

Fighting counterfeit pesticides using mid-infrared spectroscopy and chemometrics

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ABSTRACT

The use of pesticides, which are essential for agriculture and public health, poses risks when they are of out of specification or counterfeited, as they may be ineffective, toxic, or harmful to human and animal health, crops, and the environment. Traditionally, the characterisation and authentication of pesticide formulations have relied on chromatographic and mass spectrometric techniques, which provide high analytical accuracy but are often limited by their operational complexity, elevated costs and extensive sample preparation. These limitations have prompted growing interest in complementary analytical methodologies, as those based on vibrational spectroscopy. Among these, Fourier Transform Mid-Infrared (FT-MIR) spectroscopy has emerged as a powerful and versatile green analytical approach due to its high sensitivity, molecular specificity, non-use of reactive and non-destructive nature. The present study explores the application of FT-MIR as an effective analytical tool for combating pesticide counterfeiting. In this work, FT-MIR is combined with the development of an extensive spectral library and the implementation of a completed, hierarchical chemometric protocol. This methodology has been applied and validated in blind using a set of simulated counterfeit samples as well as with a real-world case with three samples supplied by a private pesticide manufacturer, thereby demonstrating its potential for routine quality control and regulatory surveillance of pesticide products.

1. Introduction

Plant protection products are used to protect crops from pests, diseases, and weeds [1–3]. They play an important role in the agricultural production systems, whether in conventional farming, integrated pest management, or organic farming (biopesticides, biocontrol products). Pesticides are used to protect plant, humans, animals, and materials from harmful organisms such as pests (insects, rodents...) and micro-organisms (fungi, bacteria) in buildings and facilities. They are essential for public health as they are used in particular to control disease vectors and infections. They are also used to protect materials such as plastics, paints, textiles, and wood against insects, microbes, and fungi. However, pesticides products must meet minimal physical-chemical quality thresholds to prevent risks for the human and animal health, the environment and the biodiversity [4].

The physical and chemical properties of pesticides influence their biological effectiveness and the risks they may pose to users, consumers,

and the environment. Poor-quality pesticides may pose problems in term of biological effectiveness, may be phytotoxic to treated plants and may be hazardous to health and the environment [5].

Counterfeit pesticides are fake products often manufactured and packaged to look like the legal product, but their composition may not match their label. Counterfeit products may have less active substance than the legal version or they may contain cheaper co-formulants, which are either banned or restricted in the EU, due to the potential risks they may pose to human health and/or the environment. They can also contain untested products and undeclared active substances that may result in unacceptable residue levels, making the crop products unmarketable. Because of this, counterfeit pesticides can be ineffective or dangerous to humans, animals and the environment. The use of counterfeit and illegal pesticides can pose very real risks to farmers, the environment and the health of crops. Unlike legal, registered products, spurious pesticides could contain unknown toxic impurities and have not been tested for human health impact. The impact of the trade of

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illegal and counterfeit pesticides in the European Union is well described in the recommendations issued by international organizations [6–9].

The widespread availability of technology needed to produce counterfeit and illegal pesticides, coupled with the lack of enforcement of existing laws and legislative loopholes all contribute to facilitate the trade of counterfeit products [10], which has become a very lucrative business, generating over €1 billion a year in Europe, and amounting to an estimated 9–14% of the European market. According to the European Anti-Fraud Office (OLAF), approximately 13.8% of all pesticides sold in EU in 2021 are counterfeits. In June that year, the EU's law enforcement agency (Europol) seized >1200 tonnes of illegal pesticides of which 100 tonnes of counterfeit pesticides seized at seller, manufacturer and logistics companies and 82 tonnes of pesticides suspected of being counterfeited. Again, in 2022, the seventh edition of Silver Axe, Europol's annual operation targeting illegal pesticides focused on ports, airports and other entry points led to the seizure of almost 5 000 tonnes of illegal and counterfeit pesticides and the targeting of a factory where pesticides were being counterfeited [11].

Complicating efforts to stop illicit trade in pesticides is the fact that they are increasingly being listed online on e-commerce platforms by unlicensed sellers. Despite the heavy regulations on pesticide trade, listings of unauthorized, banned and counterfeit pesticides can be found on virtually every e-commerce platform [9]. As an example, in December 2021, Amazon was fined USD 2.5 million as part of a settlement with the Washington state Attorney General for selling illicit pesticides that were highly toxic and restricted for use [12].

Assessment of pesticide formulations and fight against counterfeiting are currently carried out on a case-by-case basis, usually based on suspicion. Currently, the European procedures for approving active substances and zonal authorisation of formulations are already highly harmonised. The same formulation can therefore be authorised in several European Member States by national authorisation acts.

A critical requirement for pesticide monitoring is to have a well-established validated and standardized analytical method [13]. The detection and quantification technology of choice must possess several key characteristics, such as excellent sensitivity, accuracy and reproducibility. During the last decades, these important detection characteristic requirements have been fulfilled by various chromatographic based techniques (such as LC/GC–MS, HPLC, GC and TLC). In the literature, pesticides have been studied and analysed by different methods and equipment [14], such as gas chromatography (GC) [13,15,16] or liquid chromatography (HPLC) [13,17–20], both having advantages in the low limit of detection et accurate quantification of the active substance. Also, mass spectrometry (MS) is classically [21,22], among others. However, one of the drawbacks of these techniques, it is that they are time consuming, not environmentally friendly, they require a variety of sample extraction and preparation techniques, a variety of chromatographic conditions, and they are very specific methods, i.e. a certain group of pesticides can only be analysed/detected on a certain equipment or detector. Even though these methods have been evolving gradually to improve their detection capabilities, other detection technologies have also emerged that promise added benefits, such as faster detection times, simpler protocols, in situ sampling, reduced cost and portability. Those technologies include the use of vibrational spectroscopy methods. Methods such as NIR spectroscopy [23,24] have been used to develop analytical strategies capable of controlling pesticide authenticity using a simple spectral matching at a collected database or to determine prohibited components in pesticides. However, NIR spectroscopy has the drawback of low sensitivity, as the combination bands of molecular vibrations obtained are relatively weak compared to fundamental vibrations observed in mid-infrared (MIR) spectroscopy. Even if NIR involves overtone and combination bands that are intrinsically weaker than the fundamental vibrations observed in MIR, its analytical sensitivity in practical applications is often enhanced by the use of chemometric and multivariate data analysis techniques. Raman spectroscopy [25] have been used to develop an analytical tool for

routine analysis of some pesticide formulations [26] or to detect pesticide residues [27–30], among others. Moreover, Dias et al. constructed a database with Raman spectra of the main commercial pesticides currently used and they make it available to the scientific community [31]. An important advantage of the Raman technology is that the samples can be analysed through most of the transparent containers avoiding contact with the toxic substances. NIR shares this advantage only after carefully choosing the wavelength and calibrating the system while taking the container into account. However, the Raman technology may not be applicable for sensitive detection due to the inherently weak Raman signals. Even though alternative solutions have been proposed in the literature to improve this signal, such as the use of surface-enhanced Raman scattering (SERS) [32–36], the use of this technique remains limited due to the fact that many pesticide samples show fluorescence emission, regardless of the type of formulation, although it is mostly observed in granular and liquid samples. This causes a real limitation when proposing a direct method of analysis.

