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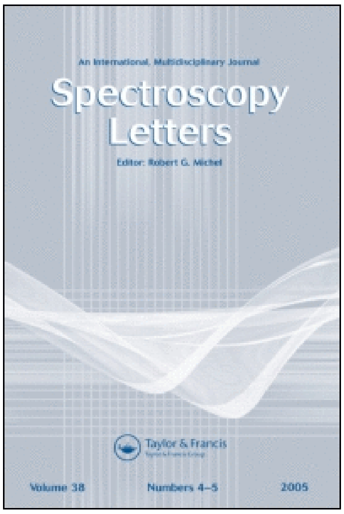

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# First-Derivative Fourier-Transform Infrared Determination of Oxadiazon in Commercial Herbicide Formulations

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**ABSTRACT** A Fourier-transform infrared (FTIR) method has been developed for the quantification of oxadiazon in herbicide formulations. The method involves the extraction of the active ingredient by sonication of the samples with $CHCl_3$ and direct measurement of the peak area values in first-order derivate spectra from 1770 $cm^{-1}$ to 1774 $cm^{-1}$ corrected with a baseline point located at 1950 $cm^{-1}$ and after a 5-point smoothing. A limit of detection (3 s) of 0.03 mg $g^{-1}$ and a typical relative standard deviation (RSD) of 1.3% were found. Results obtained were comparable with those found by liquid chromatography with UV detection. The proposed method involves a 7-times reduction in solvent consumption and 20-times increase of the sampling throughput compared with the chromatography procedure, and thus, it can be concluded that the proposed method is a sustainable alternative for quality control of commercial pesticide formulations.

**KEYWORDS** first-derivative spectroscopy, Fourier-transform infrared, herbicide formulations, oxadiazon

## INTRODUCTION

Pesticides are biologically active chemicals designed to control pests but with a residual toxicity for humans. This, it is essential that the risks they pose to human health, animals, and the environment can be properly controlled. In order to carry this out, before a pesticide can be sold, supplied, stored, used, or advertised in Spain it must be approved by the Dirección General de Salud Pública, Subdirección General de Sanidad Ambiental y Salud Laboral.[1] Additionally, the assessment of chemical preparations to be placed in the European market, must accomplish the European Union and national legislations.

Notification schemes for new chemical substances manufactured or imported within EU industries requires not only details on the notifier/manufacturer and the identity of the chemical but also a technical dossier providing information on the substance and results from analysis of physical and chemical properties,

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including quantitative data on the concentration of active principles and test reports from toxicologic and ecotoxicologic assays.[2]

Oxadiazon, 5-*tert*-butyl-3-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazol-2(3*H*)-one, is a selective pre-emergence herbicide present as active ingredient in several commercially available formulations. It is used for the control of annual grasses and many broadleaf weeds in turf and landscape ornamentals.

Products containing oxadiazon control weeds growing from seeds, not controlling those emerged or established, by killing young weed seedlings as they come in contact with oxadiazon during germination.[3,4]

After a bibliographic research in the Analytical Abstracts database for the period 1980 to February 2006, it was verified that the main part of the methods proposed for the determination of oxadiazon in different kinds of matrices such as juice,[5] honey,[6] soil,[7] wines,[8] and cereals[9] is based on chromatography techniques.

The single precedent on the determination of oxadiazon at percentage level corresponds with Liu et al.,[10] who determined oxadiazon combined with butachlor and simetryn using gas chromatography–mass spectrometry.

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However, there are no precedents about the use of infrared spectrometry or methodologies proposed for the determination of oxadiazon in commercial formulates in spite of the tremendous development of Fourier-transform infrared (FTIR)-based methods for the determination of pesticides in agrochemicals made in the past years.[11]

Thus, the aim of this study was the development of a FTIR procedure for a fast, accurate, and direct determination of oxadiazon in commercial herbicide formulations that can be used in the quality control of these products and could avoid the application of chromatography procedures that work better for residue analysis than for products containing oxadiazon at percentage level.

