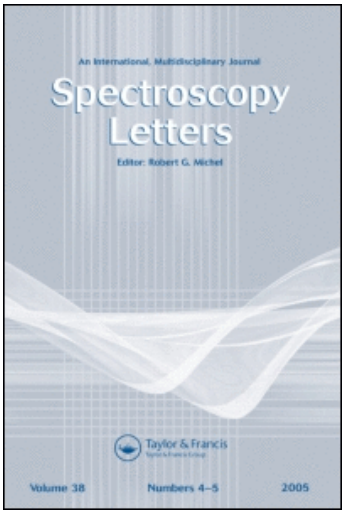

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Vibrational Spectrometry Strategies for Quality Control of Procymidone in Pesticide Formulations

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Vibrational Spectrometry Strategies for Quality Control of Procymidone in Pesticide Formulations

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Abstract: Two vibrational spectrometry–based methodologies were developed for procymidone determination in wettable powdered pesticide formulations. The Fourier-transform infrared (FTIR) procedure was based on the selective extraction of procymidone by chloroform and determination by peak area measurement between 1451 and 1441 cm^{-1}, using a baseline correction established between 1490 and 1410 cm^{-1}, and a precision of 0.4% and a limit of detection of 0.01% w/w procymidone for a sample mass of 25 mg were obtained. For FT-Raman determination, the selected conditions were peak area measurement between 1005 and 995 cm^{-1} Raman shift, with a baseline correction fixed between 1030 and 947 cm^{-1}, and a relative standard deviation of 1% and a limit of detection of 0.8% procymidone in the original sample were obtained. The sample frequency for FTIR determination was 30 hr^{-1}, lower than that for Raman with 40 hr^{-1}. FT-Raman reduces to the minimum the reagent consumption and waste generation, also avoiding the sample handling and contact of the operator with the pesticide. It can be concluded that the proposed methods are appropriate for quality control in commercial pesticide formulations.

Keywords: FTIR, pesticide formulations, powder analysis, procymidone, Raman

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INTRODUCTION

Procymidone, *N*-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide, is a dicarboximide fungicide with moderate generic activity. Although most uses involve foliar application, absorption through roots occurs with translocation to leaves and flowers. Procymidone inhibits spore germination, mycelial growth, and triglyceride synthesis in fungi. It is used in agriculture, horticulture, and viticulture against *Botrytis* sp., *Sclerotinia* sp., *Monilia* sp., *Aslternaria* sp., *Fusarium* sp., and *Rhizoctonia* sp.[1]

The main procymidone formulations commercially available are wettable powder (50% w/w), soluble concentrate (25% and 50% w/v), and water dispersable granules (50% and 75% w/w). In most cases, procymidone is not coformulated with other pesticides.[2]

Procymidone presents a low acute toxicity, its lethal dose (LD_{50}) being higher than 5000 mg/kg in rats and mice.[1]

The recommended method of the Collaborative International Pesticides Analytical Council (CIPAC) for the determination of procymidone in pesticide formulations is based on capillary gas chromatography with flame ionization detection (GC-FID) using dibutyl sebacate as internal standard.[3]

Procymidone has also been determined at trace levels in fruits and vegetables,[4,5] wine,[6] and human urine[7,8] by gas chromatography with tandem mass spectrometry; in vegetables,[9] wine,[10] and water[11] by gas chromatography with electron capture detection; in fruits and vegetables[12,13] by using micellar electrokinetic chromatography; and in synthetic mixtures by high-performance liquid chromatography (HPLC) with diode array detection.[14,15]

The use of vibrational spectrometry for pesticide analysis is a less common practice than the use of chromatography. The applicability of Fourier-transform infrared (FTIR) has been shown for the determination of carbaryl,[16] chlorpyriphos-ethyl,[17] buprofezin,[18] fluometuron,[19] chlorsulfuron,[20] folpet and metalaxyl[21] in pesticide formulations; Fourier-transform Raman spectrometry has been applied to the determination of pesticides in concentrated formulations based on the direct measurement of the Raman scattering of solid samples placed inside modified nuclear magnetic resonance tubes.[22–24] Recently, FT-Raman also has been employed for the direct determination of pesticides from solid[25] or liquid[26] samples or a previous dilution of the formulation with $CHCl_3$,[27] using in all cases standard chromatographic glass vials as a cell.

On the other hand, the development of surface-enhanced Raman scattering (SERS) increased dramatically the sensitivity of Raman measurements and provided new possibilities on the analysis of pesticides.[28,29] However, till now there exist no report on the use of FTIR nor on Raman for the determination of procymidone.

The main objective of this work was the development of fast and environmentally friendly methodologies for the analysis of pesticide formulations

containing procymidone that can be applied for quality control in the manufacturing industry.

