

**ORTEP STABILIZER TASK FORCE (STF) ANALYTICAL METHOD
GAS CHROMATOGRAPHIC ANALYSIS OF DERIVATIZED ALKYL TIN
CHLORIDES**

SUMMARY

Following extraction, the tetraalkylated derivatives of mono-, di-, and trialkyl (methyl, butyl, or octyl) tin compounds are analyzed using gas chromatography with mass spectrometry.

GENERAL INFORMATION

--This method is intended for use in conjunction with the corresponding ORTEP Association (2006) methods, *Extraction of Alkyltin Chlorides from Water* and *Extraction of Alkyltin Chlorides from Dry Animal Feed*.

--Organotin compound (OTC) - Substance with at least one Sn-C bond. The number of Sn-C bonds is a measure of the degree of alkylation of a compound.

--Organotin cation (OC) - The portion of an organotin compound containing the Sn-C bonds (i.e., without the attached anion).

--Monoheptyltin trichloride (MHTC), diheptyltin dichloride (DHTC), tripropyltin chloride (TPTC), and tetrapropyltin (TTPT) are added as internal standards during the extraction procedure.

--Boron compounds (e.g., boranes) may interfere with other compounds during GC determination and influence analyte detection. In order to protect the GC column and to reduce the likelihood of chromatographic interferences, it is recommended to apply a pre-cleaning step, such as acid-washing with 2 M HCl or silica gel cleanup, to all sample extracts prior to analysis.

--Other gas chromatography detector systems (e.g., flame photometric detection [FPD] or atomic emission detection [AED]) may be utilized for these compounds. For more information, see the German Standard Method for the determination of selected organotin compounds by gas chromatography (DIN 38407).

I. Apparatus

Autosampler

Gas Chromatograph (GC) system (e.g., Hewlett-Packard 5890)

Mass Spectrometer (MS) Detector System for EI-mode (Electron Impact), with sufficient sensitivity

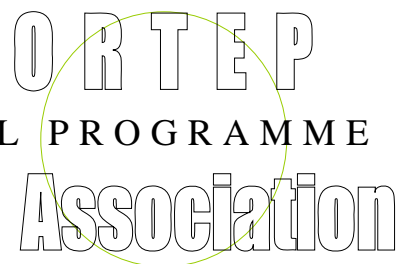
Data acquisition/processing software, compatible with the chosen detector system

II. Measurement

A. General:

1. Optimize the instrument settings according to the manufacturer's instructions. Choose the measuring conditions depending on the analytical question. Instrument signal can be evaluated using either peak

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area or peak height. In the case of discontinuous detection (e.g., MS), evaluation using peak area is recommended.

NOTE: For ease of understanding the wording in this paper is always “peak area.”

2. Example injection sequence: Hexane / blank extract / reference solution extracts (in ascending concentration) / hexane / sample extracts.

NOTE: For procedure control, it is advantageous to analyze a blank extract and a reference solution extract after about every six injections as a calibration check. If the control value for the blank does not match with the original blank value or the recalibration does not produce values within the selected precision data, repeat the last series of measurements. If necessary, investigate the procedure for sources of contamination or other changes in the instrument signal.

- B. GC Conditions: Adjust the respective chromatographic system according to the manufacturer’s instructions to operate with sufficient sensitivity and selectiveness. Chromatographic conditions should be set up to obtain a baseline resolution. The chromatographic conditions used during recent method verification and validation studies for the ORTEP method are presented in Appendix A.1.
- C. Example Detector Conditions: Following is a general example for the MS detector system. The chromatographic conditions used during recent method verification and validation studies for the ORTEP method are presented in Appendix A.1

1. MS

Transfer line:	290°C
Electron impact:	70 eV
Photomultiplier:	2000 V
Mode:	Selected ion monitoring (SIM)

NOTE: The isotope cluster of organotin compounds is formed by 10 natural tin isotopes (see Table 1). In the case of GC/MS analysis, two of the most intensive non-interfered isotope cluster ions (preferably with high mass) should be recorded by registering selected fragment ions (see Table 2).

Table 1. Masses and abundances of natural tin isotopes.