To cope with the drawbacks of NIR and Raman, among the vibrational spectroscopic techniques, Mid-infrared (MIR) or Fourier Transform Infrared (FT-MIR) spectroscopy has emerged as a powerful tool in the detection and analysis of counterfeit pesticides due to its sensitivity and specificity (the fundamental vibrations observed are stronger than in the case of NIR). In this direction FT-MIR has been shown to be effective for pesticide residues detection [37,38]. Also, for the determination of illegal substances in commercial pesticides, such as thiram and ziram [39], folpet and metalaxyl [40], malathion [41], diuron [42] and metamitron [43], among others. FT-MIR has been, recently, also be used for the determination of fungicides such as carbendazim or mancozeb [44] or for the monitoring of the counterfeit situation of pesticides [45].

This paper aims to show how FT-MIR, a solvent-free and thus green screening technology, can be a valuable tool for detecting counterfeit pesticides by offering high sensitivity, molecular specificity and non-destructive analysis to accurately identify active substances, detect modifications brought to an original formulation and ensure quality control. To this end, in a first part of this work, a complete FT-MIR spectral library of legal pesticide formulations and active substances has been established and used to develop a complete chemometric protocol including three steps based on multivariate analysis tools. In a second part of this work, this methodology has been applied and validated in blind using a set of simulated counterfeit samples as well as with a real case with three samples supplied by a private pesticide manufacturer. The aim is not to provide quantitative concentration values when detecting adulterants but making a fast methodology combining FT-MIR and simple chemometric tools to differentiate between authentic and adulterated pesticide formulations.

2. Material and methods

2.1. Principles of mid-infrared spectroscopy and instrumentation

Mid-infrared spectroscopy operates in the wavelength range of approximately 2.5 to 25 μm (4000 to 400 cm^{-1}). It is based on the absorption of infrared light by molecular bonds within a sample. When molecules absorb infrared light at specific wavelengths, they undergo transitions between vibrational energy levels. The resulting absorption spectrum is characteristic of the molecular composition and structure of the sample. MIR spectroscopy is characterized by its high sensitivity and its capacity to provide detailed information about molecular structures and functional groups.

Several techniques and types of instrumentation can be used in MIR spectroscopy for pesticide analysis. The most popular one, due to its high resolution and sensitivity is Fourier Transform Infrared (FT-MIR) Spectroscopy. It collects data over a wide spectral range, providing detailed information about the sample. Usually, FT-MIR is associated with Attenuated Total Reflectance (ATR) presentation technique. ATR- FT-

MIR is a popular technique for analyzing solid and liquid samples with minimal preparation. Alternatively, Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy (Fuller and Griffiths, 1978) can be used for analyzing powders and heterogeneous samples.

In this work, FT-MIR spectra were collected with the Attenuated Total Reflectance (ATR) 'Platinum' accessory, a single reflection monolithic diamond integrated into a Vertex 70 spectrometer (Bruker Optics, Ettlingen, Germany). It is a simple technique that can be

Table 1

list of the 38 blind samples including pure formulations (in white), formulations adulterated with solvents (in light grey and pure adulterants (in dark grey). The first column represents the sample number, the second column the formulation, the third column the manufacturing batch, the fourth column the formulation code, the fifth column the nominal content in the active substance composition, the sixth column the function of the formulation and the seventh column the percentage of adulteration (if any).

Sample Number	Formulation	Manufacturing Batch	Formulation Code	Active Substance and Nominal Content	Function	Percentage of adulteration
01	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	0%
02	CARYX	batch 1	SL	30 g/L metconazole, 210 g/L mepiquat chloride	Fungicide / Plant Growth Regulator	0%
03	REMOCCO 60	batch 2	EC	60 g/L metconazole	Fungicide	0%
04	CARAMBA	batch 2	EC	60 g/L metconazole	Fungicide	0%
05	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 50% xylene
06	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 50% DMSO
07	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 50% isooctane
08	CARYX	batch 1	SL	30 g/L metconazole, 210 g/L mepiquat chloride	Fungicide / Plant Growth Regulator	+ 50% water
09	REMOCCO 60	batch 1	EC	60 g/L metconazole	Fungicide	+ 10% isooctane
10	CARAMBA	batch 1	EC	60 g/L metconazole	Fungicide	+ 10% isooctane
11	LIBRAX	batch 1	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	0%
12	REMOCCO 60	batch 1	EC	60 g/L metconazole	Fungicide	0%
13	CARAMBA	batch 1	EC	60 g/L metconazole	Fungicide	0%
14	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 10% xylene
15	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 10% DMSO
16	LIBRAX	batch 2	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 10% isooctane
17	CARYX	batch 1	SL	30 g/L metconazole, 210 g/L mepiquat chloride	Fungicide / Plant Growth Regulator	+ 10% water
18	LIBRAX	batch 1	EC	62.5 g/L fluxapyroxad, 45 g/L metconazole	Fungicide	+ 10% isooctane
19	REMOCCO 60	batch 2	EC	60 g/L metconazole	Fungicide	+ 10% isooctane
20	CARAMBA	batch 2	EC	60 g/L metconazole	Fungicide	+ 10% isooctane
21	XYLENE	batch 1	-			100%
22	DMSO	batch 1	-			100%
23	ISO-OCTANE	batch 1	-			100%
24	SULFOSULFURON 75 WG	batch 1	WG	75% w/w sulfosulfuron	Herbicide	0%
25	SULFOSULFURON 80 WG	batch 1	WG	80% w/w sulfosulfuron	Herbicide	0%
26	SULFOSULFURON 80 WG	batch 1	WG	80% w/w sulfosulfuron	Herbicide	+ 50% CAPRI TWIN
27	MONITOR	batch 1	WG	80% w/w sulfosulfuron	Herbicide	0%
28	SULFOSULFURON 80 WG	batch 1	WG	80% w/w sulfosulfuron	Herbicide	+ 75% CAPRI TWIN
29	CAPRI TWIN	batch 1	WG	cloquintocet-mexyl, florasulam, pyroxulam	Herbicide	0%
30	Blank of PROTENDO EXTRA	batch 1	EC	all the coformulants without active substance		100%
31	PROSARO	batch 1	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	0%
32	AVIATOR XPRO	batch 1	EC	75 g/L bixafen, 150 g/L prothioconazole	Fungicide	0%
33	PROSARO	batch 1	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	+ 50% blank
34	AVIATOR XPRO	batch 1	EC	75 g/L bixafen, 150 g/L prothioconazole	Fungicide	+ 50% blank
35	PROTENDO EXTRA	batch 1	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	0%
36	PROSARO	batch 2	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	0%
37	PROTENDO EXTRA	batch 1	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	+ 50% blank
38	PROSARO	batch 2	EC	125 g/L prothioconazole, 125 g/L tebuconazole	Fungicide	+ 50% blank