EXPERIMENTAL

Apparatus and Reagents

A Nicolet (Madison, WI, USA) Magna 750 FTIR spectrometer, equipped with a temperature-stabilized deuterated tryglycine sulfate (DGTS) detector, was employed for infrared measurements, using a micro-flow cell (Graseby-Specac, Orpington, UK) with ZnSe and CaF_2 windows and a pathlength of 0.10 mm. 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.

A Bruker RFS 100/S (Bremen, Germany) spectrometer equipped with a 2 W maximum power Nd:YAG laser that emits at 1064 nm and a Ge detector cooled with N_2 was employed to obtain Raman spectra of solid samples, using 2 mL and 12 × 32 mm internal diameter standard glass chromatographic vials as sample cells.

An ultrasonic water bath (J.P. Selecta, Barcelona, Spain) was used to improve a fast pesticide extraction.

An Agilent HPLC Series 1100 High Performance Liquid Chromatograph (Madrid, Spain), equipped with a reversed phase C-18 (Kromasil), 250 × 4.6 mm i.d. and 5-μm particle diameter column, and a diode array detector (DAD) was also employed for the analysis of fungicide formulations, this methodology being used as a reference for the validation of FTIR measurements.

Procymidone PESTANAL reagent grade standard (99.1% w/w) was supplied by Fluka (Buchs, Switzerland). Analytical grade chloroform stabilized with ethanol and sodium chloride, reagent grade (99.8% w/w) and supplied by Scharlau (Barcelona, Spain), was employed for the preparation of samples and standards. Procymidone wettable powder commercial formulations with a procymidone concentration of 50% w/w were obtained directly from the Spanish market.

HPLC-DAD Reference Procedure

Sample (40 mg) was accurately weighed inside a 25-mL volumetric flask and diluted to the volume with acetonitrile (CH_3CN), being sonicated during 5 min in an ultrasonic water bath to extract procymidone from the matrix. Extract (0.1 mL) was diluted to 10 mL and filtered through a 0.22-μm polyamide filter. Filtrate (20 μl) was directly injected in a 9 : 1 acetonitrile : water mobile phase of 1 mL min^{-1} flow rate. Procymidone was determined in the

isocratic mode by absorbance measurements at 238 nm and area values of the chromatograms peak obtained at 3.7 min. An external calibration was established with standard solutions of Procymidone in acetonitrile.

FTIR Procedure

Sample (25 mg) were accurately weighed into a glass vial and dissolved with 4 g of $CHCl_3$. The vial was closed with a cap and the mixture was sonicated for 5 min in an ultrasonic water bath. After that, the sample extract was passed through a 0.22-μm nylon syringe filter and then introduced into 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 from 4000 to $900\,cm^{-1}$ using a background of the cell filled with the solvent.

Peak area values between 1451 and $1441\,cm^{-1}$, corrected with a baseline established between 1490 and $1410\,cm^{-1}$, were employed to quantify procymidone in samples using an external calibration line obtained with standard solutions of the pesticide in chloroform in the concentration range between 1.7 and 5.3 mg g^{-1}, measured in the same conditions than samples.

Raman Procedure

An amount approximately of 300 mg of commercial sample were grounded and homogenized for 5 min in an agate mortar. The sample was introduced in a chromatographic glass vial and the Raman spectra recorded between 3500 and $70\,cm^{-1}$, at $4\,cm^{-1}$ resolution and accumulating 25 scans per spectrum. The Ng : YAG laser power was fixed at 750 mW. A Blackman-Harris 4 apodization function, a scan velocity of 1.0 (2.2 kHz), a zero filling factor of 2, and an aperture of 10 mm were also employed for the acquisition of the Raman spectra.

An external calibration curve was established with a solid procymidone standard diluted with sodium chloride at different levels, for 0.25 to 0.73 g g^{-1}. For quantitative purposes, peak area values between 1005 and $995\,cm^{-1}$ corrected with a baseline defined between 1039 and $947\,cm^{-1}$ were used.

RESULTS AND DISCUSSION

FTIR Spectrum of Procymidone

Figure 1 shows the absorbance spectra, in the wavenumber range from 2000 to $1000\,cm^{-1}$, of a procymidone standard chloroformic solution of 4.2 mg g^{-1}