Mass (amu)	Abundances (%)	Relative Abundance (%)
112	0.95	2.88
114	0.65	1.97
115	0.34	1.03
116*	14.24	43.19
117	7.57	22.96
118*	24.01	72.82
119	8.58	26.02
120*	32.97	100.00
122	4.71	14.29
124	5.98	18.14

*These isotopes are preferred for MS detection

Table 2. Characteristic masses for MS identification and evaluation of ethylated alkyltin compounds

Substance	Cluster a1/a2	Cluster b1/b2	Cluster c1/c2
Monomethyltriethyltin	193.0 / 191.0	165.0 / 163.0	179.0 / 177.0
Dimethyldiethyltin	179.0 / 177.0	193.0 / 191.0	165.0 / 163.0
Trimethylethyltin	179.0 / 177.0	165.0 / 163.0	136.9 / 134.9
Monobutyltriethyltin	235.1 / 233.0	179.0 / 177.0	151.0 / 149.0
Dibutyldiethyltin	263.1 / 261.1	179.0 / 177.0	151.0 / 149.0
Tributylethyltin	291.1 / 289.1	263.1 / 261.1	179.0 / 177.0
Monooctyltriethyltin	291.1 / 289.1	179.0 / 177.0	151.0 / 149.0
Diocetyldiethyltin	375.2 / 373.2	263.1 / 261.1	151.0 / 149.0
Triocylethyltin	459.3 / 457.3	375.2 / 373.2	235.1 / 233.0
Monoheptyltriethyltin	277.1 / 275.1	179.0 / 177.0	151.0 / 149.0
Diheptyldiethyltin	347.2 / 345.2	249.1 / 247.1	151.0 / 149.0
Tripropylethyltin	249.1 / 247.1	235.1 / 233.0	193.0 / 191.0
Tetrapropyltin	249.1 / 247.1	165.0 / 163.0	151.0 / 149.0

Note: If two clusters (from a, b, c) have been chosen, use the following nomenclature:

M_{hn} : h = mass of the higher cluster, n = 1st or 2nd mass in the cluster
 M_{ln} : l = mass of the lower cluster, n = 1st or 2nd mass in the cluster

III. Identification

A. Minimal requirement for identification:

Independent of the detection system used, analyte identification may be confirmed by comparing the retention times of samples and standards. In order to achieve minimum requirements for identification, both sample and standard retention times (RT) should fall within ± 0.05 min of each other, and relative retention times (RRT) over the total run of a chromatogram should not shift more than ± 0.2 %. Additionally, there must be no evidence of interference in the method blanks.

B. Identity check

NOTE: This is only required if results may need to be legally binding, i.e., used for litigation purposes.

The identity is checked in several steps:

1. Analyte identification is thought to be probable if both the RT and the RRT meet acceptable limits for one capillary column.
2. Analyte identification is confirmed if both the RT and the RRT also meet acceptable limits on a second column of different polarity.
3. Furthermore, analyte identity is confirmed if both the RT and the RRT from one column using MS detection are in agreement and the mass spectrum over the total mass range matches sufficiently with the mass spectrum of a reference substance, or if (in the case of single ion monitoring) the characteristic masses of the isotope clusters are detected and the criteria in Appendix B are met.

Table 3. Definitions of the subscripts used in the calculation procedures that follow.

Subscript	Definition
<i>i</i>	Identity of the compound
<i>I</i>	Internal reference standard
<i>k</i>	Identity of the internal standards
<i>e</i>	Values from calibrations
<i>P</i>	Values from sample measurements
<i>J</i>	Mass portion step of the reference solutions
<i>h</i>	Higher cluster
<i>l</i>	Lower cluster

IV. Calibration

- A. Calibrate with the internal standard *I* over the total procedure (e.g., for both samples and reference standard samples) using a calibration curve. To establish a

calibration curve, measure the extracts of at least six reference solutions (see extraction procedures).

- B. The specific relative responses related to an internal reference standard (subscript *I*), e.g., diheptyltin dichloride (DHTC), are determined using the additional internal standard(s) (subscript *k*) of different alkylation degree(s). They are taken from the extract chromatograms of the reference solution. The mean response will be compared to the relative response calculated from the chromatograms of sample extracts.

NOTE: If DHTC is chosen as the internal reference standard (subscript *I*), subscript *k* is subsequently used in equation 3 for each of the other internal standards – MHTC, TPTC, and TTPT.

