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Reinvestigation of Phase-Transfer-Catalyzed Chlorpyrifos Synthesis

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Abstract:

Production of chlorpyrifos via the phase-transfer-catalyzed reaction of *O*,*O*-diethylphosphorochloridothioate and the sodium salt of 3,5,6-trichloropyridin-2-ol was reinvestigated. The formation of sulfotep (the major byproduct) and the yield are influenced by the nature and concentration of the catalysts, temperature, stirring rate, and time of the reaction. The elucidation of the roles of different parameters influencing the end of the reaction have permitted us to perform the synthesis of chlorpyrifos on bench scale (0.3 M scale) under optimized conditions—using the minimum amounts of catalysts (0.5 mol %)—with 92% yield and 98.5% purity.

Introduction

Chlorpyrifos (Dursban: *O*,*O*-diethyl-*O*-3,5,6-trichloro-2-pyridylphosphorothioate) is a broad-spectrum, commercial organophosphorus insecticide first elaborated and proposed by R. H. Rigterink et al.[1,2] The major route for the production of chlorpyrifos consists of the reaction between *O*,*O*-diethylphosphorochloridothioate (DECTP) and the sodium salt of 3,5,6-trichloropyridin-2-ol (NaTCP).[3−13]

NaTCP was formed after the reaction of a mineral base (such as NaOH) with 3,5,6-trichloropyridin-2-ol, the synthesis of which via the CuCl-catalyzed reaction of trichloroacetyl chloride and acrylonitrile has been recently reinvestigated.[14,15]

Different times of reaction and yields have been reported concerning the reaction of NaTCP with DECTP performed in a single-[1−6] or a two-phase solvent system[7−13] using several types of catalysts with different concentrations (Table 1).

The reactive form of NaTCP is the pyridinate ion (TCP^-), the concentration of which is maximized in alkaline medium at pH ≈ 10 (pK_a of 3,5,6-trichloropyridin-2-ol was estimated to be 9.8). The alkaline medium was mostly accomplished and stabilized using boric acid/borate tampon ($pK_a = 9.2$).

Two important kinds of catalysts used that gave best performance of the reaction have been tertiary amines (TA) in conjunction with phase transfer catalysts (PTC). The TA have been used to protect DECTP from hydrolysis, and the PTC, to transport pyridinate ion (TCP^-) through the organic phase for reaction with DECTP.

The main compounds used as the PTC have been BTEAC (benzyl triethylammonium chloride) or BTMAC (benzyl trimethylammonium chloride)[6,10−13] and PG 26-2 surfactant (produced from the reaction of di-*sec*-butyl phenol with ethylene oxide and propylene oxide with an HLB value in the range of 8−10) or other surfactants.[5,9]

Several types of TA with different amounts of steric hindrance have been used in the chlorpyrifos synthesis, for example, TMA (trimethylamine), DMAP (dimethyl amino pyridine), TEDA (triethylenediamine), MI (methyl imidazole), and so on.

By using a two-phase solvent system (H_2O/CH_2Cl_2) plus a dual catalyst system (the tertiary amine and phase transfer catalyst)—which was first proposed and elaborated by Kroposki et al.—the hydrolysis of DECTP which causes sulfotep ($((C_2H_5O)_2P(S))_2O$) formation was overcome, and the product was readily separated in high purity (Scheme 1).

Although several types of TA and PTC were used in the chlorpyrifos synthesis, the advantage or disadvantage of each case has not yet been discussed in detail. On the other hand, according to a two-phase system (H_2O/organic solvent), efficient stirring of the reaction mixture is of main importance in the accomplishment of the reaction and is influenced by the rate of the stirrer and the shape of the reactor.

In this contribution, we attempt to reconsider the factors leading to completion of the reaction and to define the optimized conditions for yield and purity of the product.

Results and Discussion

As mentioned earlier, a two-phase-catalyzed chlorpyrifos synthesis requires an organic/H_2O solvent system, a phase transfer catalyst, and a tertiary amine.

