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REFERENCE RAMAN SPECTRAL DATABASE OF COMMERCIAL PESTICIDES [**]

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Among several techniques used to study pesticides, Raman spectroscopy stands out for providing fast and reliable results. The objective of this work is to construct a database with Raman spectra of the main commercial pesticides currently used and make it available to the scientific community. With this aim, liquid and solid samples from 78 pesticides were collected. For the Raman spectroscopy analysis of pesticides, a portable Delta Nu Raman spectrometer with a 785 nm laser wavelength and 8 cm^{-1} resolution was used. The results obtained from the different pesticides were grouped into tables showing the action class, chemical class, active ingredient, and relative intensities of the characteristic Raman bands.

Keywords: *Raman spectroscopy, pesticides, insecticides, fungicides, herbicides.*

СПРАВОЧНАЯ БАЗА ДАННЫХ СПЕКТРОВ КОМБИНАЦИОННОГО РАССЕЯНИЯ КОММЕРЧЕСКИХ ПЕСТИЦИДОВ

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Проведен анализ жидких и твердых образцов 78 пестицидов методом спектроскопии комбинационного рассеяния света с использованием портативного спектрометра Delta Nu Raman с длиной волны 785 нм и разрешением 8 см$^{-1}$. Результаты для различных пестицидов сгруппированы в таблицы, показывающие класс действия, химический класс, активный ингредиент и относительную интенсивность характеристических полос комбинационного рассеяния.

Ключевые слова: *спектроскопия комбинационного рассеяния света, пестициды, инсектициды, фунгициды, гербициды.*

Introduction. Estimates from the United Nations [1] show that the world population may reach nine billion people by the year 2050, thus increasing the demand for food and raw materials. However, it has been observed that arable land has not kept pace with population growth or industrial expansion in the last two centuries. Nevertheless, there has been a sizable effort to increase food productivity in these areas. The fight against pests and diseases, using pesticides throughout the planting process, has been one of the capital factors boosting productivity. The term pesticide applies to any substance or mixture of substances intended for use in the prevention, destruction, or control of any pest that hinders or interferes with any form of production, storage, processing, transport, or commercialization of food or feed for humans and animals. It also refers to substances that pose restraints to agricultural production or hinder the growth of timber and wood

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products or can be administered to animals to fight insects, arachnids, or other pests (endoparasites or ectoparasites). This terminology also includes substances used as plant growth regulators, defoliants, desiccants, fruit density reducing agents or agents applied to prevent premature fruit falling, and pre- or postharvest substances utilized to prevent spoilage during storage and transportation [2].

Some advantages of the use of pesticides lie in the increase in quantity and quality of food and, consequently, fall in food prices, thanks to the improvement in yield and efficiency of the production processes. In addition, the administration of these chemical products helps protect human health by eliminating pests and diseases that can settle on fruits, vegetables, and grains. However, their use can lead to neurological, behavioral, and psychological dysfunctions, as well as hormonal imbalance and problems in the reproductive system.

The annual consumption of pesticides in the world reaches approximately 2.5 million tons. Of this total, 20% is consumed by developing countries. For example, from 2000 to 2012, the annual sales of pesticides in Brazil increased by 194% [3]. In this scenario, several studies from different areas have been conducted, aiming to evaluate the advantages and disadvantages of the use of pesticides. Several assays seek to detect the use of pesticides as pollutants in the environment (soil, water) or evaluate the occurrence of traits of these products in foods [4–7]. The Raman Spectroscopic method is one of various techniques used to detect the presence of pesticides. However, there are no free pesticide libraries, using a portable Raman spectrometer for the analysis of commercial pesticides, to assist researchers in the identification of pesticides. Thus, the objective of this work is to build a database with Raman spectra of the predominant currently used commercial pesticides and make it available for reliable identification of these chemical agents.

Experimental. For this work, 78 pesticides (13 fungicides, 33 herbicides, and 32 insecticides) and 7 adjuvants and mineral oils were collected. For measurement of the liquid samples, 2 mL of the pesticide in nature was placed in a glass vial and measured directly on the equipment. The solid samples were measured by placing them on a glass slide thick enough to prevent the interference of glass fluorescence with the spectrum. Sample handling was performed within a fume hood using protective equipment, such as gloves, mask, and coat.

