HBr was considered as follows: Organotin halides tend to interact with materials in the GC system. Tin atoms of organotin halides are positively charged owing to the electron-withdrawing nature of the halides; hence, they can attack the lone pairs of electrons on the residual silanol groups on the capillary column with the result that the organotin halides are adsorbed on the column surface. In particular, halides of TPhT have a very high polarity, and might act as a Lewis acid [eqn. (1)].



If HBr molecules are introduced onto the column, the lone pairs of electrons on the silanol groups will be attached to HBr [eqn. (2)]. This makes the organotin halides difficult to attach to the lone pairs and consequently they can elute from the column.

From the viewpoint of partition equilibrium, the following phenomenon was considered. When HBr enters the capillary column, it dissolves in the stationary phase and makes the phase acidic. With an acidic stationary phase, organotin halides, which are cationic species, easily elute from the column. Methanolic HBr solution doped prior to the injection of the organotin halides creates a large zone in the column (Fig. 7; 1). When the column temperature is raised, the methanolic HBr is

transferred towards the exit of the column with vaporization of methanol (Fig. 7; 2). With the transfer, HBr dissolves in the stationary phase making it acidic and active sites such as silanol groups are deactivated by the formation of hydrogen bonds with HBr. As a result, the partition of organotin halides between the stationary phase and the gas phase proceeds smoothly (Fig. 7; 3).

Halogen exchange reaction in the capillary

HBr doping showed superior results for the separation of organotin halides, especially for TPhT halides. As a result of HBr doping, sharp peaks were observed for the organotin halides. The halogen exchange reaction from chloride to bromide occurred easily when the organotin chlorides encountered the HBr in the column. For the chlorides, mass spectra (Fig. 5) with HBr doping show characteristic bromide fragment ions such as $[M_{Br} - R]^+$, $[M_{Br} - 2R]^+$ and $[M_{Br} - 3R]^+$ [M_{Br} = bromide molecule, R = butyl (Bu), phenyl (Ph) or pentyl (Pen)], as for the bromides. It was apparent that the formation of the bromides occurred easily and rapidly when the chlorides were chromatographed under the conditions of HBr doping [eqn. (3)].

$$R_3Sn\text{–}Cl \xrightarrow{HBr} R_3Sn\text{–}Br \quad R = C_4H_9 \text{ or } C_6H_5 \qquad (3)$$

Bromination was probably favoured because of the higher boiling-point of HBr (HBr: −67.0 °C; HCl: −84.9 °C) and the slight differences in the electronegativity and electron withdrawing ability of Br and Cl. Consequently, HBr could remain in the column slightly longer, and interact with the organotin compounds to a much greater extent than HCl. Hence, HBr pre-injected into the GC system was dissolved or adsorbed in the liquid phase of the column, and the subsequently injected organotin chlorides were converted to the respective bromides on/in the stationary phase at the front of the column and following the facile halogen exchange were eluted as bromides from the column.

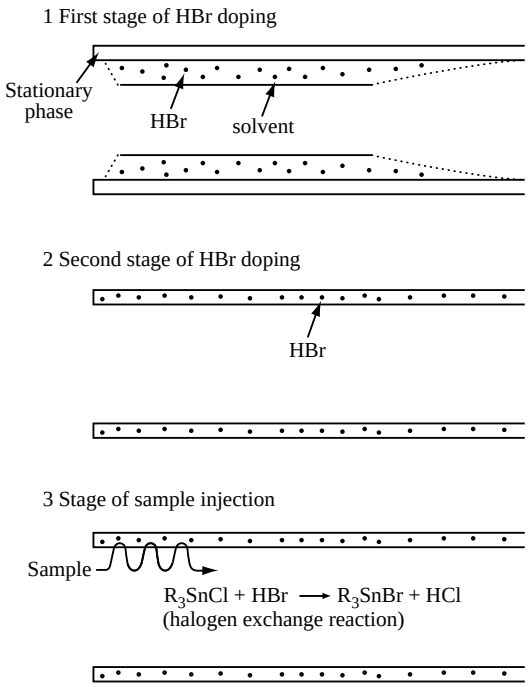


Fig. 7 Hydrogen bromide doping phenomenon and halogen exchange reaction. 1, First stage of HBr doping, 2, second stage of HBr doping, 3, stage of sample injection.

