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Solid sampling Fourier transform infrared determination of Mancozeb in pesticide formulations

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Abstract

A series of approaches have been assayed for FTIR determination of Mancozeb in several solid commercial fungicides using different calibration strategies. The simplest procedure was based on the use of the ratio between the absorbance of a characteristic band of Mancozeb and that of a KSCN internal standard measured in the FTIR spectra obtained from KBr pellets. It was employed the quotient between peak height absorbance values at 1525 cm^{-1} for Mancozeb and 2070 cm^{-1} for KSCN. In these conditions a precision as relative standard deviation (RSD) of 0.6% and a relative accuracy error of 0.8% (w/w) were found. For complex formulations, containing other compounds with characteristic absorption bands at different wavenumbers than Mancozeb, one of them was used as internal reference being employed the standard addition approach. In this case, the Mancozeb bands at 1525 cm^{-1} or at 1289 cm^{-1} were employed, being used the ferrocyanide band at 2075 cm^{-1} as internal reference. RSD values between 0.7–1.4% and a relative accuracy error of 3% (w/w) were found. A third strategy was based on the use of partial least squares (PLS) calibration. A reference set was prepared mixing Mancozeb, Kaolin, Cymoxanil and KBr, being predicted the Mancozeb concentration in pesticide formulations by using the quotient between absorbance bands of Mancozeb and those of Cymoxanil. In these conditions a relative accuracy error of 0.6% (w/w) and a relative standard deviation of 1.3% were found.

Keywords: Mancozeb; FTIR determination; Pesticide formulations; Internal standardization; Solid sampling; KBr pellets; PLS

1. Introduction

In the infrared literature it can be found a series of models for the quantitative analysis of samples based on the use of bands quotients between different components. These strategies avoid problems arising from the lack of information about the thickness of solid pellets or liquid sample drops deposited between two crystals. The aforementioned studies have been applied to the determination of the average condensation degree of surfactants [1,2] or the proportion between two active principles in a pharmaceutical formulation [3,4]. In recent years, new studies were developed to provide robust models based on the use of quotients between absorbance bands of two [5,6] or more components [7] present in the sample to avoid problems related with the election of internal standard and the compatibility with the sample components could appear [8,9].

Mancozeb, a [[1,2-etilenbisditiocarbamate](2-)] of manganese and zinc mixture, is a synthetic pesticide, which has been used since 1967 as a fungicide to prevent the growth of moulds and to protect plants and crops against damage caused by fungi. Mancozeb needs to be sprayed on surfaces of leaves and crops for protection against moulds. Fortunately the toxicity of Mancozeb is very low, with LD$_{50}$ values of the order of several g kg^{-1} [10]. It is available in commercial formulations as dusts, water-dispersible granules, wettable powders, and ready-to-use formulations. It is commonly found in combination with other pesticides like Cymoxanil, Metalaxyl, Fosetyl-Al or copper oxychloride [11].

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The analysis of alkylenebis (dithiocarbamates) of some divalent metal ions is hampered by their low solubility, low stability, and polymeric structure. Indirect methods include spectrophotometry [12,13], gas chromatography (GC) [14], or reversed phase ion-pair chromatography [15] determination of the reaction products liberated after reduction, in an acidic medium, to carbon disulfide. It is important to note that these methods are typically unable to distinguish among various dithiocarbamates since most of them can be degraded to CS_2. Other methods for determination of ethylenebisdithiocarbamates rely on the measurement of the metallic portion of the compounds, and therefore, many of these methods are similar to those for detection of inorganic manganese or zinc [16]. However, these methodologies assure the content of metal but cannot evaluate the possible degradation of pesticide molecules.

As it has been suggested by the CIPAC, chromatographic methods, based on both, gas and liquid chromatography, are currently employed for routine analysis of pesticide formulations [17]. However, recent studies have evidenced the ability of infrared spectrometry methods as an adequate alternative technique for the resolution of this analytical demand. Pyrethroids, such as cyperthrind and deltamethrin, have been analysed in emulsifiable concentrate formulations by FTIR spectrometry after separation by thin layer chromatography and re-dissolution in CCl_4 [18]. Iprodione has been determined in wettable powder after extracting with CH_2Cl_2 and measurement at 3355 cm^{-1} [19]. Attenuated total reflectance (ATR) infrared spectrometry combined with principal components regression (PCR) analysis has been applied to the determination of chlorpyrifos-ethyl in agrochemical formulations [20].

The improvement of FTIR determinations through the use of flow injection analysis has been applied to solve problems related to the determination of Carbaryl [21] and Buprofezin [22] and the simultaneous determination of active ingredients in commercial pesticide formulations [23], also including, in some cases, the sample treatment step, as for Malathion online determination [24].