routinely applied during inspections. This ATR accessory allowed analyzing liquids and powders and obtaining spectra of high quality through the use of an integrated press accessory. For powders, around 10 mg of the sample were deposited directly on the crystal and pressed against it to ensure optimum contact with the diamond. For liquids, around 20 μl were deposited directly on the crystal without the press step. Each spectrum was the average spectrum of 64 scans. The spectra ranged from 4000 to 600 cm^{-1} and the data were collected with a spectral resolution of 4 cm^{-1} . Analyses have been done in triplicate after acquiring the spectrum of the background (ambient air). The triplicate spectra were averaged to obtain one spectrum per sample. The MIR data obtained in this study are of high quality and the preprocessing approaches evaluated did not lead to any performance improvement, so the results presented in this work are obtained without any preprocessing method.

OPUS software (version 7.8) was used for MIR spectra recording as well as data treatment together with R(t-SNE).

2.2. Sample material

In a first step a complete library of FT-MIR spectra of different samples was collected to screen a variety of pesticide formulations that are authorized on the Belgian market. In total, 459 pesticides samples were available to build this spectral library. From those, 205 samples belong to the Walloon Agricultural Research Centre (CRA-W) sample bank including herbicides, insecticides and fungicides. These products are mainly used on field crops in the framework of biological efficacy studies. These are authentic authorized products obtained directly from the plant protection companies or distributors. For some products, several samples belonging to different batches have been obtained during the last 3 years. These samples were submitted by plant protection companies to perform studies conducted under a quality assurance system and were therefore considered genuine. Moreover 254 samples have been supplied by the Belgian Federal Agency for the Safety of the Food Chain (FASFC). These samples were collected in the framework of its control programs on pesticide formulations. The samples that were not originating from companies and regulatory contexts were subjected to chromatographic confirmation. The conclusions of the spectroscopic rapid screening were confirmed by a GC-MS screening / profiling of volatile compounds (active substances, co-formulants and impurities), and by a LC-HRMS (Q-TOF) exploratory determination of high-molecular weight compounds. A group of 38 samples has been sent to FT-MIR analysis in blind as a real external validation set. Table 1 shows the composition of those samples. 15 samples correspond to original formulations (in white), 19 samples correspond to the formulations internally adulterated with 10% or 50% solvent in order to mimic counterfeiting (in light grey); and the 4 remaining samples (in dark grey) correspond to the adulterating solvents (xylene, dimethyl sulfoxide, isooctane, water). The 10% and 50% adulterations levels with solvents were selected to evaluate the sensitivity of the spectrometric method and to detect modifications that would trigger further analytical confirmation. These adulteration levels were considered “economically valuable” for a counterfeiter. The relevant regulatory guidelines (“Guidance document on significant and non-significant changes of the chemical composition of authorised plant protection products under Regulation (EC) No 1107/2009 of the EU Parliament and Council on placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC.” SANCO/12,638/2011” and the “Guidance document on significant and non-significant changes of the chemical composition of authorised plant protection products under Regulation (EC) No 1107/2009 of the EU Parliament and Council on placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. SANCO/12,638/2011) give some recommendations on acceptable changes and on modifications that would indicate a major change of the formulation. The nature of the samples has not been communicated before analysis to

mimic the conditions of an actual control (unknown samples). The aim of the tests was the comparison of new samples to reference samples already available in the data libraries.

In addition, three other samples were subjected to FT-MIR analysis. These samples, supplied by a private pesticide manufacturer, reflect a real-world case study comprising: (i) an original, legally registered formulation (SP1 in Table 2; MOVENTO, containing spirotetramat as the active substance); (ii) an authorized parallel trade product (SP2; VSM SPIROTETRAMAT, equivalent to MOVENTO); and (iii) a suspicious formulation (SP3; falsely declared as a parallel trade product equivalent to MOVENTO). All samples were analysed under blind conditions, being treated as unknown formulations to objectively assess the discriminatory capability of the FT-MIR method.

2.3. Data treatment / chemometric approach

Several chemometric approaches were implemented, and a three-step protocol was established to ensure the systematic treatment and interpretation of data derived from the FT-MIR spectroscopic analysis of the samples:

- 1) The first step in this protocol is the use of a LOCAL-based method: the Bruker search algorithm. Bruker Optics' new band-based algorithm can be used for both: searching for a pure component or searching for a single component within a mixture. This is only possible, because of the band-based search algorithm, where the band positions are used to find matches in the database. A unique three level database search compares the band position, relative intensities and the band half width. The algorithm enhances the influence of spectral regions characterized by distinct absorption bands, while down-weighting areas lacking significant spectral information. Local analytical performance is evaluated through a scoring metric, where scores above 990 denote acceptable analytical quality, and values below this threshold identify samples requiring further investigation. This threshold was empirically established based on the set of pure pesticide formulation samples, selecting the value that allowed correct identification of all reference samples. This threshold was subsequently applied to the entire dataset. While no specific bibliographic reference supports this choice, the approach is data-driven and ensures methodological consistency.
- 2) Once the Bruker search suggests a potential match for a given sample, the result must be subsequently validated. The second step therefore involves the application of the exploratory technique t-SNE (t-distributed Stochastic Neighbor Embedding) [46]. This dimensionality reduction method enables visualization of the intrinsic structure of multivariate data in a two-dimensional space, where the likelihood of two points being located in proximity is determined by the spectral similarity between the corresponding samples.
- 3) The third step consists of applying another exploratory visualization tool, Principal Component Analysis (PCA). This multivariate statistical technique transforms the original correlated variables into a reduced set of uncorrelated variables, known as principal components (PCs), which are linear combinations of the initial features. The PCs are ordered by decreasing explained variance, with the first components capturing most of the variability within the dataset. As PCA was selected as a visualization tool, different combinations of PCs were explored. An optimal number of principal components was not defined, as the method was not intended for model construction but only for data visualization.

Python 3.12 (using the scikit-learn library) was used for PCA and t-SNE analyses.

When required, spectral visualization is additionally carried out to aid interpretation.

Table 2

Three samples representing a real case counterfeiting scenario. The first column represents the sample number, the second column the formulation name, the third the formulation code, the fourth column the nominal content in active substance composition, the fifth column the function and the sixth column includes information about the legal status of the samples.

Sample Number	Formulation	Formulation Code	Active Substance and Nominal Content	Function	Legal status of the samples
SP1	MOVENTO	SC	100 g/L spirotetramat	insecticide	Legitimate authorized original product
SP2	VSM SPIROTETRAMAT	SC	100 g/L spirotetramat	insecticide	Legitimate authorized parallel trade product
SP3	Labeled as SPIROMAT	SC	Labeled as 100 g/L spirotetramat	insecticide	Suspicious product

3. Results

All available samples were analysed using the FT-MIR system described in [Section 3.1](#), following standardized acquisition parameters. For each individual sample, three independent spectral replicates were recorded under identical instrumental conditions. This approach was adopted to enhance measurement reliability, minimize random instrumental noise, and account for potential sample heterogeneity or variability arising from differences in physical state, surface texture or

moisture content.

The resulting dataset comprises a comprehensive spectral library including the FT-MIR spectra of all 459 samples described in [Section 2.2](#), accompanied by the corresponding metadata (e.g., sample identification code, trade name, formulation type, function, production year, provider and active substance content). All spectra were stored in their raw and pre-processed forms to enable subsequent chemometric analysis. Data acquisition, management, and preliminary processing (including pre-processing and spectral quality evaluation) were performed using the

Table 3

Results obtained after the application of the three-step chemometric protocol to the FT-MIR spectra of the 38 validation samples.

Sample description			Results of the three-step chemometric protocol on the FT-MIR data			
Sample Number	Formulation	Percentage of adulteration	OPUS score	Results based on target OPUS score > 990	Results based on t-SNE, PCA and visualisation of spectra	Found adulterant
01	LIBRAX	0%	1000	PASS	Detected as LIBRAX	-
02	CARYX	0%	980	FAIL	Detected as CARYX	-
03	REMOCCO 60	0%	999	PASS	Detected as CARAMBA	-
04	CARAMBA	0%	999	PASS	Detected as CARAMBA	-
05	LIBRAX	+ 50% xylene	684	FAIL	Detected as adulterated LIBRAX	xylene
06	LIBRAX	+ 50% DMSO	690	FAIL	Detected as adulterated LIBRAX	DMSO
07	LIBRAX	+ 50% isooctane	966	FAIL	Detected as adulterated LIBRAX	-
08	CARYX	+ 50% water	654	FAIL	Detected as adulterated CARYX	water
09	REMOCCO 60	+ 10% isooctane	989	FAIL	Detected as adulterated CARAMBA	-
10	CARAMBA	+ 10% isooctane	989	FAIL	Detected as adulterated CARAMBA	-
11	LIBRAX	0%	999	PASS	Detected as LIBRAX	-
12	REMOCCO 60	0%	999	PASS	Detected as CARAMBA	-
13	CARAMBA	0%	999	PASS	Detected as CARAMBA	-
14	LIBRAX	+ 10% xylene	903	FAIL	Detected as adulterated LIBRAX	-
15	LIBRAX	+ 10% DMSO	891	FAIL	Detected as adulterated LIBRAX	DMSO
16	LIBRAX	+ 10% isooctane	997	PASS	Detected as adulterated LIBRAX	-
17	CARYX	+ 10% water	939	FAIL	Detected as adulterated CARYX	water
18	LIBRAX	+ 10% isooctane	982	FAIL	Detected as adulterated LIBRAX	-
19	REMOCCO 60	+ 10% isooctane	989	FAIL	Detected as adulterated CARAMBA	-
20	CARAMBA	+ 10% isooctane	989	FAIL	Detected as adulterated CARAMBA	-
21	xylene	100%	430	FAIL	Detected as xylene	-
22	DMSO (dimethyl sulfoxide)	100%	890	FAIL	Detected as dimethyl sulfoxide	-
23	isooctane	100%	740	FAIL	Detected as isooctane	-
24	SULFOSULFURON 75 WG	0%	862	FAIL	Detected as MONITOR	-
25	SULFOSULFURON 80 WG	0%	957	FAIL	Detected as MONITOR	-
26	SULFOSULFURON 80 WG	+ 50% CAPRI TWIN	852	FAIL	Detected as adulterated MONITOR	CAPRI TWIN
27	MONITOR	0%	998	PASS	Detected as MONITOR	-
28	SULFOSULFURON 80 WG	+ 75% CAPRI TWIN	483	FAIL	Detected as adulterated MONITOR	CAPRI TWIN
29	CAPRI TWIN	0%	948	FAIL	Detected as CAPRI TWIN	-
30	Blank of PROTENDO EXTRA	100%	740	FAIL	No match found	-
31	PROSARO	0%	993	PASS	Detected as PROSARO	-
32	AVIATOR XPRO	0%	999	PASS	Detected as AVIATOR XPRO	-
33	PROSARO	+ 50% blank	940	FAIL	Detected as adulterated PROSARO	PROTENDO EXTRA blank
34	AVIATOR XPRO	+ 50% blank	968	FAIL	Detected as adulterated AVIATOR XPRO	PROTENDO EXTRA blank
35	PROTENDO EXTRA	0%	997	PASS	Detected as PROSARO	-
36	PROSARO	0%	993	PASS	Detected as PROSARO	-
37	PROTENDO EXTRA	+ 50% blank	947	FAIL	Detected as adulterated AVIATOR XPRO	PROTENDO EXTRA blank
38	PROSARO	+ 50% blank	939	FAIL	Detected as adulterated PROSARO	PROTENDO EXTRA blank

OPUS 8.7 software package (Bruker Optics GmbH, Ettlinger, Germany).