Calculate the relative response as follows:

$$R_{Ikej} = \frac{F_{Iej} \cdot m_{kej}}{F_{kej} \cdot m_{Iej}} \quad (3)$$

Where:

R_{Ikej} is the relative response of the internal standard *k*, in relation to the internal reference standard *I* in the calibration *e*, mass portion step *j*

F_{Iej} is the peak area of the internal reference standard *I* in the calibration *e*, mass portion step *j*

m_{kej} is the mass of the internal standard *k* in the calibration *e*, mass portion step *j*, in nanograms

F_{kej} is the peak area of the internal standard *k* in the calibration *e*, mass portion step *j*

m_{Iej} is the mass of the internal reference standard *I* in the calibration *e*, mass portion step *j*, in nanograms

- C. Derive the typical alkylation degree-specific intralaboratory relative response by calculation of the mean value from all mass portion steps:

$$R_{Ike} = \frac{1}{j} \cdot \sum_{j=1}^j R_{Ikej} \quad (4)$$

Where:

R_{Ike} is the mean relative response of the internal standard *k*, related to the internal reference standard *I* in the calibration over all mass portion steps *j*

R_{Ikej} is the relative response of the internal standard *k* related to the internal reference standard *I* in the calibration mass portion step *j*

- D. Calculate the standard deviation of the typical alkylation degree-specific intralaboratory relative response as follows:

$$S_{R_{Ike}} = \sqrt{\frac{\sum (R_{Ike} - R_{Ikej})^2}{j-1}} \quad (5)$$

Where:

SR_{Ike} is the standard deviation of the mean relative response of the internal standard k related to the internal reference standard I in the calibration over all mass portion steps j

R_{Ike} is the mean relative response of the internal standards k related to the internal reference standard I in the calibration over all mass portion steps j

R_{Ikej} is the relative response of the internal standard k related to the internal reference standard I in the calibration, of the mass portion step j

j is the mass portion step

- E. Calculate the relative standard deviation (RSD) as follows:

$$RSD = \frac{SR_{Ike}}{R_{Ike}} \cdot 100 \quad (6)$$

Where:

RSD is the relative standard deviation of the mean relative response of the internal standard k related to the internal reference standard I in the calibration over all mass portion steps i , in percent

SR_{Ike} is the standard deviation of the mean relative response of the internal standard k related to the internal standard I in the calibration over all mass portion steps j

R_{Ike} is the mean relative response of the internal standard k related to the internal reference standard I in the calibration over all mass portion steps j

The relative standard deviation (RSD) should not exceed 10%. If the RSD exceeds 10% the procedure may need to be repeated (including the extraction).

- F. MS detection may be based on either the peak area for the most intensive mass (base peak) from a non-interfered cluster (see Appendix B.; preferably the higher cluster) of OTC_{*i*}, or on the sum of the peak areas for this cluster ($F_{Mh1} + F_{Mh2}$ respectively $F_{Ml1} + F_{Ml2}$).

Integrate the peak areas (F) of the OTC_{*i*}, the internal reference standard (I), and each OTC_{*i*}. Calculate a calibration curve for each working range, according to equation 7:

$$y = (a_1 * x) + a_0 \quad (7)$$

Where:

- y is the mass of OTC_i in a calibration of one working range
- a₁ is the slope of calibration curve
- x is the value calculated from peak area and mass of internal reference standard (subscript I) and peak area of OTC_i
- a₀ is the intercept of calibration curve

G. Calculate the coefficients of equation 7 according to equations 8 and 9:

$$a_1 = \frac{\sum (x_{ij} - \bar{x}_i) \cdot (y_{ij} - \bar{y}_i)}{\sum (x_{ij} - \bar{x}_i)^2} \text{ with } \bar{x}_i = \frac{1}{j} \cdot \sum_{j=1}^j x_{ij}, \bar{y}_i = \frac{1}{j} \cdot \sum_{j=1}^j y_{ij} \text{ and } x_{ij} = \frac{F_{iej}}{F_{Iej}} \cdot m_{Ie} \quad (8)$$

$$a_0 = \bar{y}_i - a_1 \cdot \bar{x}_i \quad (9)$$

Where:

- a₁ is the slope of calibration curve
- a₀ is the intercept of calibration curve
- y_{ij} is the mass of OTC_i in a calibration of one working range, mass portion step j (= m_{iej})
- x_{ij} is the value calculated from peak area and mass of internal reference standard (subscript I); and peak area of OTC_i in a calibration of one working range, mass portion step j
- F_{Iej} is the peak area of internal reference standard I in a calibration of one working range, mass portion step j
- F_{iej} is the peak area of OTC_i in a calibration of one working range, mass portion step j
- m_{Ie} is the mass of internal reference standard I in a calibration of one working range, in nanograms
- \bar{x}_i is the mean of all x_{ij} in a calibration of one working range for one OTC_i
- \bar{y}_i is the mean of all y_{ij} in a calibration of one working range for one OTC_i

H. Alternatively, an "adjusted single reference calibration" can be applied. Integrate the peak areas (F) of the OTC_i, the internal reference standard (I), and each OTC_i to obtain the mass portion dependant response factors Rf_{iej}.

$$Rf_{iej} = \frac{F_{iej} \cdot m_{Ie}}{F_{Iej} \cdot m_{ie}} \quad (10)$$

Where:

- Rf_{iej} is the response factor for the OC_i during calibration, mass portion step j
- F_{Iej} is the peak area for the internal reference standard I in the calibration, mass portion step j
- m_{ie} is the mass of the OC_i in the calibration, in nanograms
- F_{iej} is the peak area for the OTC_i in the calibration, mass portion step
- m_{Ie} is the mass of the internal reference standard I in the calibration, in nanograms

V. Evaluation (Note: chromatography software will perform many of these steps)

- A. Calculate from the chromatograms of the calibration solutions the alkylation degree-specific, intralaboratory relative response (see equation 4) of the internal standards related to the internal reference standard, e.g., MHTC, DHTC, etc., and its response and the respective standard deviation (equation 5). Calculate from the chromatograms of the sample extracts the relative response of the internal standards related to the reference standard (according to equation 3) and compare it to the alkylation degree-specific, intralaboratory relative response. Depending on the alkylation degree and the sample, state the relative response in the calibration, including the respective standard deviation and the relative response in the test report.
- B. Calculate the mass m_i of OTC_i in the sample extract with equation 11:

$$m_i = a_1 \cdot \frac{F_i \cdot m_I}{F_I} + a_0 \quad (11)$$

Where:

- m_i is the mass of the OC_i in the sample extract, in nanograms
- F_i is the peak area OTC_i in the sample measurement
- m_I is the mass of the internal reference standard I in the extract as OC , in nanograms
- F_I is the peak area for the internal reference standard I in the sample measurement
- a_1, a_0 are the coefficients from equation 7

If the OC_i is to be quantified by the “adjusted single-reference calibration”, use as a basis the response factor Rf_{iej} for the mass portion step j , which is nearest to the peak area F_{ie} for the measured value F_i .

- C. Calculate the mass m_i of the OC_i in the sample extract according to equation 12:

$$m_i = \frac{Rf_{iej} \cdot F_i \cdot m_I}{F_I} \quad (12)$$

Where:

m_i is the mass of the OC_i in the pre-treated sample extract, in nanograms

Rf_{iej} is the mean response factor OC_i at the mass portion step j

F_i is the peak area OC_i in the sample measurement

m_I is the mass of the internal reference standard I in the pre-treated extract as OC , in nanograms

F_I is the peak area for the internal reference standard I in the sample measurement

D. Water analysis

The mass concentration w_i of the OC_i in the water sample is calculated according to equation 13:

$$w_i = \frac{m_i}{V_p} \quad (13)$$

Where:

w_i is the mass concentration for the OC_i in the water sample, in ng/L

m_i is the mass OC_i in nanograms according to equation 11 or 12

V_p is the volume of the water sample used for analysis, in L

E. Air monitoring The mass concentration w_i of the OC_i in the air monitoring sample is calculated according to equation 14:

$$w_i = \frac{m_i}{V_p} \quad (14)$$

Where:

w_i is the mass concentration for the OC_i in the sample, in ng/m³

m_i is the mass OC_i in nanograms according to equation 11 or 12

V_p is the volume of air sampled onto the XAD-2 sampler analysis, in m³

F. Animal feed analysis The mass concentration w_i of the OC_i in the dry animal feed sample is calculated according to equation 15:

$$w_i = \frac{m_i}{m_p} \quad (15)$$

Where:

w_i is the mass concentration for the OC_i in the rat feed sample, in ng/g

m_i is the mass OC_i in nanograms according to equation 11 or 12

m_p is the mass of dry animal feed used for analysis, in g

VI. Statement of Results

- A. Report the results in appropriate units with three significant figures.