Dithiocarbamate pesticides, such as Ziram and Thiram can be directly analyzed from solid formulations using chloroform as a solvent [25]. Ziram has been also determined after acid decomposition and the CS_2 generated measured by vapour phase FTIR [26].

Due to the extremely low solubility of Mancozeb in common organic solvents employed for FTIR spectrometry, also including polar ones such as alcohol or water, this pesticide can not be easy analyzed in dissolution and it is necessary to obtain the infrared spectra directly from the solid sample using diffuse reflectance (DR), attenuated total reflectance (ATR), photoacoustic or absorbance measurements in KBr pellets.

The aim of this study has been the development of simple strategies which could be used for routine determination of Mancozeb in commercial formulated fungicides based on the use of FTIR transmittance measurements in KBr pellets and thus, a series of direct measurements of the quotient between absorbance bands of Mancozeb and those of selected internal reference were suggested for the analysis of different pesticide formulations.

The use of the quotient between the absorbance of Mancozeb and that of a reference compound was employed on using: (i) external calibration, (ii) standard addition approach, and (iii) partial least squares calibration; thus offering a series of alternatives to solve the problem of the direct analysis of solid samples by transmittance FTIR without a previous dissolution.

2. Experimental

2.1. Apparatus and reagents

A Mattson Research RS1 Fourier transform infrared spectrometer (Madison, WI, USA) equipped with a temperature-stabilized DGTS detector with a Ge/KBr beamsplitter and precise digital signal processing (DSP) was employed for all the IR spectral measurements with a nominal resolution of 4 cm^{-1} and accumulating 25 scans.

For the mass measurements it was used a Mettler Toledo AG285 (Columbus, OH, USA) balance with a precision of ±0.01 mg.

PLS data treatment was carried out using Omnic Quant IR (version 1.2) software from Nicolet (Madison, WI, USA).

Mancozeb (88.1% (w/w)), Cymoxanil (98.0% (w/w)) and Kaolin, technical products were supplied by Laboratorios Afrasa S.A. and commercial formulations were obtained from the Spanish market. All the disks were prepared using KBr, spectroscopy IR grade, from Panreac (Barcelona, Spain). Analytical reagent grade potassium thiocyanate from Panreac (Barcelona, Spain) was employed as internal standard.

2.2. Recommended procedure

2.2.1. External calibration in the presence of an added internal standard

An accurately weighted amount of 1.50 mg (±0.01 mg) KSCN was added to 2.00 mg (±0.01 mg) sample and 500.0 mg (±0.1 mg) KBr. The mixture was grounded and homogenized for 5 min in an agate mortar. The mixture was pressed at 10 tones in a 13 mm diameter evacuable pellet die and the FTIR spectrum of the resultant KBr disk recorded in the range from 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution and accumulating 25 scans for spectrum. The background spectrum was established, under identical instrumental conditions, from the air.

An external calibration curve was established with KBr disks containing different amounts of Mancozeb in the presence of KSCN as internal standard, using the quotient between the bands at 1525 cm^{-1}, with a baseline established between 1556 and 1430 cm^{-1} for Mancozeb and that of KSCN of 2070 cm^{-1}, with a baseline established between 2233 and 1930 cm^{-1}.

2.2.2. *Standard addition in the presence of a well known sample component*

An accurate weight of the order of 25 mg of a commercial formulation which contains also ferric ferrocyanide and copper oxychloride, was mixed with 300 mg KBr. On the other hand a stock mixture of pure Mancozeb and KBr (20 mg Mancozeb in 250 mg KBr) was prepared. From mixtures of the diluted sample and the stock powder, it was prepared a series of standards with a constant concentration of ferric ferrocyanide and different added amounts of Mancozeb.

Solid mixtures were pressed and the FTIR spectra of the KBr disks recorded using the aforementioned instrumental conditions. Peak area and peak height measurements corresponding to Mancozeb bands were divided by data corresponding to the 2075 cm^{-1} ferrocyanide band, using a baseline between 1986 and 2158 cm^{-1}, and Mancozeb determined using the standard addition aproach from absorbance quotient data as a function of added mg of the pesticide, being selected the peak height data at 1289 cm^{-1} for Mancozeb corrected with a baseline located at 1272 cm^{-1}.

