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ADVANTAGES AND DISADVANTAGES OF PESTICIDE ANALYSIS METHODS USED IN AGRICULTURAL SAMPLES

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Abstract

Pesticides are substances (herbicides, fungicides, insecticides, plant growth regulators etc.) used primarily for pest control that can occur in both animals and plants. Unfortunately, besides beneficial effects, their use also has many disadvantages, these being toxic to humans and environment. For this reason, it is very important to have precise and accurate analytical methods for pesticide determination and quantification. The main purpose of this paper was to provide a description of the most commonly used methods of analysis and sample preparation for qualitative and quantitative determination of pesticides. The field of agriculture was analysed as a field of use of pesticides. Thus it has been highlighted that current analysis methods heavily rely on the use of gas chromatography analysis tools and in regard to the methods of agricultural samples preparation, these are in general extraction methods. The paper presents the advantages and disadvantages of the mentioned methods, in qualitative and quantitative assessment of pesticide present in agricultural biomass.

Key words: *pesticides, agriculture, analytical method, chromatography.*

INTRODUCTION

Pesticides are substances used primarily for pest control (US Environmental, 2007) that can occur in both animals and plants.

There are several classes of pesticides, the most common ones being:

- Organochlorine pesticides: DDT is the most used pesticide from this class and although its use has been restricted, there are countries that are thinking of reintroducing it (Turusov et al., 2002; Van den Berg, 2009);
- Organophosphorus pesticides: although they are said to be a more ecological option, many of the substances from this class have been associated with an endocrine disrupting potential (Mnif et al., 2011; Karami-Mohajeri et al., 2011);
- Carbamate pesticides: unfortunately the use of this class of pesticide can lead to a series of negative activity on the human body such as: possible reproductive disorders (Jamal et al., 2015), genotoxic effects in hamster ovarian cells (Soloneski et al., 2015) and last but not least increased risk for dementia (Lin et al., 2016).

There are three ways in which humans can be affected by pesticides (Yusà, Coscollà and Millet, 2014) and the most important source is through diet or ingestion.

Another way is through dermal contact, a way that it’s more and more encountered due to household use of pesticides.

And a third way is by inhalation of contaminated air, particularly for those are staying nearby the agriculture areas.

Pesticides besides activities that have a negative impact on the health of people, affect on long term all type of water (surface and underground), air, soil and also soil organisms (Sarfraz et al., 2009)

To understand better the importance of pesticide use a short history of these compounds have been summarised in Table 1.

Table 1. Brief history of pesticide use (Jojiya et al., 2017)

Period	Type of pesticide used
Ancient time	Ashes, common salts and bitters
1st century	Arsenic, suggestion of soda and olive oil for treatment of legumes (Pliny the Elder, a Roman naturalist-Historia naturalis)
16th century	Arsenicals and nicotine in the form of tobacco extracts (Chinese farmers)
1850	Pyrethrum, soap and a wash of tobacco, sulfur and lime also used
1867	The pigment Paris green (impure form of copper arsenite), Paris green and kerosene oil emulsion
1896	Bordeaux mixture ($CuSO_4$ and $Ca(OH)_2$) and selective chemical herbicides
1900	Dilute sulfuric acid, copper nitrates and potassium salts
1900-1950	Sodium arsenite solutions become the standard herbicides and are used in large quantities
1913	Organomercury seed dressing
1913-1939	Dithiocarbamates fungicides used in US
1939	Insecticidal potential of DDT discovered in Switzerland. Chlorinated hydrocarbons (DDT, BHC, dieldrin, aldrin and chlordane)
1950s	Fungicides captan, glyodin and organophosphorus insecticide: malathion
1961	DDT registered for use on 34 different crops as pesticide usage dramatically increases
1962	Bio accumulation and long-term toxicity and pest resistance became evident. Stoppage of DDT usage and other chlorinated compounds by farmers. Favor of the use of Organophosphates and Carbamates
1972	Environmental Protection Agency revoked the use of DDT on all food sources in the United States. The World Health Organization, however, still reserves the right to use DDT on particularly virulent outbreaks of malaria
1972-1980	Herbicidal sulfonylureas, neonicotinoids, glyphosate, synthetic fungicides such as metaxyl and triadimefron and light-stable pyrethroid pesticides are introduced
1990s	Integrated pest management, intensified research on biological pest control methods and other alternatives to pesticides
1990-1995	Increased interest in Integrated Pest Management (IPM) programs
2000	Wide spread usage of IPM techniques organic farming excluding the usage of synthetic pesticides.
2010-2015	Involvement of genetic engineering and biotechnological methods to control the usage of pesticides eg. baculoviruses

EXTRACTION METHODS OF PESTICIDES

A novel method for sample extraction that it is used more and more is QuEChERS (Sherish et al., 2017).

