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MONITORING THE BREAKDOWN OF DINOCAP IN SPIKED SOIL, WINE AND GRAPE SAMPLES BY GC/MS AND FTIR/ATR

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Abstract

Capillary gas chromatography coupled with mass spectrometry technique was used for the assessment of low concentration of dinitrophenol pesticide, Dinocap in different spiked samples. For this purpose it has been spiked with Dinocap (15- 200 µg/mL) five environmental matrices (a soil sample and two each samples of wine and grapes). The Dinocap degradation grade in these samples was also monitored. The extraction was performed in dichloromethane. The assessment of the Dinocap in the samples were also achieved by FTIR/ATR and reveals that after 18 days of pesticide application the recovery level of Dinocap decreased from 64% to 3% in grape, from 72% to 9% in soil, from 82% to 10% in wine at 18 days after pesticide application. The method described in this paper could be used for screening and identification of the named pesticide in other environmental samples with a spiking level as low as 2-20 µg/mL.

Keywords: dinitrophenol pesticide, dinocap, FTIR, GC/MS, wine

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1.Introduction

1.1. Methods for pesticide and pesticide residues quantification

Pesticides have largely benefited the human life through enhancement of agricultural products but in turn have influenced human health. The potential health impact of using the aforementioned huge amounts has merit increasing concerns in the public opinion. As consequence, different analytical methods for detection of pesticides and their potential degradation products in environmental samples and in foodstuff were developed. The analytical methods for the determination of pesticides depend on the matrix complexity origin, pesticide concentration in the sample and of the chemical classes (Madjar et al., 2014).

The *extraction methods* are an important aspect of the pesticides analysis and depend of sample origins. The procedure consists in selected organic solvent if the extraction technique is direct solid–liquid extraction (SLE) or liquid–liquid extraction (LLE). There are studies (Rial Otero et al., 2003) that present the analysis of 14 fungicides in white grapes for vinification using different extraction procedures, such as liquid-liquid extraction (LLE) method and solid phase extraction (SPE) method associated with liquid chromatography and diode array detection (HPLC-DAD). Furthermore, fungicides cyprodinil, fludioxonil, procymidone and vinclozoline, which are widely used to control grey mold in vineyards, from commercially sterilized white grape juice were determined using liquid–liquid extraction (LLE) and gas chromatographic separation, followed by mass

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spectrometric detection (GC–MSD) (Pose-Juan et al., 2006).

In the last decade was reported for solid sample in pesticides extraction two more new methods pesticide supercritical fluid extraction (SFE) and accelerated solvent extraction (ASE). Microwave-assisted extraction (MAE) has also been tested for both organochlorine pesticides (OCP) and organophosphorus pesticides (OPP) extractions. Matrix solid-phase dispersion (MSPD) has been applied to the extraction of both OCP and OPP residues and combines sample homogenisation, disruption, extraction, fractionation, and cleanup within a single process (Pareja et al., 2011).

Quaternary ammonium herbicides (diquat, paraquat, difenzoquat) are difficult to be analyzed, but there are researches (Pateiro-Moure, 2008) that present some procedures as such as digestion-based methods, shaking extraction and microwave-assisted extraction (MAE). Clean-up of extracts was performed by solid-phase extraction (SPE) using silica cartridges. Detection of these herbicides was performed using liquid chromatography (LC) coupled to UV detection and mass spectrometry (MS) as confirmatory technique.

Solid-phase extraction (SPE) is the most common technique for isolation and concentration of pesticides from water (López-Blanco et al., 2002) and it is used for quality tests in the laboratories of water analyses and beverage industries (Rial-Otero et al., 2006). Some studies (Rial-Otero et al., 2006) present the results of diquat and paraquat screening in drinking waters using SPE and liquid chromatography and diode array detection. SPE was also used in order to isolate some pharmaceutical compounds from river aqueous matrix (Iancu et al., 2017).

Solid phase microextraction (SPME) procedure has been developed, validated and reported for different pesticides, as it follows: cyprodinil and fludioxonil in white wine samples (Rial Otero et al., 2002), carbofuran (López-Blanco et al., 2002), α- and β-endosulfan in waters (López-Blanco et al., 2002), carbamates and phenylurea pesticide residues in fruit juices (Sagratini et al., 2007). SPME was employed in extraction of organochloride pesticides in some medicinal plants from Botswana (Gondo et al., 2016).

A new and efficient extraction technique reported in literature (López-Blanco et al., 2003; 2005) using single-drop microextraction (SDME) and gas chromatography with electron capture detector for determination of carbamates and organophosphorus pesticides in natural waters.

In separation and determination of the pesticides, *gas chromatography* (GC) is the most used method but *liquid chromatography* (LC) is also used for measuring levels of some pesticide and residues of pesticides in foods. Multi-residue methods including GC–mass spectroscopy (MS) have been developed for the routine analysis of pesticides from different classes, including OCPs, OPPs, pyrethroid pesticides (PYRs), triazines (TRZs), and their degradation products, in composite foods (Crnogorac et al., 2009; Rao et al., 1989).