The remaining samples were analysed under blind conditions using the FT-MIR system, including both the set of 38 test samples and the three formulations originating from the real-case scenario. The acquired spectra were subsequently processed following, in a hierarchical way, the three-step chemometric protocol combining spectral database matching and multivariate data exploration. In a first step, all the spectra were projected to the Bruker LOCAL band-search algorithm to identify potential spectral matches based on band position, relative intensity, and half-width. Only spectra achieving similarity scores above 990 were considered to meet the threshold for acceptable analytical quality, whereas samples scoring below this value did not correspond to what was expected. In a second step and for all the samples to be predicted, t-SNE was used to visualize spectral similarities and clustering patterns in two-dimensional space. And finally, PCA was performed to examine variance structure and confirm grouping trends. The combined interpretation of these three analytical steps of the chemometric protocol yielded the final classification outcome for each sample. The results obtained by t-SNE were consistent with those obtained using PCA and did not provide additional relevant information. Therefore, the corresponding plots were not included in the paper.

3.1. Results obtained for the blind original and adulterated samples

The results presented in Table 3 summarize the outcomes obtained from the analysis of the three-step chemometric protocol for the 38 blind samples. The first column lists the sample numbers, while the second and third columns indicate the original formulation and the percentage of adulterant (if present), respectively. The subsequent four columns summarize the outcomes from the three-step protocol. Column 4 reports the OPUS score, which quantifies the degree of similarity or correspondence between the sample to be predicted and the reference samples

stored in the database, obtained after the first step of the protocol. Column 5 specifies whether the sample passes or fails this step. Samples with an OPUS score larger than 990 are considered to meet the expected criteria, whereas those with scores below this threshold are classified as failing. Column 6 presents the results derived from the steps 2 and 3 of the defined protocol. Finally, column 7 indicates the adulterant found using the protocol, if any.

Samples indicated in grey correspond to cases in which the classification algorithm assigned the sample to a formulation category that did not correspond to its verified identity, or where the specific adulterant could not be determined, or both.

As can be seen in Table 3, most of the formulations have been correctly identified. Fig. 1 illustrates several representative cases in which the three-step chemometric protocol effectively identified the formulation names of unknown samples. Each figure presents the FT-MIR spectrum obtained for a given sample (01 and 31 respectively) together with its corresponding original formulation from the spectral database. The strong spectral resemblance observed across spectra clearly demonstrates the capacity of the protocol to detect a certain formulation. All these samples achieved similarity scores exceeding 990 and the complementary visualizations based on PCA and t-SNE provide additional insight into the positioning of the samples to be predicted relative to the formulations included in the spectral database. The close spatial clustering of the unknown samples with their corresponding formulation groups supports the consistency of the correct identification of the samples. This is indicated in Fig. 2, where the two previous samples have been projected into the PCA space defined by the reference samples in the spectral database. The PCA analysis was not restricted to the first two PCs, as higher-order PCs may still contain relevant information. In this case, PC3 explains a non-negligible proportion of the variance (13%), which justifies its inclusion in the visualization. The PC1 vs PC3 representation was therefore selected because it provided a

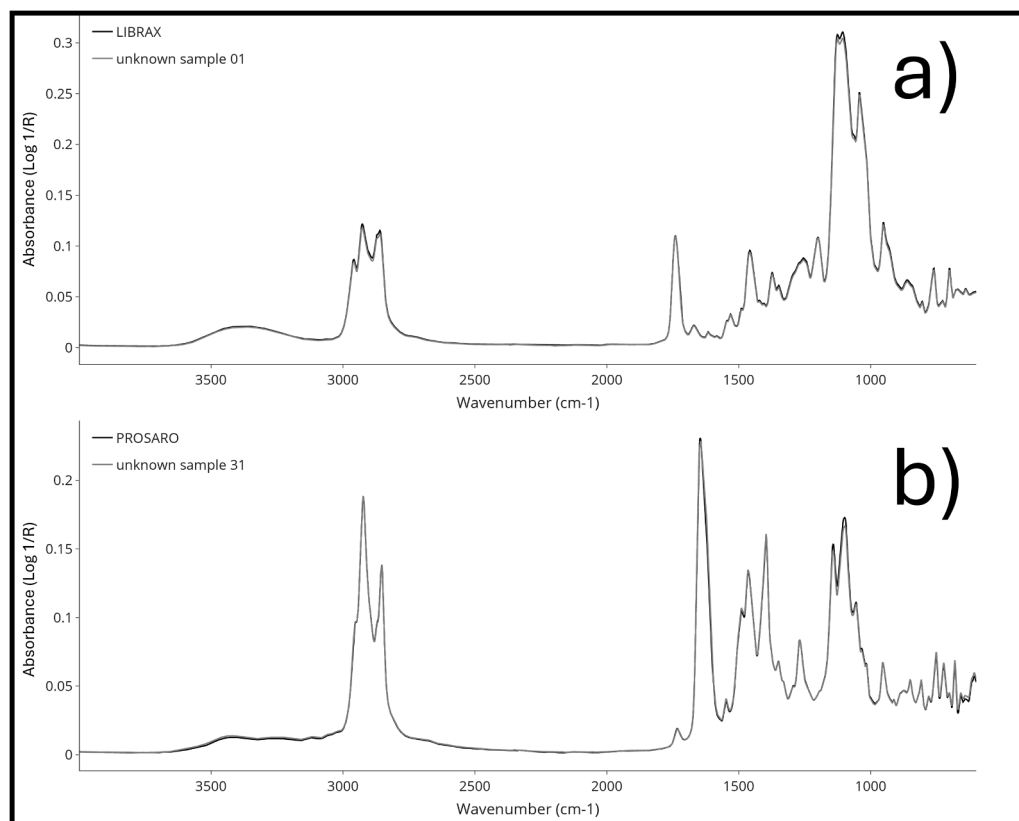


Fig. 1. a) Spectra of the sample 01 and its reference in the spectral database (LIBRAX); b) Spectra of the sample 31 and its reference in the spectral database (PROSARO).