# MATERIALS AND METHODS

## Apparatus and Reagents

A Magna 750 FTIR spectrometer from Nicolet (Madison, WI, USA), equipped with a temperature-stabilized deuteratedtriglycine (DTGS) detector, a long-lasting Ever-Glo source, and a KBr beamspliter, was employed for spectral measurements, using a Specac microflow cell with ZnSe and $CaF_2$ windows and 0.11-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 data.

A Gilson P-2 Minipuls peristaltic pump (Villiers-le-Bel, France) furnished with Viton (iso-versinic) tubes (1 mm i.d. and 3 mm o.d.) resistant to chlorinated solvents, which provides flow rates from 0.2 to 3 mL $min^{-1}$, and polytetrafluoroethylene (PTFE) tubes of 1.6 mm o.d. and 0.8 mm i.d were used to introduce solutions into the microflow cell.

A Hewlett-Packard HPLC Series 1050 High Performance Liquid Chromatograph (Waldbronn, Germany), equipped with a Kromasil C-18 column (250 × 4.6 mm i.d. and 5 μm particle diameter) and a variable-wavelength UV-Vis detector was employed for the analysis of oxadiazon formulations, this methodology being used as a reference procedure for the validation of the FTIR method.

Oxadiazon standard (99.7%, w/w) was supplied by Fluka (Buchs, Switzerland). Analytical grade chloroform stabilized with 150 mg $l^{-1}$ amylene and acetonitrile were obtained from Scharlau (Barcelona, Spain) and were employed for the preparation of samples and standards. Emulsifiable concentrate commercial formulations containing oxadiazon 25% (w/v) were obtained directly from the Spanish market.

## Reference Procedure

Twenty-five milligrams sample was accurately weighed, inside a 25-mL volumetric flask and diluted to the volume with $CH_3CN$, then sonicated during 5 min in an ultrasound water bath to extract oxadiazon from the matrix and to ensure a complete homogenization. One milliliter of the extract was diluted to 10 mL and filtered through an 0.22-μm nylon filter. Twenty microliters of this latter solution was directly injected in a Kromasil C-18 (250 × 4.6, 5 μm) column using an 80:20 acetonitrile:water mobile phase at a flow rate of 1 mL $min^{-1}$. Oxadiazon was determined in the isocratic mode by absorbance measurements at 292 nm using area values of the chromatogram peak obtained at a retention time of 10.37 min for samples and interpolating them in an external calibration line established from five oxadiazon standard solutions in acetonitrile in the concentration range 3.81–38.1 ppm measured in the same conditions as samples.

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## FTIR Recommended Procedure

Fifty milligrams sample was diluted with 7 g $CHCl_3$ and sonicated for 5 min. This solution was passed through an 0.22-μm nylon filter and then introduced in a FTIR measurement microflow cell by using a peristaltic pump. The spectra were obtained in the stopped-flow mode from 4000 to 850 $cm^{-1}$ at 4 $cm^{-1}$ nominal resolution and accumulating 25 scans per spectrum, each averaged spectrum requiring an acquisition time of 30.9 s. The background was established from the cell filled with the solvent.

Peak area values of the first-order derivative spectra between 1770 and 1774 $cm^{-1}$, corrected with a single point baseline established at 1950 $cm^{-1}$ after a 5-point smoothing, were employed to quantify oxadiazon. Data found from samples were interpolated in an external calibration line obtained with 5 standard solutions of the pesticide in the concentration range between 0.68 and 2.91 mg $g^{-1}$ and measured in the same conditions as samples.

# RESULTS AND DISCUSSION

## Absorbance Spectra of Oxadiazon

Examples of zero-order absorbance spectra from 4000 to 850 $cm^{-1}$ of both an oxadiazon standard dissolved in chloroform and an extract of a commercial sample are shown in Fig. 1.

The band located at 1782 $cm^{-1}$ is due to the carbonyl group, that at 1616 $cm^{-1}$ could be assignable to the -C=N-N group torsion, and the band observed at 1489 $cm^{-1}$ could be related to the O-CH group deformation from the aliphatic ether.[12]

Other characteristic bands appear at 1423 $cm^{-1}$ due to benzene ring torsions, 1327 $cm^{-1}$ corresponding with the interaction between $CH_3$ groups from *t*-butyl group, 1249 $cm^{-1}$ (aryl-O torsion from the aromatic ether), and 1040 $cm^{-1}$ (O-CH torsion from the aromatic ether, too).