Gas chromatography equipped with an ion trap mass spectrometry detector (GC–ITMS) was used to determine tebuconazole residues in grapes, musts and wines, meanwhile liquid chromatography equipped with triple quadrupole mass spectrometer (LC–MS/MS) was used to determine tebuconazole residues in synthetic must and wine used for *in vitro* assays (González-Rodríguez et al., 2009). Gas chromatography coupled with mass spectrometry (GC/MS) is by far the most frequent analysis tool for identifying the pesticides and the degradation products of its. Important advantages of the GC/MS based methods are: (i) the high amount of structural information yielded and the possibility of using commercial libraries which make the identification of unknown of degradation products feasible; (ii) the ruggedness and reliability of the GC/MS interface; and (iii) the high sensitivity and separation efficiency which avoid the overlapping of compound with similar structures.

The dithiocarbamate (DTC) fungicide residues in foodstuffs were assessed by photometric carbon-disulfide (CS_2) methods after acid digestion of DTC or by GC or LC combined with MS. DTCs rapidly degrade and will decompose into carbon disulfide (CS_2) and the respective amine under acid digestion. The DTC-residue analysis consist in collecting evolving CS_2 and a direct consequence is that maximum residue limits (MRLs) are specified as mg CS_2/kg food (Crnogorac et al., 2009; Rao et al., 1989).

Gas chromatography with specific detectors is used mainly, depending on the class of pesticides to be quantified. Electron capture detection (ECD) has usually been employed for OCPs and PYR analyses (Chung et al., 2011). Both flame photometric detection (FPD) with phosphorus filter and nitrogen–phosphorus detection (NPD) have been used for OPP detection. For example, six organophosphate pesticides (azinphosethyl, chlorfenvinphos, chlopyriphos, ethoprophos, fenamiphos, malathion) and two organonitrogen pesticides (alachlor and deltamethrin) from water were considered as target analytes for determination based on solid phase extraction (SPE) followed by gas chromatography with nitrogen-phosphorus detector (GC-NPD) (Lopez-Blanco et al., 2006). Gas chromatography coupled to high-resolution time-of flight mass spectrometry (GC-HR-TOF-MS) is an analytical technique that present an accurate-mass and high sensitivity measurements. GC-TOF-MS it is one of the most promising techniques to investigate the presence of organic compounds in different fields (Hernández et al., 2011).

Liquid chromatography (LC) has been used for the analysis for which GC conditions were not suitable, mainly carbamates and their metabolites and degradation products. LC has also been combined with conventional detectors such as fluorescence or UV detectors for identifying and quantifying pesticide residues.

LC has been coupled with different kinds of MS detectors, including single quadrupole, ion trap, tandem-MS, and time-of-flight-mass spectroscopy (TOF-MS) in order to determine pesticide residue levels and/or to elucidate their structures in aqueous and solid environmental samples as well as in foods of vegetable origin. More selective techniques for the analysis of DTCs include various HPLC approaches. Reversed phase chromatography (RP-HPLC) and ion-pair chromatography (IPC) followed by UV detection for the analysis of Thiram, Dibam, Ferbam, Metam-sodium, Ziram, Mancozeb, Zineb, and Propineb or with chemiluminescence detection for the separation of Mancozeb and Propineb. The compounds were analyzed in plants, soil and foods (Szolar, 2007).

RP-HPLC interfaced to MS via atmospheric pressure chemical ionisation (APCI) and electrospray ionisation (ESI) was applied to the analysis of Thiram, Disulfiram, Dazomet (3,5-dimethyl-1,3,5-thiadiazinane-2-thione), ethylenethiourea (ETU), and propylenethiourea (PTU) in fruits and vegetables. Thiram and degradation of DTCs as ETU and PTU in fruits and vegetable was analyzed in normal phase liquid chromatography (NP-HPLC) and UV detection. HPLC methods for the detection and quantification of the pesticide residues presence in juice and wine could employ UV absorption, UV diode array, fluorescence (FL) and chemiluminescence (CL) detection (Jin et al., 2007; Szolar, 2007).

Dithiocarbamate fungicides (DTC) in 150 samples of that are provided from products from Spain were quantified after different extraction and purification stages and liquid chromatography and diode array detection separation. The analyses indicated that the residue fungicide limits (MRLs) exceeding was found in 6% of the samples analyzed, specifically on lettuces and peppers (López-Fernández et al., 2012).

Assessments of residual levels of Mancozeb after spiking in smooth and curly lettuces at two different concentrations followed by different washing treatments (with tap water, Amukine, hydrogen peroxide, acetic acid, and ammonium hydroxide) at varying time and temperature were carried out by using acetonitrile extraction and high performance liquid chromatography with diode array detection (HPLC-DAD) (López- Fernández et al., 2013).

1.2. Nitrophenol pesticide quantification

The nitrophenol derivatives have valuable properties for applications to the biomedical and pharmaceutical domain, as well as to the agricultural and defense fields, with the risks of potential hazardous to the environment (Černohlávková et al., 2009; Kilgore and Cheng, 1963; Ju and Parales, 2010). The persistence of these compounds in the environment and the toxicity need the development of methods for detection of the presence at low levels of analytes and decontamination procedures (Calin et al., 2011; Zitko et al., 1976). The estimation of the presence of the pollutants in environmental sample supposes a preliminary separation. Extraction must achieve the transfer of the pesticide residue from each sample matrix into the organic phase and the clean up step is designed to protect the chromatographic system from the matrix ingredients which cause the efficiency of the chromatographic separation to deteriorate rapidly or impair the sensitivity of the selected detector (Cox et al., 2000).