VII. Analytical Report

- A. The report shall refer to this method and contain the following details:
- 1) Identity of the sample (including sample ID, sample date, matrix, etc.);
 - 2) Information on sampling and sample pre-treatment (if any);
 - 3) Detailed description of the procedure (e.g., extraction method, cleanup steps performed, GC conditions, etc.);
 - 4) Procedure used for identification and quantification of the single components (statement of calibration and calculation mode);
 - 5) Statement of result according to Section VI;
 - 6) QC sample results (e.g., blank results, matrix spike/duplicate recoveries, matrix spike/duplicate RPDs, etc.);
 - 7) Any deviations from the procedure and statement of all circumstances that may have influenced the results; and
 - 8) Relative response from the calibration and the sample solutions.

VIII. References

de Wolf, J.M. and R. Schilt. 2004. Validation of analysis of organotin chlorides MMTC, MBTC, DBTC, MOTC, DOTC and TOTC, and tetraalkyltins TTOT and TTBT in RM3 rodent diet. TNO Report V4921. Study conducted by TNO Nutrition Research, Analytical Sciences for the ORTEP Stabilizer Task Force. Zeist, The Netherlands.

de Wolf, J.M., R. Schilt, and H.A. Meinema. 2004. Validation of analysis of organotin chlorides MMTC, DMTC, MBTC, DBTC, MOTC and DOTC in water. TNO Report V4766. Study conducted by TNO Nutrition Research, Analytical Sciences for the ORTEP Association Stabilizer Task Force. Zeist, The Netherlands.

DIN Deutsches Institut für Normung e.V. 2001. DIN 38407 – 13:2001-03 German Standard Methods for the Examination of Water, Waste Water and Sludge – Jointly Determinable Substances (Group F) – Part 13: Determination of selected organotin compounds by gas chromatography (F13). Beuth Verlag, 10772 Berlin, Germany.

ORTEP Association. 2006a. ORTEP Stabilizer Task Force (STF) Analytical Method - Extraction of Alkyltin Chlorides From Dry Animal Feed. Revision 3.0. January 2006.

ORTEP Association. 2006b. ORTEP Stabilizer Task Force (STF) Analytical Method - Extraction of Alkyltin Chlorides From Water. Revision 3.0. January 2006.

APPENDIX A

A.1 Chromatographic conditions - method verification and validation studies for the ORTEP method

Column: fused silica HP5 MS, 30 m, 0.25 mm ID, 0.25µm film
 Pre-column: fused silica HP5 MS, 2.5 m, 0.25 mm ID, 0.25µm film
 Column temperature: 45°C for 3 min → +5°C/min → 80°C → +15°C/min → 260°C for 15 min
 Carrier: helium; 1.5 mL/min constant flow
 Injection volume: 1 µL
 Injection temperature: 60°C → +14.5°C/second → 300°C for 5 min
 Injection method: splitless
 Ionization: electron impact, 70 eV
 Mass range: 60-400 amu

Table A.1 Characteristic masses used for MS identification and quantitation of tetraalkylated organotin compounds

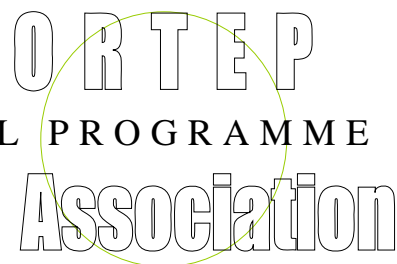
Substance	Mass Fragment 1 (m/z)	Mass Fragment 2 (m/z)	Mass Fragment 3 (m/z)
MMT	<u>193</u>	165	179
DMT	<u>179</u>	193	165
MBT	<u>235</u>	179	151
DBT	<u>263</u>	179	151
MOT	<u>291</u>	179	151
DOT	<u>375</u>	263	151
TOT	<u>375</u>	263	459
TTBT	<u>291</u>	235	179
TTOT	<u>459</u>	347	235
MHT	<u>277</u>	179	151
DHT	<u>347</u>	249	179
TPT	<u>235</u>	249	193
TTPT	<u>249</u>	--	--
Naphthalene*	<u>128</u>	--	--

Underlined mass fragments were used for quantitation.

* - Internal standard compound used to check the injection of the sample into the GC instrument (see ORTEP extraction methods for water and feed).