In conclusion, the halogen exchange reaction to form the bromides and phase acidification with HBr facilitated the elution of the halides from the capillary column and made the peaks sharp. From the results in Figs. 3 and 4, doping with 0.5 mM methanolic HBr solution seemed to be adequate for analyzing TBuT and TPhT halides on a 15 m DB-1 capillary GC column.

This acid doping technique might be applicable to the analysis of other organometallic halides which are difficult to analyze directly by GC because of their high polarity. We have already reported the direct GC determination of methylmercury chloride by using HBr pre-treatment of the column.[31] The chromatograph, detector and column did not suffer any damage due to HBr doping. The peak shape has remained fairly constant.

Analytical characteristics

Linearity and detection limits

Under the proposed experimental conditions, linear calibration graphs were obtained for the determination of TBuT and TPhT. TPenT was added to the extracting solvent to control the precision of the manual injection.

The values for the calibration graphs are summarized in Table 2. The detection and determination limits were defined as the concentrations of the analyte giving signals equivalent to three and ten times, respectively, the blank standard deviation.[32] The data yielded a good linearity within the range 0.1–0.6 μg ml^{-1}. To check the linearity of the calibration graph, the lack-of-fit test[33] was applied for triplicate measurements. Linear regression of the responses (peak area ratio) on concentration gave rise to a residual sum of squares (SSr) of 0.3643 for TBuT and 0.01888 for TPhT with 16 degrees of freedom. Analysis of variance for pure error gave the values shown in Table 3. The 5% point of $F_{4,12}$, 3.26, is larger than the mean square of lack-of-fit/mean square of pure error of 0.45 for TBuT and 0.44 for TPhT, showing that there is no significant lack-of-fit to the linearity.

Reproducibility

The reproducibility for the analytes was determined by performing ten consecutive manual injections of 1 μl of a standard solution containing 0.1 ng of TBuTCl and TPhTCl. The peak area measurement gave relative standard deviations (RSDs) of 1.5 and 2.3%, respectively. TPenTCl (0.1 ng) gave an RSD of 1.8%.

Table 2 Analytical figures for the determination of TBuT and TPhT by the proposed method

Analyte	Calibration equation*	*r*	Linear range/μg ml^{-1}	Detection limit/μg g^{-1}	Determination limit/μg g^{-1}
TBuT	$y = 13.858x - 0.054$	0.998	0.1–0.6	0.002	0.007
TPhT	$y = 3.631x + 0.014$	0.998	0.1–0.6	0.004	0.014

* y = TBuT : TPenT peak area ratio; x = concentration of the analyte in μg ml^{-1}.

Table 3 Analysis of residual variance

	Sum of squares			Mean square		*F*	
Source of variation	TBuT	TPhT	DOF*	TBuT	TPhT	TBuT	TPhT
Residuals	0.3643	0.01888	16				
Pure error	0.3169	0.01645	12	0.0264	0.00137		
Lack-of-fit	0.0474	0.00243	4	0.0119	0.00061	0.45	0.44
						$< F_{4,12}$, 3.26	

* Degrees of freedom.

Accuracy

To validate the method, the analysis of the CRM NIES No. 11 (fish tissue) was performed. The results are shown in Table 4. The values obtained as TBuTCl (means of three replicates on two different days) match well the certified value, 1.3 ± 0.1 μg g^{-1}.[31] The values obtained for TPhTCl (means of three replicates on two different days) also match well the indicative value reported by the NIES, 6.3 μg g^{-1}.[34]

Recoveries

Spiked experiments were performed using a fish sample (sea bass) by analysing five replicates at three concentration levels. The results are presented in Table 5. The average recoveries and RSDs ranged from 95.0 to 98.0% and from 2.30 to 4.12%, respectively. Quantitative recoveries of TBuT and TPhT from the fish sample were achieved.