Dinocap is the ISO common name for (RS)-2,6-dinitro-4-octylphenyl crotonates and (RS)-2,4-dinitro-6-octylphenyl crotonates, and it was used frequently in agriculture in European Union countries together with other pesticides of dinitrophenol type. (Koskela et al., 2006). The use of pesticides became a mandatory factor for an efficient agriculture in order to have a good production and control of diseases (Aravena et al., 2010).

The method frequently used for the detection of Dinocap residues requires different steps in the sample preparation procedures of evaporation, distillation, extraction and finally color development with a pyridine-water or ethanolictetraethylammonium hydroxide reagent. In literature there are few reports regarding spectral procedures correlated to phenol derivatives (Arancibia et al., 2005; Aysal et al., 2007; Grube et al., 2008; Mayer et al., 1995; Wackerbarth et al., 2010; Üzer et al., 2006;). It were reported also determinations of the presence of Dinocap by gas chromatograph/Fourier transform infrared spectrometer/mass spectrometry.

The Fourier Transform Infrared (FTIR) spectroscopy gave consistent data regarding the functional groups of the interest chemicals from environmental samples (Ahmad et al., 1996; Linker et al., 2005; Nyquist and Settineri, 1990; Picó and Kozmutza, 2007; Stahl and Tilotta, 2001), on pure chemicals or complex mixtures, without any sample preparation. The detection of the presence of Dinocap was made on different samples, a typical agricultural soil, 2 types of wines and 2 types of grapes, taken at different stage of experiment. The rate of degradation of Dinocap was also investigated in the named samples by GC/MS and FTIR.

2. Material and methods

2.1. Chemicals

Certified reference chemical of the test pesticide Dinocap technical mixture was of 89% purity and purchased from the SIGMA-ALDRICH (article no. 45452, batch SZE6017X). Dichloromethane was purchased from Merck-Darmstadt, Germany, natriumsulphate anhydrous was analytical reagent grade and purchased from Fluka.

2.2. Apparatus

A gas chromatograph GC Focus equipped with a mass detector DSQII and AI800 autosampler, Thermo Electron Corporation was used. Capillary column was TR5MS (30 m x 0.25 mm i.d., 0.25-µm

film). The column temperature was programmed from 40^0 C to 300^0 C at 10^0 C/min and held at final temperature for 7 minutes. Split mode with time of 10 minutes and injector temperature 250 ^{o}C was used. The ionization mode was electron impact (70 eV). The ATR FTIR measurements were performed by a FTIR 6300 Able@Jasco system with a single reflection diamond ATR crystal, an incidence angle of $30^0$and the transmission spectra used KRS - 5 windows. It were aquired 3630 data points per each spectrum, over the range of 500 - 4000 cm^{-1} with a resolution of 4 cm^{-1}. The nitro bands are situated at 1346 and 1545 cm^{-1}. For monitoring of the degradation process of the nitrocompound, the reference chemical was acquire and select the characteristic absorption bands.

The used equipment included analytical balance KERN ABJ – capable of accurately weighing to the nearest 0.0001 g; Water bath Aqua-wave 9377, Barnstead/Lab-Line – capable of holding a steady temperature of 50 ^{0}C; Memmert oven; rotaevaporatory Laborota 4000, Heidolph. The used glassware included screw-capped bottles 2, 4 and 8 ml (Pyrex), volumetric flasks of 10 mL, Pasteur pipettes – 0.1 to 5,000 µL, variable-volume autopipettes with disposable plastic tips; plastic bottles – plastic bottles should be of high-density polyethylene (HDPE), Teflon, or some other material to which Dinocap will not adsorb; separatory funnels of 50 mL equipped with polytetrafluoroethylene (PTFE) stopcock; and sample filters – nominal 0.45 µm, Millipore Millex-HV.

2.3. Standard solutions

The stock solution was prepared by accurately weighing 20 mg (±0.01 mg) Dinocap in volumetric flask (certified 'A' class) and dissolving in 10 mL dichloromethane. A 10-fold dilution was made from original stock solution to prepare the working solution with concentrations of about 200 µg/mL. The dilution was repeated for the preparation of working solution with concentrations of about 20 µg/mL. Exact concentrations of Dinocap in the working standard solutions are presented in the following table (Table 1). The solutions were stored in a refrigerator at 4^{o}C.