Moreover, a series of bands at 1193, 1123, 1110, and 1094 $cm^{-1}$ corresponding with the several torsions of C-Cl bonds from the benzene ring could be identified.[12]

All the aforementioned bands are also present in the sample extract, and additional bands correspond with other formulation components as that of 1704 $cm^{-1}$, which corresponds with cyclohexanone, a usual co-formulated agent present in this kind of formulation.

## Selection of the Appropriate Bands for Oxadiazon Determination

In order to obtain the best analytical performance of the FTIR determination of oxadiazon in formulated samples, several peak area and peak height measurements using different baseline criteria were tested. Table 1 summarizes the most relevant results obtained.

In terms of sensitivity, it can be appreciate that peak area measurements provide one order of magnitude better sensitivity than peak height values and that the band at 1489 $cm^{-1}$ is that which provides the lowest accuracy errors. Because of this, peak area measurements between 1494 and 1482 $cm^{-1}$ corrected with a baseline point established at 1436 $cm^{-1}$ could be considered the

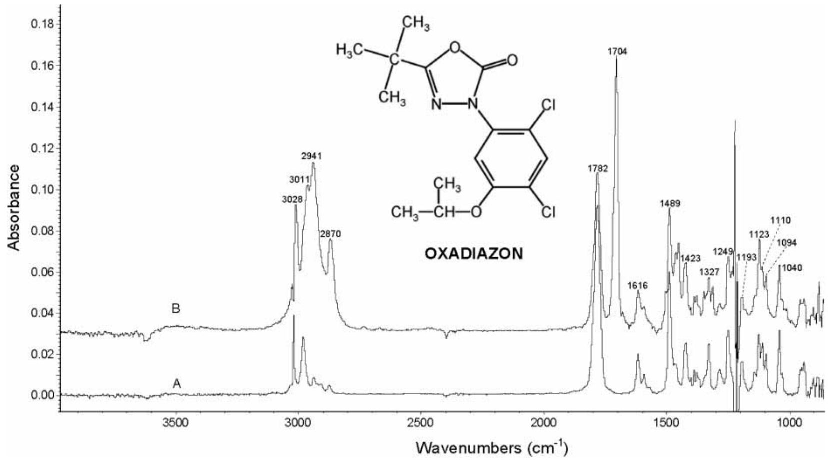

**FIGURE 1** Zero-Order Absorbance FTIR Spectra of an Oxadiazon Standard and a Sample Extract. (A) Spectra of a 1.63 mg $g^{-1}$ Oxadiazon Standard in $CHCl_3$ and (B) A Commercial Sample Extract. *Note*: Spectra were Shifted on the *y* Axis to Clearly Show their Bands. Inset: A Molecule of Oxadiazon. Instrumental Conditions: 25 Scans, 4 $cm^{-1}$ Nominal Resolution using a Background of the Cell Filled with $CHCl_3$.

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**TABLE 1** Analytical Characteristics of FTIR Determination of Oxadiazon in Agrochemicals Using Different Measurement Modes from Zero Order Absorbance Spectra