Application to the analysis of a fish sample

The applicability of the proposed method was studied by the analysis of a fish sample. A 5 g fish sample (sea bass, wet) was analyzed according to the procedure outlined in Fig. 1. A volume of 1 μl of sample solution was injected into the GC–FPD system with doping with 0.5 mM HBr. The chromatogram obtained is shown in Fig. 8. The method was suitable for the determination of TBuT and TPhT compounds in fish samples.

Conclusions

The direct and simultaneous GC analysis of two polar organotin (TBuT and TPhT) halides (chloride and bromide) using an apolar capillary column and FPD was investigated. The GC system was doped with dilute methanolic HBr solution immediately before the injection of a standard or sample solution to prevent the adsorption of the analytes onto the column. Under the acidic conditions of doping, the organotin halides did not adsorb on the active sites and were eluted from the column; the peaks were sharp and symmetrical. HBr doping was effective and showed excellent results for the analysis of the halides. Using a 15 m DB-1 capillary column and doping with 0.5 mM methanolic HBr solution, three organotin halides including TPenT were determined efficiently and rapidly. TPenT was used as an internal standard. Calibration graphs for both TBuTCl and TPhTCl were linear in the range 0.1–0.6 μg ml^{-1}. The bromides showed almost identical results as the chlorides.

Table 4 Analysis of the NIES No. 11 fish tissue CRM for the determination of TBuTCl and TPhTCl on two different days (three determinations on each day)

Day	TBuTCl/μg g^{-1}	RSD (%)	TPhTCl/μg g^{-1}	RSD (%)
A	1.29	3.5	6.42	3.0
B	1.30	3.1	6.37	3.6

Table 5 Recoveries of TBuTCl and TPhTCl from a fish sample* (n = 5)

TBuTCl				TPhTCl			
Added/ng	Found/ng	Recovery (%)	RSD (%)	Added/ng	Found/ng	Recovery (%)	RSD (%)
0	0.116			0	0.050		
0.10	0.212	96.4	3.97	0.10	0.145	95.0	4.12
0.20	0.311	97.4	2.62	0.20	0.245	97.7	2.80
0.50	0.597	96.2	2.71	0.50	0.540	98.0	2.30

* Fish sample: sea bass; sample mass, 5 g (wet).

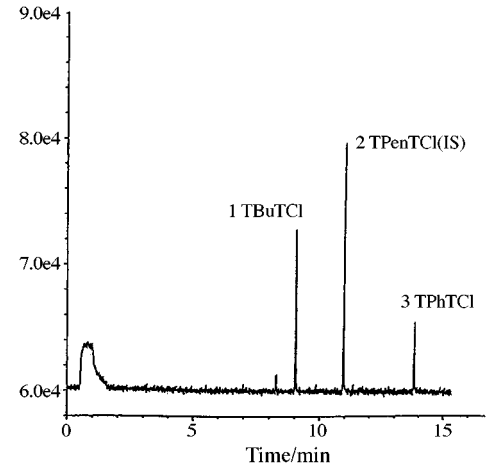


Fig. 8 Gas chromatogram of fish (sea bass) sample. Column: DB-1, 15 m × 0.25 mm id, 0.1 μm film thickness. Experimental conditions; 0.5 mM HBr doping; sample mass, 5 g (wet); IS, TPenTCl (0.1 μg ml^{-1}); injection volume, 1 μl.

The mass spectra of organotin halides separated on the HBr doped column confirmed that a halogen exchange reaction occurred during GC analysis. The mechanism of organotin halide elution and peak sharpening by acid doping, and the halogen exchange reaction of organotin halides was considered from a chromatographic viewpoint.

The proposed method was suitable for the determination of TBuT and TPhT compounds in fish samples. The GC system did not suffer any damage from the acid doping.

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