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A validated and fast procedure for FTIR determination of Cypermethrin and Chlorpyrifos

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Abstract

A FTIR methodology has been developed for the simultaneous determination of Cypermethrin and Chlorpyrifos in pesticide commercially available formulations. The method involves the extraction of both active principles with $CHCl_3$ and direct measurement of the peak area values between 1747 and 1737 cm^{-1} corrected with a baseline defined at 2000 cm^{-1} for Cypermethrin and peak height values established at 1549 cm^{-1} corrected using a baseline situated at 1650 cm^{-1} for Chlorpyrifos.

The limits of detection achieved were of the order of 0.7 and 0.4% (w/w), and the relative standard deviation 0.4 and 0.2% for Cypermethrin and Chlorpyrifos, respectively. The developed procedure provided statistically comparable results with those obtained by HPLC, for a series of commercial samples, which validated the FTIR method. The procedure developed reduces organic solvent consumption, per sample preparation, from 51 ml CH_3CN required for HPLC to 2.5 ml $CHCl_3$, and reduces waste generation also increasing the sample measurement frequency, from 3 to 30 samples/h, as compared with the HPLC–UV reference method.

Keywords: Cypermethrin; Chlorpyrifos; Pesticide formulations; FTIR

1. Introduction

Cypermethrin, (*R*,*S*)-alpha-cyano-3-phenoxybenzyl(1*RS*)-*cis*,*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate, is a synthetic pyrethroid insecticide used to control many pests, including moth pests of cotton, fruit and vegetable crops. It is also used for crack, crevice and spot treatment to control insect pests in stores, industrial buildings, laboratories and on ships, buses and aircraft. It may be also used in non-food areas in schools, nursing homes, hospitals, restaurants, in food processing plants and as a barrier treatment insect repellent for horses. This pesticide is light stable and it is available as an emulsifiable concentrate or wettable powder (WP) [1].

Cypermethrin is an alpha-cyano (type II pyrethroids) that causes neurotoxicity in mammals and insects. It is a moderately toxic material by dermal absorption or ingestion [2,3]. EPA reports an oral LD_{50} of 150–500 mg/kg in rats [3].

Chlorpyrifos, *O*,*O*-diethyl-*O*-3,5,6-trichloro-2-pyridyl phosphorothioate, is a broad-spectrum organophosphate insecticide. Chlorpyrifos is effective in controlling cutworms, cockroaches, flea beetles, flies, termites and lice. It is used as an insecticide on grain, cotton, field, fruit, nut and vegetable crops and well as on lawns and ornamental plants. It is also registered for direct use on sheep and turkeys, for horse site treatment, domestic dwellings, farm buildings, storage bins and commercial establishments. This product is available as granules, wettable powder, dustable powder and emulsifiable concentrate [1].

Chlorpyrifos is moderately toxic. The oral LD_{50} for chlorpyrifos in rats is 95–270 mg/kg, 60 mg/kg in mice and 1000 mg/kg in rabbits [4].

Chlorpyrifos has a half-life between 16 and 72 days, depending on the pH of the solution. Direct photo transformation was observed in buffer solutions and river waters, under both natural and artificial lighting conditions [5].

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The use of agrochemical formulations with more than one active principle is a common practice in order to improve their crop protective action. The determination of several active principles in a same formulation requires, in many cases, the use of different analytical techniques, thus involving long and tedious procedures. The Collaborative International Pesticide Analytical Council (CIPAC) recommends the use of high performance liquid chromatography with UV detection (HPLC-UV) or gas chromatography with flame ionization detection (GC-FID) for the determination of Cypermethrin [6] and the use of high performance liquid chromatography with UV detection for the determination of Chlorpyrifos [7].

In recent years, it has been published a series of procedures based on gas chromatography with mass spectrometry detection (GC-MS) for the simultaneous determination of Cypermethrin and Chlorpyrifos in different matrices, such as fruits and vegetables [8], food [9], soil [10], plants [11] or water [12]. All these methods are very convenient for determination of residues at trace levels, but not well justified for the analysis of formulations.