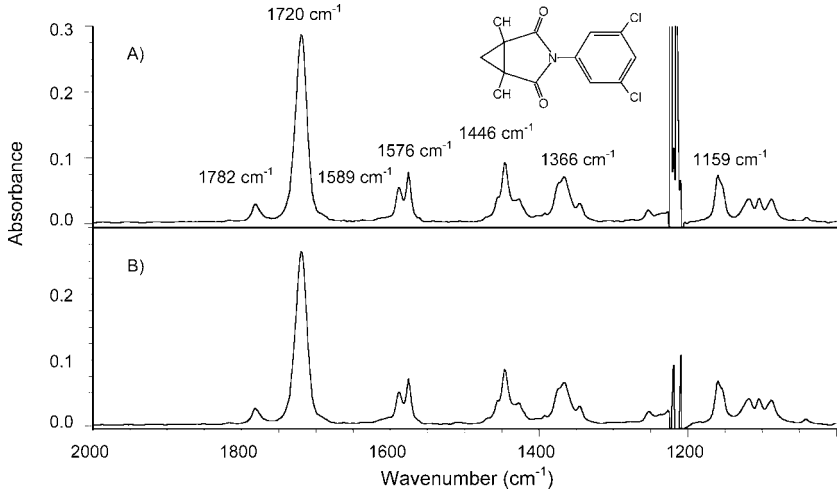

Figure 1. FTIR spectra of a 4.2 mg g^{-1} procymidone in $CHCl_3$ standard (top) and a $CHCl_3$ extract containing a concentration of 3.8 mg g^{-1} of procymidone of a sample (bottom).

and that of a fungicide sample extract with a concentration of procymidone of 3.8 mg g^{-1} both obtained using a background established with the cell filled with $CHCl_3$. As can be seen in this figure, the spectra of both sample and standard present the same bands. The most intense bands were the carbonyl band in cyclic imides (in and out of phase) at 1720 and 1782 cm^{-1} and the pseudosymmetric N–C═O stretching at 1446 cm^{-1}. Other absorption bands located at 1576 and 1589 cm^{-1}, due to C═C stretching bands in chloroalkenes, at 1366 and 1159 cm^{-1} corresponding to the benzene ring stretching and breathing, respectively, can be also identified in this spectra[30] and all those seem appropriate for procymidone determination in pesticide formulations

Effect of FTIR Measurement Conditions on Procymidone Determination

The effect 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}.

As can be seen in Fig. 2A, the higher signal to noise ratio was found for a 4 cm^{-1} nominal resolution, these values also corresponding to the best repeatability. On the other hand, in Fig. 2B it can be seen that the most intense and precise results were those obtained when accumulating

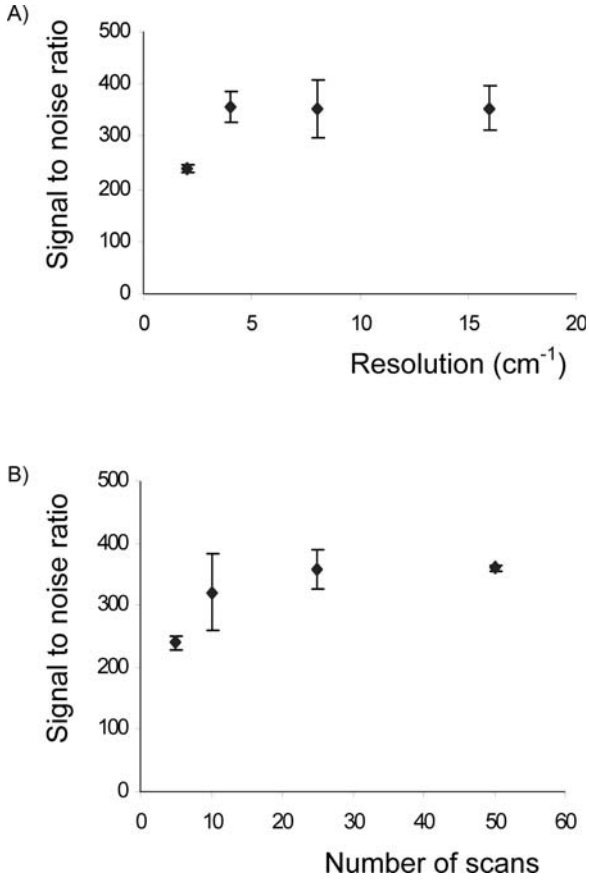

Figure 2. (A) Effect of the nominal resolution on signal to noise ratio of a procymidone standard of 3.31 mg g^{-1} obtained accumulating 25 scans for spectrum. (B) Effect of the number of accumulated scans on the signal to noise ratio. Data were obtained using a nominal resolution of 4 cm^{-1}. The signals were established for a procymidone standard of 3.31 mg g^{-1}.

50 scans, but in order to ensure a compromise between measurement frequency and precision values, 25 accumulated scans was selected.

