

Residues

Definition

Pesticides

1. The designation pesticide applies to any substance or mixture of substances intended to prevent, destroy, or control any unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of pure articles. The designation includes substances intended for use as growth regulators, defoliants, or desiccants, and any substance applied to crops before or after harvest to protect the product from deterioration during storage and transport.
2. Pesticides are commonly used in agriculture. Pesticides may stay in small amounts (called residues) in or on fruits, vegetables, grains, and other foods. To make sure the food is safe for consumption, official bodies like the United States Environmental Protection Agency (EPA) regulates the amount of each pesticide that may remain in and on foods.
3. Pesticides are categorized into four main substituent chemicals: herbicides; fungicides; insecticides and bactericides.

Antibiotics

1. During their lifetime animals may have to be treated with different medicines for prevention or cure of diseases. In food producing animals such as cattle, pigs, poultry and fish this may lead to residues of the substances used for the treatment in the food products derived from these animals (e.g. meat, milk, eggs). The residues should however not be harmful to the consumer. To guarantee a high level of consumer protection, legislation requires that the toxicity of potential residues is evaluated before the use of a medicinal substance in food producing animals is authorized. If considered necessary, maximum residue limits (MRLs) are established and in some cases the use of the relevant substance is prohibited.

Further reading on pesticide and antibiotic residues:

<http://www.fda.gov/Food/FoodSafety/FoodContaminantsAdulteration/Pesticides/default.htm>

<http://www.epa.gov/pesticides/index.htm>

<http://www.agf.gov.bc.ca/pesticides/>

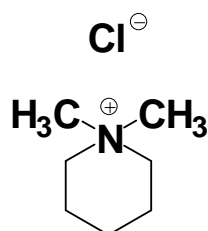
http://ec.europa.eu/food/food/index_en.htm

http://ec.europa.eu/food/plant/protection/pesticides/index_en.htm

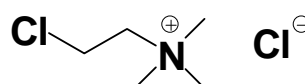
http://ec.europa.eu/sanco_pesticides/public/index.cfm

<http://en.wikipedia.org/wiki/Pesticide>

Pesticides



Mepiquat



Chlormequat

Pesticides are biological (such as a virus, bacterium, antimicrobial or disinfectant) or chemical substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest. Target pests can include insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes (roundworms), and microbes that destroy property, cause nuisance, spread disease or are vectors for disease.

There are currently 507 pesticides that are listed with maximum residue limits by the European Union. Many of these are difficult to analyze using traditional methods. For example chlormequat and mepiquat are two very hydrophilic pesticides, they are widely used as plant growth regulators. They act by inhibition of vegetative growth and promotion of flowering in a wide range of fruits, vegetables, cereals and cotton. They are eliminated in soil through microbiological processes and the end-product is carbon dioxide, but can accumulate in plants, animals and humans. The US-EPA (Environmental Protection Agency) has listed the compounds and hence it requires to be measured.

In the following example, strategies for determination of mepiquat and chlormepiquat are presented.

Detection of Mepiquat and Chlormequat using HILIC–MS in Positive Mode

SeQuant® ZIC®–HILIC

Column: SeQuant® ZIC®–HILIC (3.5 µm, 200Å) PEEK 100×2.1 mm (1.50447.0001)

Recommended Solvents and Reagents

Acetonitrile: isocratic grade for HPLC LiChrosolv® (1.14291)

Water: Water for chromatography LiChrosolv® (1.15333)
or freshly purified water from Milli-Q® water purification system

Ammonium acetate for analysis EMSURE® ACS, Reag. Ph Eur (1.01116)

Recommended filtration tools

Mobile phase filtration:

PTFE coated with funnel, base, stopper clamp (XX1004720)