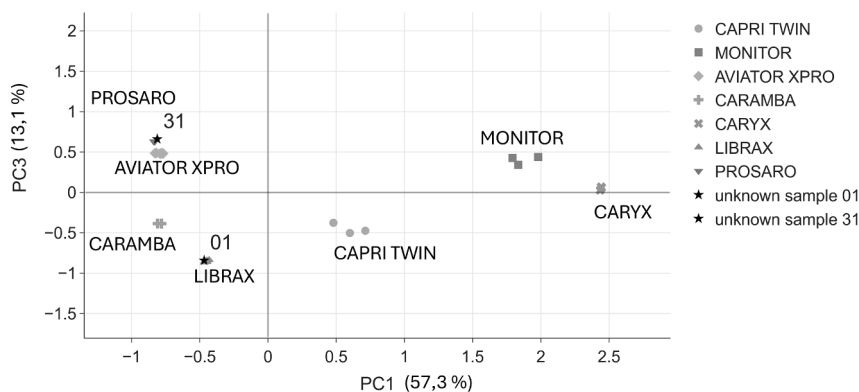


Fig. 2. PCA space defined by the reference samples in the spectral database and the projection of samples 01 and 31.

clearer separation of the samples compared to the conventional PC1 vs PC2 plot. Several interesting observations can be extracted from this figure. First, samples 01 and 31 are projected toward the LIBRAX and PROSARO clusters respectively, demonstrating the spectral resemblance already observed in Fig. 1. Second, the PCA plot reveals the proximity between PROSARO and AVIATOR XPRO, as well as between CARAMBA and LIBRAX. This can be attributed to compositional similarities among the formulations: PROSARO and AVIATOR XPRO both contain prothioconazole as active substance, while CARAMBA and LIBRAX contain metconazole.

Few samples have been incorrectly detected. Such misclassifications are most frequently associated with formulations exhibiting highly similar or nearly identical chemical or spectral profiles, often originating from distinct manufacturers or production batches or from samples coming from parallel markets. Moreover, these discrepancies may arise also when a given formulation is absent from the constructed spectral library. In most of these cases, the three-step protocol tends to assign the sample to the most spectrally or compositionally similar class, typically one that shares the same principal active substance or exhibits closely related matrix characteristics.

As shown in Table 2, the pairs of commercial formulations CARAMBA / REMOCCO 60, MONITOR / SULFOSULFURON 80 WG or SULFOSULFURON 75 WG, and PROSARO / PROTENDO EXTRA represent typical examples of equivalence between products marketed under different trade names. Each pair appears to correspond to formulations with chemically identical or nearly identical composition. In all three cases, the products share the same declared active substance, equivalent concentration, and comparable mode of action, resulting in analogous biological efficacy. For instance, REMOCCO 60 and CARAMBA both contain metconazole as unique active substance, MONITOR and SULFOSULFURON 80 WG or SULFOSULFURON 75 WG are formulations based on sulfosulfuron, and PROSARO and PROTENDO EXTRA both contain prothioconazole and tebuconazole in similar proportions. The differences observed among these paired products are shown in Fig. 3 and are mostly branding, label details and possibly minor formulation differences (e.g. exact solvent or co-formulant composition). In the case of MONITOR and SULFOSULFURON 80 WG or SULFOSULFURON 75 WG, more differences are observed in the spectra (Fig. 3b). This is due to matrix effects from the water dispersible granules (WG) formulations. The physical nature of WG formulations, comprising granulated solids designed to be dispersed in water, produces distinctive scattering and baseline variations in the FT-MIR spectra. These spectral artifacts differ significantly from those of more common liquid or emulsifiable concentrate (EC) formulations included in the database, thereby confounding automated spectral comparison routines. In all cases, from an analytical point of view, these compositional similarities imply that the FT-MIR spectral profiles of such equivalent products are expected to be comparable, often rendering their differentiation challenging.

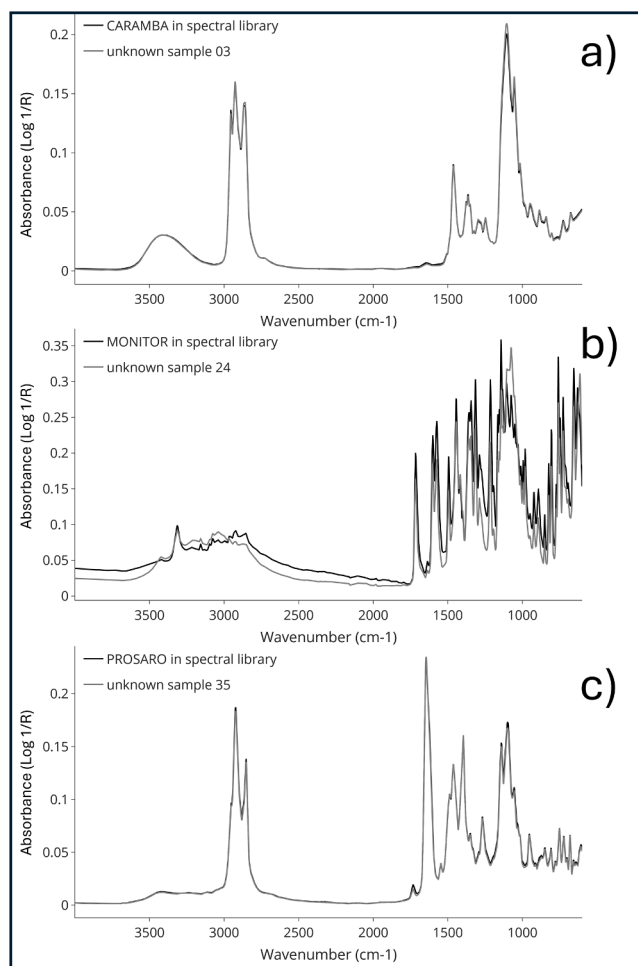


Fig. 3. three typical examples of equivalence between products marketed under different trade names: a) sample 03 (REMOCCO 60) detected as CARAMBA; b) sample 24 (SULFOSULFURON 75 WG) detected as MONITOR and c) sample 35 (PROTENDO EXTRA) detected as PROSARO.