Selection of FTIR Bands for Procymidone Determination

In order to select the best measurement conditions for FTIR procymidone determination, several bands, base-line criteria, and measurement mode (peak height and peak area values) were assayed and evaluated in terms of sensitivity, repeatability, and limit of detection. Table 1 shows the main

Table 1. Analytical features of the FTIR determination of procymidone using different bands, baseline criteria, and measurement modes

Measurement mode	Wavenumber (cm^{-1})	Baseline correction	Procymidone calibration curve [$y = a + b\ C$ (mg g^{-1})]				
			$a \pm s_a$	$b \pm s_b$	R^2	% RSD[a]	LOD[b] (% w/w)
Height	1782	1805–1757	0.0002 ± 0.0001	0.00564 ± 0.00004	0.9994	0.17	2.9
Area	1787–1777		-0.0002 ± 0.0008	0.0505 ± 0.0003	0.9996	0.3	1.0
Height	1720	1760–1666	0.0020 ± 0.0009	0.0656 ± 0.0003	0.9997	0.13	0.1
Area	1725–1715		0.014 ± 0.007	0.589 ± 0.002	0.9998	0.06	0.03
Height	1589	1631–1529	0.0000 ± 0.0002	0.01214 ± 0.0006	0.9996	0.4	1.2
Area	1594–1584		-0.001 ± 0.002	0.1070 ± 0.0006	0.9996	0.4	0.5
Height	1576	1631–1529	-0.0002 ± 0.0003	0.01787 ± 0.00008	0.9997	0.07	0.8
Area	1581–1571		-0.002 ± 0.002	0.1233 ± 0.0005	0.9997	0.3	0.2
Height	1446	1490–1410	-0.0003 ± 0.0003	0.02048 ± 0.00009	0.9997	0.4	0.4
Area	1451–1441		-0.003 ± 0.002	0.1611 ± 0.0007	0.9998	0.4	0.01
Height	1366	1410–1318	-0.0002 ± 0.0002	0.01522 ± 0.00006	0.9997	0.2	0.6
Area	1371–1361		-0.002 ± 0.002	0.1374 ± 0.0005	0.9998	0.13	0.2
Height	1159	1186–1138	-0.0002 ± 0.0003	0.0158 ± 0.0001	0.9994	0.3	1.2
Area	1164–1154		-0.006 ± 0.002	0.1474 ± 0.0008	0.9996	0.2	0.4

[a]RSD: Relative standard deviation for five measurements.
[b]LOD: Limit of detection in pesticide formulations for a sample mass of 25 mg and stablished for a probability level of 99.6%.

figures of merit of different external calibration lines obtained from the main procymidone bands in the spectral region from 2000 to 1000 cm^{-1}.

The limits of detection established from three times the standard deviation of blank values divided by the slope of the calibration line varied from 0.01% to 2.9% w/w procymidone for an original sample mass of 25 mg this being adequate for the determination of this active main component in commercially available formulations. A repeatability between 0.06% and 0.4% in terms of relative standard deviation of a solution containing 4.3 mg g^{-1} procymidone was obtained, thus indicating the good stability of FTIR measurements.

In terms of sensitivity, it is clear that peak area measurements provides one order of magnitude better sensitivity than peak height values, but the repeatability of area measurements in some cases works better than that of peak height.

The band at 1446 cm^{-1} was selected because is not overlapped with any excipient band and due to the higher selectivity of this band in front of the carbonyl band at 1720 cm^{-1}. As can be seen in Table 1, peak area values provided lower % RSD and % LOD than the use of peak height, so this measurement mode was selected.

FT-Raman Spectra of Procymidone

Figure 3 shows the FT-Raman spectra of a solid procymidone standard diluted in sodium chloride of 48.9% w/w of procymidone, a commercial fungicide

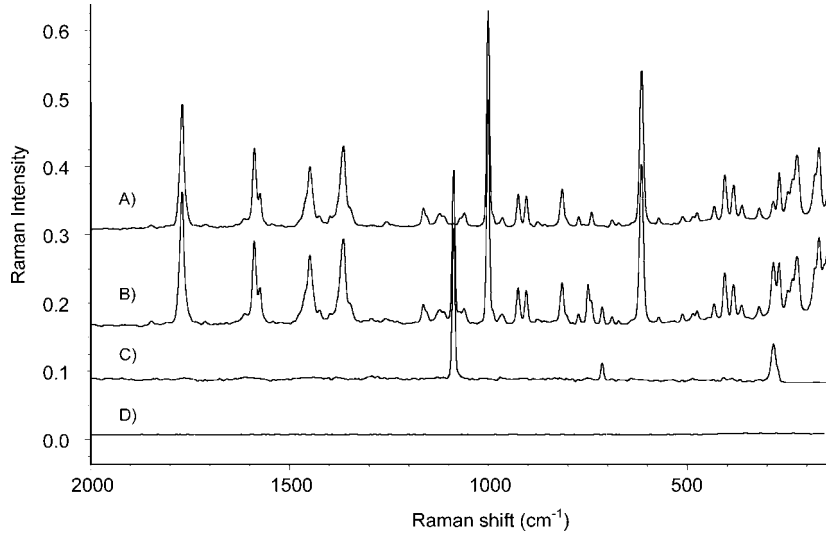

Figure 3. Raman spectra of a 48.9% w/w procymidone standard diluted in sodium chloride (A), a commercial sample containing a concentration of 50% w/w of procymidone (B), calcium carbonate (C), and sodium chloride (D) employed for the preparation of standards.