For calculation of the amount of monoalkyl tin compounds, the peak area of MHT was used as an internal standard. For calculation of the amount of dialkyl tin compounds, the peak area of DHT

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was used. For calculation of the amount of tri- and tetraalkyl tin compounds, the peak areas of TPT and TTPT, respectively, were used. Quantitation was conducted using the calibration graph constructed from the organotin calibration solutions (Q-value (ratio of peak area test substance/peak area internal standard vs. concentration)).

A.2 ORTEP METHOD VALIDATION SUMMARY RESULTS

A summary of the water and dry animal feed method validation results for monomethyltin trichloride (MMTC), dimethyltin dichloride (DMTC, water only), monobutyltin trichloride (MBTC), dibutyltin dichloride (DBTC), mono-octyltin trichloride (MOTC), dioctyltin dichloride (DOTC), trioctyltin chloride (TOTC, feed only), tetrabutyltin (TTBT, feed only), and tetraoctyltin (TTOT, feed only) are presented in Tables A.2 (de Wolf et al. 2004) and A.3 (de Wolf and Schilt 2004).

Table A.2 Summary of GC/MS method validation results in water.

Analyte	Dose Level (mg/L)	LOD (mg/L)	LOQ (mg/L)	Overall Mean Recovery (%)	RSD (%)
MMTC	0	0.05	0.2	--	--
	10.75			99	1.0
	107.5			100	2.1
DMTC	0	0.05	0.2	--	--
	9.97			101	2.2
	99.7			100	5.1
MBTC	0	0.05	0.2	--	--
	10.98			101	1.6
	109.8			95	4.3
DBTC	0	0.003	0.01	--	--
	1.02			101	3.0
	10.2			102	2.3
MOTC	0	0.002	0.005	--	--
	0.0498			94	2.0
	0.498			100	3.1
DOTC	0	0.003	0.01	--	--
	0.0566			101	3.5
	0.113			101	2.6

DBTC – Dibutyltin dichloride
 DMTC – Dimethyltin dichloride
 DOTC – Dioctyltin dichloride
 LOD – Level of detection
 LOQ – Level of quantitation
 MBTC – Monobutyltin trichloride
 MMTC – Monomethyltin trichloride
 MOTC – Monoctyltin trichloride
 RSD – Relative standard deviation



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Table A.3 Summary of GC/MS method validation results in dry animal feed.

Analyte	Dose Level (mg/Kg)	LOD (mg/Kg)	LOQ (mg/Kg)	Overall Mean Recovery (%)	RSD (%)
MMTC	0	2	5	--	--
	50			97	6.7
	250			97	2.2
	750			97	1.6
	1500			95	2.4
MBTC	0	5	15	--	--
	100			102	3.0
	300			94	4.2
	1000			99	9.3
	5000			90	4.6
DBTC	0	1	3	--	--
	30			86	5.4
	90			75	3.4
	270			92	11
	1080			95	11
MOTC	0	0.5	2	--	--
	10			91	1.1
	30			85	3.0
	100			103	4.6
	300			98	7.0
DOTC	0	0.5	2	--	--
	15			91	2.4
	50			91	0.6
	150			84	12
	500			80	11
TOTC	0	15	50	--	--
	30			91	4.1
	1000			91	1.6
	5000			86	10
	10000			81	5.5



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Table A.3 Summary of GC/MS method validation results in dry animal feed (continued).

Analyte	Dose Level (mg/Kg)	LOD (mg/Kg)	LOQ (mg/Kg)	Overall Mean Recovery (%)	RSD (%)
TTBT	0	5	15	--	--
	100			83	5.3
	500			84	4.1
	2000			83	3.5
	10000			88	3.3
TTOT	0	5	15	--	--
	100			77	6.4
	500			76	4.9
	2000			100	8.4
	10000			89	13

DBTC – Dibutyltin dichloride
 DMTC – Dimethyltin dichloride
 DOTC – Dioctyltin dichloride
 LOD – Level of detection
 LOQ – Level of quantitation
 MBTC – Monobutyltin trichloride
 MMTC – Monomethyltin trichloride
 MOTC – Monoctyltin trichloride
 RSD – Relative standard deviation
 TOTC – Trioctyltin chloride
 TTBT – Tetrabutyltin
 TTOT - Tetraoctyltin

APPENDIX B

B.1 Special criteria for the mass spectrometric (MS) identification: This section is important to single ion measurements

B.1.1 The ratios of peak areas of the respective isotope clusters of a compound may be mass-portion dependant and may differ due to the parameter settings and type of MS system used. From the chromatograms of the reference solution extracts and the sample extracts, the peak areas of the chosen four masses from Table 2 (section II.c) are determined (F_{Mh1} , F_{Mh2} , F_{Ml1} , and F_{Ml2}).

