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Control of Pesticides 2019

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Editors:
Christina Østerballe Pedersen, Danish Technological Institute
Sine Abraham Johannesen, Danish Technological Institute
Eva Jacobsen, Danish Technological Institute

Graphics: Danish Technological Institute

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Preface

This report describes the analytical chemical control of pesticides on the Danish market, which was carried out in 2019 by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the Danish National Plan of Pesticides 2017-2021. Samples of selected types of pesticides on the Danish market were collected and analysed to verify whether or not the content of active substances in the pesticides complies with the product specifications, the labelled content and the information given to the Danish Environmental Protection Agency.

The Danish National Plan of Pesticides 2017-2021 is also engaged to act against illegal and counterfeit pesticides. Therefore, the objective of the analyses was also to investigate the existence of illegal or counterfeit pesticides.

Sammenfatning og konklusion

Denne rapport beskriver den analytisk kemiske kontrol af pesticidprodukter (plantebeskyttelsesmidler) på det danske marked, der er udført af Miljøstyrelsens Kemikalieinspektion i 2019 (Ref. 1, 2).

Kontrolkampagnen dækkede 24 aktive stoffer i forskellige kombinationer i 30 plantebeskyttelsesprodukter (pesticider). Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold. Der blev udført i alt 36 analyser for aktivstoffer.

Grænsen for en accepteret afvigelse i indholdet af et aktivstof i forhold til det deklarerede indhold og produktspecifikationen er fastsat i bekendtgørelsen om bekæmpelsesmidler nr. 815 af 18/06/2018 og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler (Ref. 3, 4).

Følgende typer af produkter blev analyseret (se tabel på næste side):
- 1 acaricid indeholdende bifenazat
- 5 fungicider indeholdende dithianon, kalium phosphonat, pencycuron, proquinazid og pyraclostrobin.
- 19 herbicider indeholdende aclonifen, bentazon, caprinsyre, clomazon, diflufenican, ethofumesat, fenoxaprop-P-ethyl, glyphosat, halauxifen-methyl, pelargonsyre, picloram, propaquizafop og pyridat.
- 5 insekticider indeholdende abamectin, acetamiprid, imidacloprid, pirimicarb og tau-fluvalinat.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i 27 af de 30 produkter, idet resultaterne er indenfor tolerancen.

Der blev udført i alt 98 fysisk-kemiske test:
- Densitet blev målt på 25 produkter
- Udseende blev vurderet for 30 produkter
- Vedvarende skumdannelse blev bestemt for 22 produkter
- Emulsionsstabilitet blev vurderet for 12 produkter
- Suspensibilitet blev målt for 9 produkter.

Tre produkter, som blev testet for fysisk-kemiske parameter, var ikke i overensstemmelse med produkternes specifikationer. Uoverensstemmelsen gjaldt for henholdsvis vedvarende skumdannelse, emulsionsstabilitet og udseende af de respektive produkter.

Et pesticidprodukt blev analyseret for urenheden 1,2-dichloroethan.

Der blev foretaget screeninger af to parallelprodukter og de tilhørende originalprodukter for at undersøge, om der var forskel på formuleringsingredienser. Der blev fundet forskel mellem det ene af parallelprodukterne og originalen.

Yderligere tre pesticidprodukter blev screenet for solventer med GC-MS for at verificere indholdet af det specificerede solvent.

Oversigt over analyserede produkter.

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
Abamectin	1	1	
Acetamiprid	1	1	
Aclonifen	1	1	
Aclonifen & clomazon	1	1	
Bentazon	1	1	
Bifenazat	1	1	
Clomazon	1	1	
Diflufenican & glyphosat	1	1	
Dithianon & kaliumphosphonat	1	1	
Ethofumesat	2	2	
Fenoxaprop-p-ethyl	2	2	
Halauxifen-methyl & picloram	1	1	
Imidacloprid	1	1	
Pelargonsyre	4	4	
Pelargonsyre & caprinsyre	1		1
Pelargonsyre & glyphosat	1	1	
Pencycuron	1	1	
Pirimicarb	1	1	
Propaquizafop	2	2	
Proquinazid	1	1	
Pyraclostrobin	2	2	
Pyridat	1		1
Tau-fluvalinat	1		1
TOTAL	**30**	**27**	**3**

