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Determination of Butyltin and Phenyltin by GC–FPD Following Ethylation by $NaBEt_4$

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An organotin speciation method was optimized for the simultaneous determination of mono-, di- and tri-butyltin compounds and mono-, di- and tri-phenyltin compounds in water. The procedure was based on a one-step simultaneous ethylation and extraction using the sodium tetraethylborate reagent directly in the aqueous phase in the presence of an isooctane layer. Direct extract analysis was performed using capillary gas chromatography and flame photometric detection (GC–FPD). This derivatization procedure reduces drastically the number of analytical steps, thus saving time and improving reliability. Relative detection limits range from 0.4 to 0.8 ng dm^{-3} for butyltin species and from 0.7 to 2.1 ng dm^{-3} for phenyltin species; the linearity ranges from 0 to 400 ng dm^{-3}. Analysis of environmental aqueous samples and a Certified Reference Material (CRM) demonstrates the accuracy of the analytical method.

Keywords: ethylation; sodium tetraethylborate; butyltin; phenyltin; gas chromatography; flame photometric detector

INTRODUCTION

During the last few decades organotin compounds have been extensively used as biocides, especially in antifouling paints, as thermal and light stabilizers for plastics such as poly(vinyl chloride) and as catalysts in the production of polyurethane foams.[1] The compounds most widely used as biocides, tributyltin (TBT) and triphenyltin (TPhT), have been recognized as toxic.

Many analytical procedures based on chromatographic separation coupled to various detection techniques have been developed. A derivatization step is usually necessary in order to convert alkyltin species into forms suitable for gas chromatography.[2] Derivatization methods include: hydridization[3–8] using sodium borohydride ($NaBH_4$) or alkylation with Grignard reagents such as methyl,[9–14] ethyl,[15–20] propyl,[21–24] pentyl[25–31] or hexyl magnesium halides.[12, 32, 33] Hydridization followed by volatilization cannot be effective when organotin species (e.g. phenyl-, octyl-tin) do not produce sufficiently volatile hydrides.[34] The Grignard derivatization procedure is time-consuming, involves many sample-handling steps and can lead to losses of organotin compounds or contamination by reagent impurities.[2, 17]

A new organotin derivatization procedure directly applied in the aqueous phase using sodium tetraethylborate has been proposed recently. This method has been used for the speciation analysis of organolead-, organomercury-, organotin-[34] and selenium-containing compounds.[35] With our procedure, both derivatization and extraction of derivatives are performed in a single operating flask. Speciation of butyl- and phenyl-tin derivatives may be carried out simultaneously and more rapidly than with the Grignard reaction.

In this paper, optimal conditions for the determination of butyl- and phenyl-tin compounds have been evaluated, after a systematic examination of each operating parameter and its influence on the analytical procedure. The optimized method was applied to the analysis of spiked water samples, environmental polluted water samples and a certified reference material.

MATERIALS AND METHODS

All organotin concentrations reported in this paper are expressed as the mass of tin per mass or volume unit, i.e. ng g^{-1} or ng dm^{-3}, except in Table 7.

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Reagents and standards

Tripropyltin chloride (TPT, 98%), monobutyltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 97%), tributyltin chloride (TBT, 96%), monophenyltin trichloride (MPhT, 98%), diphenyltin dichloride (DPhT, 96%) and triphenyltin chloride (TPhT, 95%) were purchased from Aldrich. Tetrabutyltin (TeBT, 98%) was obtained from Fluka. The organotin stock solutions containing 1000 mg dm^{-3} as tin (Sn) were prepared in methanol. When stored in the dark at +4 °C, stock solutions were stable for at least one year.[36] They were diluted weekly to 10 mg dm^{-3} in methanol and stored in the dark at +4 °C; 100 μg dm^{-3} working solutions were prepared daily in methanol.

Methanol and sodium acetate were purchased from Prolabo. Nitric acid and acetic acid were obtained from Merck, and iso-octane from Fluka. The deionized water used was 18 MΩ (Millipore system).

Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemical. A working solution was made up daily by dissolving 0.02 g in 1 cm^3 of deionized water and storing in the dark at +4 °C.

Glassware was rinsed in deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again.