For assessment of the Raman spectra of the samples, a Delta Nu portable Raman spectrometer was used, containing a laser with a 785 nm wavelength and maximum power of 120 mW, with a resolution of 8 cm^{-1} and reach between 200 and 2000 cm^{-1}. This equipment was selected as it is portable and can be taken to the field to conduct *in situ* measurements. The equipment belongs to the Laboratory of Applied Nuclear Physics (LFNA) of the State University of Londrina (UEL).

To obtain the best spectrum of each sample, some factors was considered, namely, the distance of the sample from the laser focal point, the laser power, and the measuring time. The evaluation of these parameters was always adjusted to obtain the best signal-to-noise ratio.

The Raman band intensities of each sample were characterized through comparison with the most intense band of the spectrum. The different intensities were grouped into 5 classes: very strong (vs) 90–100%, strong (s) 70–90%, medium (m) 30–70%, weak (w) 10–30%, and very weak (vw) 0–10%.

Results and discussion. The results obtained for the samples of different pesticides, adjuvants, and mineral oils were grouped into tables containing the class, chemical class, active ingredient, and their characteristic Raman bands. As the spectra were obtained from natural samples, the bands present in the Raman spectra are not necessarily only those of the active ingredients of the pesticide. In fact, the Raman bands identified are characteristic of the final formulation of the commercial pesticide.

Table 1 shows the Raman bands of the 13 assessed fungicides. A more accurate analysis of Table 1 reveals that there is a difference in the Raman band fungicides. Carbendazim, difeconazole, mancozeb, and tebuconazole fungicides, for example, have different Raman spectra, allowing differentiation between them (Fig. 1). However, this task requires caution, since a fungicide containing trifloxystrobin and tebuconazole as active ingredients has a different spectrum from a pesticide containing only tebuconazole.

Table 2 shows the Raman band intensities of the 33 insecticides measured. Some of the most commonly used insecticides are abmectin, methomyl, acephate, and dimethoate. Their Raman spectra (Fig. 2) have different bands, enabling their characterization.

Commercial pesticides with the same active ingredient may present different Raman spectra (Fig. 3). This contingency occurs since, together with the active ingredient of the product, companies add other secret ingredients that make the final formulation of the pesticide different between brands, hampering characterization of the pesticide through the Raman spectrum. Thus, a more accurate analysis should be conducted.

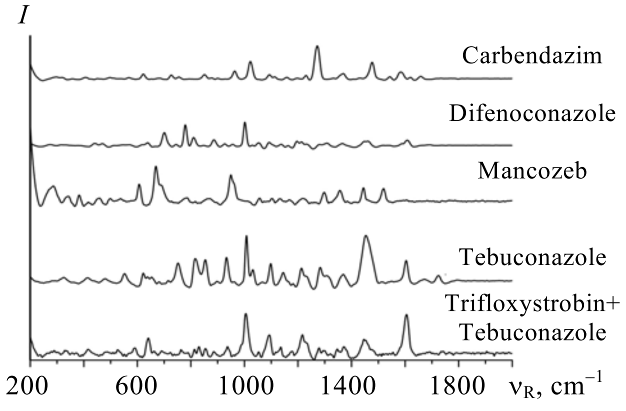

Fig. 1. Raman signal spectra of some commercial fungicides as a function of wavenumber.

TABLE 1. Class, Chemical Class, Active Ingredients and Relative Intensities of the Raman Bands of Commercial Fungicides