The ratios V_h (higher cluster) and V_l (lower cluster) are determined.

$$V_h = \frac{F_{Mh1}}{F_{Mh2}} \quad (1)$$

$$V_l = \frac{F_{Ml1}}{F_{Ml2}} \quad (2)$$

Where:

V_h is the ratio of the peak areas of the higher isotope cluster (subscript h) in the chromatograms

V_l is the ratio of the peak areas of the lower isotope cluster (subscript l) in the chromatograms

F_{Mh1} is the peak area of the higher mass (subscript 1) in the higher isotope cluster (subscript h)

F_{Mh2} is the peak area of the lower mass (subscript 2) in the higher isotope cluster (subscript h)

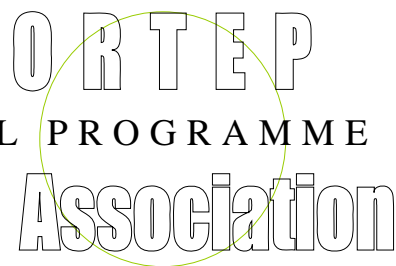
F_{Ml1} is the peak area of the higher mass (subscript 1) in the lower isotope cluster (subscript l)

F_{Ml2} is the peak area of the lower mass (subscript 2) in the lower isotope cluster (subscript l)

B.1.2. Assumed that the cluster ions in the chromatograms of the extracts from the reference solutions are not interfered with and the peak area ratios are calculated (V_{he} and V_{le}) and compared with the respective peak area ratios (V_{hp} and V_{lp}) from the chromatograms of the sample extracts. The identity of an analyte is confirmed if one of the following criteria {A through C} is met:

$$\frac{V_{he}}{V_{hp}} = 1.00 \pm a \quad \text{and} \quad \frac{V_{le}}{V_{lp}} = 1.00 \pm b \quad \{A\}$$

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$$\frac{V_{he}}{V_{hP}} = 1.00 \pm c \quad \text{and} \quad \frac{V_{le}}{V_{lP}} = 1.00 \pm b \quad \{B\}$$

$$\frac{V_{he}}{V_{hP}} = 1.00 \pm a \quad \text{and} \quad \frac{V_{le}}{V_{lP}} = 1.00 \pm d \quad \{C\}$$

Where:

V_{he} , V_{le} are the peak area ratios of the higher (subscript h) and lower (subscript l) isotope clusters in the chromatograms of the reference solutions (subscript e), respectively

V_{hP} , V_{lP} are the peak area ratios of the higher (subscript h) and lower (subscript l) isotope clusters in the chromatograms of the sample extracts (subscript P), respectively

a, b, c, d are the mass portion and matrix dependant tolerances of the peak area ratios (see Table B.1)

If criterion {A} is fulfilled, both isotope clusters are regarded as not interfered. If criterion {B} is fulfilled, the lower cluster is regarded as not interfered. If criterion {C} is fulfilled, the higher cluster is regarded as not interfered. In any other cases, both clusters are interfered and the identity is not confirmed.

Calculate the apparatus (and possibly the mass portion) dependant ratios (V_{he} and V_{le}), by injection of the reference solution extract nearest to the expected mass ratio of the sample.

Table B.1.1. Mass portion and matrix dependant tolerances of the peak area ratios.

Tolerances	Concentration of solution subjected to GC		
	10 ng/ml to 35 ng/ml	40 ng/ml to 240 ng/ml	250 ng/ml to 1000 ng/ml
a	0.3	0.1	0.05
b	0.3	0.1	0.05
c	0.5	0.25	0.15
d	0.5	0.25	0.15

NOTE: These data were derived from three different calibrations (I): 10,15,20,25,30, and 35 ng/ml; (II): 40, 80, 120, 160, 200, and 240 ng/ml and (III): 250, 400, 550, 700, 850, and 1000 ng/ml (concentration of solution subjected to GC)