Apparatus

A Varian 3300 Gas Chromatograph (GC) was used for this study. It was fitted with a split/splitless injector, a J and W Scientific capillary column coated with polydimethylsiloxane (inner diameter 250 μm, length 30 m, film thickness 0.25 μm) and a flame photometric detector (FPD). The detector was operated with a 610-nm optical filter (from MTO Optique Instrumentale) and an air/hydrogen flame. Nitrogen was used as carrier gas. GC–FPD conditions are reported below.

Samples

All samples were preserved in polyethylene bottles by addition of 10 cm^3 acetic acid per dm^3 of sample and stored at +4 °C in the dark. Bottles were cleaned with a 10% (v/v) nitric acid solution and rinsed in deionized water before they were used.

For the recovery studies, deionized water, freshwater sampled from the L'Yse brook near Pau (France) and seawater from Arcachon Bay (France) were spiked with known amounts of MBT, DBT, TBT, MPhT, DPhT and TPhT: 20 ng dm^{-3} as Sn in each case. Both environmental waters were found to be free of organotin compounds before spiking.

To validate the method, environmental polluted samples were analysed. Sampling locations are explained below.

Analytical procedure

A 100 cm^3 portion of sample adjusted to pH 4.6 with acetic acid/sodium acetate buffer was introduced into a glass reactor (170 cm^3 volume) closed by a polyethylene cap. The geometry of this reactor had been optimized.

Sodium tetraethylborate (100 μl of working solution) and iso-octane (0.4 cm^3) were then added successively. After mechanical shaking (20 min), the organic phase was collected (Fig. 1). Then 2 μl was injected into the chromatograph by means of a syringe.

Quantitation procedure

Peak heights were routinely used for quantitative calculations, the same results being obtained from peak areas due to their shape. Peaks were assigned to individual compounds on the basis of retention times and were confirmed by standard additions.

Organotin concentrations in samples were determined from five replicate analyses using TPT as internal standard and by standard addition in triplicate to compare analytical performances.

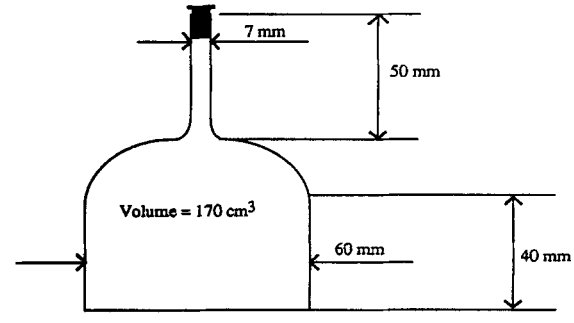

Figure 1 Glass reactor for organotin ethylation/extraction.

RESULTS AND DISCUSSION

Extraction and derivatization conditions

All extraction and derivatization conditions have been defined using a mixture of MBT, DBT, TBT, MPhT, DPhT and TPhT in deionized water. The concentrations were 250 ng dm^{-3} as Sn of each compound.

Geometry of the reactor vessel

On the one hand, the reactor geometry had to allow the best shaking in order to achieve the best efficiency of ethylation and extraction. On the other hand, the collection of the organic phase had to be as easy as possible.

For the first condition a reactor volume significantly larger than the sample volume was necessary. The sample volume being set at 100 cm^3, the reactor volume has been fixed at 170 cm^3 as a compromise between high sensitivity and sampling requirements.

In order to satisfy the second condition with a low iso-octane volume, the reactor neck diameter had to be narrow: a 7 mm diameter was chosen, allowing both reliable sample introduction and efficient cleaning.

The geometry of the reactor is described in Fig. 1.

Choice of the nature and the volume of solvent

Fully alkylated tin compounds are extracted in a non-polar solvent prior to injection into the chromatograph. Hexane and iso-octane were studied.[37-41] Preliminary experiments carried out with both solvents did not show any difference and iso-octane was retained because of its higher boiling point and its lower solubility in water.

The volume of iso-octane necessary to extract 100 cm^3 aqueous samples was tested in the range 0.3 to 1 cm^3. Peak heights as a function of iso-octane volume are presented on Fig. 2. The variation is not linear. However, too small a solvent volume led to a difficult phase separation. Therefore 0.4 cm^3 was chosen in order to allow easy and rapid collection of the organic phase containing tetra-alkylated organotin compounds.