Class	Chemical Class	Active Ingredient	Raman bands, cm^{-1}
Systemic	Benzimidazole	Carbendazim	622w, 727w, 755w, 851w, 964m, 1023vs, 1093w, 1113w, 1158vw, 1230w, 1272w, 1369m, 1477vs, 1543w, 1584m, 1658w
Contact	Inorganic	Sulfur	288m, 327w, 341w, 472vs
Protector, systemic, contact and ingestion	Strobilurins, benzimidazole and pyrazole	Pyraclostrobin + Methyltiophanate + Fipronil	686m, 742m, 777w, 819vw, 1082vw, 1214m, 1340w, 1539vs
Systemic and contact	Benzimidazole and dimethyl-dithiocarbamate	Carbendazim + Thiram	281w, 397m, 446w, 560vs, 850w, 970w, 1018w, 1267m, 1366m, 1477w, 1598w
Mesothermal	Strobilurin and triazolinthione	Trigloxystrobin + Prothioconazole	609vs, 681m, 996m, 1163m, 1639m, 1674w, 1753s, 1780s, 1859m, 1932s
Systemic and contact	Strobilurin and triazole	Epoxiconazole + Kresoximmethyl	278w, 320vw, 341w, 386vw, 421w, 457w, 494vw, 545vw, 636w, 701vw, 754w, 784w, 811w, 843w, 870vw, 903vw, 949vw, 980vw, 1013m, 1033s, 1053vs, 1126vw, 1162m, 1205vw, 1241s, 1292m, 1347vw, 1379w
Systemic and Mesothermal	Strobilurin and triazole	Trifloxy-strobin+Tebuconazole	416vw, 591w, 641m, 830w, 937w, 1005vs, 1093m, 1136w, 1217m, 1279w, 1371w, 1446m, 1605vs
Systemic	Triazole	Tebuconazole Company B	325vw, 415vw, 480vw, 553w, 622w, 752m, 817m, 854m, 933m, 1008vs, 1031w, 1098m, 1145w, 1213w, 1283w, 1307w, 1369w, 1453vs, 1604m, 1672m, 1724w
Systemic	Triazole	Tebuconazole Company A	275vw, 332vw, 414vw, 551w, 622w, 653w, 753m, 813m, 933m, 1009w, 1032w, 1098m, 1125w, 1212m, 1309m, 1370w, 1449vs, 1602w, 1682vw, 1743vw
Systemic	Dicarboximide	Procymidone	274m, 614m, 1000vs, 1388w, 1448w, 1587w, 1769w
Contact	Dithiocarbamate	Mancozeb	287m, 342w, 383w, 607m, 670vs, 950s, 1298w, 1357m, 1444m, 1519m
Local systemic	Acetamide and Dithiocarbamates	Cymoxanil + Mancozeb	289w, 341w, 606m, 668vs, 949s, 1296m, 1354m, 1441m, 1518m
Systemic	Triazole	Altered ester Difenoconazole	442vs, 470vs, 639w, 701m, 779s, 811m, 886w, 1002vs, 1054w, 1092w, 1196w, 1213w, 1308vw, 1365vw, 1461w, 1608w

TABLE 2. Class, Chemical Class, Active Ingredient, and Relative Intensities of Raman Bands of Commercial Insecticides

Class	Chemical Class	Active Ingredient	Raman bands, cm^{-1}
Systemic	Neonicotinoid and pyrethroid	Imidacloprid + Beta-cyfluthrin	290m, 328w, 359w, 423w, 480m, 570w, 634w, 756w, 820m, 892w, 963m, 1001m, 1055w, 1112m, 1235w, 1282vs, 1375m, 1484vs, 1586m
Contact and ingestion	Keto-enol	Spiromesifen	518vw, 577s, 663w, 771m, 896w, 1091w, 1145w, 1216w, 1303w, 1382w, 1447m, 1614w, 1675vs, 1749m
Contact	Avermectin	Abamectin Company C	231vw, 622w, 753m, 853w, 896vw, 933w, 1033vw, 1085vw, 1130w, 1272w, 1308m, 1448vs, 1660m
Contact and ingestion	Anthranilamide and Diamide	Clorantraniliprole	280w, 451w, 511w, 585w, 666s, 837w, 1034s, 1252m, 1325vs
Contact	Organophosphorus	Pirimiphos + methyl	331vw, 395vw, 472vw, 580s, 638m, 658w, 723w, 749w, 824vw, 966w, 1000vs, 1082w, 1252w, 1383w, 1447w, 1603w
Contact and ingestion	Organophosphorus	Malathion + xylene	435vw, 500vw, 657w, 883vs, 1052w, 1277vw, 1455w
Mesothermal and Systemic	Strobilurin and triazole	Trifloxystrobin + tebuconazole	282vw, 337vw, 421w, 530vw, 592w, 642m, 766w, 815w, 831w, 856w, 887vw, 938w, 1006vs, 1091m, 1134w, 1218m, 1282w, 1373w, 1451m, 1606vs
Systemic	Phenylpyrazole	Fipronil	306vw, 507vw, 559vw, 659vw, 722vw, 750vw, 774w, 837w, 897w, 1006w, 1065vw, 1140vw, 1165vw, 1253vw, 1307w, 1386vw, 1457vs, 1613vw
Systemic	Neonicotinoid	Acetamiprid	289w, 324w, 361vw, 431w, 479w, 545w, 627vs, 683vw, 741vw, 781w, 819w, 847m, 917w, 956m, 1022vw, 1089m, 1142vw, 1176vw, 1195vw, 1221m, 1268w, 1292w, 1346m, 1428m, 1498m, 1587m, 1621 w
Contact	Organophosphorus	Clorpirifos	347m, 461vw, 490vw, 540w, 573vw, 637m, 681w, 730w, 773w, 833w, 971vw, 1007vs, 1036w, 1105w, 1168vw, 1208w, 1250vw, 1282w, 1384vw, 1457vw 1572vw, 1610vw
Systemic	Neonicotinoid	Imidacloprid	323w, 415vw, 478vw, 553w, 623w, 754m, 818m, 852vs, 935m, 1009w, 1029w, 1066vw, 1099w, 1134w, 1212m, 1309m, 1371w, 1454vs, 1602w, 1679w, 1743w
Systemic	Neonicotinoid	Thiamethoxam	276m, 347w, 500w, 538w, 749w, 776w, 853w, 878vw, 959w, 1173m, 1239m, 1323w, 1358vs, 1378s, 1482vs, 1588s
Systemic	Spinosyn	Spinosad	501w, 547m, 596m, 773s, 850w, 936m, 1004m, 1061vs, 1101w, 1164m, 1267vs, 1335w, 1380w, 1449m, 1544m, 1599s
Systemic, contact and ingestion	Organophosphorus	Acephate	279vw, 329w, 407m, 500w, 567s, 704vs, 808w, 875m, 960w, 1228m, 1434w, 1696w
Systemic and ingestion	Diamide and antranilic	Clorantraniliprole	278w, 339w, 424w, 445w, 499w, 580w, 675w, 686w, 765w, 797w, 872w, 919w, 981w, 1077w, 1177m, 1221m, 1285m, 1351m, 1429m, 1539w, 1617vs