Among the factors that influence the completion of the reaction in the two-phase system is the addition sequence

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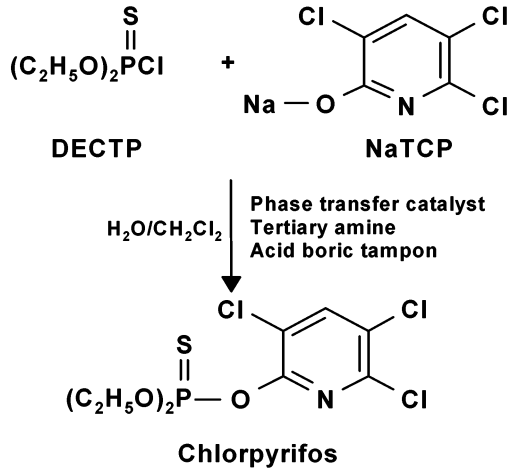
Table 1. **Some of the reported data concerning the use of the solvent system, tertiary amine and phase transfer catalyst in the chlorpyrifos synthesis[a] via the reaction of DECTP with NaTCP**

solvent system	tertiary amine (mol %)	phase transfer catalyst (mol %)	time (h)	temp (°C)	yield (%)	purity (%)	reference
MeCN	−	−	6	50	43	−	3
H_2O	DMAP	−	1.5	60	98	−	4
H_2O	DMAP (1)	PG 26−2	2	45	95	98.5	5
CH_2Cl_2	−	BTEAC (30)	2	45	88	99	6
H_2O/ CH_2Cl_2	TEDA (1)	−	5	40	99	95	7
H_2O/Toluene	−	−	4.5	25	95.5	−	8
H_2O/ CH_2Cl_2	DMAP (0.1)	PG 26−2	2	45	95.5	97	9
H_2O/ CH_2Cl_2	DMAP (10)	BTMAC (10)	1	−	89	−	10, 11
H_2O/ CH_2Cl_2	TMDA (10)	BTEAC (10)	3	−	91	−	10, 11
H_2O/ CH_2Cl_2	TMA (10)	BTEAC (10)	1	−	94	−	10, 11
H_2O/ CH_2Cl_2	MI (1)	BTEAC (1)	1.5	42	94	99.5	12
H_2O/ CH_2Cl_2	TEDA (1)	BTEAC (1)	1.5	42	97	99	13

[a] In most cited references the reaction has been performed in 0.05 M scale.

Scheme 1. **Phase-transfer-catalyzed chlorpyrifos synthesis**



of the starting materials and the quantities of the solvents used.

The solutions of PTC, NaCl, NaOH, and boric acid in H_2O and TA in organic solvent (CH_2Cl_2 or $CHCl_3$) were separately prepared and mixed in the reactor which contains NaTCP, before dropwise addition of DECTP dissolved in organic solvent.

The total amounts of water and organic solvent used are optimized for the synthesis of chlorpyrifos, respecting the minimum volume of the reactor and other vessels required for the separation, washing, and drying of the organic solvent. The lesser amounts of water and organic solvent have increased the viscosity of the mixture in the beginning of the reaction and influenced the efficiency of the stirring and separation of organic phase.

The purity of the product and the yield depend on other different factors such as the PTC and TA and their respective concentrations, the reaction temperature and time, the stirrer type, and the stirring rate. Considering these factors, the types of catalysts and their concentrations were first optimized on 0.003 M scale (Table 2, experiments 1−11). The optimized parameters were applied to bench scale (0.3 M scale) (Table 2, experiment 12) where the stirring rate and the DECTP addition rate were then optimized.

To follow the reaction, ^{31}P NMR was chosen as the most appropriate technique to analyze the composition of the phosphorus-containing compounds present in the organic phase.

In the first four experiments (Table 2, experiments 1−4), the reaction was performed in $H_2O/CHCl_3$ at 60 °C using triethylamine (TEA) as tertiary amine in the absence or presence of BTEAC (phase transfer catalyst). In the absence of BTEAC (Table 2, experiment 1), most of the starting DECTP was found unreacted in the organic phase after 3 h. Upon addition of BTEAC, the conversion rate was increased (Table 2, experiment 2−4). In the presence of TEA, the rate enhancement was BTEAC concentration dependent (1−4 mol %). The substitution of BTEAC for pyridinium chloride (PTC) (Table 2, experiment 5) showed almost the same conversion rate as that in experiment 4 except that a considerable amount of undesirable byproduct, sulfotep (12%), was formed.