2.2.3. *Partial least squares calibration in the presence of an internal standard*

About 4 mg Cymoxanil and different quantities of Mancozeb, from 40 to 55 mg, and Kaolin (a coadyuvant present in the formulations), from 41 to 56 mg, were mixed with KBr in order to prepare a calibration set. Two milligrams of sample were diluted with 250 mg KBr and the FTIR spectra of the KBr pellets were recorded. Absorbance data corresponding to Mancozeb were divided by those corresponding to Cymoxanil, employed as internal standard, and from these data a PLS model was established on using the calibration set, being predicted Mancozeb concentration in commercially available samples by using a three factors model and the spectral range between 1579 and 1269 cm^{-1} corrected with a two points baseline situated between 1581 and 1269 cm^{-1} for Mancozeb and the measurement of peak height at 1705 cm^{-1} corrected with a baseline established between 1786 and 1689 cm^{-1} for the internal reference of Cymoxanil.

2.3. *Mathematical treatments assayed*

The determination of Mancozeb, from its characteristic bands obtained in solid KBr pellets, can be carried out by using an internal standard in order to avoid the problems related to establish quantitative data in conditions for which it is difficult to fix the bandpass.

Three alternatives were assayed in the present study.

2.3.1. *External calibration by using an added internal standard*

The quotient between the absorbance at two characteristic bands of each compound, A_M and A_K, respectively, in a series of standards containing the same amount of component *K*, provides a regression line of A_M/A_K versus $[M]/[K]$ which pass through the origin, being independent on the optical pathlength because for each KBr pellet disk the bandpass is the same for both compounds. So, the regression line $A_M/A_K = \varepsilon_M/\varepsilon_K \times [M]/[K]$, in which ε_M and ε_K are the absorption coefficients of M and K at the corresponding bands considered, could be used to obtain the concentration of the analyte in unknown samples to which the internal standard was added.

2.3.2. *Standard addition analysis using an internal reference*

For samples containing mixtures of different compounds, which present their characteristics absorption bands at different wavenumbers, it can be established a relationship between the absorbance at two wavenumbers (each of one corresponding to each compound), considered for a same spectrum, which will be independent on the bandpass and will depend on the proportion between the concentrations of the two compounds.

The addition of different amounts of the analyte to be determined to a series of fixed aliquots of the sample to be analysed provides a typical standard addition expression

$$\frac{A_M}{A_K} = \frac{\varepsilon_M}{\varepsilon_K} \times \frac{M_{\mathrm{sample(mg)}}}{K_{\mathrm{(mg)}}} + \frac{\varepsilon_M}{\varepsilon_K} \times \frac{M_{\mathrm{standard(mg)}}}{K_{\mathrm{(mg)}}}$$

being ε_M and ε_K the absorption coefficient of the analyte, (*M*), and the reference compound, (*K*), at the considered wavenumbers. From the quotient between the intercept, $\varepsilon_M/\varepsilon_K \times [M]_{\mathrm{sample}}/[K]$ and the slope $\varepsilon_M/\varepsilon_K \times [K]$, it can be obtained the mass in mg of the analyte in the aliquot taken from the sample.

2.3.3. *Partial least squares using internal reference*

For the determination of Mancozeb in samples containing a second active ingredient which affects the Mancozeb signal but can be easy and accurately analysed, thus latter compound can be used as an internal reference and a PLS treatment of relative absorbance values could be used. It can be prepared a series of matched standards containing well known amounts of the reference and the analyte in order to develop a calibration model in which absorbance band quotients, instead of pure absorbance data at fixed wavenumbers, will be used.

An appropriate data adjustment of the calibration set could be useful for obtaining the concentration of the analyte in an unknown solid sample in which the reference compound has been previously determined after leaching it with an appropriate solvent. So, absorbance bands quotient data and reference concentration can be used for prediction of the insoluble analyte.