Gas chromatography with electron capture detection (GC-ECD) or nitrogen–phosphorous detection (GC-NPD) [13], high performance liquid chromatography with mass spectrometry (HPLC-MS) [14] or fluorescence detection (HPLC-FLD) [15], thin layer chromatography (TLC) [16] and micellar electrokinetic chromatography (MEKC) [17] have been also proposed for the determination of Cypermethrin and Chlorpyrifos.

The concentration range in which Cypermethrin and Chlorpyrifos are individually present in commercial formulations varies between 0.33–20% (w/w) and 1.5–75% (w/w), respectively [18]. On the other hand, when both pesticides are co-formulated, the concentration of Cypermethrin and Chlorpyrifos is between 2.0 and 4.5% (w/w) and from 36 to 45.5% (w/w), respectively [18].

FTIR spectrometry has been employed for the determination of different active principles in commercially available pesticide formulations such as Buprofezin [19], Fluometuron [20] and Folpet and Metalaxyl [21] showing the high suitability of FTIR to carry out this kind of analysis.

The single FTIR precedents concerning the determination of the aforementioned pesticides in formulations correspond to the work of Almond et al. [22], who determined Chlorpyrifos by ATR-FTIR on using multivariate spectroscopy on samples dissolved in Solvesso and that of Sharma et al. [23], who determined Cypermethrin in emulsifiable concentrated formulations after thin layer chromatography separation and dissolution of the compound in $CHCl_3$ measuring the absorbance at 1749 cm^{-1} with a baseline established between 1770 and 1720 cm^{-1}.

The evaluation of the experimental conditions for FTIR determination of Chlorpyrifos and Cypermethrin in pesticide formulations has been the main objective of the present work.

2. Experimental

2.1. Apparatus and reagents

A Magna 750 FTIR spectrometer (Nicolet, Madison, WI, USA.), equipped with a temperature-stabilized DGTS detector, a long-lasting Ever-Glo source and a KBr beamsplitter, was employed for spectral measurements, using a microflow cell (Specac, Orpington, UK) with ZnSe and BaF_2 windows and 0.10 mm pathlength. The equipment employs the 2.1 version of the OMNIC software developed by Nicolet Corporation, for the acquisition and processing of the FTIR absorbance data.

It has been employed a Gilson Minipuls 2 peristaltic pump (Villiers-le-Bel, France) equipped with solvent resistant viton tubes of 3 mm o.d. and 1 mm i.d. for the introduction of samples and standards in the flow cell.

A Hewlett-Packard HPLC Series 1050 High Performance Liquid Chromatograph (Palo Alto, CA, USA), equipped with a Kromasil column (C-18, 250 mm × 4.6 mm i.d. and 5 μm particle diameter), and a variable wavelength UV–vis detector was employed for the analysis of pesticide formulations.

Chlorpyrifos PESTANAL® reagent grade standard was obtained from Fluka (Buchs, Switzerland). Cypermethrin technical standard was supplied by Afrasa, S.A. (Valencia, Spain). Extra pure chloroform stabilized with 150 ppm of amylene and HPLC grade acetonitrile were supplied by Scharlau (Barcelona, Spain) and were employed for the preparation of samples and standards, using also Mili-Q grade water for the mobile phase.

Emulsifiable concentrates (EC) and wettable powder formulations containing Cypermethrin or/and Chlorpyrifos were obtained directly from the Spanish market. Sample 1 (EC) contains a nominal concentration of 10.0% (w/w) Cypermethrin. Samples 2 (EC) and 3 (EC) contain 46.0 and 50.0% (w/w) Chlorpyrifos, respectively. Sample 4 (WP) contains 2.1% (w/w) Cypermethrin and 37.0% (w/w) Chlorpyrifos and sample 5 (WP) contains 4.3% (w/w) Cypermethrin and 45.0% (w/w) Chlorpyrifos.