The preliminary test with BTEAC (4 mol %) and TEDA (2 mol %) indicated that TEDA (as tertiary amine) was much better than TEA (Table 2, experiments 6 and 7). Under these conditions and after 1 h, no starting DECTP was detected in the ^{31}P NMR spectrum of the organic phase, while 6% sulfotep was formed.

Among the TA used in the literature, DMAP—as a more sterically hindered amine—was successfully applied in our next experiments (Table 2, experiments 8−12). The replacement of TEDA by DMAP caused the enhancement of sulfotep byproduct formation from 6 to 12% while maintaining the same amount of chlorpyrifos formed (88%). To eliminate the byproduct formation via DECTP hydrolysis and to keep the concentration of unreacted DECTP as low as possible, the concentrations of both the phase transfer catalyst and tertiary amine were reduced as was the reaction time (Table 2, experiments 9−10).

As presented in Table 2, 0.5 mol % of DMAP and BTEAC and a 15-min reaction time were enough for the maximum conversion rate of DECTP with the minimum formation of sulfotep at 60 °C using $H_2O/CHCl_3$ as solvent system (Table 2, experiment 10). These optimized conditions were then applied to the H_2O/CH_2Cl_2 solvent system, and it

Table 2. **Proportional composition (%)[a] of the organophosphorus compounds in the organic phase of the phase-transfer-catalyzed reaction of NaTCP with DECTP under different conditions**

experiment[b]	solvent system	tertiary amine (mol %)	phase transfer catalyst (mol %)	time (h)	temp (°C)	sulfotep (53.8 ppm)	DECTP (69.8 ppm)	chlorpyrifos (60.9 ppm)
1	$H_2O/CHCl_3$	TEA (1)	–	3	60	1	90	9
2	$H_2O/CHCl_3$	TEA (1)	BTEAC (1)	3	60	–	78	22
3	$H_2O/CHCl_3$	TEA (1)	BTEAC (2)	3	60	–	61	39
4	$H_2O/CHCl_3$	TEA (1)	BTEAC (4)	3	60	–	41	59
5	$H_2O/CHCl_3$	TEA (1)	Pyridine-HCl (4)	3	60	12	32	56
6	$H_2O/CHCl_3$	TEA (2)	BTEAC (4)	1	60	–	68	32
7	$H_2O/CHCl_3$	TEDA (2)	BTEAC (4)	1	60	6	6	88
8	$H_2O/CHCl_3$	DMAP (2)	BTEAC (4)	1	60	12	–	88
9	$H_2O/CHCl_3$	DMAP (1)	BTEAC (0.5)	0.5	60	8	3	89
10	$H_2O/CHCl_3$	DMAP (0.5)	BTEAC (0.5)	0.25	60	8	3	89
11	H_2O/CH_2Cl_2	DMAP (0.5)	BTEAC (0.5)	0.5	40	0	6	94
12	H_2O/CH_2Cl_2	DMAP (0.5)	BTEAC (0.5)	2	40	0	0	100

[a] Based on ^{31}P NMR spectroscopy. [b] Experiments 1−11 and experiment 12 were performed in 0.003 and 0.3 M scale, respectively.

was realized that the production of sulfotep could be prevented under such conditions (Table 2, experiment 11) under which the reaction temperature was stabilized by the reflux condition of CH_2Cl_2 (40 °C). Use of a more appropriate industrial solvent such as ethylene dichloride (CH_2ClCH_2Cl) did not afford this opportunity.

Thus, the optimized conditions used in experiment 11 were applied to the bench scale (0.3 M scale) production of chlorpyrifos, where in 2 h complete conversion of DECTP was observed without any formation of sulfotep (Table 2, experiment 12).

The mixing and DECTP addition rates were optimized in bench scale so that the temperature was stabilized at 30 °C and the mixture became homogeneous. The surface area separating the two phases should be large enough to provide the best mixing with a suitable stirrer. In 0.003 M scale, the reaction, performed in a three-necked 25-mL flask equipped with a magnetic stirrer, lasted 30 min. However, on 0.3 M scale, in a 1000-mL reactor equipped with a mechanical stirrer, the complete conversion required 2 h, after which the mixture became completely clear as a sign of the end of reaction. The reactor used in bench scale (0.3 M scale) had 10 cm as the internal diameter and 20 cm as height. Consequently, it seems that a suitable proportional ratio of internal diameter to height of the reactor should be at least 0.5. The mixing rate and the shape of the mechanical stirrer (one or a multiple set of four-blade turbines, etc.) determine the time of the reaction and control the formation of the byproducts. We used a mechanical stirrer with one four-blade turbine and a rate of 1500 rpm. Using other mechanical stirrers with more efficient shapes can afford the same results in lesser time.