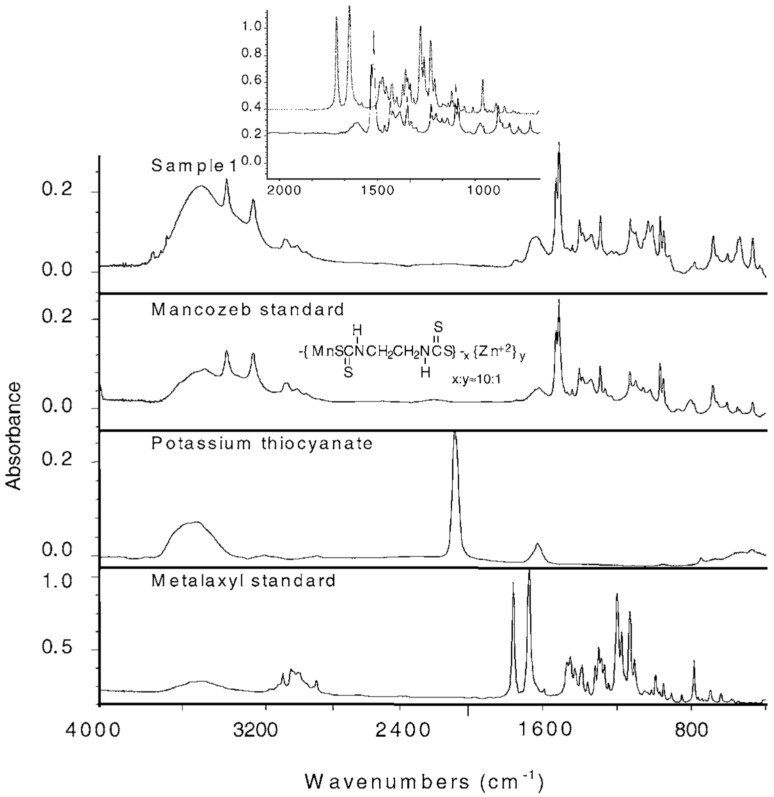

Fig. 1. FTIR spectra of KBr disks of a commercial fungicide sample which contains Mancozeb and Metalaxyl (Sample 1), Mancozeb, KSCN and Metalaxyl standards. Inset: FTIR spectra of a Mancozeb standard of 0.4 mg g^{-1} (bottom) and a Metalaxyl standard of 0.4 mg g^{-1} (top). All the spectra were recorded between 4000 and 400 cm^{-1}, at 4 cm^{-1} resolution, accumulating 25 scans for spectrum and the background was established, under identical conditions, from air.

3. Results and discussion

3.1. *Determination of Mancozeb by addition of a reference compound*

3.1.1. *FTIR absorbance spectra*

Fig. 1 shows the FTIR spectra of KBr disks of a Mancozeb standard, a commercial fungicide (Sample 1) containing 64% (w/w) Mancozeb and 8% (w/w) Metalaxyl, a Metalaxyl standard, and potassium thiocyanate, which will be employed as added reference compound for internal standardization.

Metalaxyl, methyl-*N*-(2,6-dimethylphenyl)-*N*-(2-xylyl)-DL-alaninate, is a systemic benzenoid fungicide used in mixtures as a foliar spray for tropical and subtropical crops, as a soil treatment for control of soil-borne pathogens, and as a seed treatment to control downy mildews.

As can be seen in the spectrum of Sample 1 are present the characteristic bands of Mancozeb, the most intense of these being those at 1525 and 1510 cm^{-1} which correspond to amide II band in CSNHR structures [27].

On the other hand, the thiocyanate stretching band at 2070 cm^{-1} could be used as reference to process absorbance band quotients between Mancozeb and KSCN in both, samples and standards, due to the absence of absorption at this wavenumber by all the compounds present in the sample.

3.1.2. *Selection of the appropriate bands for the FTIR measurement of Mancozeb*

As depicted in the inset of Fig. 1 the Mancozeb bands at 1525 and 1510 cm^{-1} do not overlap with any Metalaxyl band. So these bands are appropriate for Mancozeb determination in pesticide formulations containing Metalaxyl.

A series of Mancozeb standards, also containing KSCN as internal reference, with a Mancozeb/KSCN ratio between 5 and 1 were prepared according the recommended procedure for the external calibration. From the FTIR spectra of the aforementioned standards, and in order to choose the best analytical performance for the Mancozeb determination, different bands, measurement modes and baseline criteria were evaluated as can be seen in Table 1. This table shows the equations of the calibration lines, precision and accuracy values obtained for each band considered. The sensitivity of FTIR determination of Mancozeb varies from slope values of 0.109–0.60, being peak height based calibrations more sensitive than those obtained employing peak area measurements.

Table 1 evidences low correlation coefficients for calibrations established for area measurements, due to the appearance of a deformation of the thiocyanate band as a function of the relationship between Mancozeb and KSCN, as can be seen in Fig. 2. This deformation is probably due to the substitution of K^{+} in KSCN by the Zn^{2+} of Mancozeb. So,

Table 1
Selection of IR bands for Mancozeb determination by using external calibration and KSCN as internal reference