Continue Table 2

Class	Chemical Class	Active Ingredient	Raman bands, cm^{-1}
Ingestion	Microbial	Bacillus thuringiensis	893vw, 1065vw, 1078vw, 1149vw, 1303w, 1446vs
Systemic, contact and ingestion	Organophosphorus	Acephate	323vw, 363vw, 452vw, 566w, 620vw, 703m, 808vw, 872vw, 978vs, 1229w
Physiological	Benzoylurea	Lufenuron	617w, 677w, 807vw, 851w, 930vw, 1003vs, 1028w, 1114vw, 1163vw, 1277w, 1316vw, 1454vw, 1602w, 1717w
Contact and ingestion	Organophosphorus	Chlorpyrifos	1382vs
Systemic and contact	Methylcarbamate	Methomyl	284w, 731w, 887vs, 1096w, 1458w, 1591w
Contact	Avermectin	Abamectin Company A	317w, 441w, 562vw, 618m, 747m, 842w, 889w, 928m, 989vw, 1027vw, 1070vw, 1140w, 1228vw, 1301m, 1455vs, 1654w
Systemic	Neonicotinoid	Imidacloprid	262w, 327s, 390w, 416w, 483w, 635w, 666w, 755w, 828m, 849w, 886w, 965m, 997vs, 1051w, 1109m, 1213w, 1282s, 1371s, 1468w, 1488w, 1558s, 1586vs
Ingestion	Keto-enol	Spiromesifen	339vw, 455vw, 517vw, 576s, 667w, 769m, 854vw, 896w, 928vw, 1000vw, 1092w, 1143w, 1216w, 1309w, 1382w, 1444m, 1615w, 1676vs, 1751m
Systemic	Neonicotinoid	Imidacloprid	289m, 328w, 360w, 422w, 478m, 634m, 689w, 754m, 818s, 891w, 963m, 1001s, 1056m, 1113m, 1145w, 1196w, 1235w, 1281s, 1375m, 1455w, 1486vs, 1570m, 1585m
Contact and ingestion	Pyrethroid	Lambda-cyhalothrin	452m, 571w, 1002vs, 1213m, 1303w
Systemic and contact	Organophosphorus	Dimethoate	407vw, 502m, 534w, 584vw, 658vs, 727m, 751m, 838m, 906vw, 1001m, 1316vw, 1381w, 1450w
Contact and ingestion	Pyrethroid	Cypermethrin	662vw, 732w, 772w, 824w, 1008vs, 1035vw, 1212w, 1457vw, 1618w
Systemic, contact and ingestion	Methylcarbamate	Methomyl	449vw, 482vw, 664w, 726w, 882vs, 945vw, 1048vw, 1091vw, 1276vw, 1453w, 1587w
Contact and ingestion	Pyrethroid Ester	Beta-cypermethrin	767m, 1000w, 1378vs
Contact and ingestion	Oxadiazine	Indoxacarb	849vw, 974vw, 1003w, 1073w, 1102m, 1206w, 1266m, 1304w, 1442s, 1605m, 1654vs
Contact and ingestion	Avermectin	Abamectin Company B	328w, 446w, 554s, 623vw, 751w, 812w, 892w, 844m, 892m, 933w, 1147m. 1287m, 1462vs
Systemic	Neocotinoide	Imidacloprid + Thiodicarb	684w, 751m, 1148w, 1346m, 1457w, 1582vs
Contact and ingestion	Pyrethroid	Fenpropathrin	536vw, 580vw, 662w, 730m, 830vw, 1002vs 1382vw, 1604vw