2.2. Reference procedure

Ten milligrams of sample were accurately weighted, inside a 25 ml volumetric flask and diluted to the volume with CH_3CN. One milliliters of the solution was diluted to 10 ml and filtered through a 0.22 μm nylon filter. Twenty microliters of this latter solution were directly injected in a 80:20 acetonitrile:water mobile phase using 1 ml min^{-1} carrier flow. Both pesticides were determined in the isocratic mode by absorbance measurements at 278 nm. For quantification, it was used area values of the chromatographic peaks obtained for Chlorpyrifos at a retention time of 11.9 min. In the case of Cypermethrin, the sum of the areas of the peaks found at 16.8, 17.2 and 17.6 min for the pesticide isomers were employed. Data found for samples were interpolated in external calibration lines established from the measurement of six standard

solutions of 4.32–43.2 μg g^{-1} Chlorpyrifos and from 4.64 to 46.4 μg g^{-1} Cypermethrin.

2.3. FTIR procedure

Twenty-five milligrams of sample were accurately weighted and diluted with 4 g of $CHCl_3$. The sample slurry were passed through a 0.22 μm nylon filter and then introduced in the FTIR measurement cell by using a peristaltic pump. The spectra were obtained in the stopped flow mode, at 4 cm^{-1} nominal resolution and accumulating 25 scans per spectrum, in the range from 4000 to 850 cm^{-1} and using a background of the cell filled with the solvent.

The concentrations of Cypermethrin and Chlorpyrifos in commercial formulations were calculated by interpolating absorbance values measured in the sample spectra in external calibration lines.

Two individual sets of Cypermethrin (five standards from 0.64 to 1.87 mg g^{-1}) and Chlorpyrifos (five standards from 1.61 to 4.70 mg g^{-1}) external standard solutions in $CHCl_3$ were prepared and their FTIR spectra were obtained in the same conditions as samples. A calibration line was established for Cypermethrin by measuring peak area values between 1747 and 1737 cm^{-1}, corrected using a baseline defined at 2000 cm^{-1}. For Chlorpyrifos determination, measurements of the peak height at 1549 cm^{-1}, corrected using a baseline established at 1650 cm^{-1}, were employed.

3. Results and discussion

3.1. FTIR spectra of Cypermethrin and Chlorpyrifos

Fig. 1 shows the absorbance FTIR spectra in the wavenumber region from 2000 to 900 cm^{-1} of pure standard solutions in $CHCl_3$ of Cypermethrin and Chlorpyrifos and different sample extracts in chloroform. As can be seen in this figure, the Cypermethrin spectrum has absorption bands at 1742, 1587,1488, 1449 and 1076 cm^{-1}, due to carbonyl stretching, C=C stretching in chloroalkenes, ring vibration of benzene, CH_2 deformation in R–CH_2–CN structure and (C=O)–O– stretching, respectively.

The absorption bands of Chlorpyrifos are located at 1549, 1412, 1339, 1165, 1088, 1025 and 968 cm^{-1}, due to C=N stretching, pyridine stretching, ring vibration, ring breathing, Cl–C stretching, trigonal ring breathing and P=S stretching [24], respectively.

Sample spectra provide the characteristic bands of the active principles additionally than some small bands coming from inert and solvent components of the pesticide formulations.

3.2. Measurement conditions

The effects of the number of accumulated scans and the nominal resolution employed for data acquisition were evaluated in order to improve the measurement conditions. The number of accumulated scans was modified from 5 to 50, and the nominal resolution varied from 2 to 16 cm^{-1}.