Bands				Calibration line[a]		R^2	R.S.D.[b]	Mancozeb concentration[c] (% w/w) ± s	Er (%)[d]
Compound	Measurement mode	Wavenumber (cm^{-1})	Baseline (cm^{-1})	$a \pm s_a$	$b \pm s_b$				
Mancozeb	Height	1525	1556–1430	−0.06 ± 0.02	0.42 ± 0.01	0.998	0.2	64.5 ± 0.4	0.8
KSCN	Height	2070	2233–1930						
Mancozeb	Height	1510	1553–1428	−0.09 ± 0.04	0.60 ± 0.02	0.993	0.4	64.8 ± 0.4	1.2
KSCN	Height	2070	2233–1930						
Mancozeb	Area	1536–1518	1556–1451	−0.015 ± 0.006	0.109 ± 0.003	0.995	0.5	66.9 ± 0.3	5
KSCN	Area	2139–2013	2233–1930						
Mancozeb	Area	1519–1492	1553–1428	−0.02 ± 0.01	0.179 ± 0.007	0.993	1.0	68 ± 2	6
KSCN	Area	2139–2013	2233–1930						
Mancozeb	Area	1542–1485	1555–1427	−0.04 ± 0.02	0.30 ± 0.01	0.993	0.8	68 ± 2	6
KSCN	Area	2139–2013	2233–1930						

[a] Regression line: $A_{\mathrm{Mancozeb}}/A_{\mathrm{KSCN}} = a + b\,C_{\mathrm{Mancozeb}}$ (mg)/C_{KSCN} (mg).
[b] R.S.D.: Relative standard deviation for a ratio Mancozeb/KSCN of 1.25 in KBr disk established from 5 different KBr pellets of a sample.
[c] Mancozeb concentration established in Sample 1, by using different criteria, in terms of % (w/w) ± S.D.
[d] Accuracy relative error, taking into account a reported concentration of 64% (w/w).

in this study, peak height data measurements of Mancozeb at 1525 cm^{-1} (corrected with a baseline established between 1556 and 1430 cm^{-1}) related to those of KSCN at 2070 cm^{-1} (with a baseline fixed between 2233 and 1930 cm^{-1}) will be recommended.

One commercial pesticide formulation containing Mancozeb and Metalaxyl was analyzed by the proposed procedure and as can be seen in Table 1 Mancozeb concentration found is comparable to that reported by the manufacturer. A relative error lower than 1% (w/w) and a repeatability of the 0.6% (expressed as a relative standard deviation) were obtained in the aforementioned conditions.

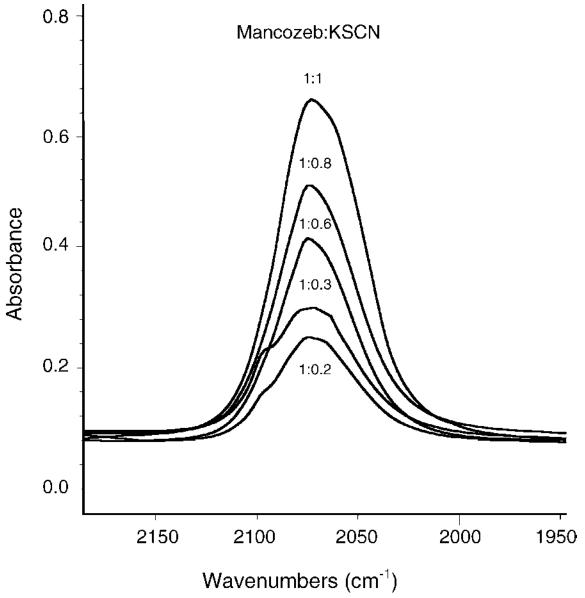

Fig. 2. Deformation on the thiocyanate band at 2070 cm^{-1} due to the presence of Mancozeb. Values indicated correspond to the Mancozeb:KSCN ratio in (w/w).

3.2. Determination of Mancozeb by standard addition analysis using an internal reference

3.2.1. FTIR absorbance spectra

FTIR spectra of KBr disks of a sample containing Mancozeb, ferric ferrocyanide and copper oxychloride and those of the different components considered can be seen in Fig. 3. The commercial sample (Sample 2) spectrum shows a higher number of bands than Mancozeb spectrum, due to the presence of ferric ferrocyanide and copper oxychloride in this product which avoid the use of KSCN as internal reference but provides another way for Mancozeb determination.

As can be seen in Fig. 3, the copper oxychloride (technical product) utilized in the manufacture of this commercial sample contains ferric ferrocyanide, evidenced by the presence of the band that appears at 2080 cm^{-1} due to $-C{\equiv}N$ stretching [27]. The presence of ferrocyanide in oxychloride, which not affects the Mancozeb determination, was used as internal reference because the quantity of ferrocyanide belong constant in each sample and for the analysis of this kind of sample the strategy adopted was based on the use of the standard addition approach, being added increasing amounts of Mancozeb to constant sample aliquots.