with a concentration of procymidone of 50% w/w, calcium carbonate, the main coadjuvant present in the sample, and that of a blank of sodium chloride. As can be seen, the spectrum of the sample and that of the standard present practically the same bands except those typical of $CaCO_3$, which can be clearly identified in the sample. The most intense bands in procymidone spectra are those present at 1770 and 1000 cm $^{-1}$ Raman shift due to C═O stretching and trigonal ring breathing, respectively. Other less important bands are those located at 1588, 1449, 1365, and 615 cm^{-1} due to C═C stretching in chloroalkenes, pseudosymmetric N–C═O stretching, ring stretching in benzene and C–Cl stretching, respectively.[30]

Raman Measurement Conditions

In order to improve the Raman measurement conditions, the effect of the number of accumulated scans, the laser power, and the nominal resolution employed for data acquisition were evaluated for a standard of procymidone diluted in a sodium chloride matrix with a concentration of 48.9% w/w. The number of accumulated scans was modified from 5 to 50, the laser power changed between 250 and 1000 mW and the nominal resolution varied from 2 to 16 cm^{-1}.

The most precise and sensitive results were those obtained when accumulating 50 scans for a laser power of 1000 mW (Fig. 4A). However in order to ensure a compromise between measurement frequency and precision and to avoid the use of a high laser power, which can affect the thermal stability of samples, 25 accumulated scans and 750 mW were selected, also being confirmed that, for a nominal resolution of 4 cm^{-1} and 25 accumulated scans, the best signal to noise ratio was found on using 750 mW (Fig. 4B).

Concerning the nominal resolution, it was found that the use of a resolution between 2 and 16 cm^{-1} provided a signal to noise ratio, established as the ratio between the peak area measurement between 1005 and 995 cm^{-1} Raman shift, with a baseline correction between 1030 and 947 cm^{-1}, and the noise of a blank established in the same region, of the order 10,000 (Fig. 5), but a 4 cm^{-1} resolution was the best compromise between sensitivity and sampling speed, a sample measurement throughput of 40 hr^{-1} for this value being obtained.

The repeatability of procymidone Raman measurements in solid phase can be affected by the vial and sample holder position. In order to evaluate the effect of these variables, a procymidone standard was measured changing the vial position randomly and using different vials for the same sample. A relative standard deviation of 2.9% and 5.3%, respectively, was found for the Raman intensity of a 48.9% w/w procymidone standard determined with peak area values between 1005 and 995 cm^{-1}, which is acceptable to carry out determination of this pesticide in commercial formulations.

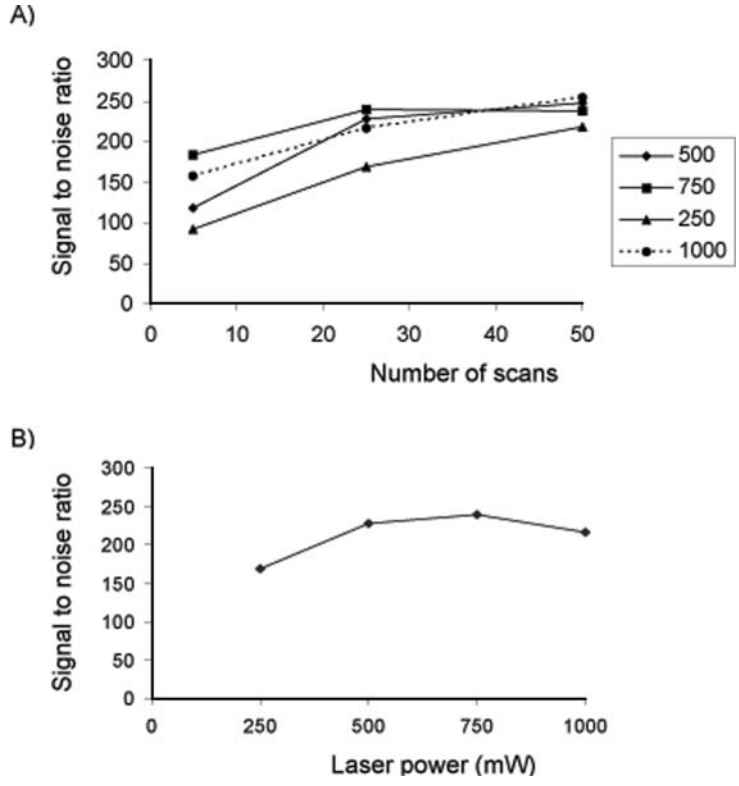

Figure 4. (A) Effect of the number of accumulated scans on the signal to noise ratio for different laser power. Data were obtained from the area between 1005 to 995 cm^{-1} shift of a standard containing 48.9% w/w procymidone. Experimental measurements were carried out with a nominal resolution of 4 cm^{-1} and laser powers between 250 and 1000 mW. (B) Signal to noise dependence from the laser power for 1000 cm^{-1} peak of a spectrum of a procymidone standard of 48.9% w/w obtained accumulating 25 scans per spectrum at a nominal resolution of 4 cm^{-1}.