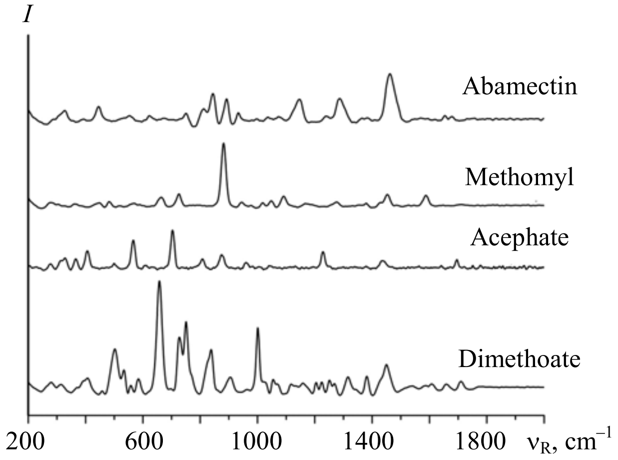

Fig. 2. Raman signal spectra of some commercial insecticides as a function of wavenumber.

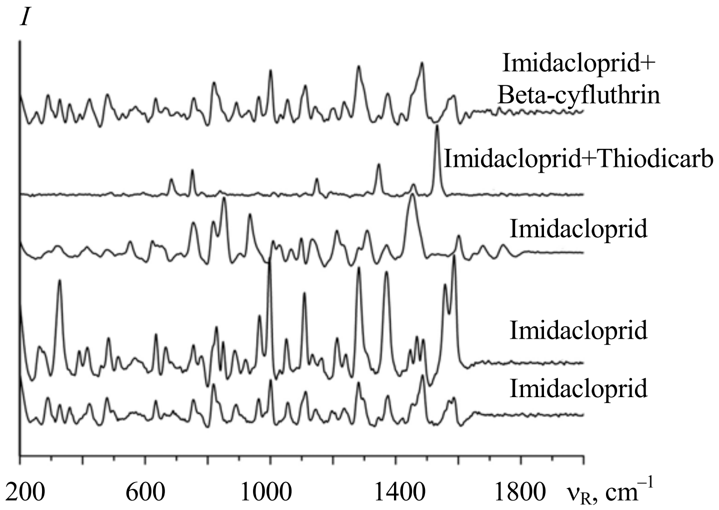

Fig. 3. Raman signal spectra of insecticides containing the imidacropid active ingredient in their formulation.

Table 3 shows the intensities of the Raman bands of the 32 evaluated herbicides. Figure 4 presents some herbicides analyzed in this work, among them, the most commonly used in agriculture. Different commercial herbicides have distinct Raman spectra that allows for their differentiation and identification.