| Peak height/ area (cm$^{-1}$) | Baseline criteria (cm$^{-1}$) | Regression line $y = (a \pm s_a) + (b \pm s_b)\ C_{Oxa}$ | $r^a$ ($n = 15$) | RSD (%)$^b$ | LoD$^c$ (mg g$^{-1}$) | LoQ$^d$ (mg g$^{-1}$) | Oxadiazon concentration (% w/v)$^e$ |  | Accuracy error (%)$^f$ |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | FTIR | HPLC |  |
| 1782 | 1950 | $y = (-0.0010 \pm 0.0004) + (0.0405 \pm 0.0002)\ C_{Oxa}$ | 0.9998 | 0.15 | 0.004 | 0.012 | 26.48 ± 0.14 | 24.9 ± 0.2 | 6.4 |
|  |  |  |  |  |  |  | 26.20 ± 0.12 | 25.0 ± 0.2 | 4.8 |
|  |  |  |  |  |  |  | 26.46 ± 0.17 | 24.9 ± 0.3 | 6.3 |
| 1787–1777 | 1950–1550 | $y = (-0.009 \pm 0.004) + (0.442 \pm 0.002)\ C_{Oxa}$ | 0.9998 | 0.07 | 0.0007 | 0.0024 | 26.51 ± 0.12 | 24.9 ± 0.2 | 6.5 |
|  |  |  |  |  |  |  | 26.29 ± 0.11 | 25.0 ± 0.2 | 5.2 |
|  |  |  |  |  |  |  | 26.53 ± 0.10 | 24.9 ± 0.3 | 6.5 |
| 1489 | 1473 | $y = (0.0000 \pm 0.0002) + (0.01960 \pm 0.00014)\ C_{Oxa}$ | 0.9997 | 1.0 | 0.03 | 0.10 | 23.37 ± 0.15 | 24.9 ± 0.2 | −6.1 |
|  |  |  |  |  |  |  | 23.39 ± 0.18 | 25.0 ± 0.2 | −6.4 |
|  |  |  |  |  |  |  | 23.7 ± 0.3 | 24.9 ± 0.3 | −4.8 |
|  | 1436 | $y = (-0.0003 \pm 0.0003) + (0.02380 \pm 0.00014)\ C_{Oxa}$ | 0.9998 | 0.6 | 0.06 | 0.18 | 25.6 ± 0.3 | 24.9 ± 0.2 | 2.7 |
|  |  |  |  |  |  |  | 25.4 ± 0.11 | 25.0 ± 0.2 | 1.4 |
|  |  |  |  |  |  |  | 25.6 ± 0.2 | 24.9 ± 0.3 | 2.9 |
| 1494–1482 | 1473 | $y = (0.002 \pm 0.003) + (0.2003 \pm 0.0017)\ C_{Oxa}$ | 0.9995 | 1.2 | 0.04 | 0.12 | 22.7 ± 0.3 | 24.9 ± 0.2 | −8.8 |
|  |  |  |  |  |  |  | 22.75 ± 0.17 | 25.0 ± 0.2 | −9.0 |
|  |  |  |  |  |  |  | 23.0 ± 0.4 | 24.9 ± 0.3 | −7.5 |
|  | 1436 | $y = (-0.002 \pm 0.002) + (0.2571 \pm 0.012)\ C_{Oxa}$ | 0.9999 | 0.6 | 0.04 | 0.14 | 25.6 ± 0.2 | 24.9 ± 0.2 | 2.8 |
|  |  |  |  |  |  |  | 25.35 ± 0.07 | 25.0 ± 0.2 | 1.4 |
|  |  |  |  |  |  |  | 25.58 ± 0.12 | 24.9 ± 0.3 | 2.7 |
| 1423 | 1436 | $y = (0.00028 \pm 0.00015) + (0.00831 \pm 0.00008)\ C_{Oxa}$ | 0.9993 | 0.6 | 0.12 | 0.39 | 27.9 ± 0.3 | 24.9 ± 0.2 | 12 |
|  |  |  |  |  |  |  | 27.9 ± 0.3 | 25.0 ± 0.2 | 12 |
|  |  |  |  |  |  |  | 28.4 ± 0.4 | 24.9 ± 0.3 | 14 |
| 1428–1416 | 1436 | $y = (0.0005 \pm 0.0010) + (0.0853 \pm 0.0005)\ C_{Oxa}$ | 0.9997 | 1.5 | 0.07 | 0.22 | 26.9 ± 0.2 | 24.9 ± 0.2 | 8.2 |
|  |  |  |  |  |  |  | 27.0 ± 0.3 | 25.0 ± 0.2 | 8 |
|  |  |  |  |  |  |  | 27.4 ± 0.4 | 24.9 ± 0.3 | 10 |
| 1327 | 1363 | $y = (0.00030 \pm 0.00011) + (0.00912 \pm 0.00006)\ C_{Oxa}$ | 0.9997 | 0.5 | 0.04 | 0.13 | 26.9 ± 0.2 | 24.9 ± 0.2 | 8.1 |
|  |  |  |  |  |  |  | 26.7 ± 0.2 | 25.0 ± 0.2 | 6.9 |
|  |  |  |  |  |  |  | 27.0 ± 1.0 | 24.9 ± 0.3 | 8.2 |
| 1333–1321 | 1363 | $y = (0.0024 \pm 0.0011) + (0.0817 \pm 0.0006)\ C_{Oxa}$ | 0.9996 | 0.7 | 0.04 | 0.13 | 27.6 ± 0.3 | 24.9 ± 0.2 | 11 |
|  |  |  |  |  |  |  | 27.5 ± 0.3 | 25.0 ± 0.2 | 10 |
|  |  |  |  |  |  |  | 27.7 ± 1.1 | 24.9 ± 0.3 | 11 |