3.2.2. Selection of the appropriate bands for the FTIR determination of Mancozeb by standard addition

As can be seen in the inset of Fig. 3 the FTIR spectrum of the commercial sample presents a series of characteristic bands of Mancozeb in the wavenumber range from 1550 to 1250 cm^{-1}. These bands do not overlap with bands of the other compounds present in the formulation. So, it is possible to process these data related to the absorbance at 2075 cm^{-1}. Table 2 shows the characteristic bands chosen for this study, processed with the previously defined standard addition model based on the use of the ratio between peak area or peak height of the selected absorbance bands. In all the cases, calibration lines were prepared as indicated in the

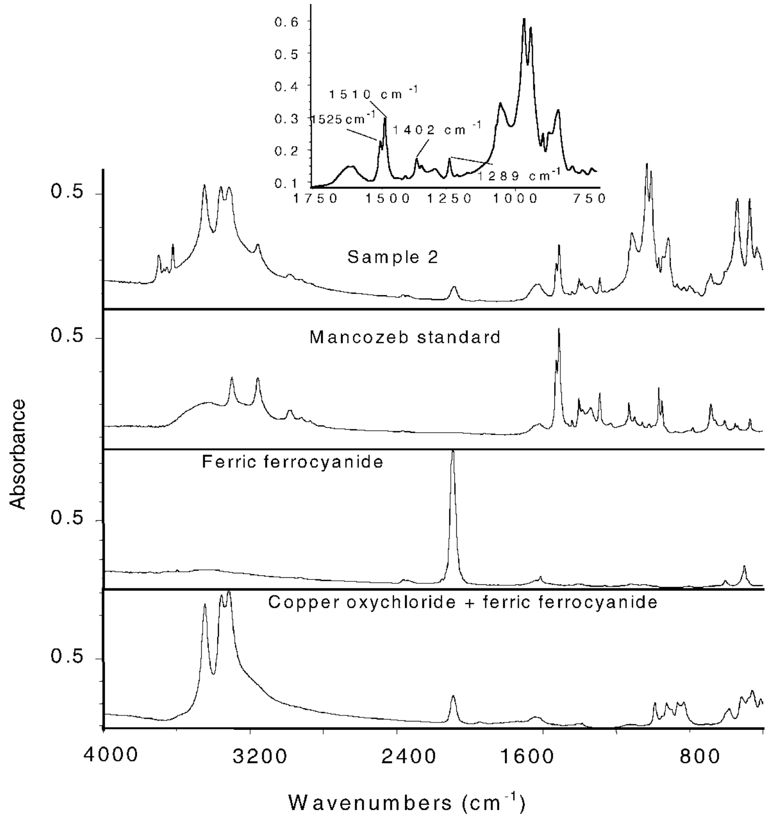

Fig. 3. FTIR spectra of KBr disks of a commercial fungicide which contains Mancozeb cooper oxychloride and ferric ferrocyanide (Sample 2), Mancozeb standard, ferric ferrocyanide and copper oxychloride with ferric ferrocyanide technical mixture. Inset: detailed spectrum of Sample 2 showing the bands selected for the determination of Mancozeb. All the spectra were recorded between 4000 and 400 cm^{-1}, at 4 cm^{-1} resolution, accumulating 25 scans for spectrum and the background was established, under identical conditions, from air.

Table 2
Selection of IR bands for determination of Mancozeb in a commercial sample using the standard addition method and ferrocyanide as internal reference

Bands				Calibration line[a]		R^2	R.S.D.[b]	Mancozeb concentration[c] (% w/w) ± s	Er (%)[d]
Compound	Measurement mode	Wavenumber (cm^{-1})	Baseline (cm^{-1})	$a \pm s_a$	$b \pm s_b$				
Mancozeb	Height	1525	735–1567	1.59 ± 0.17	3.27 ± 0.13	0.9967	1.4	18 ± 2	3
Ferrocyanide	Height	2075	1986–2158						
Mancozeb	Height	1510	1428–1554	2.4 ± 0.3	4.2 ± 0.2	0.9949	2	21 ± 3	20
Ferrocyanide	Height	2075	1986–2158						
Mancozeb	Height	1401	1425	0.74 ± 0.07	1.35 ± 0.06	0.996	0.9	20 ± 2	14
Ferrocyanide	Height	2075	1986–2158						
Mancozeb	Height	1289	1272	0.62 ± 0.05	1.31 ± 0.04	0.998	0.7	17 ± 1	−3
Ferrocyanide	Height	2075	1986–2158						
Mancozeb	Area	1557–1517	1557	0.97 ± 0.10	1.83 ± 0.08	0.9962	2	19 ± 2	8
Ferrocyanide	Area	2109–2050	2142–1994						
Mancozeb	Area	1517–1485	1554–1428	1.51 ± 0.18	2.68 ± 0.15	0.9938	2	20 ± 3	14
Ferrocyanide	Area	2109–2050	2142–1994						
Mancozeb	Area	1415–1391	1427	0.47 ± 0.06	0.73 ± 0.05	0.9923	1.5	23 ± 3	30
Ferrocyanide	Area	2109–2050	2142–1994						
Mancozeb	Area	1300–1279	1275	0.24 ± 0.03	0.50 ± 0.02	0.996	1.3	17 ± 2	−3
Ferrocyanide	Area	2109–2050	2142–1994						

[a] Regression line: $A_{\text{Mancozeb}}/A_{\text{Ferrocyanide}} = a + b\,C_{\text{Mancozeb added}}$ (mg).