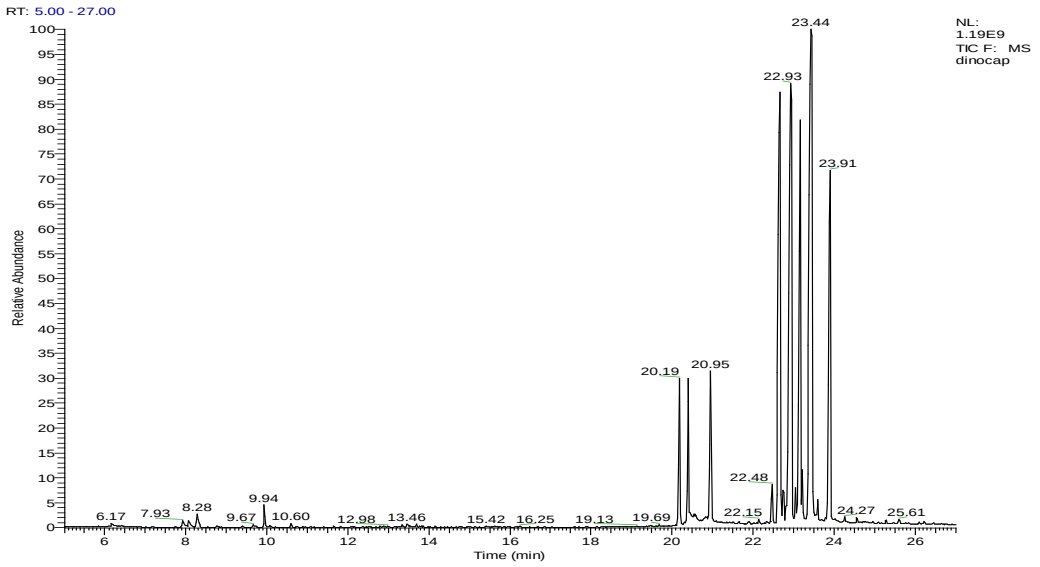
Table 1. Concentrations of Dinocap in the dilution

Sample code	***Concentration level (µg/mL) in CH_2Cl_2***
S0D	1780
S1D	178
S2D	17.8
S3D	1.78 (0.488 µM)

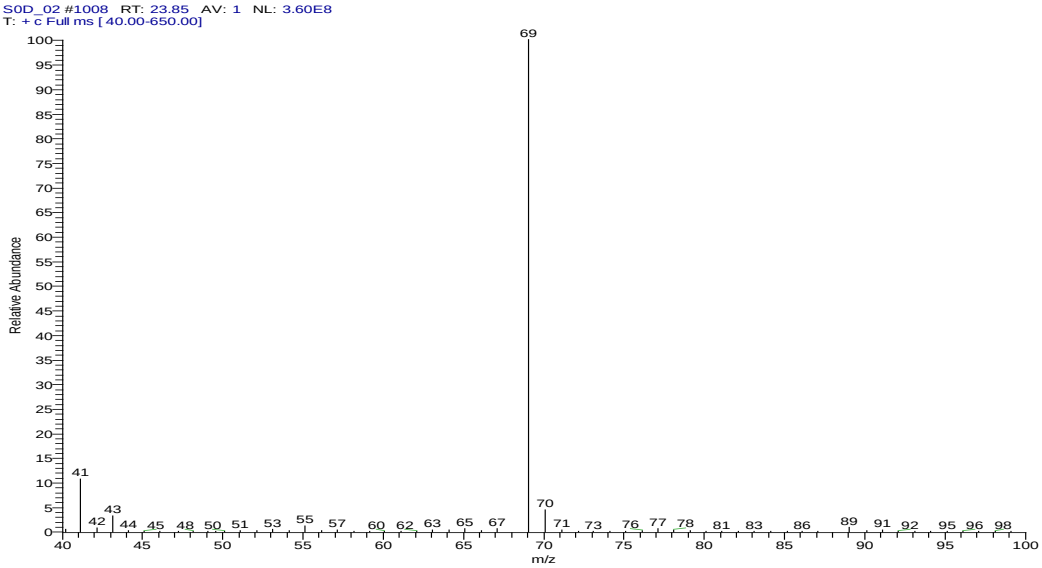
GC chromatogram of Dinocap displays the isomers of 9.94, 22.67, 22.93, 23.16, 23.44 and 23.91 min, respectively (Fig. 1a). The mass spectra of the isomer of Dinocap at 23.85 min. of retention timeare presented also (Fig. 1b). The Dinocap presents in FTIR spectrum many bands in order with the complicate structure. In accordance with its ATR FTIR and literature (Green and Lauwers, 1971; Rusu et al., 2010) the almost equal intensities of of $\nu_{sim}(NO_2)$ at 1545 cm^{-1} and of $\nu_{sim}(NO_2)$ at 1346 cm^{-1} are due to the isomer 2,6-dinitro-4-octylphenyl crotonate. The CH units from aliphatic segments are at 2859 – 2959 cm^{-1}, C-H bands of methyl and methylene groups are at 2931 cm^{-1} (CH asymmetric stretch) and at 2859 cm^{-1} (CH symmetric stretch). The bands of C=O group and C=C double bond from ester moiety are situated at 1759 and 962 cm^{-1}.

2.4. Spiking samples

Laboratory determinations were made on arable soil (coded S1D) from Prahova region with an intensive agriculture, red and white wine, coded V1D and V2D, respectively, and red and white grapes, coded STRA2RD and STR1AD, respectively. Rosé wine was namely "Busuioaca de Bohotin" and the white wine was namely "Tamaioas aromaneasca". As grape samples were used fresh red and white grapes above varieties.