[a] Multiple correlation coefficient for a set of 15 standard measurements.

[b] Relative standard deviation for 3 independent measurements of a oxadiazon standard solution of 1.63 mg g$^{-1}$.

[c] Limit of detection established from three times (a probability level of 99.6%) the standard deviation of a blank solution divided by the slope of the calibration line.

[d] Limit of quantification values established as 10 times the standard deviation of a blank solution divided by the slope of the calibration line.

[e] Concentration values are the average of three independent analysis measured in triplicate ± the corresponding standard deviation of all values found for an emulsifiable concentrate formulation with a declared value of 25% w/v.

[f] Mean accuracy error (%) found from the comparison with result obtained by HPLC.

most appropriate criterion for the determination of oxadiazon.

Table 1 also reports the limit of detection (LOD) values found on using different bands. LOD values were established, as recommended by the IUPAC, as the pesticide concentration, which provides an absorbance value equal to 3 times the standard deviation of 10 measurements of a blank solution (99.6% confidence level). Additional indicators such as the r value, relative standard deviation (RSD), or limit of quantitation (LOQ) are also reported, confirming that the use of zero-order absorbance spectra of oxadiazon provides good linearity in the experimental conditions chosen with a LOD of 0.04 mg $g^{-1}$ and a LOQ of 0.14 mg $g^{-1}$ with RSD values of the order 0.6%.

However, the accuracy errors remain in the range +1.4% to +2.8% compared with data found by HPLC.

This fact could be due to the influence of formulation components that can be co-extracted with oxadiazon in $CHCl_3$ and can affect the sample spectra.

## First-order Derivative FTIR Measurements

The use of derivative spectra instead of zero-order ones in analytical spectroscopy is a single and easy way to correct for irrelevant background absorption and has been widely used in multicomponent analysis and to avoid matrix effects on selected bands.

Because of that, in the current study we evaluated the use of first-order derivative spectra to determine oxadiazon in sample extracts in order to avoid matrix effects that could be the reason for the high accuracy errors observed on using zero-order spectra.[13,14]

Figure 2 shows the first-order derivative spectra in the region 2000–1000 $cm^{-1}$of an oxadiazon standard dissolved in chloroform together with that of a chloroform extract of pesticide formulation sample.

As can be appreciated, in the derivative spectra the band intensity and consequently the signal-to-noise ratio decrease compared with the zero-order ones (see Fig. 1). In this sense, based on the previously obtained results, the carbonyl band at 1782 $cm^{-1}$ has been selected because of its high intensity for the determination of oxadiazon.

The inset in Figure 2 shows in detail the first-order derivative for carbonyl band in the spectral range compressed between 1870 $cm^{-1}$ and 1650 $cm^{-1}$ and for smoothed spectra.