Mixing effect

The reagents were all introduced in the reactor and mixed during the ethylation–extraction step. The mixing efficiency must be adequate to perform an efficient extraction of ethylated derivatives in iso-octane.[37] According to the literature, the mixture could be shaken manually during 5 min[39,40] or be stirred magnetically,[37,38,41] depending on the authors.

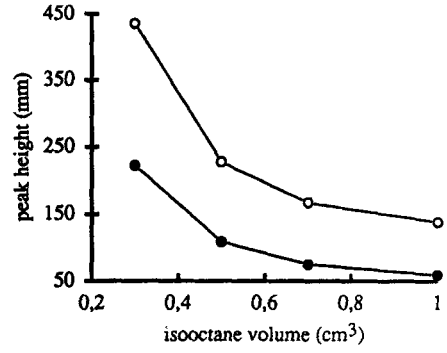

Figure 2 Effect of iso-octane volume on peak heights for butyltin compounds (MBT, DBT, TBT, TeBT) and for phenyltin compounds (MPhT, DPhT, TPhT) in deionized water [250 ng(Sn) dm^{-3}]. The three butyltin derivatives and the three phenyltin derivatives had the same behaviour. ○, Butyltin compounds; ●, phenyltin compounds.

Three mixing procedures were investigated: (1) magnetic stirring; (2) ultrasonic bath; (3) mechanical rotary shaker. Ethylation–extraction yields were calculated using TeBT height as reference because this compound was not subject to an ethylation step. The results are compared in Table 1. The ethylation–extraction step was never complete when sonication in an ultrasonic bath was used (2). A mechanical rotary shaker (3) gave higher and more reproducible ethylation–extraction yields than magnetic stirring (1), because of its vigorous and regular mixing. Therefore mechanical rotary shaking was chosen for all the following experiments.

Effect of reaction/extraction time

Reaction time cannot be separated from extraction time. It was studied between 0 and 30 min and the results are reported in Fig. 3.

Optimal efficiency is reached within 20 min with the mixing conditions described above. These results are in agreement with ethylation–extraction times reported in the literature, ranging from 5 to 60 min depending on the mixing procedure.

Effect of reaction pH

The addition of alkaline sodium tetrathylborate increased the pH of unbuffered water samples.[41] It was therefore necessary to determine the true

Table 1 Effect of mixing on ethylation/extraction yields[a]

Compound	Ethylation/extraction yield (%)		
	(1) Magnetic stirring	(2) Ultrasonic bath	(3) Mechanical rotary shaker
MBT	87	28	100
DBT	56	40	88
TBT	52	68	85
MPhT	31	14	34
DPhT	65	27	79
TPhT	37	40	45

[a] Deionized water is spiked with 250 ng(Sn) dm^{-3} of MBT, DBT, TBT, MPhT, DPhT and TPhT.

effect of pH on the ethylation reaction.

The peak heights are given as a function of pH in the range 2–8.3 in Fig. 4. The best performances were achieved at pH values ranging between 4 and 5. An acetate buffer was finally chosen to fix the pH to 4.6 during the derivatization step.

These findings are in agreement with the results reported by Ceulemans *et al.*[38–40]

GC–FPD conditions

GC–FPD conditions were optimized using a mixture of MBT, DBT, TBT, MPhT, DPhT and TPhT in deionized water. The concentrations were 250 ng dm^{-3} as Sn, of each compound.

Analytical conditions are summarized in Table 2 and a chromatogram is given as Fig. 5.

It is interesting to note that the injection temperature (290 °C) was found to be slightly higher than those reported in the literature[10, 17, 23–25, 27, 30, 37, 41] for example 250 °C for Müller[17] and Gomez-Ariza *et al.*[27] or 270 °C for Higashiyama.[23]

Concerning flame composition, a hydrogen-rich flame was found to improve selectivity and sensitivity.[17, 27] Using capillary GC with a low flow rate of carrier gas, the compounds have to be carried to the flame by a make-up of nitrogen flow. This flow is a significant parameter because it allows the flame to remain in performance by reducing the background noise.[10]

Calibration, reproducibility and detection limits

External calibration was performed for MBT, DBT, TBT, TeBT, MPhT, DPhT and TPhT in