(a)



(b)

Fig. 1. (a) EI total ion chromatogram of Dinocap solution in dichloromethane; the isomers are at the retention times of 9.94, 22.67, 22.93, 23.16, 23.44 and 23.91 min, respectively. (b) EI mass spectra of Dinocap isomer at 23.85 min of retention time

Pesticide contamination consisted in spiking of 20 mg Dinocap aqueous solution over the tested samples of about 100 g, equivalent with doses that reach in soil during application. The Dinocap concentration of the spiked samples is presented in the following table (Table 2). The sample materials before analysis were kept under ambiental conditions. A soil sample, red and white wine and fresh grapes, which did not receive any treatment of the pesticide were used as blank.

Table 2. Dinocap concentration of the spiked samples

Sample code	***Dinocap concentration [µg/g]***
S1D	183
STR1AD	190
STR2RD	200
V1D	154
V2D	192

2.5. Method quantification

The quantification of the interest analyte, Dinocap, was based on five-point calibration graph obtained by plotting the area ratio of the target compound and concentration of the calibration standards. The detection limit parameter was determining by considering a signal to noise ratio of 4 with reference to the background noise obtained from the blank sample, whereas, the limit of quantification (LOQ) was determined by considering a signal to noise ratio of 13.

The measurements follows the untreated samples, and treated samples after one hour after the pesticide application, and were coded E1. At each sampling, two samples of each matrix were taken and the analyses were performed immediately. The dichloromethane was chosen for the extraction procedure.

From each sample 10 g was extracted two times, with a volume of dichloromethane equal to two times the weight of the sample. After the separation, centrifugation steps, the organic extract was filtered with a HPLC filter unit (0.45 µm, Millipore Millex-HV) and dried for one hour with Na_2SO_4. The resulting extracts were concentrated in a gentle flow of nitrogen at 20 – 25 ºC to a volume of 1000 µL. The analyses were performed by GC/MS, and after that, the samples were evaporated to dryness and the residue was analyzed by infrared spectroscopy.

The extraction efficiency of the above batch was determined by GC/MS and the monitoring of the pesticide at the different stage of the experiment was done by FTIR and GC/MS, respectively. The GC chromatogram of the soil organic extract coded S1E1, red and white wine organic extracts coded V1DE1 and V2DE1, red and white grapes organic extracts coded STR1ADE1 and STR2RDE1, and of the standard solution of 1780 µg/ml, coded S0D is presented (Fig. 2). The recovery grade of the pesticide from the soil spiked sample, extracted after one hour of application, was about 72%, for STR1ADE1 of 64%, STR2RDE1 of 63%, V1DE1 of 75% and for V2DE1 of 82%.

The monitorin of Dinocap was performed by FTIR spectroscopy by the vibrations of nitro group. We have also performed preliminary investigations by FTIR/ATR spectroscopy on spiked samples in natural state.

The comparative FTIR spectra of the residue of the soil sample extracted in dichloromethane, after one hour of pesticide application, sample code S1DE1, the spiked soil as such, code Sol, in comparison with the reference chemical, sample code Dinocap are presented below (Fig. 3).

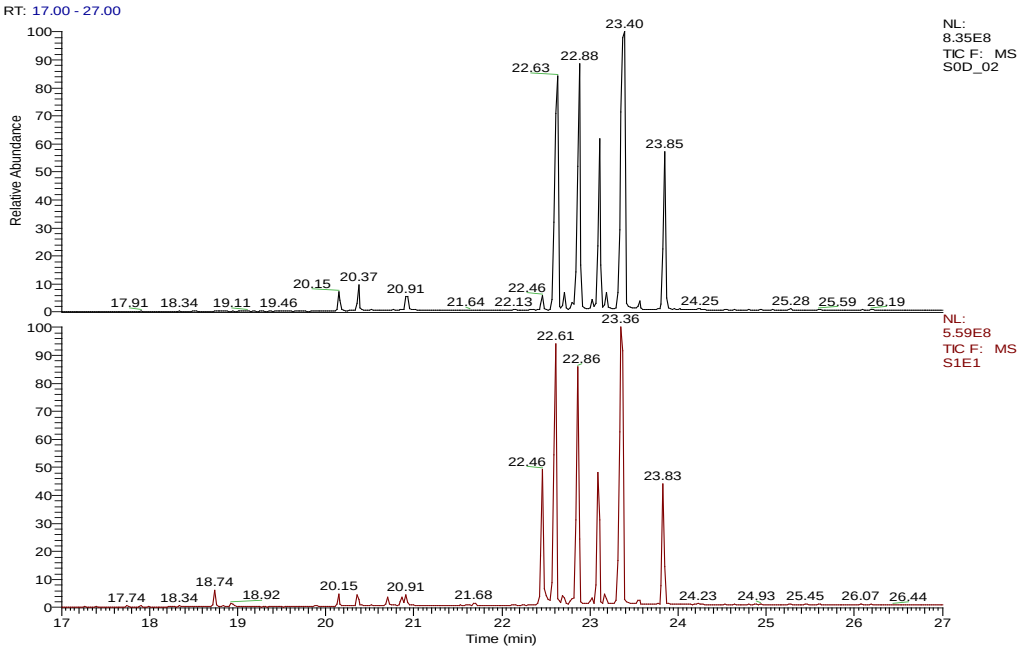


Fig. 2. EI total ion chromatogram of the Dinocap standard solution of 1780 µg/ml (upper), sample code S0D, and soil organic extract, sample code S1E1