TABLE 3. Relative Intensities of the Raman Bands of the Herbicides Analyzed

Class	Chemical Class	Active Ingredient	Raman bands, cm^{-1}
Systemic non-selective	Glycine	Glyphosate Company B	309vw, 474vw, 580vw, 724vw, 775w, 811vs, 895w, 939m, 985m, 1084w, 1171vw, 1325w, 1385vw, 1405vw, 1464w
Non-Selective of systemic action	Glycine	Glyphosate Company C	477vw, 723vw, 778vw, 812vs, 895w, 941w, 989vw, 1082w, 1325vw, 1385vw, 1405vw, 1465w
Systemic selective	Benzothiadiazinone	Bentazone	282w, 453w, 590w, 672s, 842m, 987w, 1040vs, 1256m, 1331s, 1600w
Systemic non-selective	Triazolone	Carfentrazone ethyl	291w, 575w, 689m, 716w, 742m, 836w, 999vs, 1246w, 1377 w, 1430m, 1611vs

Continue Table 3

Class	ChemicalClass	Active Ingredient	Raman bands, cm^{-1}
Systemic	Cyclohexanedione oxime	Clethodim	287m, 513m, 577m, 741s, 1383vs
Systemic selective	Triketone	Tembotrione	396vw, 530w, 809m, 845vs, 930w, 995vw, 1048vw, 1090vw, 1146vw, 1306vw, 1466m
Systemic non-selective	Urea and Bipyridylium	Paraquat + Diuron	287m, 842m, 1200m, 1307vs, 1658s
Systemic non-selective	Bipyridylium	Diquat	737w, 1077m, 1199m, 1326vs, 1534w, 1586m, 1618m
Systemic selective	Aryloxyphenoxypropionic	Quizalofop-p-methyl	287vw, 326vw, 453vw, 475vw, 559w, 580w, 660w, 722w, 748m, 774vw, 822vw, 865vw, 929vw, 1006s, 1052vw, 1065vw, 1132w, 1183vw, 1252w, 1303vw, 1332vw, 1385vs 1464w, 1583vw, 1612w
Systemic selective	Aryloxyalkanoic	Acetic	279w, 354w, 399s, 415s, 655m, 726m, 844vs, 859m, 898m, 921w, 947w, 1028w, 1048w, 1112m, 1160m, 1243m, 1293vw, 1342m, 1416w, 1477w, 1589m
Systemic selective	Chloroacetanilide	S-metolachlor	282vw, 372vw, 445vw, 500vw, 546m, 614w, 701m, 791vs, 873w, 983w, 1006vw, 1053m, 1111w, 1172w, 1264vs, 1382m, 1459w, 1591m, 1670w
Systemic non-selective	Homoalanine	Glufosinate + ammonium salt	699w, 852m, 893w, 968w, 1031vs, 1066m, 1133w, 1202w, 1347vw, 1453m
Systemic non-selective	Glycine	Glyphosate Company A	476vw, 721vw, 777vw, 811vs, 892w, 938w, 987vw, 1081w, 1170vw, 1323w, 1385vw 1405vw, 1464w
–	–	Chlorpyrifos	338vs, 566m, 595w, 731w, 897m, 1012vw, 1124w, 1187w, 1245m, 1384vw, 1472vw, 1566w
Selective Emerging	Cyclohexanone oxime	Sethoxydim	576w, 703w, 781s, 877w, 1003vs, 1217w, 1384w, 1462w, 1614w
Selective pre-emerging	Aryloxyphenoxypropionic acid	Haloxyfop-p-Methyl	284vw, 320vw, 436vw, 527vw, 554vw, 577w, 654w, 694vw, 720m, 743m, 850w, 924vw, 1002vs, 1031vw, 1059vw, 1096vw, 1163vw, 1246w, 1325vw, 1381w, 1449w, 1610w
Selective systemic	Isoxazolidinone	Clomazone	541w, 580vw, 685w, 720m, 739m, 809vw, 835vw, 1006m, 1045vs, 1204w, 1450w, 1600w, 1660w
Residual selective	Triazinone	Metribuzim	280w, 327vw, 376vw, 444vw, 515w, 589vw, 663m, 715w, 814w, 912w, 940vw, 1061m, 1216w, 1239w, 1307w, 1393w, 1469vs, 1526w, 1684w
Selective Emerging	–	Clomazone + Carfentrazone-ethyl	392vw, 452vw, 542w, 581vw, 686w, 719m, 740m, 809vw, 825vw, 857vw, 1006w, 1046vs, 1136vw, 1166vw, 1204w, 1253vw, 1385vw, 1451w, 1580vw, 1600w, 1660vw
–	Aryloxyphenoxypropionic acid	Propaquizafop	325vw, 476w, 560w, 582w, 662w, 724m, 750s, 866w, 932m, 1007s, 1069vw, 1134vw, 1184w, 1253m, 1334w, 1388vs, 1402vs, 1453m, 1584w, 1614w
Selective Systemic	Cyclohexanedione oxime	Tepraloxydim	451w, 520w, 572w, 703w, 771m, 1004w, 1054w, 1024w, 1382vs, 1469w