[b] R.S.D.: Relative standard deviation for a sample with a 10 mg g^{-1} Mancozeb standard added (mg), established from 5 different KBr pellets of the sample.

[c] Mancozeb concentration established in Sample 2, by using different criteria, in terms of % (w/w) ± S.D.

[d] Accuracy relative error, taking into account a reported concentration of 17.5% (w/w).

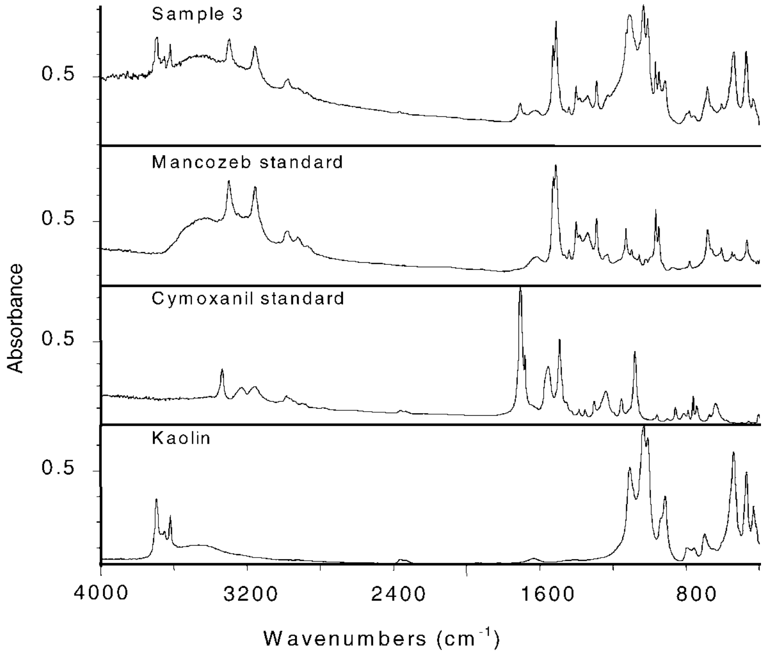

Fig. 4. FTIR spectra of KBr disks of a commercial fungicide containing Mancozeb, Kaolin and Cymoxanil (Sample 3), Mancozeb, Cymoxanil and Kaolin standards. All the spectra were recorded between 4000 and 400 cm^{-1}, at 4 cm^{-1} resolution, accumulating 25 scans for spectrum and the background was established, under identical conditions, from air.

Experimental section, by adding increasing amounts of Mancozeb to a fixed amount of sample.

The use of peak height ratio values provides a higher sensitivity than that obtained by the corresponding peak area measurements. The use of absorbance height data of Mancozeb at 1289 cm^{-1} and those of ferrocyanide at 2075 cm^{-1} provided the best regression coefficient and the best relative standard deviation. From the quotient between the intercept and the slope of the standard addition curve, a percentage of 17 ± 1% (w/w) of Mancozeb was obtained for the sample analyzed, that is a 3% lower than that indicated by the manufacturer.

3.3. Determination of Mancozeb by PLS–FTIR using an internal reference

3.3.1. FTIR absorbance spectras

Fig. 4 shows the FTIR spectra in KBr disk of Mancozeb, Cymoxanil and Kaolin standards, and that of a commercial fungicide sample containing 46.5% (w/w) Mancozeb and 4% (w/w) Cymoxanil.

Cymoxanil, 2-cyano-*N*-[(ethylamino)carbonyl]-2-(methoxyimino) acetamide, is an aliphatic nitrogen fungicide highly soluble in $CHCl_3$ [28], which can be determined by direct FTIR measurement at 1720 cm^{-1} after leaching with chloroform.

As can be seen, sample spectrum provides the typical bands corresponding to Mancozeb and the other compounds present in this formulation. Based on the fact that this formulation contains a 4% (w/w) Cymoxanil and this pesticide can be easily determined, it can be employed as internal reference, being possible to use the band at 1705 cm^{-1} to obtain absorbance data independent to the bandpass of each KBr disk measured.