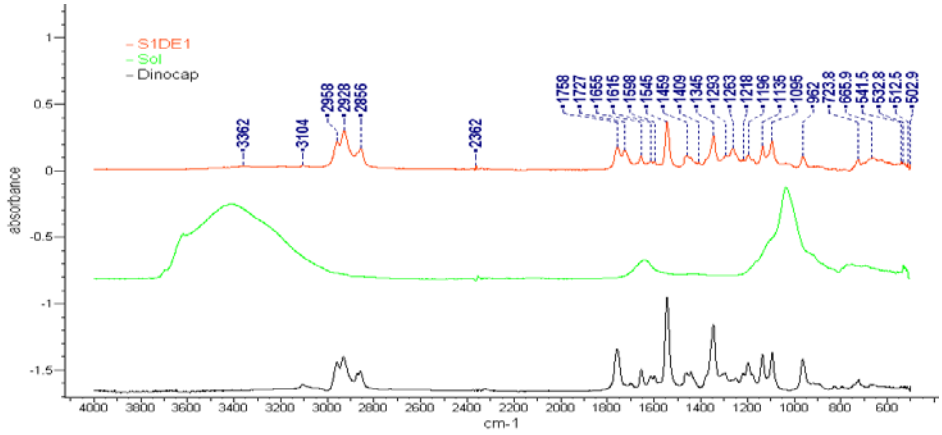


Fig. 3. FTIR spectra of the residue of the soil sample extracted in dichloromethane, after one hour of pesticide application, sample code S1DE1, the spiked soil as such, code Sol, in comparison with the reference chemical, sample code Dinocap

2.6. Stability test of the pesticide in the wine-growing products

The samples were taken at the chosen period of 7 days after pesticide application and the organic extracts were coded E2, after 15 days, coded E3, and 18 days, coded E4, respectively.

3. Results and discussion

The chromatographic monitoring revealed that after 18 days of the pesticide application, the organic extracts coded E4 showed about 3-16% of the Dinocap presence. The recovery grade of dinocap decrease from 63% to 3% in STR2RDE4, 72% to 9% in S1DE4, 82% to 10% in V2DE4, 64% to 15% in STR1ADE4, 75% to 16% in V1DE4, at 18 days after pesticide application. The degradation timetable of Dinocap in the spiked samples is presented in the Table 3 and Fig. 4. The area of the sample extracts are plotted versus the dichloromethane extracts of each spiked samples, at the initial contact of sample with the pesticide Dinocap.

As it is expected, due to natural environment the decreasing of the Dinocap content in spiked samples occurs, due to the intensity of the nitro band that has been diminished (Fig. 5), at 1544 cm^{-1} and 1344 cm^{-1}. The IR vibrations of nitro group was better evidenced in the dichloromethane extracts of soil, wine and grapes as is presented in their spectra. The intensity of nitro bands seems to increase and decrease the nitroaromatic content in samples. Also, the intensity of the absorption band with assymmetric vibration of nitro groups at 1620 cm^{-1} decrease in the time, correlating with decreasing of the content of Dinocap in the spiked samples. The 1100 – 1700 cm^{-1}

region of FTIR microspectra of the residue of organic extracts of the spiked samples after 18 days of pesticide application: soil, sample code S1DE4; red wine, sample code V1DE4; white wine, sample code V2DE4; red grape, sample code STR2RDE4, and white grape, sample code STR1ADE4 are presented (Fig. 5). The IR vibrations at 1759 cm^{-1} that correspond with C=O group and of C=C at 962 cm^{-1} within Dinocap molecule were monitorized by FTIR. It is possible that a degradation product of Dinocap can occur in the degradation process, due to chances in the absorption at 1759 cm^{-1} and a new peak at 3424 cm^{-1}. After 54 days of the Dinocap application to the soil sample, sample code S1DE7, it was evaluated the dichloromethane extract by GC/MS. The total ion chromatogram (Fig. 6), in comparison with the organic extract after 18 days of pesticide application, sample code S1DE4, and theDinocap solution of about 2 µg/mL, sample code S2D is presented. The degradation product at 22.46 minutes retention time has the mass spectrum presented (Fig. 7), with a possible structure from the NIST database.

One of the possible degradation products of Dinocap in the wine-growing products studied could be 9-octadecenamide, by the bands of 3193 cm^{-1} ($NH_2C=O$), 3360 cm^{-1} of NH (stretch) primary amide, and 1632-1660 cm^{-1} from –CO from the primary amide, overlapped by C=C from alkylene. The IR bands from 950-1225 cm^{-1} that belongs to the aromatic ring are dissapeared from the soil sample analyzed after 54 days of pesticide application.