A particular case is represented by sample 30, for which the three-step chemometric protocol failed to identify the correct formulation. This limitation arises because the sample corresponds to the blank formulation of PROTENDO EXTRA, i.e. a formulation without the active substance and, in addition, not included in the spectral database.

Moreover, in most of the cases and as specified in the last column in Table 3, the protocol was able to identify the specific adulterant present, indicating the good performances of the proposed methodology for both

detection and identification tasks. Nevertheless, a few samples proved to be more challenging.

Among those, two special cases can be distinguished: 1) all samples adulterated also with isooctane (samples 07, 09, 10, 16, 18, 19 and 20) and 2) the case of sample 14 corresponding to LIBRAX adulterated with xylene.

In the case of samples 07, 09, 10, 16, 18, 19 and 20, the addition of isooctane appears to induce detectable modifications in the FT-MIR spectra (Fig. 4), manifested as spectral abnormalities deviating from the reference profiles of the respective formulations (LIBRAX, REMOCCO 60 and CARAMBA). These deviations are due to the presence of isooctane that influences the molecular vibrational modes captured by the FT-MIR analysis. As this work is done in blind, a definitive identification of isooctane could not be established. However, the band around 2950 cm^{-1} corresponds to the asymmetric stretching of the $-\text{CH}_3$ groups in isooctane and evolves according to the level of isooctane in the sample. The opposite is observed in band 1100 cm^{-1} , which corresponds to C–O stretching of an ester or C–N stretching of an amine group, probably in one of the co-formulant present in the formulation.

In the case of sample 14 (LIBRAX) that was intentionally adulterated with 10% of xylene, the protocol successfully detected spectral irregularities indicative of adulteration, confirming the sensitivity of the proposed methodology to compositional changes. However, as for the previous case, the adulterant could not be identified. This may be explained by the relatively low concentration of xylene, which could have resulted in insufficient signal intensity for reliable spectral discrimination.

3.2. Assessment of a real counterfeiting case scenario

As described in Section 2.2, a set of samples (Table 2), provided by a private pesticide manufacturer, were subjected to analytical evaluation. These samples were selected to reflect a realistic case study scenario and have been analysed following the same procedure as in the previous case. To ensure the accuracy of the obtained results, confirmatory analyses were additionally conducted using chromatographic and mass

spectrometric techniques.

The formulations under investigation, commercially known as MOVENTO for the original, legally registered formulation, were treated as blind samples throughout the analytical challenge. All three formulations contained spirotetramat as the declared active substance. For comparison and reference purposes, the analytical standard of spirotetramat was also available in the spectral database.

Fig. 5 shows the FT-MIR spectra of the original, legally registered formulation (SP1) and the authorized parallel trade product (SP2). No clear differences are observed between the two formulations, indicating their compositional equivalence. In contrast, Fig. 6 presents the spectra of the suspicious formulation (SP3) together with the active substance, spirotetramat. For sample SP3, a very low local score was obtained, suggesting a limited correlation between this sample and the reference spirotetramat spectrum in the database. Spectral analysis indicates the presence the characteristic absorption bands of spirotetramat in SP3, however, variations in the OH related bands, around 3200 cm^{-1} and 1640 cm^{-1} , suggest a certain dilution of the active substance with water.

Results obtained by FT-MIR were confirmed by performing screenings by gas chromatography with mass spectrometry detection (GC–MS) and liquid chromatography with high resolution (time of flight) mass spectrometry detection (LC–HRMS (Q–TOF)).

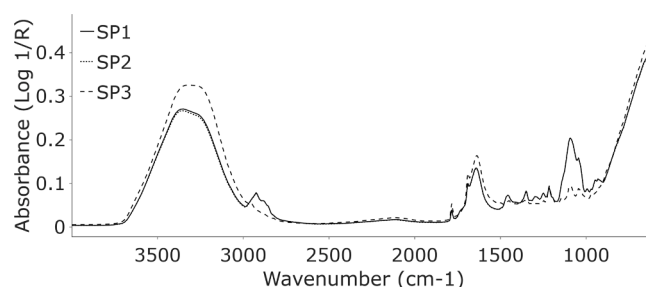


Fig. 5. FT-MIR spectra of the original, legally registered formulation (SP1), the authorized parallel trade product (SP2) and the counterfeit product (SP3).

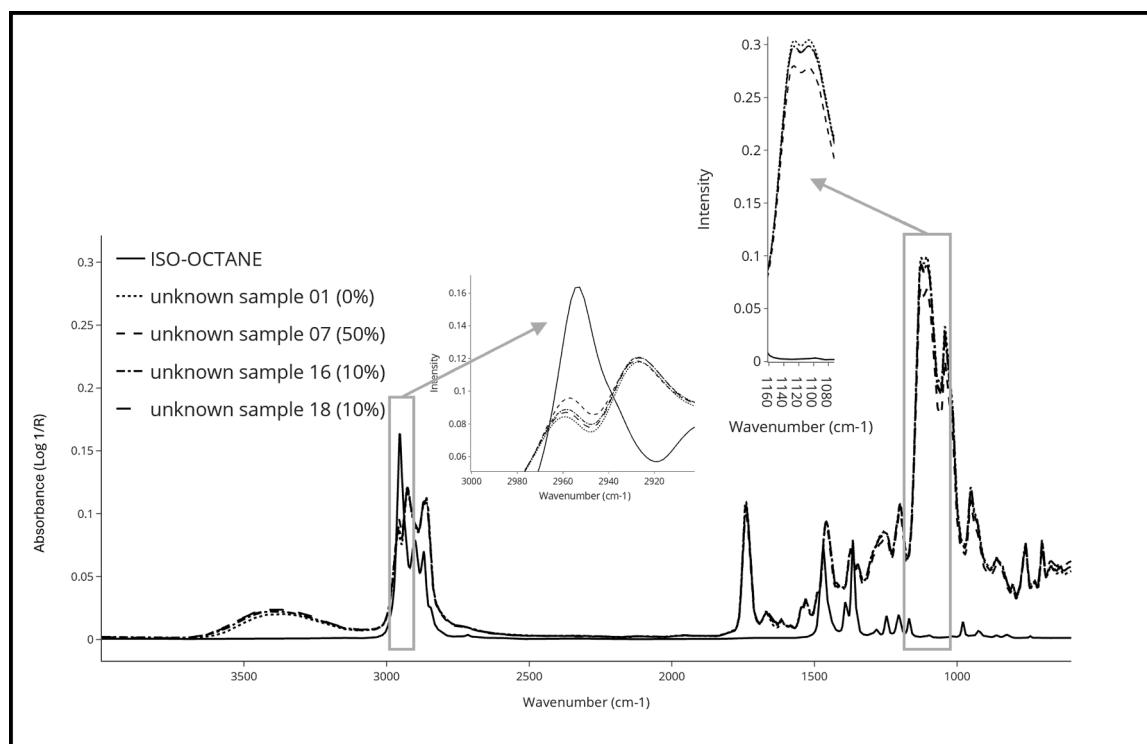


Fig. 4. different LIBRAX samples pure and adulterated with isooctane at different levels (10% and 50%) as well as the spectra of the solvent isooctane.