One study use QuEChERS for the determination of seven pesticides from Okavango Delta water samples and present a detection limit situated between 0.102 μg/L-1.693 μg/L and a recovery value situated between 61% and 95% (V.C. Obuseng et al., 2013). Correia-Sa et al. have analysed soil samples with organic carbon over 2.3% and obtained 3.42-23.77 μg/kg limit detection and 70%-120% recovery (Correia-Sa et al., 2012).

Fresh peppermint samples were analysed by Magdalena Slowik-Borowiec et al. using this type of extraction method and obtain 0.01 mg/kg limit of detection and 100% recovery (Slowick-Borowiec et al., 2012). This method has several advantages such as: environmentally friendly and is simple and fast.

Another type known and used extraction method is Supercritical Fluid Extraction (SFE) which can be used for both solid and semi-solid samples. It is a recently developed method. The main advantage is that SFE is simple and less time consuming. Teresa Castelo-Grande et al. developed a SFE method for pesticides from soil and obtain a recovery of atrazine higher that 96% (Teresa Catselo-Grande et al., 2005). Tatsuo Yoshida et al. obtain a value for recovery of Isotianil extracted from rice and rice cultivation soil between 95.1% and 99.3% (T. Yoshida et al., 2013).

Hiroaki Chikushi et al. (H. Chikushi et al., 2009) evaluated the presence in water sample and proposed a method with low limit of detection: 0.002-2.3 μg/l.

A quite new extraction method is accelerated solvent extraction (ASE). Important points in this technique are temperature and pressure and also have advantages like speed and simplicity. Another plus is represented by the volume of reactive which is relatively low. Michelle L. Hladik et al. have analysed environmental sediment samples and obtain 81-101% recovery and 0.6-3.1 μg/kg limit of detection (Michelle L. Hladik et al., 2012).

Beside the extraction methods mentioned above, there are presented in Table 2 other data obtained by using different types of extractions.

Table 2. Extraction method of pesticide

Extraction method	Recovery/Limit of detection (LOD)	Sample	Advantages/Disadvantages	Reference
Headspace Single-Drop Micro-extraction (HS-SDME)	LOD = 0.07-12.54 μg/kg Recovery = 74-102%	Honey	Advantages: Possibility of using various solvents; Very good for extraction of diazinon; Possibility of extracting volatile and water-soluble analytes.	Amvrazi et al., 2012
Solid Phase Extraction (SPE)	LOD = 0.01-0.088 μg/L Recovery = 74.2-116.4%	Water samples	Advantages: Can be used to determine may types of pesticides; Present very good limit of detection; Rapid and efficient method.	Lopez-Mesas et al., 2007
Dispersive liquid–liquid micro-extraction (DLLME)	LOD = 0.0032-0.0174 μg/L Recovery = 84-108 %	Water samples	Advantages: Fast; Sensitive; Multi-residue method; Very good recovery. Disadvantages: Limited solvent choice; It's not suitable when the matrix composition is complex.	Abdullash et al., 2017
Solvent-based de-emulsification dispersive liquid–liquid micro-extraction (SD-DLLME)	Recovery = 60-120%	Water samples	Advantages: Environmentally friendly; Less expensive than other techniques; Can be applied also for pharmaceuticals and personal care products. Disadvantages: same as DLLME.	Caldas et al., 2016
Accelerated solvent extraction (ASE)	LOD = 0.6-3.1 μg/kg Recovery = 81-101%	Sedimentation of agricultural drainage samples	Advantage: Small volumes of solvents; Fast, easy and simple. Disadvantages: Relatively high price of the equipment.	Hladik et al., 2012
	LOD = 0.8-3.4 μg/kg Recovery = 75-102%	Sediment samples from the estuary		
Solid-phase extraction (D-SPE) by quick, easy, cheap, effective, rugged and safe (QuEChERS)	LOQ = 0.1-100 μg/kg	Rice paddy soils	Advantages: Alternative materials are more effective and less expensive than traditional sorbents Disadvantages: Limited solvent choice for extraction.	Arias et al., 2014
QuEChERS	Recovery = 70-120%	Cereals (corn, wheat flour and rice)	Advantages: Multi-residue analysis; Simple and with satisfactory accuracy.	He et al., 2015
Direct immersion solid-phase micro-extraction (DI-SPME)	LOD = 0.015-0.13 μg/L	Aqueous samples	Advantages: Can be applied on all types of water samples; Multi-residue analysis. Disadvantages: Relatively expensive because of fiber cost; Matrix effects.	Tankiewicz et al., 2013
Microwave-assisted extraction (MAE)	Recovery = 81.5-108.4%	Grass samples; Vegetation from the contaminated industrial area of Torneiros	Both methods are suitable for chlorinated pesticides analysis. Advantages MAE: shorter extraction times, higher extraction rates.	Barriada-Pereira et al., 2003
Soxhlet extraction	Recovery = 75.5-132.7%			