Retention times of chlorpyrifos and 2,3,5,6-tetrachloropyridine (used as the internal standard) determined by HPLC in the conditions stated in Experimental Section are respectively 4.49 and 3.38 min.

The ^1H, ^{13}C, and ^{31}P NMR spectra have demonstrated the absence of other organic impurities and of sulfotep as the main byproduct (Figure 1).

The fine structure of the peaks in different regions in the ^1H and ^{31}P NMR have permitted us to determine the coupling

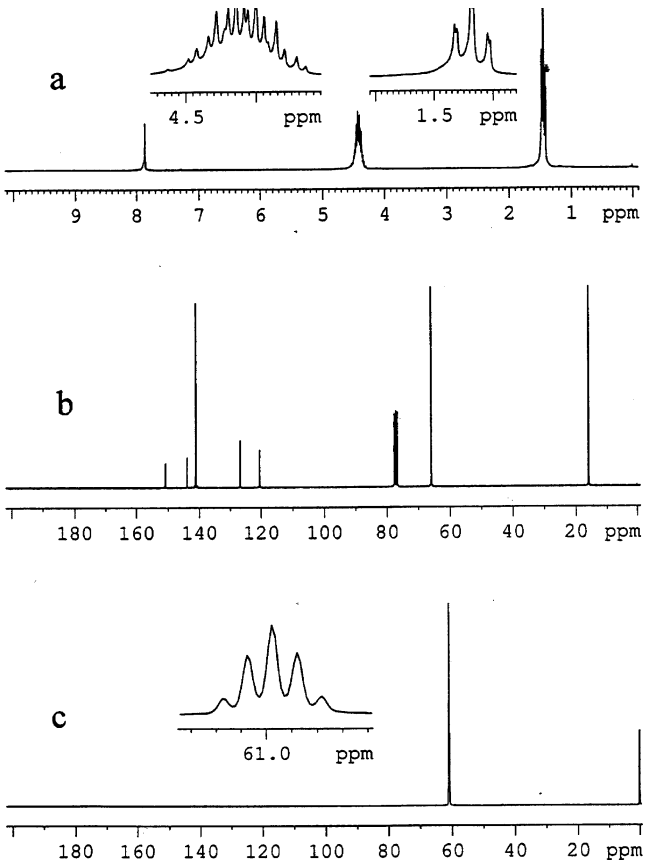
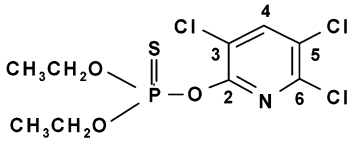


Figure 1. **^1H (a), {^1H}^{13}C (b), and ^{31}P (c) NMR spectra of chlorpyrifos sample (in $CDCl_3$).**

constants between different protons and phosphorus atoms (see Experimental Section).

The ^{13}C NMR characteristics of chlorpyrifos are outlined in Table 3 and Figure 2. It was found that $^3J_{CH3-P}$ was greater than $^2J_{CH2-P}$: 8 vs 5 Hz. CH_3 and CH_2 carbons further couple to adjacent protons. The same feature was observed concerning the coupling constants $^3J_{C3-P}$ and $^2J_{C2-P}$. The aromatic carbons C2, C3, C5, and C6 couple both with phosphorus and C4−H hydrogen, giving rise to dd peaks (Figure 2). C4 carbon resonance appears at 141.1 ppm as does a dd. The greater $^3J_{C2-H}$ and $^3J_{C6-H}$ values relative to those of $^2J_{C3-H}$

Table 3. **^{13}C NMR characteristics of chlorpyrifos (in $CDCl_3$)**



^{13}C NMR characteristics	CH_3	CH_2	C_2	C_3	C_4	C_5	C_6
δ (ppm)	15.8	65.8	150.8	120.4	141.1	126.7	143.9
J_{C-H} (Hz)	127, 2.5	149, 4.5	9	4	173	3	9
J_{C-P} (Hz)	8	5	6	7	~0.5	~0.5	~0.5