Selection of Bands for Raman Determination of Procymidone

As indicated in Table 2, different bands were tested to do the Raman determination of procymidone in solid pesticide formulations. Peak height and peak area values were measured, also evaluating the use of different baseline criteria. The table shows the equations of the calibration lines obtained in each condition considered. It can be seen that the sensitivity of FT-Raman determination of procymidone varies from 0.215 to 5.6 intensity units (g^{-1} g), where peak height measurements are one order of magnitude less sensitive than when using peak area. In all the cases assayed, the limit of detection found was of the order 0.1% to 1.0% w/w independently of sample amount if it was enough to be excited and the emission could be done.

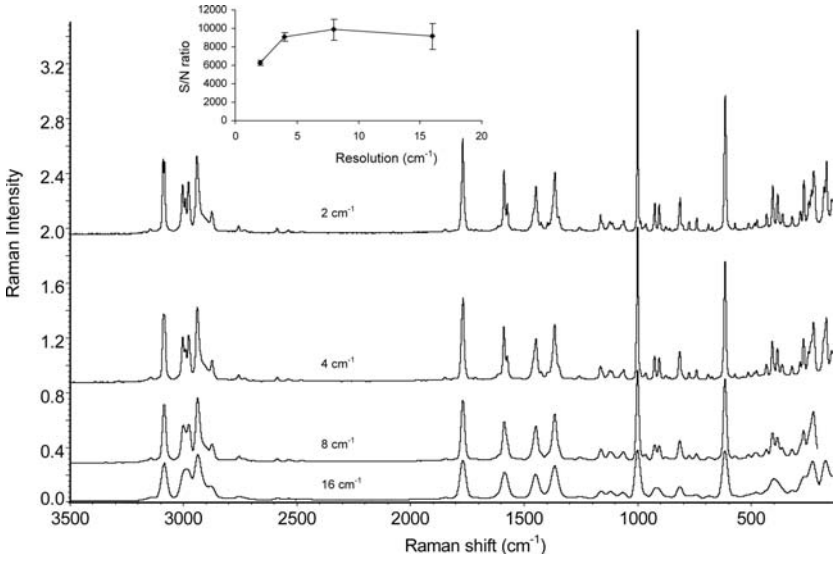

Figure 5. Effect of the nominal resolution on the Raman spectrum of a procymidone standard of 48.9% w/w obtained accumulating 25 scans for spectrum and a laser power of 750 mW. Inset: Signal to noise effect for peak area values between 1005 to 995 cm^{-1} Raman shift.

The use of the peak area measurement between 1005 and 995 cm^{-1} with a baseline fixed between 1030 and 947 cm^{-1} was selected because it presented the best sensitivity, a limit of detection of 0.8% w/w, and accuracy errors of the order 1.0%.

Analytical Figures of Merit of the Developed Procedures

The main characteristics of the FTIR method developed for the determination of procymidone in formulated products are indicated in Table 1. For peak area measurements between 1451 and 1441 cm^{-1}, corrected with a baseline established between 1490 and 1410 cm^{-1}, a calibration line [Absorbance = $(-0.003 \pm 0.002) + (0.1611 \pm 0.0007)\, C_{mg\,g^{-1}}$] with a correlation coefficient $R^2 = 0.9998$, a precision of 0.4%, and a limit of detection of 0.01% w/w procymidone for a sample mass of 25 mg were obtained.

For FT-Raman determination, the selected conditions were peak area measurement between 1005 and 995 cm^{-1} Raman shift, with a baseline correction fixed between 1030 and 947 cm^{-1}, obtaining a calibration line [Signal = $(0.00 \pm 0.06) + (5.6 \pm 0.2)\ C_{g\,g^{-1}}$, with a correlation coefficient $R^2 = 0.993$, a relative standard deviation of 1%, and a limit of detection of 0.8% Procymidone in the original sample.