DETERMINATION METHODS OF PESTICIDES

Javad Ghodsi and Amir Abbas Rafati have developed a method for the determination of diazinon made by use of a MWCNTs/TiO2NPs nanocomposite sensor (J. Gjodsi et al., 2017). Comparative with other methods used such as gas chromatography, high-performance liquid chromatography (HPLC), mass spectrometry method, spectrophotometry, infrared spectroscopy and an enzyme immunoassay (M. Khadem et al., 2017; T.D. Lazarevic-Pasti et al., 2013; G. Erdogdu, 2003) that are expensive, time-consuming and with the need of trained employers, this method has shown to be sensitive, fast and use an easy fabricate sensor that is not so expensive. Also the method presents a good limit of detection of 3 nM.

The real samples have included city piped and agricultural water.

Another determination method that uses HPLC/MS/MS was developed by Hwa-mi Lee et al. They analyse 56 residual pesticides from commercial crops and obtain a recovery value between 65-82% and a detection limit up to 11.54 µg/kg (Hwa-mi Lee et al., 2013).

Hirahara et al. described a screening method for determination of 200 pesticides using GC/MS/MS.

The method present a recovery value situated in 50-150% interval and a good limit of quantification of 0.01 mg/kg (Hirahara et al., 2006).

There are many methods for determination of pesticides, some of which are presented in the Table 3.

Table 3. Determination method of pesticide

Determination method	Recovery/ Limit of detection (LOD)	Sample	Advantages/Disadvantages	Reference
GC-ìECD	LOD = 0.07-19 µg/kg	Honey	Very good for determination of organochlorines and organophosphorus pesticides; Highly sensitive; Low detection limit.	Amvrazi et al., 2012
GC/MS	LOD = 0.6-3.1 µg/kg Recovery = 81-101%	Sedimentation of agricultural drainage samples	Very good recovery value; Sensitive method.	Hladik et al., 2012
	LOD = 0.8-3.4 µg/kg Recovery = 75-102%	Sediment samples from the estuary		
Micellar electro-kinetic chromatography–electrospray–mass spectrometry (MEKC-ESI-MS/MS)	LOD = 0.001-0.144 µg/L Recovery = 83-101%	Environmental or drinking water samples	Advantages: Low limit of detection Disadvantages: Relatively high price of the equipment	Moreno-Gonzalez et al., 2012
Ultra-high-performance liquid chromatography/time-of-flight mass spectrometry (UHPLC/TOF-MS)	Recovery = 74-111%	Vegetable and fruit samples	Multi-residue method; suitable for routine quantitative analyses of pesticide	Sicaperumal et al., 2015
GC/SQ-MS	LOD = 0.4-48.2 µg/kg Recovery = 70-110%	Grape, lemon, onion and tomatoes	Advantages: The method is repeatable; Can be used in many types of matrices Disadvantages: Lemon and onion showed poor recoveries	Lesueur et al., 2008
HPLC/IT-MS	LOD = 1-115 µg/kg Recovery = 70-110%			
GC-MS/MS	Recovery = 96 ± 9%	Cereal samples (wheat, rye, barley, oats, maze, buckwheat)	Improved analytical performance parameters Multi-residue method.	Walorczyk et al., 2012

CONCLUSIONS

Due to the numerous negative effects on human and environmental, it is important and there is still a need to develop precise, sensible and robust extraction and analysis methods to determine the amount of pesticides and to keep them in conformity with applicable laws. Taking into account all these aspects, in this paper we have briefly discussed the most commonly used extraction and determination method for pesticides mainly from agriculture domain and also from other fields.

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