Analytical features obtained using different measurement modes and baseline criteria are reported in Table 2. It can be observed that, based on first-order derivative spectra measurements, the accuracy errors were reduced significantly by a factor of three compared with the best results found with absorbance

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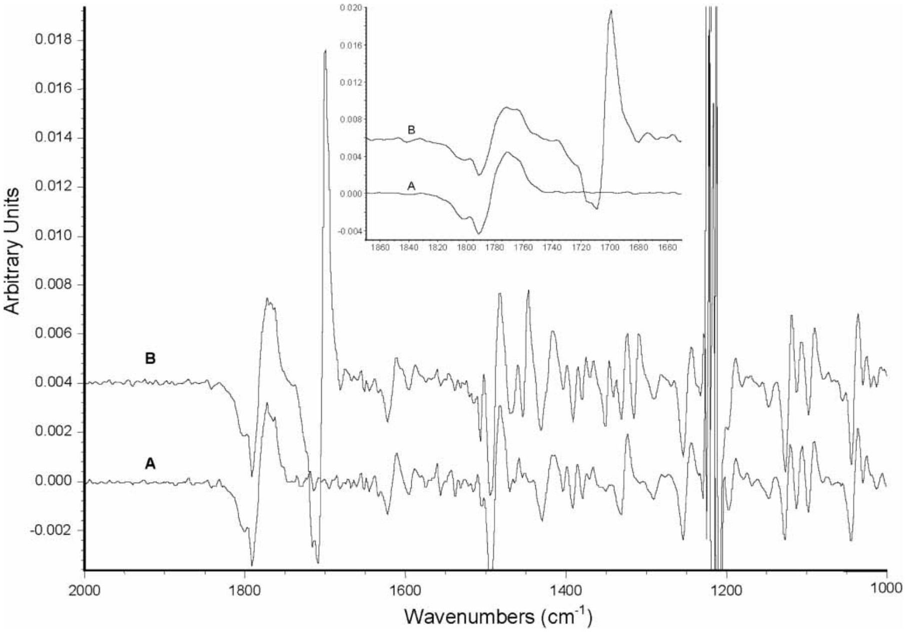

**FIGURE 2** First-Order Derivative FTIR Spectra of (A) An Oxadiazon Standard and (B) A Sample Extract. Inset: Detail of the Derivative Spectra in the Range between 1870 $cm^{-1}$ and 1650 $cm^{-1}$ after a 5-Point Smoothing. *Note*: Experimental Conditions as Indicated Fig. 1 legend.

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**TABLE 2** Analytical Features for the Determination of Oxadiazon in Emulsifiable Concentrate Formulates Based on First-Order Derivative Spectra of the Carbonyl Band

| Height/area ($cm^{-1}$) | Baseline criteria ($cm^{-1}$) | Regression line $y = (a \pm s_a) + (b \pm s_b)\,C_{Oxa}$ | $r^a$ ($n = 15$) | RSD (%)[b] | LoD[c] ($mg\,g^{-1}$) | LoQ[d] ($mg\,g^{-1}$) | Oxadiazon concentration (% w/v)[e] FTIR | Oxadiazon concentration (% w/v)[e] HPLC | Accuracy error (%)[f] |
|---|---|---|---|---|---|---|---|---|---|
| 1792 | 1950 | $y = -(-0.00002 \pm 0.00002) + (0.002001 \pm 0.000012)\,C_{Oxa}$ | 0.9998 | 2.2 | 0.03 | 0.10 | 24.4 ± 0.3 | 24.9 ± 0.2 | −2.2 |
| | | | | | | | 24.3 ± 0.4 | 25.0 ± 0.2 | −2.7 |
| | | | | | | | 24.4 ± 0.2 | 24.9 ± 0.3 | −2.0 |
| 1771–1773 | 1950 | $y = (-0.00017 \pm 0.00004) + (0.00374 \pm 0.00002)\,C_{Oxa}$ | 0.9998 | 2.2 | 0.03 | 0.11 | 25.2 ± 0.6 | 24.9 ± 0.2 | 1.1 |
| | | | | | | | 25.0 ± 0.4 | 25.0 ± 0.2 | −0.15 |
| | | | | | | | 25.3 ± 0.5 | 24.9 ± 0.3 | 1.4 |
| 1772 | 1950 | $y = (0.00001 \pm 0.00002) + (0.001998 \pm 0.000012)\,C_{Oxa}$ | 0.9998 | 2.2 | 0.06 | 0.20 | 24.4 ± 0.3 | 24.9 ± 0.2 | −2.2 |
| | | | | | | | 24.3 ± 0.4 | 25.0 ± 0.2 | −2.7 |
| | | | | | | | 24.4 ± 0.2 | 24.9 ± 0.3 | −2.0 |
| 1770–1774 | 1950 | $y = (-0.00006 \pm 0.00007) + (0.00729 \pm 0.00004)\,C_{Oxa}$ | 0.9998 | 1.6 | 0.04 | 0.13 | 24.7 ± 0.4 | 24.9 ± 0.2 | −0.9 |
| | | | | | | | 24.7 ± 0.3 | 25.0 ± 0.2 | −1.2 |
| | | | | | | | 24.73 ± 0.18 | 24.9 ± 0.3 | −0.7 |