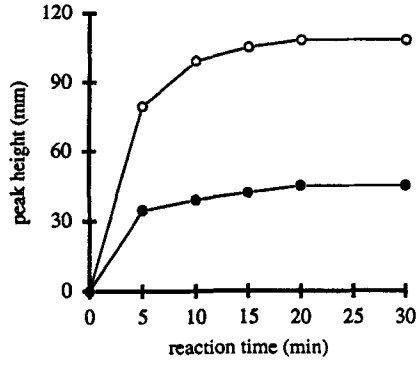

Figure 3 Effect of reaction time on peak heights for butyltin compounds (MBT, DBT, TBT, TeBT) and for phenyltin compounds (MPhT, DPhT, TPhT) in deionized water [250 ng(Sn) dm^{-3}]. The three butyltin derivatives and the three phenyltin derivatives had the same behaviour. ○, Butyltin compounds; ●, phenyltin compounds.

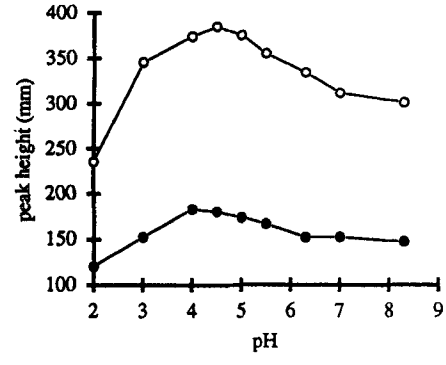

Figure 4 Effect of pH on peak heights for butyltin compounds (MBT, DBT, TBT, TeBT) and for phenyltin compounds (MPhT, DPhT, TPhT) in deionized water [250 ng(Sn) dm^{-3}]. The three butyltin derivatives and the three phenyltin derivatives had the same behaviour. ○, Butyltin compounds; ●, phenyltin compounds.

Table 2 Analytical conditions for determination of organotin compounds by GC–FPD

Injector parameters	
Sample volume	2–4 μl
Injection temperature	290 °C
Relay	
Initial relay	+1 (splitless)
Relay time	1 min
Final relay	−1 (split)
GC parameters	
Carrier gas	Nitrogen
Flow rate	0.7 $cm^3 min^{-1}$
Oven programme	
Initial temperature	70 °C for 1 min
First heat-up rate	30 °C min^{-1}
Intermediate temperature	190 °C for 0 min
Second heat-up rate	15 °C min^{-1}
Final temperature	270 °C for 5 min
FPD parameters	
Detection temperature	290 °C
Flame	Air/Hydrogen
Hydrogen flow rate	185 $cm^3 min^{-1}$
Air flow rate	250 $cm^3 min^{-1}$
Make-up	Nitrogen
Flow rate	30 $cm^3 min^{-1}$

deionized water using concentrations of 0–500 ng(Sn) dm^{-3}. Calibration curves were plotted using the values of peak heights; they were linear in the whole concentration range except for monosubstituted species, which showed a linear response ranging from 0 to 400 ng dm^{-3} only.

Table 3 Reproducibility test in deionized water[a]

Sample	TPT	MBT	DBT	TBT	TeBT	MPhT	DPhT	TPhT
1	41	20	33.5	33.3	39	16.3	34.5	23.5
2	42.5	18.2	34	36.2	43	17	35.2	23.7
3	47.5	17.2	38.5	33.7	42	17	37	26.7
4	47.2	17.2	37.7	38	42.5	15	34.7	23.7
5	47	16.7	38.2	37.2	40.2	14.5	37.5	23.7
6	43	17.5	35.5	34.2	38.2	15.2	36.2	26.2
Average	44.7	17.8	36.2	35.4	40.8	15.8	35.9	24.6
σ	2.61	1.08	2.01	1.80	1.80	0.98	1.14	1.33
RSD (%)	6.4	6.7	6.1	5.6	4.8	6.8	3.5	5.9

[a] Concentration of each tin compound is equivalent to 100 ng dm^{-3} as Sn. Response studied is peak height.

Reproducibility was studied using a mixture of TPT, MBT, DBT, TBT, TeBT, MPhT, DPhT and TPhT in deionized water (100 ng(Sn) dm^{-3} each). The raw results of six replicate analyses are reported in Table 3.