Table 2. Analytical features of the Raman determination of procymidone using different bands, baseline criteria and measurement modes

Measurement mode	Wavenumber (cm^{-1})	Baseline correction	Procymidone calibration curve [$y = a + b\ C$ ($g\ g^{-1}$)]				
			$a \pm s_a$	$b \pm s_b$	R^2	% RSD[a]	LOD[b] (% w/w)
Height	1770	1800–1720	0.000 ± 0.004	0.45 ± 0.01	0.995	0.6	0.6
Area	1775–1765		0.01 ± 0.04	3.6 ± 0.1	0.993	0.5	0.5
Height	1588	1606–1551	0.000 ± 0.003	0.269 ± 0.008	0.993	0.6	0.9
Area	1593–1583		-0.01 ± 0.03	2.11 ± 0.07	0.991	0.6	0.2
Height	1419	1499–1414	0.000 ± 0.003	0.215 ± 0.007	0.991	1.5	0.9
Area	1454–1444		-0.01 ± 0.03	2.12 ± 0.07	0.992	1.5	0.1
Height	1365	1409–1320	0.000 ± 0.003	0.285 ± 0.008	0.993	0.8	1.0
Area	1454–1444		0.00 ± 0.03	2.51 ± 0.08	0.992	0.7	0.7
Height	1000	1030–947	0.002 ± 0.007	0.78 ± 0.02	0.996	1.1	0.5
Area	1005–995		0.00 ± 0.06	5.6 ± 0.2	0.993	1.0	0.8
Height	615	660–592	0.001 ± 0.006	0.56 ± 0.02	0.993	1.0	0.3
Area	620–610		0.00 ± 0.05	4.5 ± 0.1	0.993	0.9	0.1

[a]RSD: Relative standard deviation for five measurements.
[b]LOD: Limit of detection in pesticide formulations for a sample mass of 25 mg and stablished for a probability level of 99.6%.

Calibration line obtained from solid standards of procymidone stored standard chromatographic glass vials present a good stability, having obtained after 3 months storage a calibration equation [Signal = $(-0.01 \pm 0.05) + (5.5 \pm 0.1)\ C_{g\,g^{-1}}$], with a correlation coefficient $R^2 = 0.997$, which is statistically comparable to those previously indicated for these standards.

To evaluate the accuracy of both procedures, a series of recovery studies was carried out on commercial samples spiked with different amounts of procymidone and diluted with $CHCl_3$ or NaCl, with a total procymidone concentration from 3.26 to 8.49 mg g^{-1} and 9.2% to 62.5% w/w, for FTIR and FT-Raman determination, respectively. As can be seen in Table 3, the average recovery of Procymidone from spiked samples was $101 \pm 2\%$ and $97 \pm 3\%$.

Application to Multicomponent Formulations

In order to evaluate how far along the vibrational spectrometry could be useful as an alternative to chromatographic procedures in the analysis of pesticide formulations, the existence of agrochemicals containing additional pesticides than procymidone was checked and it was found that chlorothalonil is coformulated with the aforementioned compound.[31]

As it can be seen in Fig. 6, in both the FTIR (Fig. 6A) and Raman (Fig. 6B) spectra, the selected bands employed through this study can be clearly differentiated with those obtained for chlorothalonil, thus evidencing the tremendous possibilities to extract direct information from the vibrational spectra of mixtures of compounds, based on the presence of several isolated bands for each one of the compounds considered.

However, for complex mixtures containing several principles and additives, it must be employed a chemometric-based methodology for the calibration of signals based on a series of well-analyzed samples as we have suggested.[32]

Comparison Between Different Methodologies Developed

The different methodologies developed for the determination of procymidone in pesticide formulations provide statistically comparable results for a probability level of 95% (student statistical, calculated value, t_{exp}, being lower than 1.812, the theoretical one for 10 degrees of freedom, t_{tab}), as can be seen in Table 4.

The advantages offered by the vibrational procedures is a strong reduction of the volume of organic solvent required for the analysis (41.3 mL acetonitrile for HPLC-DAD, 2.7 mL chloroform for FTIR, and no solvent for FT-Raman) and the increase of the sampling frequency from 8.6 hr^{-1} on the case of HPLC-DAD to 30 hr^{-1} for FTIR and 40 hr^{-1} for FT-Raman.

Table 3. Recovery studies on procymidone added to formulate samples by using FTIR and FT-Raman spectrometry

FTIR				FT-Raman			
Total content of procymidone (mg g^{-1})	Procymidone found (mg g^{-1})	% Recovery	Mean recovery ± s	Total content of procymidone (% w/w)	Procymidone found (% w/w)	% Recovery	Mean recovery ± s
3.27	3.34	101.9 ± 0.3		9.26	9.04	99 ± 2	
	3.32				9.34		
	3.33				9.20		
5.19	5.32	102.5 ± 0.2		12.97	12.99	102 ± 2	
	5.33				13.02		
	5.33				13.57		
6.40	6.35	99.1 ± 0.2	101 ± 2	17.15	16.87	98 ± 2	97 ± 3
	6.33				16.90		
	6.34				16.51		
7.07	7.19	101.72 ± 0.09		40.1	37.76	93 ± 1	
	7.19				37.77		
	7.18				37.00		
8.49	8.43	99.0 ± 0.2		62.6	61.19	95 ± 3	
	8.39				58.68		
	8.41				57.90		