*Note*: For details, see the footnotes of Table 1.

measurements for the band at 1489 $cm^{-1}$. Other quality parameters such as the linearity of the model fitting, the signal repeatability (evaluated for the RSD), the LOD, and the LOQ are also detailed in Table 2.

Ensuring a compromise between all the aforementioned parameters, the area measurements in the first-order derivative spectra, between 1770 $cm^{-1}$ and 1774 $cm^{-1}$ with a baseline correction point established at 1950 $cm^{-1}$, were selected to carry out the quantification of oxadiazon in herbicide formulates.

## Smoothing Treatment on First-Derivative FTIR Spectra of Oxadiazon

It can be noticed that for the successful application of differentiation in quantitative analytical applications, it is essential to use differentiation in combination with sufficient data smoothing in order to optimize the signal-to-noise ratio.[15] However, this treatment implies several drawbacks such as peak height reduction or peak shape modification.

To select the best smoothing conditions, we evaluated the effect of smoothing from 5 to 25 points on the analytical features of oxadiazon determination.

The results obtained are reported in Table 3. As it can be seen, a slight improvement in accuracy errors was achieved when 5-point smoothing correction treatment was applied. In short, the use of first-order derivative smoothed data reduces the accuracy errors (relative values in %) to a range between +0.15% and −0.6%.

## Analytical Figures of Merit of the Proposed Procedure

In addition to reported features, we evaluated the recovery percentage of added oxadiazon on commercial samples spiked with different amounts of this pesticide from 1.38 to 3.75 mg $g^{-1}$, and the average recovery of oxadiazon was 101.5 ± 0.8%.

The absence of matrix effects was confirmed by comparing the slopes of external calibration and standard addition regression lines. The equations obtained in the same measurement session were $y = (0.01086 \pm 0.00004) + (0.00756 \pm 0.00003)C_{Oxa}\,mg\,g^{-1}$ with $r = 0.9999$ ($n = 18$) and $y = (0.00008 \pm 0.00003) + (0.007596 \pm 0.000016)C_{Oxa}\,mg\,g^{-1}$ with $r = 0.99996$ ($n = 18$), for the standard addition and external

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**TABLE 3** Effect of Smoothing of the First-Order Derivative Spectra on the Analytical Features of the FTIR Determination of Oxadiazon