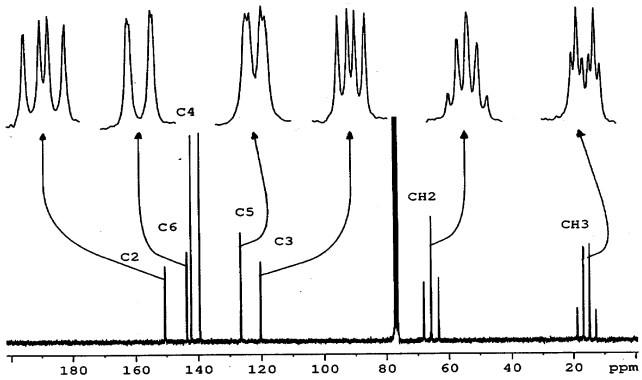


Figure 2. **^{13}C NMR spectra of chlorpyrifos sample (in $CDCl_3$) and the multiplicity of the different peaks.**

and $^2J_{C5-H}$ conform to the C−H coupling constants in aromatic compounds.[21]

Summary

In summary, both yield and purity of chlorpyrifos produced by the reaction of DECTP with NaTCP using a phase-transfer-catalyzed system are influenced by different factors such as the catalysts, temperature, and stirring of the reaction mixture. The tertiary amine catalyst should act as a protecting agent to prevent the DECTP hydrolysis (and sulfotep formation) and, at the same time, act as a suitable leaving group to permit the reaction of DECTP with NATCP to occur. TEA was a good protecting agent but an undesirable leaving group. Therefore, despite a very slow reaction in the presence of TEA, sulfotep was not formed, except in the presence of pyridinium chloride that catalyzed its formation. On the other hand, both DMAP and TEDA were suitable as temporary protecting agents and better leaving groups facing NaTCP. Therefore, in the presence of DMAP or TEDA, the reaction time must be at minimum to prevent DECTP hydrolysis. This was accomplished by choosing a suitable reactor and stirring time.

The 0.5 mol % of DMAP and BTEAC were enough for the reasonable conversion rate with the minimum formation of sulfotep in 60 °C (using $CHCl_3/H_2O$ as solvent system). Performing the reaction under optimized conditions concerning the phase transfer catalyst and tertiary amine at 40 °C (using CH_2Cl_2/H_2O as solvent system) eliminated the formation of sulfotep and caused the formation of chlorpyrifos on bench scale (0.3 M scale) after 2 h with 92% yield and 98.5% purity.

Experimental Section

General Procedures. NMR spectra were recorded on a Bruker DPX-250 instrument (250 MHz for ^{1}H, 62.5 MHz for ^{13}C and 100 MHz for ^{31}P), and CDCl3 was used as solvent; chemical shifts were reported in δ (ppm) from TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P) with downfield shifts positive. Electronic ionization GC−MS spectra were recorded on a Varian (SATURN 4D) spectrometer with capillary column (DB-5MS, 0.1 μ, 30 m × 0.250 mm). Only *m*/*z* values having intensities of more than 20% were given, and retention time was reported using temperature programming (100−250 °C, 10 °C/min) with He flow rate of 10 mL/min. IR spectra were recorded on a Perkin-Elmer 783 instrument using KBr pellet. Melting point was obtained on a Mettler FP61 apparatus. HPLC analysis was performed using a Cecil 1100 instrument.