One more degradation product could be the 2,6-dinitro-4-octylphenol by the presence of the IR peak at 1728 cm^{-1} and 1688 cm^{-1}that belongs to carboxylic acid –COOH α, β unsaturated, and the dissapearing of the IR peaks at 1759 cm^{-1} and 1615 cm^{-1} from CO esters α, β unsaturated. The new peaks at 1261 cm^{-1} and 1035 cm^{-1} are corresponding with –OH group from Aryl-OH; 773.9 cm^{-1} and 799.9 cm^{-1} for 1,2,3 trisubstitute aromatic ring; a large band at 3420 cm^{-1} for –OH and NH groups from alcohols, phenols and carboxylic acids, amines or amides; and 1688 cm^{-1} carboxylic acid –COOH α, β unsaturated.

Table 3. Degradation by GC/MS of Dinocap in spiked samples

Extraction code of the sample	***Sample type/Area***				
	S1	***V2***	***V1***	***STR1A***	***SRT2R***
S0D (1780 µg/mL)	11067				
E1/1st day	6455	9009	7577	5351	5070
E2/ 7 days	6363	1017	7346	6054	3946
E3/15 days	1866	810	6676	4457	4646
E4/18 days	1034	1178	6676	1618	415

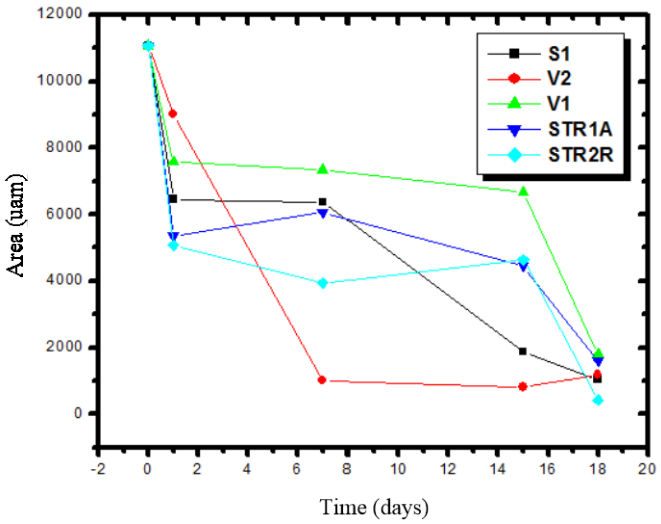


Fig. 4. Dinocap degradation grade in the spiked samples: soil sample, code S1; white wine, code V2, red wine, code V1, white grape, code STR1A, red grape, code STR2R

4. Conclusions

The rate of degradation of Dinocap was investigated in the analyzed samples by GC/MS and FTIR/ATR. Analytical studies were carried out on samples of arable soil, red and white wine, red and white grapes that have been spiked with Dinocap at concentrations that ranged 15- 200 µg/mL. The recovery grade of the pesticide from the soil spiked sample, extracted after one hour of application, was about 72%, for soil. In the case of white grapes was 64%, for red grapes was 63% meanwhile for red wine was 75% and for white wine was 82%. The recovery grade of Dinocap decreased from 64% to 3% in grape, from 72% to 9% in soil, from 82% to 10% in wine at 18 days after pesticide application. After 54 days of the Dinocap application to the soil sample was found degradation compounds of Dinocap.

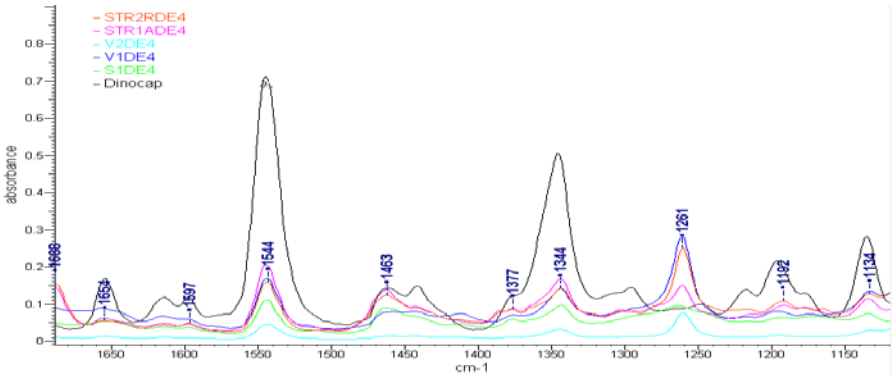


Fig. 5. 1100 – 1700 cm^{-1} region of FTIR microspectra of the residue of organic extracts of the spiked samples after 18 days of pesticide application: soil, sample code S1DE4; red wine, sample code V1DE4; white wine, sample code V2DE4; red grape, sample code STR2RDE4, and white grape, sample code STR1ADE4