Continue Table 3

Class	ChemicalClass	Active Ingredient	Raman bands, cm^{-1}
Selective Systemic	Pyridinecarboxylic acid	Picloram	283w, 351s, 398w, 416m, 606m, 655m, 729m, 844vs, 920m, 1111s, 1163w, 1245w, 1344m, 1459w, 1590m
Selective emerging	Dinitroaniline	Trifluralin	313m, 558vw, 580w, 662w, 723w, 748m, 804vs, 1006m, 1105m, 1166w, 1252w, 1353vs, 1450w, 1551w, 1630w
Non-selective Systemic	Diphenyl ether	Fomesafen	710vw, 748vw, 865w, 986vw, 1079w, 1151vw, 1218w, 1247vw, 1356vs, 1481vw, 1585w, 1618vw
Selective systemic	Aryloxyalkanoic acid	2,4- D, dimethylamine salt	279w, 354w, 399s, 415s, 655m, 726m, 844vs, 859m, 898m, 921w, 947w, 1028w, 1048w, 1112m, 1160m, 1243m, 1293vw, 1342m, 1416w, 1477w, 1589m
Selective systemic	Pyridinecarboxylic acid	Fluroxypyr-meptyl + fluroxypyr + alkyl-benzene	605vs, 1007w, 1126w, 1320w, 1451m
Selective post-emerging	Aryloxyphenoxypropionic acid	Fenoxaprop-p-ethyl+aromatic hydrocarbon, C11	451vw, 519w, 703w, 770w, 1025w, 1382vs, 1467w
Selective systemic	Triacetone	Mesotrione	520w, 570vw, 704w, 769w, 1002vw, 1022w, 1381vs, 1466w, 1579w
Selective pre- and post-emerging	Triazine	Atrazine	327m, 373vw, 421w, 546w, 647w, 686w, 839m, 977vw, 924w, 963vs, 993w, 1063vw, 1085vw, 1132vw, 1254m, 1321vw, 1344vw, 1448m, 1553vw, 1601w
Selective non systemic	Triazine	S-metolachlor + atrazine	327m, 546w, 687w, 794w, 966vs, 1255m, 1460m, 1596m
Selective systemic	Triazine	Atrazine	329m, 374w, 421w, 549w, 651w, 689w, 842w, 928w, 967vs, 996w, 1067vw, 1136vw, 1256m, 1453w, 1605w
Non-selective Systemic	Glycine	Isopropylamine salt of glyphosate	477vw, 723vw, 778vw, 812vs, 895w, 941w, 989vw, 1082w, 1325vw, 1465w

In the case of glyphosate, we measured three samples from different manufacturers (Fig. 5). Although it is possible to differentiate the herbicide glyphosate from other herbicides (Fig. 4), for the studied samples, it is not possible to differentiate between the companies that market it.

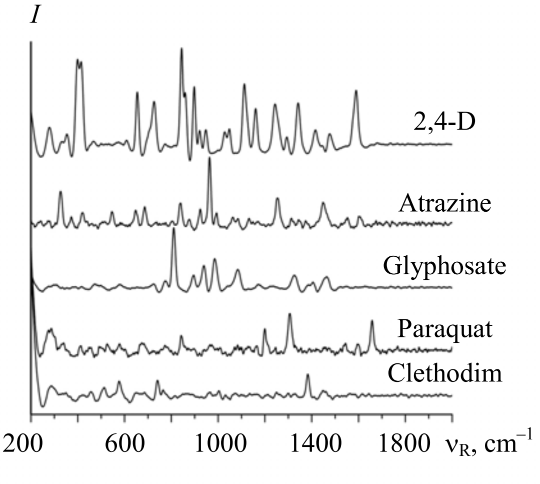

Fig. 4. Raman signal spectra of some commercial herbicides as a function of wavenumber.