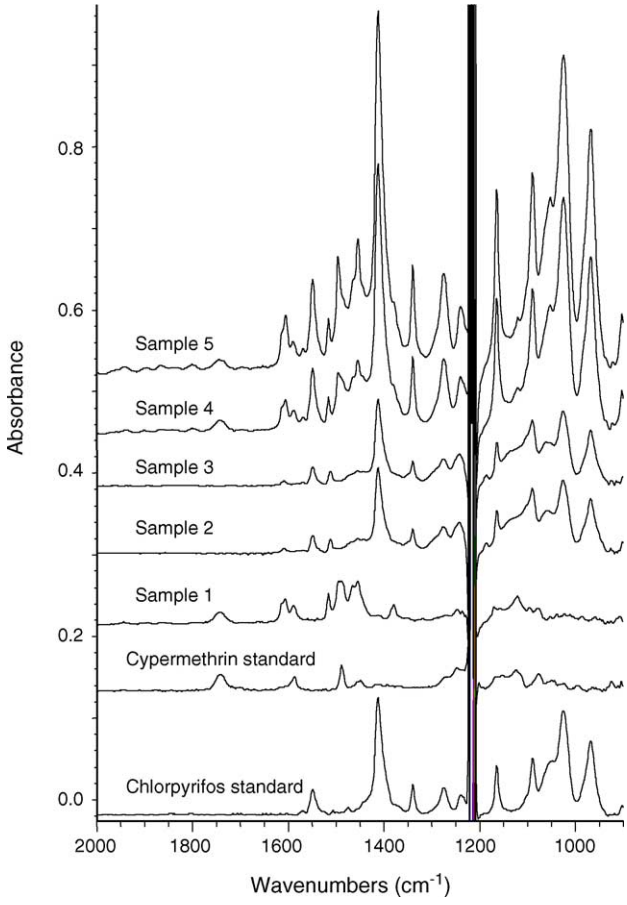

Fig. 1. FTIR spectra of $CHCl_3$ solutions of Cypermethrin, Chlorpyrifos and five commercial pesticide formulations containing these compounds. Spectra are the average of 25 accumulated scans using a nominal resolution of 4 cm^{-1}. Concentrations of standards correspond to 6.73 mg g^{-1} Cypermethrin and 5.36 mg g^{-1} Chlorpyrifos. Thirty-three milligrams of sample 1, 29 mg of sample 2, 24 mg of sample 3, 170 mg of sample 4 and 120 mg of sample 5 were diluted with 4 g $CHCl_3$ to obtain these spectra.

As can be seen in Fig. 2, the highest signal to noise ratio, established as the ratio between the spectral area calculated between 1747 and 1737 cm^{-1} corrected with a single point baseline established in 2000 cm^{-1}, for a 1.21 mg g^{-1} Chlorpyrifos standard and the noise measured in the same region for a blank spectrum and expressed as root mean square (RMS) was found for a 2 cm^{-1} nominal resolution and accumulating 50 scans per spectra. However, in order to ensure a compromise between measurement frequency and sensitivity, 25 accumulated scans and a nominal resolution of 4 cm^{-1} were selected with a relative loss of sensitivity of 7% as compared with the best signal, but reducing the measurement time from 109 to 30 s.

3.3. Band selection

In order to choose the best analytical performance of the FTIR determination of Cypermethrin and Chlorpyrifos in for-

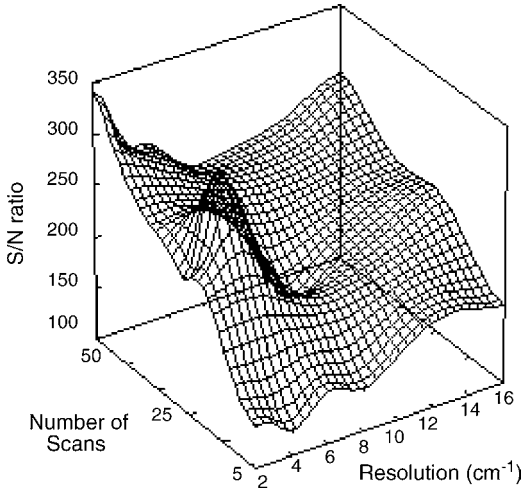

Fig. 2. Effect of the nominal resolution and number of accumulated scans on signal to noise ratio of a Chlorpyrifos standard of 1.21 mg g^{-1}.

mulated samples, different bands and baseline criteria were evaluated, as can be seen in Table 1. In every case, it was also considered the use of both, peak height and peak area, absorbance measurements.

In terms of sensitivity, it is clear that peak area measurements provide one order of magnitude better sensitivity than peak height values, but in general, all the studied conditions provide appropriate characteristics for pesticide formulations analysis. Peak area measurements between 1747 and 1737 cm^{-1} were selected for the determination of Cypermethrin because for these conditions, no overlapping effects were found in all samples analysed. On the other hand, the peak height at 1549 cm^{-1} was selected for Chlorpyrifos determination because in these conditions there is no overlapping with any Cypermethrin band.