3.3.2. PLS treatment of FTIR data

A calibration set integrated by 4 matched standards with a constant mass of Cymoxanil of 4 mg and quantities of Mancozeb from 40 to 55 mg, and Kaolin from 56 to 41 mg was used for PLS modelization. FTIR spectral data were mean centered after the appropriate selection of the spectral region in terms of both, wavenumber range and peak area or peak height. Additionally, in order to establish the best calibration model, different criteria to select the internal standard spectral data (see Table 3) and the number of factors were selected, taking into consideration the minimum value of the predicted residual error sum of squares (PRESS) for cross validation.

As can be seen in Table 3, when a wide spectral range was selected, it was obtained an excessively high standard deviation, which indicates that the calibration set for matched standards is unable to reproduce exactly the matrix of samples. The most accurate results were obtained for the region between 1579 and 1269 cm^{-1} (corrected with a baseline between 1581 and 1269 cm^{-1}), in which the most important bands of Mancozeb are present, and employing as internal standard the peak height of Cymoxanil at 1705 cm^{-1} (baseline established between 1786 and 1689 cm^{-1}). Under these conditions a root mean square error of calibration (RMSEC) of 0.10% (w/w), an accuracy relative error of 0.6% (w/w) and a precision, as relative standard deviation, of 1.3% were found for a sample con-

Table 3
Analytical features of the different regions employed in PLS calibration for Mancozeb determination in solid samples and using Cymoxanil as internal standard

Data employed					Analytical characteristics found			
Mancozeb		Internal standard			Factors[a]	Calibration error[b]	Mancozeb concentration[c]	E_r (%)[d]
Measurement region (cm^{-1})	Baseline (cm^{-1})	Measurement mode	Wavenumber (cm^{-1})	Baseline (cm^{-1})				
1581–399	1583	Height	1705	1786–1689	5	0.07	50 ± 30	8
1581–399	1583	Area	1713–1695	1786–1689	5	0.03	50 ± 30	8
1579–1269	1581–1269	Area	1713–1695	1786–1689	3	0.08	47.0 ± 1.5	1.2
1579–1269	1581–1269	Height	1705	1786–1689	3	0.10	46.8 ± 0.6	0.6
1581–1471	1583–1471	Height	1705	1786–1689	3	0.09	49 ± 2	5
1578–841	1578–841	Height	1705	1786–1689	3	0.11	48.6 ± 0.4	4
1577–1520	1577–1452	Height	1705	1786–1689	4	0.25	42 ± 7	−10

[a] The number of factors was chosen in order to obtain the minimum PRESS.
[b] Calibration mean error was found from the cross-validation for a set of standards with ratios between Mancozeb and Cymoxanil from 8.9 to 12.9.
[c] Results obtained for a Mancozeb concentration in terms of % (w/w) ± the corresponding standard deviation of 3 analysis.
[d] Accuracy error in % calculated for 3 independent determination of Mancozeb samples containing 46.5% (w/w).

taining 46.5% (w/w) Mancozeb and 4% (w/w) Cymoxanil.

4. Conclusions

The proposed calibration strategies for FTIR Mancozeb determination in different types of fungicide formulations, based on the use of KBr disks and absorbance bands ratio respect to different internal references, provide comparable results to those reported by the manufacturer with relative errors which varied from +0.8 to −3.0% (w/w). The methodologies developed are adequate for quality control of these fungicide formulations and provided the first precedent on the use of FTIR for the determination of Mancozeb.

The developed methods do not require any chemical pretreatment of samples. The use of reagents is reduced to the minimum because samples were processed without solvents, except in the case of PLS calibration with matched standards for prediction of Mancozeb concentration in samples containing Cymoxanil, in which case this latter compound, used as internal reference, must be determined separately by leaching with 3 ml $CHCl_3$.

On comparing the different strategies assayed, it can be concluded that the use of an internal standard, added to both, samples and standards, could be the simplest methodology but it requires the presence of a well defined and not interfered analyte band. However, it is clear from the examples provided through this study that for complex formulations it is not a good alternative.

The use of a sample component, as internal reference, involves the need of a separate determination of the concentrations of the reference compound. However, the use of the standard addition methodology avoids this problem, but increases the sample manipulation.

In this study we have presented different strategies for FTIR analysis of pesticides that can not be measured in solution and we let in the hands of the reader to choose the most appropriate strategy to be adopted as a function of sample composition and facilities to find an internal standard or to carry out additional determinations.

In fact, all the strategies commented here increase the applicability of traditional FTIR measurements on KBr disks from qualitative purposes to quantitative exploration of samples and offer a good alternative for the analysis of low soluble active ingredients like Mancozeb in pesticide formulations.

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