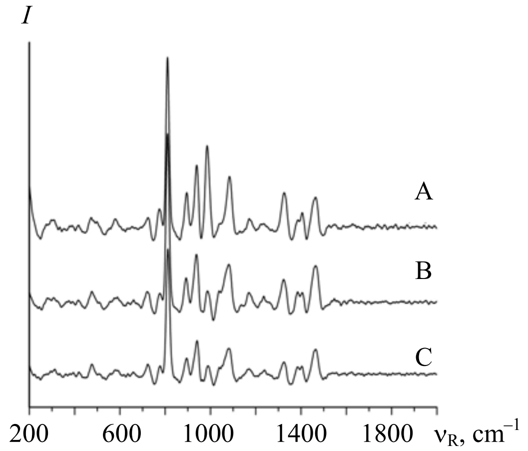

Fig. 5. Raman signal spectra of glyphosate from different companies A, B, and C.

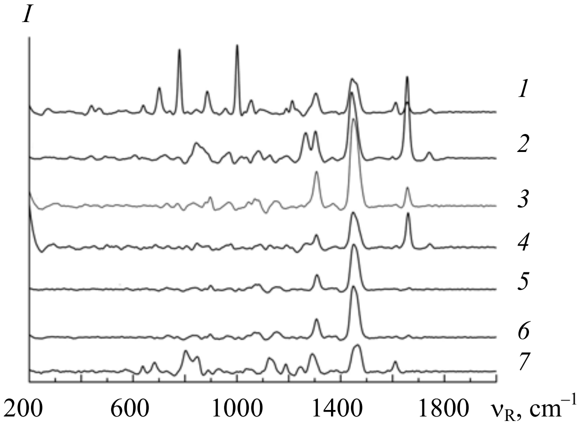

Fig. 6. Raman signal spectra of some adjuvants and mineral oils as a function of wavenumber: 1– mixture of methyl esters, aromatic hydrocarbons, unsaturated fatty acid, and surfactant; 2 – soybean oil methyl ester; 3 – paraffinic mineral oil; 4 – ethoxylated alkyl ester of phosphoric acid; 5 – paraffinic hydrocarbon mixture, cycle paraffinic and aromatic saturated and unsaturated oil obtained by distillation mineral oil; 6 – paraffinic hydrocarbon mixture, paraffinic and aromatic saturated and unsaturated cycle from the distillation of petroleum mineral oil; 7 – Nonyl phenoxy poly(ethyleneoxy)ethanol

TABLE 4. Relative Intensities of the Raman Bands of the Adjuvants and Oils Analyzed

Active Ingredient	Raman bands, cm^{-1}
Paraffinic mineral oil	897w, 1070vw, 1307m, 1449vs, 1658w
Nonylphenoxypolyethanol	292vw, 571vw, 638w, 683m, 803s, 848m, 929vw, 1043vw, 1125m, 1189w, 1246w, 1291m, 1466vs, 1611m
Mixture of paraffinic hydrocarbons, paraffinic cycle and saturated and unsaturated aromatics from petroleum distillation	734vw, 842vw, 897vw, 1069vw, 1154w, 1307m, 1449vs
Mixture of paraffinic hydrocarbons, paraffinic cycle and saturated and unsaturated aromatics from petroleum distillation	730m, 838m, 899s, 1086w, 1152vw, 1309m, 1450vs
Mixture of methyl esters, aromatic hydrocarbon, unsaturated fatty acid and surfactant	440vw, 468vw, 639vw, 701m, 779vs, 886m, 956vw, 1001vs, 1055w, 1090vw, 1191vw, 1213w, 1305w, 1445m, 1613w, 1656w
Soybean methyl ester	844w, 970vw, 1083vw, 1265m, 1303m, 1443s, 1656vs
Ethoxylated alkyl ester of phosphoric acid	1306m, 1448vs, 1660vs

Adjuvants and mineral oils can be added to pesticides to increase efficiency in application and the effect of the product. Table 4 shows the Raman band intensities of the 7 adjuvants and mineral oils evaluated. The Raman spectra of the adjuvants and mineral oils have two bands in common: in the 1310 and 1450 cm^{-1} regions (Fig. 6). The other bands are characteristic of every mix and can be used for the characterization of these products.

Conclusion. The substantial increase in the use of pesticides in recent decades has triggered a rise in the number of works in this area, with diverse study objectives: from investigations on the deposition of pesticides in samples of soil, water, and plant products to the damage they can cause to living things. In this connection, Raman spectrometry can be of invaluable help to researchers as it allows characterization of different commercial pesticides. This work characterized 78 pesticides through Raman spectroscopy by surveying the relative intensity of their characteristic bands.

Conflict of interest. The authors report there are no conflicts of interest.

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