Data in Table 1 also reports the limit of detection (LOD) values found on using different bands. LOD's were established, as recommended by the IUPAC as the pesticide concentration, which provides an absorbance value equal to three times the standard deviation of 10 blank solutions (99.6% confidence level). The aforementioned values divided by the slope of the calibration line and multiplied by the sample dilution factor used in the recommended procedure provided the limit of detection in the actual samples in terms of %, w/w.

3.4. Study of interferences

From sample spectra reported in Fig. 1, it can be seen that the main bands correspond to those of Cypermethrin and Chlorpyrifos being absent the characteristic bands of the typical excipients employed in these formulations like calcium carbonate, surfactants, cyclohexanone and other solvents. So, the mutual overlapping of bands of the considered pesticides could be the main source of interferences. It was carried out a series of mutual interference studies to verify the possibilities of the simultaneous determination of Cypermethrin and Chlorpyrifos in a same sample.

It was studied the effect on the absorbance measurements at 1548 cm^{-1} of increasing Cypermethrin concentrations, from 0 to 19.88 mg g^{-1}, for a fixed concentration of 2.39 mg g^{-1} Chlorpyrifos. On the other hand, it was evaluated the interference of increasing Chlorpyrifos concentrations, from 0 to 20.00 mg g^{-1}, for a fixed concentration of 1.47 mg g^{-1} Cypermethrin. In both cases, it can be concluded that in the selected conditions, the simultaneous determination of Cypermethrin and Chlorpyrifos could be done without interferences. The methodology developed is extremely valuable for the simultaneous determination of the two considered

Table 1
Analytical features of the FTIR determination of Cypermethrin and Chlorpyrifos using different bands and baseline criteria

Measurement mode	Wavelength (cm^{-1})	Baseline correction	$a \pm s_a$	$b \pm s_b$	r^2	R.S.D. (%)	L.O.D. (% w/w)	L.O.Q. (% w/w)
Cypermethrin calibration curve ($y = a + b\,C$ (mg g^{-1}))								
Height	1742	2000	0.0002 ± 0.0001	0.00953 ± 0.00004	0.9993	0.3	0.6	2
Area	1747–1737	2000	0.0017 ± 0.0008	0.1007 ± 0.0008	0.9998	0.4	0.7	2.3
Height	1587	1650	0.00031 ± 0.00009	0.00926 ± 0.00003	0.9999	0.9	0.3	1
Area	1592–1982	1650	0.002 ± 0.001	0.082 ± 0.001	0.9997	0.8	0.5	1.7
Height	1488	1530	0.0003 ± 0.0002	0.01514 ± 0.00005	0.9998	1.0	0.3	1
Area	1493–1483	1530	0.000 ± 0.002	0.147 ± 0.002	0.9995	1.1	0.6	2
Height	1076	1097–1061	0.0003 ± 0.0002	0.00558 ± 0.00008	0.997	1.2	1.4	4.7
Area	1081–1071	1097–1061	0.000 ± 0.002	0.070 ± 0.002	0.998	0.9	1.0	3.3
Chlorpyrifos calibration curve ($y = a + b\,C$ (mg g^{-1}))								
Area	1554–1544	1650	0.002 ± 0.001	0.0527 ± 0.0004	0.9993	0.10	0.2	0.67
Height	1549	1650	0.0009 ± 0.0002	0.00639 ± 0.00007	0.9993	0.2	0.4	1.3
Height	1549	1650–1527	0.0004 ± 0.0002	0.00600 ± 0.00004	0.9992	0.2	0.5	1.7
Height	1412	2000	0.0006 ± 0.0004	0.0290 ± 0.0001	0.9996	0.3	0.2	0.67
Area	1417–1407	2000	0.009 ± 0.005	0.270 ± 0.002	0.9995	0.4	0.9	3
Height	968	2000	0.0008 ± 0.0003	0.01839 ± 0.00009	0.9996	0.4	0.9	3
Area	973–963	2000	0.007 ± 0.004	0.207 ± 0.002	0.9994	0.6	0.8	2.7

Note: The linear range was in all the cases from 0.64 to 1.87 mg g^{-1} Cypermethrin and from 1.61 to 4.70 mg g^{-1} Chlorpyrifos, being employed five standard solutions measured three times each one to make the calibration.