| Smooth points | Dataspacing ($cm^{-1}$)[a] | Spectral range ($cm^{-1}$) | Regression line $y = (a \pm s_a) + (b \pm s_b)\ C_{Oxa}$ | $r$ ($n = 15$) | RSD (%)[b] | LOD ($mg\ g^{-1}$) | LOQ ($mg\ g^{-1}$) | Oxadiazon concentration (% w/v) |  | Accuracy error (%) |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  |  | FTIR | HPLC |  |
| 5 | 9.642 | 1770–1774 | $y = (-0.00009 \pm 0.00007) + (0.00721 \pm 0.00004)\ C_{oxa}$ | 0.9998 | 1.3 | 0.03 | 0.10 | 24.8 ± 0.3 | 24.9 ± 0.2 | − 0.4 |
|  |  |  |  |  |  |  |  | 24.9 ± 0.3 | 25.0 ± 0.2 | − 0.6 |
|  |  |  |  |  |  |  |  | 24.94 ± 0.15 | 24.9 ± 0.3 | 0.15 |
| 7 | 13.500 | 1769–1773 | $y = (-0.00042 \pm 0.00011) + (0.00730 \pm 0.00006)\ C_{oxa}$ | 0.9996 | 1.0 | 0.02 | 0.08 | 25.1 ± 0.5 | 24.9 ± 0.2 | 0.9 |
|  |  |  |  |  |  |  |  | 25.0 ± 0.3 | 25.0 ± 0.2 | −0.13 |
|  |  |  |  |  |  |  |  | 25.3 ± 0.5 | 24.9 ± 0.3 | 1.6 |
| 9 | 17.357 | 1769–1773 | $y = (-0.00036 \pm 0.00009) + (0.00722 \pm 0.00005)\ C_{oxa}$ | 0.9997 | 0.6 | 0.02 | 0.07 | 25.3 ± 0.5 | 24.9 ± 0.2 | 1.5 |
|  |  |  |  |  |  |  |  | 25.1 ± 0.2 | 25.0 ± 0.2 | 0.4 |
|  |  |  |  |  |  |  |  | 25.4 ± 0.4 | 24.9 ± 0.3 | 2 |
| 11 | 21.213 | 1768–1772 | $y = (-0.00029 \pm 0.00008) + (0.00721 \pm 0.00004)\ C_{oxa}$ | 0.9998 | 0.3 | 0.011 | 0.04 | 25.4 ± 0.4 | 24.9 ± 0.2 | 1.8 |
|  |  |  |  |  |  |  |  | 25.12 ± 0.18 | 25.0 ± 0.2 | 0.5 |
|  |  |  |  |  |  |  |  | 25.5 ± 0.3 | 24.9 ± 0.3 | 2 |
| 17 | 32.784 | 1768–1772 | $y = (-0.00020 \pm 0.00007) + (0.00723 \pm 0.00004)\ C_{oxa}$ | 0.9998 | 0.17 | 0.002 | 0.008 | 25.76 ± 0.11 | 24.9 ± 0.2 | 3 |
|  |  |  |  |  |  |  |  | 25.34 ± 0.14 | 25.0 ± 0.2 | 1.3 |
|  |  |  |  |  |  |  |  | 25.66 ± 0.18 | 24.9 ± 0.3 | 3 |
| 25 | 48.212 | 1766–1770 | $y = (-0.00009 \pm 0.00005) + (0.00628 \pm 0.00003)\ C_{oxa}$ | 0.9999 | 0.17 | 0.010 | 0.03 | 25.62 ± 0.07 | 24.9 ± 0.2 | 3 |
|  |  |  |  |  |  |  |  | 25.35 ± 0.10 | 25.0 ± 0.2 | 1 |
|  |  |  |  |  |  |  |  | 25.62 ± 0.15 | 24.9 ± 0.3 | 3 |

[a] Wavenumber range employed by the software for the adjust at the polynomial function for a nominal resolution of 4 $cm^{-1}$.

*Note*: For details about the rest of parameters see footnotes in Table 1.

calibration, respectively; observing that the slope values of these lines are statistically comparable.

Moreover, in the aforementioned conditions, results obtained for three different herbicide formulates were statistically comparable for a probability level of 99.5% with those obtained by HPLC.

## CONCLUSIONS

From the results obtained, it can be concluded that the FTIR procedure developed is a simple, fast, accurate, and environmentally friendly alternative to HPLC methods for the quality control analysis of herbicide formulates containing oxadiazon.

Both the reagents consumed and waste generation were minimized, and the FTIR procedure used only 4.8 mL chloroform instead of 35 ml acetonitrile per sample analyzed.

In spite of the fact that HPLC provides a LOD of 0.022 $\mu$g mL$^{-1}$ for oxadiazon, which is three orders of magnitude lower than that found by FTIR, it can be concluded that relatively low sensitivity associated with FTIR spectrometry is not a problem in the analysis of pesticide formulations that contain the active ingredient at a percentage level.

The FTIR procedure developed in this work provides statistically comparable results with those obtained by HPLC, for a probability level of 95%, and permits a measurement sampling throughput of 116 h$^{-1}$, nearly 20 times higher than that found by HPLC, which is the order of 6 h$^{-1}$.

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