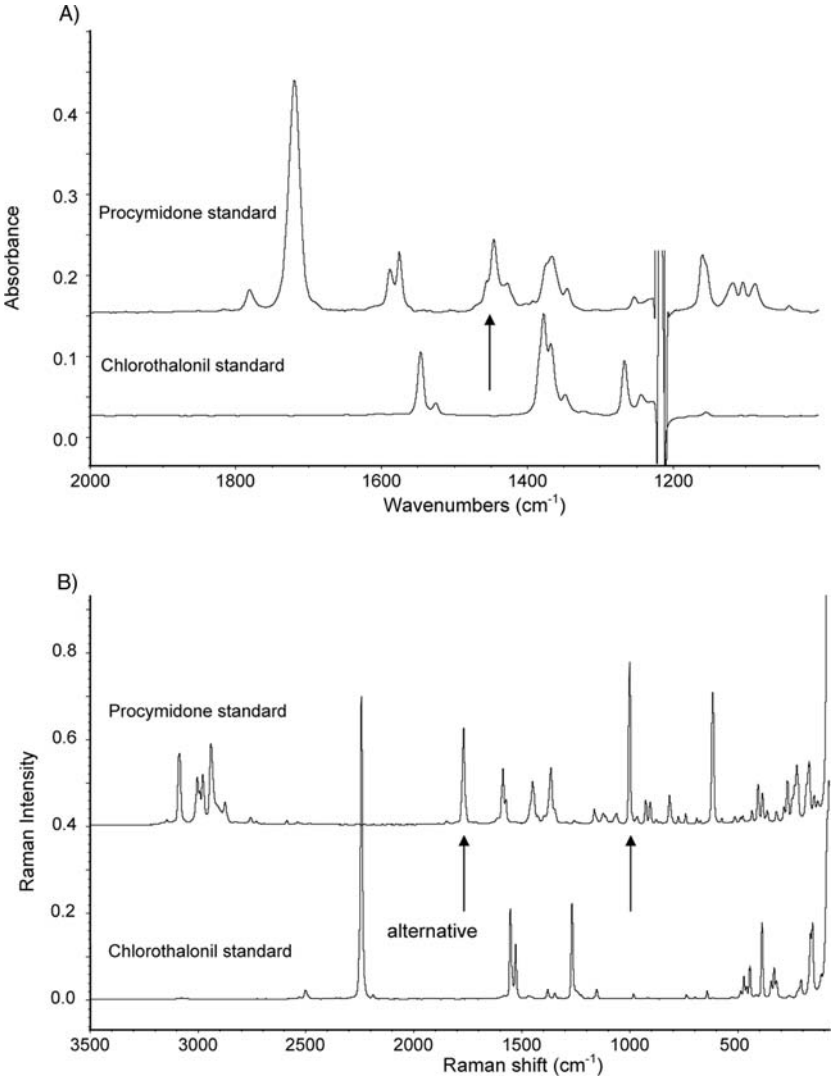

Figure 6. Vibrational spectra of procymidone and chlorothalonil: (A) FTIR spectra of standards dissolved in $CHCl_3$; (B) FT-Raman spectra obtained directly from the solid standards.

CONCLUSIONS

Results obtained in this paper show the possibilities of the absorption (FTIR) and emission (FT-Raman) vibrational techniques for the determination of principle active components in pesticide formulations.

Table 4. Results obtained in the analysis of commercial samples

Sample	HPLC-DAD (% w/w)	FTIR (% w/w)	t_{exp}	FT-Raman (% w/w)	t_{exp}
1	50.6 ± 0.4	50.1 ± 0.9	1.13	50.4 ± 0.5	0.70
2	51.6 ± 0.2	51.2 ± 0.2	1.8	51 ± 1	1.32
3	50.5 ± 0.3	50.7 ± 0.3	1.05	51 ± 1	1.07

t_{exp} = calculated value of the Student statistical.

t_{tab} = 1.812, theoretical Student statistical for a probability level of 95% and 10 degree of freedom.

FTIR determination sample frequency was $30\,hr^{-1}$, lower than the Raman ones of $40\,hr^{-1}$, but both were clearly higher than the HPLC-DAD ones ($8.6\,hr^{-1}$). FT-Raman reduces to the minimum the reagent consumption and waste generation, also avoiding sample handling and the contact of operator with the pesticide.

It can be concluded that the proposed spectrometric methodologies are a fast and environmentally friendly alternative for the classic chromatographic procedures for quality control in pesticide commercial formulations.

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