To investigate the lowest limits of detection, experiments were carried out using a volume of 1 dm^3 of a mixture of organotin compounds in deionized water. The concentrations were

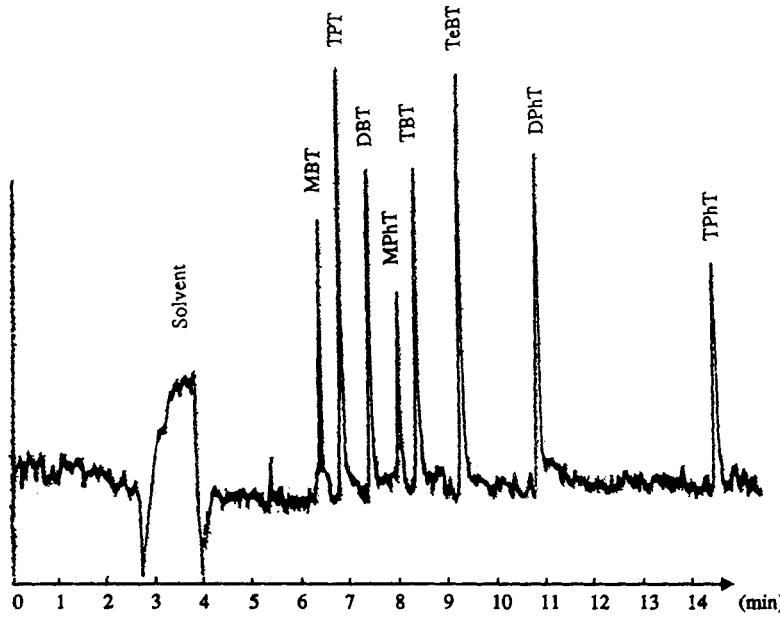

Figure 5 Typical GC–FPD chromatogram for organotin compounds. The amount of each compound injected was equivalent to 40 pg as tin.

Table 4 Theoretical detection limits 3 SD of blank values[a]

Compound	Relative detection limit ng(Sn) dm^{-3}	Absolute detection limit (pg)
TPT	0.4	4
MBT	0.8	8
DBT	0.5	5
TBT	0.4	4
TeBT	0.4	4
MPhT	2.1	21
DPhT	0.7	7
TPhT	1.1	11

[a] Concentration of each tin compound is equivalent to 10 ng dm^{-3} as Sn. Response studied is peak height. Relative detection limits refer to the water sample and absolute ones to amounts injected (injected volume was 4 μl).

10 ng(Sn) dm^{-3} of each. The results obtained in optimal gas-chromatographic conditions are given in Table 4. In routine analytical conditions these values are ten times higher.

The present limits of detection are similar to those reported by Michel and Avery[37] for butyltin compounds. They are all the more interesting as they were obtained with a commercially available GC–FPD apparatus, without any modification, unlike the detectors described by Aue and Flinn[42] or Michel and Avery,[37] which were modified by fitting a quartz burner.

Moreover, the present limits of detection are lower than those described by Choi *et al.*[41] (5.25, 7.55 and 15.65 pg for TBT, DBT and MBT, respectively) which use the same procedure. They are also much lower than those found by Gomez-Ariza *et al.*[27] (300, 280, 320, 470, 480 and 530 pg for TBT, DBT, MBT, MPhT, DPhT and TPhT, respectively). These authors used a Grignard derivatization procedure and converted organotin compounds into pentylated derivatives.

Recoveries of organotin species in spiked water

The efficiency of this speciation procedure has been checked by analysing spiked water samples, i.e. deionized water, freshwater and seawater samples.

Results given in Table 5 show satisfactory recoveries of all analytes in deionized water samples. In freshwater too high a concentration of MPhT and too low a concentration of TPhT were found; they could be explained by a partial degradation of the triphenyltin compound. This phenomenon was not observed in seawater but the concentration of DPhT was found to be low. The correlation between determinations given by internal standard and standard addition confirms the reliability of both procedures.