Preparation of *O,O*-Diethyl-*O*-3,5,6-trichloro-2-pyridylphosphorothioate (Chlorpyrifos). Into a 1000-mL, three-necked, double-glass-walled reactor (with water at desired temperature circulating between the walls), equipped with a mechanical stirrer (made up of one four-blade turbine), a condenser, a dropping funnel, and a thermometer, was placed 73.2 g (0.33 mol) of NaTCP. Then, two solutions of 3.48 g (0.057 mol) of boric acid, 1.59 g (0.027 mol) of NaCl, 1.89 g (0.048 mol) of NaOH, and 0.342 g (1.5 mmol) of BTEAC in 375 mL of water—the pH of this solution was 9.9 at 25 °C—and 0.183 g (1.5 mmol) of DMAP in 150 mL of CH_2Cl_2 were placed into the reactor. The temperature of the reaction mixture was stabilized at 30 °C using a water circulator, while stirring at 1500 rpm, and a solution of 56.1 g (0.3 mol, 46.8 mL) of DECTP in 105 mL of CH_2Cl_2 was added dropwise during 15 min. The reaction mixture was maintained at 40 °C, and the vigorous stirring continued. The reaction mixture turned to a milky viscous suspension within 30 min. The stirring was continued for a further 1.5 h, until the mixture became completely clear. The organic and aqueous layers (pH = 9.2 at 25 °C) were separated. The unreacted NaTCP was recovered from the aqueous layer by filtration. The organic layer was washed with water (2 × 50 mL) and dried by 30 g of $CaCl_2$. After vacuum stripping, the product was found to consist of 94 g containing 98.5% chlorpyrifos with 0.015% acidity (FAO specifications for technical chlorpyrifos concerning purity and acidity are respectively 94% and 0.1%).[16] The overall yield based on the amount of DECTP used was calculated to be 92%. ^{1}H NMR ($CDCl_3$): 1.43 (t, J_{H-H} = 7.5 Hz, J_{H-P} = 2 Hz, 3H, CH_3), 4.41 (m, J_{H-H} = 7.5 Hz, J_{H-P} = 10 Hz, 2H, CH_2), 7.86 (s, 1H, C_5HCl_4) ppm (in agreement with lit.[17]). ^{13}C NMR ($CDCl_3$): 15.8, 65.8, 120.4, 126.7, 141.1, 143.9, 150.8 ppm, ^{31}P NMR ($CDCl_3$): 60.98 (m, J = 10 Hz) ppm (lit.[18] 61.53 ppm). Mp = 43.5−44.5 °C (lit.[19,20] 42−43.5 °C). GC−MS: retention time = 13 min; *m*/*z* (intensity (%)): 47 (39),

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65 (31), 97 (92), 98 (26), 107 (22), 109 (22), 197 (59), 199 (56), 208 (26), 210 (25), 258 (71), 260 (48), 286 (40), 288 (35), 314 (100), 316 (71), 350 (27), 352 (27). IR (KBr pellet): 644 (m), 669 (m), 710 (m), 739 (m), 840 (vs), 959 (vs), 1016 (vs), 1053 (s), 1082 (s), 1160 (s), 1233 (m), 1263 (m), 1328 (m), 1402 (vs), 1538 (m), 2910 (w), 2970 (w), 3025 (w) cm^{-1}.

HPLC Analysis of Chlorpyrifos Sample. The sample was dissolved in acetonitrile solution containing 2,3,5,6-tetrachloropyridine (mp = 90−91 °C) as internal standard. The chlorpyrifos content was determined by a HPLC instrument equipped with a pumping system able to maintain a pressure of 11 Mpa, a UV spectrophotometer detector (with 1.0 AUFS sensitivity), and a reverse-phase column (C-18, 250 mm × 4.6 mm). A mixture of acetonitrile (82 mL), water (17.5 mL), and acetic acid (0.5 mL) was used as the mobile phase with the flow rate of 2 mL/min at 30 °C. All solvents were HPLC grade, and chlorpyrifos of known purity was used as standard. The UV absorbance was measured at 300 nm.

The internal standard solution was made by dissolving 150 mg of 2,3,5,6-tetrachloropyridine in acetonitrile and diluting to 250 mL using a volumetric flask. The calibration solution was prepared by weighing 80 mg of chlorpyrifos standard into a 50-mL glass-stoppered conical flask and mixing with 25 mL of internal standard solution. The sample solution was prepared as the calibration solution using 80 mg of the chlorpyrifos sample, the purity of which was to be determined.

A 10-μL amount of each calibration and sample solution with sufficient interval time was injected, and the peak area of chlorpyrifos with that of internal standard (R) was compared. Then, using the following formula, the purity of the chlorpyrifos sample was determined.

$$\text{chlorpyrifos content (g/kg)} = (R_2 \times m_1 \times P)/(R_1 \times m_2)$$

R_1 = ratio of chlorpyrifos peak area to internal standard peak area for calibration solution

R_2 = ratio of chlorpyrifos peak area to internal standard peak area for sample solution

m_1 = mass of chlorpyrifos standard in the calibration solution

m_2 = mass of chlorpyrifos sample in the sample solution

P = purity of chlorpyrifos standard (g/kg)

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