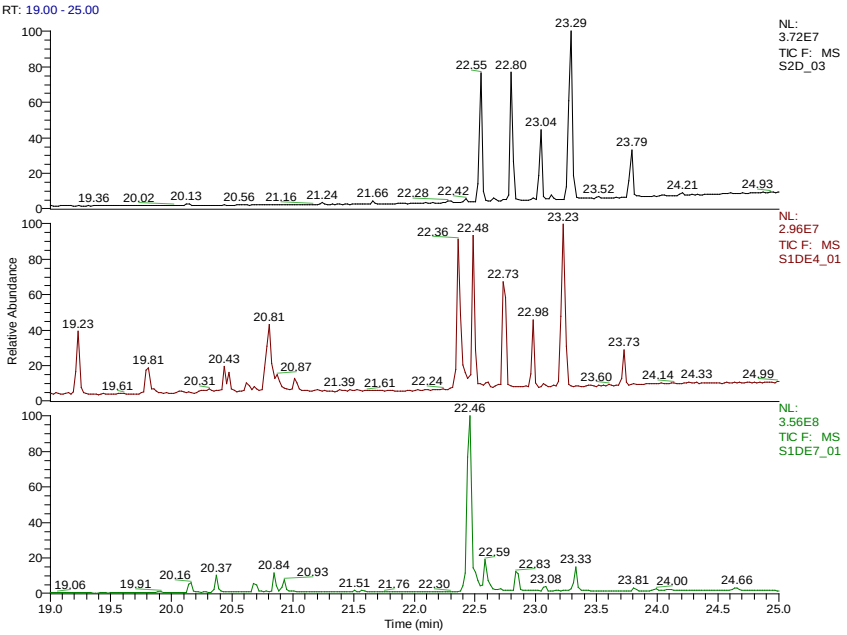
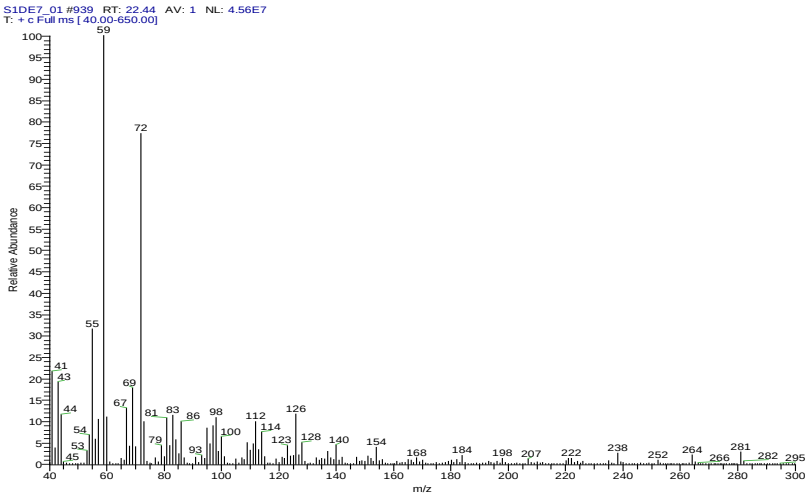
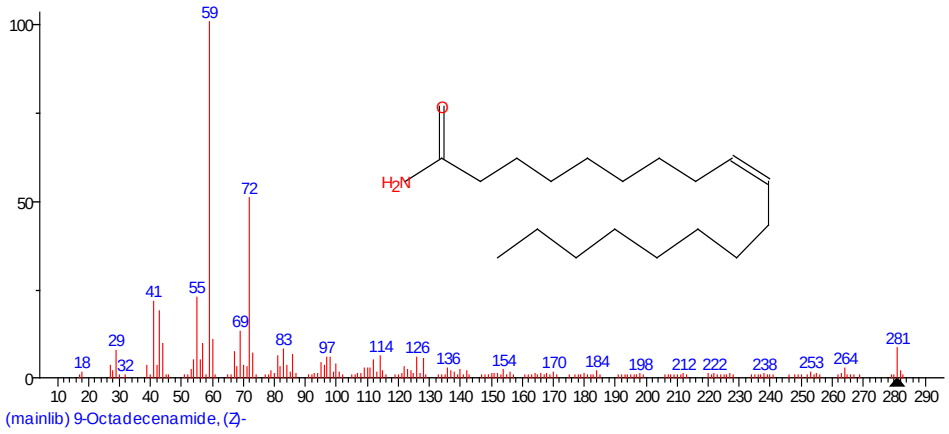


Fig. 6. EI total ion chromatogram of the dichloromethane extract of soil sample spiked with Dinocap, after 54 days of the application, sample code S1DE7 in comparison with the organic extract after 18 days of pesticide application, sample code S1DE4, and theDinocap solution of about 2 µg/mL, sample code S2D. The interest analyte is almost completely degradated by the presence of the chemical at 22.46 minutes



(a)



(b)

Fig. 7. (a) Mass spectrum of the chemical at 22.44 minutes
from the sample coded S1DE7 and (b) the reference from the NIST database

This study has demonstrated that GC/MS is an exquisite method for identification and quantification of Dinocap pesticide from different matrices using organic solvent extraction. The analysis can be conducted from a sample with a spiking level as low as 2-20 µg/mL. Qualitative analyses performed by IR spectroscopy showed the presence of Dinocap at about 20 µg/mL spiking level, at 1546 cm^{-1} and 1345 cm^{-1} in the FTIR absorption spectra, corresponding to NO_2 symmetric groups. The position of the IR peaks can be used for the degradation process of nitro aromatics monitoring, based on the sample extracts in dichlorometane.

The main benefits from the presented method for the presence detection of Dinocap from wine-growing products are:

- confirmation of the analyte by two different spectrometric techniques (GC/MS and FTIR/ATR);
- the same preparation procedure applied involves a considerable saving in experimental time, a smaller quantity of the extraction solvent volume that involves lower chemical waste.

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