Analysis of environmental water samples

The analysis of actual environmental samples demonstrated the applicability of the method: a coastal seawater sampled in Britanny (France), an industrial waste water sampled near Rouen (France) and a domestic waste water sampled

Table 5 Concentrations of organotin compounds analysed in various water samples[a]

	Average in concentration±SD, $n=8$ [ngISn) dm^{-3}] (Recovery, %)		
Compound	Deionized water	Freshwater	Seawater
MBT	20.6±0.1 (103)	19.8±0.2 (99)	21.5±0.9 (108)
DBT	18.6±0.1 (93)	20.3±0.2 (102)	20.7±0.5 (104)
TBT	20.3±0.1 (102)	19.4±0.2 (97)	22.8±0.4 (114)
Σ Butyultins	59.5±0.3 (99)	59.5±0.6 (99)	65±1.8 (108)
MPhT	20.2±0.2 (101)	23.4±0.3 (117)	21.9±0.9 (110)
DPhT	17.9±0.1 (90)	20.3±0.2 (102)	17.1±1.1 (86)
TPhT	18.7±0.1 (94)	16.7±0.1 (84)	21.1±1.0 (106)
Σ Phenyltins	56.8±0.4 (95)	60.4±0.6 (101)	60.1±3 (100)

Deionized water, freshwater and seawater were spiked with 20 ng dm^{-3} as Sn of MBT, DBT, TBT, MPhT, DPhT and TPhT. Response studied was peak height.

Table 6 Analysis of environmental water samples[a]

Compound	Coastal seawater	Industrial waste water	Domestic waste water
MBT	9.6±0.9	152±6	58±4
DBT	2.8±0.3	234±11	27±2
TBT	11.5±0.8	44±2	56±4
MPhT	7.4±0.9	72±4	108±8
DPhT	n.d.[b]	n.d.	n.d.
TPhT	8.3±0.7	n.d.	n.d.

[a] Organotin concentrations in samples were determined from analysis of five replicates using TPT as internal standard.
[b] n.d., not detected.

near Pau (France). The results of five replicate analyses are reported on Table 6.

The three butyltin compounds and MPhT were detected in all samples. These compounds have entered the seawater through leaching from antifouling paints. Organotin pollution of the domestic waste water sample might result from leaching of PVC materials and from domestic washing waters. Some running waters contaminated by agricultural biocides might be mixed by chance with the analysed waste water.

In the seawater, all butyltin compounds, MPhT and TPhT were detected at very low levels in the ng dm^{-3} range. This demonstrates that the determination of butyl- and phenyl-tin compounds by this method in environmental samples is possible.

Determination of organotin compounds in a certified reference material

There is no certified reference material for the determination of organotin compounds in water. Therefore this method was validated by the analysis of the certified reference material: CRM 462, a marine sediment certified for its TBT and DBT contents.[43]

Organotin compounds were extracted from 2 g of sediment in 20 cm^3 of acetic acid using the procedure described by Desauziers *et al.*[44] or Astruc *et al.*[45] Five extractions were made and each extract was analysed five times.

Results given in Table 7 are in agreement with the certified values.[43] This demonstrates, in a quite difficult situation (a low-concentration sediment), that determinations of DBT and TBT by this method are accurate.

CONCLUSION

After optimization of the operating conditions, butyltin and phenyltin species were determined in aqueous samples. The results show that the one-step aqueous ethylation–extraction/capillary gas chromatography–flame photometric detection method is a convenient analytical technique for the determination of butyltin and phenyltin compounds in aqueous samples such as river water, waste water or seawater.

The one-step ethylation/extraction operation is easy and rapid to perform. It allows a simultaneous determination of butyltin and phenyltin species; other organotin compounds could also be determined in the same analysis. Derivatization with sodium tetraethylborate is much less time- and manpower-consuming than the Grignard reaction. This makes the method appropriate to routine analysis, especially for pollution control of natural aquatic environments, and industrial or urban waste waters.

Furthermore, the method can be extended to the determination of organotin compounds in other samples of environmental interest such as sediments and tissues.

Table 7 Analysis of the certified reference material CRM 462 (internal standard procedure)

Compound	Analysis by ethylation–GC–FPD [ng(as compound) g^{-1}]	Certification[a] [ng(as compound) g^{-1}]
MBT	102±7	—
DBT	105±11	128±16
TBT	70±6	70±14
MPhT	40±7	—

[a] From ref. 43.

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