Table 2
Determination of Cypermethrin and Chlorpyrifos in pesticide formulations by HPLC-UV and FTIR procedures

Sample	Active substance	HPLC-UV[a]	FTIR[a]	Relative accuracy error (%)[b]	t_{exp}
1	Cypermethrin	12.1 ± 0.1	12.2 ± 0.1	0.82	1.58
2	Chlorpyrifos	46.2 ± 0.2	46.4 ± 0.8	0.4	0.54
3	Chlorpyrifos	50.2 ± 0.1	50.3 ± 0.5	0.20	0.44
4	Chlorpyrifos	37.2 ± 0.5	37.6 ± 0.8[a]	1.08	0.95
	Cypermethrin	2.10 ± 0.05	2.08 ± 0.07	−0.9	0.52
5	Chlorpyrifos	45.3 ± 0.3	45.1 ± 0.2[a]	−0.44	1.24
	Cypermethrin	4.35 ± 0.04	4.32 ± 0.05	−0.69	1.05

t_{tab} = 1.812 with a probability level of 95% and 10 freedom degree.
[a] Concentration values (%, w/w) are the average of three independent duplicate analyses ± standard deviation.
[b] %Error calculated as 100 × ([FTIR] − [HPLC])/[HPLC], where [FTIR] and [HPLC] are the concentrations found using the FTIR procedure and the HPLC-UV one, respectively.

pesticides in a same sample containing a big range of relative concentrations.

4. Determination of Cypermethrin and Chlorpyrifos in pesticide formulations

To validate the proposed FTIR procedure, one sample containing Cypermethrin, two samples with Chlorpyrifos and two samples with the two aforementioned active principles were analysed by both, the FTIR developed procedure and the HPLC reference method, and results found are indicated in Table 2.

The accuracy errors obtained from the difference between results found by FTIR and HPLC range from −0.9 to 0.82% in the case of Cypermethrin and from −0.44 to 1.08% for Chlorpyrifos.

On the other hand, the regression between all the data found for samples assayed provided regression equation of $C_{FTIR} = (-0.014 \pm 0.016) + (1.002 \pm 0.002)C_{HPLC}$ with $r^2 = 0.9997$ for Cypermethrin and $C_{FTIR} = (0.0 \pm 0.9) + (1.00 \pm 0.02)C_{HPLC}$ with $r^2 = 0.996$ for Chlorpyrifos. Statistically, the aforementioned regression lines present slope and intercept values comparable with 1 and 0, respectively, which evidence that, as compared with the reference method, the developed FTIR procedure does not need any blank correction and does not present constant relative errors.

On the other hand, the statistical comparison of paired results (summarized in Table 2) provides t_{exp} values that are, in all the cases, lower than 1.82, the theoretical t value for a confidence level of 95%.

5. Conclusions

The FTIR procedure developed in this work provides statistically comparable results, for a probability level of 95%, with those obtained by the HPLC reference method.

In spite of the fact that HPLC provides a LOD of 0.24 and 0.16 mg l^{-1} for Cypermethrin and Chlorpyrifos, respectively, which are three orders of magnitude lower than those found by FTIR, it can be concluded that both techniques are appropriate for the concentration of pesticides in commercial formulations.

The reagent consume and waste generation were minimized, and then the FTIR procedure used only 2.5 ml of chloroform instead of 51 ml acetonitrile per sample required in the HPLC–UV method.

The sample analysis frequency was increased from 3 to 30 samples/h, by reducing the sample pre-treatment, being unnecessary any clean-up previous step to the FTIR measurement of the sample extracts.

So, it can be concluded that the FTIR procedure developed is a simple, fast and accurate alternative for the quality control analysis of pesticide formulations containing Cypermethrin and Chlorpyrifos, and provides an enhanced methodology as compared with previous studies focussed on FTIR measurement of Cypermethrin after a long and tedious treatment or that based on a multivariate approach for Chlorpyrifos determination.

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