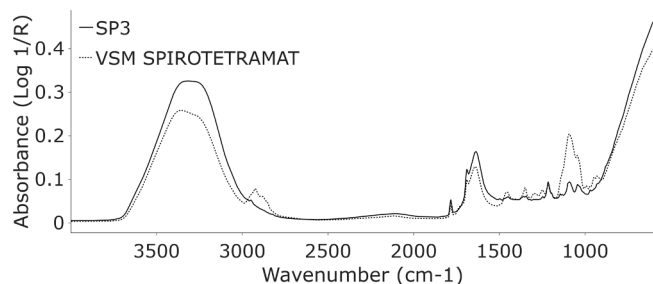


Fig. 6. FT-MIR spectra of suspected counterfeit formulation (SP3) and the analytical standard of spirotetramat.

The samples of MOVENTO, original, legally registered formulation (SP1) and of the suspected counterfeit formulation (SP3) were analysed by GC–MS in full scan mode, using two columns of different polarity (DB-5 and DB-Wax) after dilution with acetone and hexane, respectively. The chromatographic setup comprised a Shimadzu GC-TQD system equipped with an automatic liquid sampler and a splitless injection system. Detection was performed using a Shimadzu GCMS-QP2010 Ultra with a capillary direct interface. Data acquisition and analysis were conducted using Real Time Analysis and Post Run Analysis software. Helium served as the carrier gas at a constant flow rate of 1 mL/min. The inlet temperature was maintained at 200 °C, and the oven temperature started at 40 °C for 0 min, then ramped to 250 °C at 5 °C/min and held for 10 min, with a total run time of 62 min. The injection volume was 1 µL. The capillary interface was set to 250 °C, while the ionization source operated at 280 °C using electron impact (EI) ionization. Mass spectra were acquired in full scan mode over the m/z range 40–700. Two different anti-freezing agents were identified, respectively in the sample SP1 and SP3, confirming the difference of composition of the two formulations.

The two samples were also analysed by LC–HRMS (Q-TOF), using a reversed phase column (Acquity HSS T3) after dilution with methanol. The analysis employed a Shimadzu Nexera UHPLC system with an autosampler, pump, and column oven, coupled to an ABSciex X-500R Q-TOF Quadrupole time-of-flight mass spectrometry spectrometer. Data were processed using ABSciex Sciex OS software. Chromatographic separation was achieved on an Acquity HSS T3 column (1.7 µm, 100 × 2.1 mm), with mobile phases consisting of water with 0.1% Formic acid (Phase A) and methanol with 0.1% Formic acid (Phase B). The flow rate was set at 0.3 mL/min, with a column temperature of 40 °C and an injection volume of 10 µL. The spirotetramat content in the counterfeit sample SP3 was 9% lower than the content of the original sample SP1. Moreover, the impurity spirotetramate ci-enol was detected in the counterfeit sample SP3.

These results confirm that predictions obtained by the three-step chemometric protocol on the FT-MIR spectral data.

4. Conclusion

This work demonstrates that FT-MIR spectroscopy, when combined with a three-step chemometric protocol, represents a powerful, reliable and environmentally sustainable tool for the qualitative screening of pesticide formulations. Although the technique does not provide quantitative determination of active substances and co-formulants, its qualitative discriminant capability allows for effective differentiation between authentic and counterfeit products, as well as for the verification of formulation integrity. The proposed protocol can be considered a green screening technique, as it is solvent-free, non-destructive and requires minimal sample preparation, reducing, then, chemical waste and environmental impact. These characteristics, combined with its rapidity, cost-effectiveness and ease of implementation, make FT-MIR spectroscopy ideally suited for routine quality control and high-throughput screening applications.

Currently, authentication of pesticide formulations and the detection of counterfeit products are often performed on a case-by-case basis, typically following suspicion. A more effective and harmonized strategy could be achieved through the establishment of centralized FT-MIR spectral databases of legally authorized formulations at the European level. Given the existing harmonization of active substance approval and zonal authorisation procedures within the European Union, identical formulations are often marketed across multiple Member States. Therefore, a standardized FT-MIR spectral repository, managed by official control laboratories, regulatory authorities, or product authorization holders, could serve as a comprehensive reference tool for the identification of suspect samples during routine screening. Samples exhibiting spectral deviations from authentic profiles could then be subjected to confirmatory analyses using classical chromatographic or mass spectroscopic techniques.

While certain challenges remain, such as spectral band overlapping and mainly the need for extensive and continuously updated reference databases, FT-MIR spectroscopy combined with the proposed three-step chemometric protocol has proven to be a robust, rapid and green analytical methodology for combating pesticide fraud. Continued research, expansion of spectral libraries, and technological refinement will further enhance its applicability, contributing to the protection of agriculture, the environment and public health against the growing threat of counterfeit pesticide products.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used CHATGPT to synthesize the text and improving language and readability. After using this tool/service, the authors reviewed and edited the content as needed and take(s) full responsibility for the content of the published article.

CRedit authorship contribution statement

Juan Antonio Fernández Pierna: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Quentin Arnould:** Writing – review & editing, Validation, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Delphine Delhotte:** Writing – review & editing, Validation, Investigation, Formal analysis, Data curation, Conceptualization. **Pierre Hucorne:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation. **Gilles Rousseau:** Writing – review & editing, Investigation. **Jérôme Bodart:** Data curation. **Vincent Baeten:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Olivier Pigeon:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

All authors reports financial support was provided by Belgian Federal Public Service of Public Health, Food Chain Safety and Environment. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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