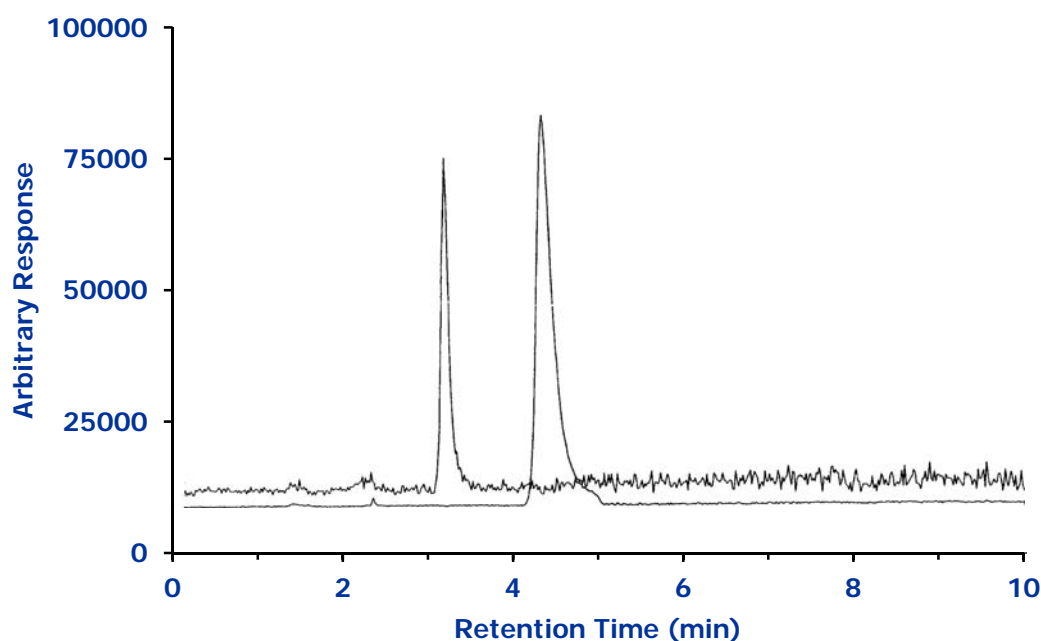
Omnipore PTFE membrane filter 0.45µm (JHWP04700)

Detection of Mepiquat and Chlormequat using HILIC-MS in Positive Mode

SeQuant® ZIC®-HILIC

Chromatographic Conditions

Column: SeQuant® ZIC®-HILIC (3.5 µm, 200Å) PEEK 100x2.1 mm 1.50447.0001
 Injection: 20 µL
 Detection: Electrospray-MS in positive mode (ESI+). Single ion monitoring (SIM) at m/z 114 and 122
 Flow Rate: 0.2 mL/min.
 Mobile Phase (v/v): Acetonitrile and 25 mM ammonium acetate (80:20)
 Temperature: Ambient
 Diluent: Mobile phase
 Sample: Standard injection of chlormequat and mepiquat



By courtesy of: Dr.-Ing. Ludmila Havlik, Chemisches Labor Dr. Wirts + Partner, Hannover, Germany, www.wirts.de

Chromatographic Data

No.	Compound	Time (min)	Retention Factor
	Void volume (t ₀)	1.6	–
1	Chlormequat	3.1	0.9
2	Mepiquat	4.3	1.7

Determination of Mepiquat and Chlormequat in seed by HILIC-MS/MS

Column: SeQuant® ZIC®-HILIC (3.5 µm, 200Å) PEEK 100x2.1 mm (1.50447.0001)

Mobile phase: Acetonitrile, ammonium acetate buffer (25 mM overall ionic strength), formic acid (80:19.5:0.5)

Flow rate: 0.4 mL/min

Injection: 1 µL

Detection: MS/MS, using an Agilent 1200 RRLLC system and 6410 QQQ System.

Compound	Precursor Ion (m/z)	Product Ion (m/z)	Fragmentor	Collision Energy (eV)
Chlormequat-D4	126	58.1	140	35
Chlormequat	122	58.1	140	35
Mepiquat-D3	117.1	98.2 (Quant)	140	30
		61.1 (Qual)	140	30
Mepiquat	114.1	98.2 (Quant)	140	30
		58.1 (Qual)	140	140

Sample preparation

Briefly (for seed samples):

- Weigh 10 g of seed
- Grind and add 20 mL of Milli-Q® plus 40 mL ethanol with ISTD
- Take an aliquot of 5 mL of extraction solvent
- Add the appropriate amount of standard to the standard samples
- Filtration

For further details please refer to the presentation:

<http://amcham.dk/dl/esac/ESAC08-5.pdf>