Summary and conclusion

This report describes the analytical chemical control of plant protection products (pesticide products) on the Danish market that was carried out by the Danish Environmental Protection Agency (Danish EPA), Chemical Inspection Service, in 2019. (Ref. 1, 2)

The control campaign covered 24 active substances in different combinations in 30 plant protection products (PPP, pesticides). The products were analysed to verify whether the content of the active substances in the products in question complies with the product specification and the declared content. 36 analyses were carried out for active substances.

The tolerance of an accepted deviation in the content of an active substance compared to the declared content and product specification is determined in the Danish Statutory Order on Pesticides No. 815 of 18/06/2018 as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products. (Ref. 3, 4)

The following products were analysed (see table on next page):
- 1 acaricide containing bifenazate.
- 5 fungicides containing dithianon, potassium phosphonate, pencycuron, proquinazid, and pyraclostrobin.
- 19 herbicides containing aclonifen, bentazone, capric acid, clomazone, diflufenican, ethofumesate, fenoxaprop-P-ethyl, glyphosate, halauxifen-methyl, pelargonic acid, picloram, propaquizafop, and pyridate.
- 5 insecticides containing abamectin, acetamiprid, imidacloprid, pirimicarb, and tau-fluvalinate.

The measured content of active substances complied with the declared content in 27 out of 30 of the selected products as the results were within the range of tolerance.

In total, 98 physical-chemical tests were performed:
- Density was measured on 25 products.
- Appearance was assessed for 30 products.
- Persistent foaming was performed on 22 products.
- Emulsion stability was performed on 12 products.
- Suspensibility was performed on 9 products.

Three products that were tested for physical-chemical parameters did not comply with the specified values for persistent foaming, emulsion stability and appearance, respectively.

One product was analysed for the content of the impurity 1,2-dichloroethane.

Screening was performed on two parallel products and the corresponding original products to examine whether there was a difference between the formulation chemicals. For one of the parallel products a difference from the original product was found.

Additionally, three products were screened for solvent by GC-MS to verify that the correct solvent was used.

Overview of the number of analysed products.

Active substance	No. of analysed products	No. within tolerance	No. outside tolerance
Abamectin	1	1	
Acetamiprid	1	1	
Aclonifen	1	1	
Aclonifen & clomazone	1	1	
Bentazone	1	1	
Bifenazate	1	1	
Clomazone	1	1	
Diflufenican & glyphosate	1	1	
Dithianon & potassium phosphonate	1	1	
Ethofumesate	2	2	
Fenoxaprop-p-ethyl	2	2	
Halauxifen-methyl & picloram	1	1	
Imidacloprid	1	1	
Pelargonic acid	4	4	
Pelargonic acid & capric acid	1		1
Pelargonic acid & glyphosate	1	1	
Pencycuron	1	1	
Pirimicarb	1	1	
Propaquizafop	2	2	
Proquinazid	1	1	
Pyraclostrobin	2	2	
Pyridate	1		1
Tau-fluvalinate	1		1
TOTAL	**30**	**27**	**3**

1. Control campaign 2019

1.1 Collecting products

The Danish control campaign conducted in 2019 covered 24 active substances in different combinations in 30 plant protection products (PPP, pesticides). The active substances were selected according to the amount of active substance sold in previous years as well as to when the active substances lately were included in the control campaign. The Danish Chemical Inspection Service of the Danish Environmental Protection Agency collected all products during the period from March to July 2019. The product samples were collected either from wholesale dealers/importers or at retailer outlets. A summary of the selected active substances is given in TABLE 1.

TABLE 1. Outliner of selected active substances in the 2019 control campaign.

Area of application	Active substance	CAS no.
Acaricide	Bifenazate	149877-41-8
Fungicide	Dithianon	3347-22-6
	Potassium phosphonate	13977-65-6
	Pencycuron	66063-05-6
	Proquinazid	189278-12-4
	Pyraclostrobin	175013-18-0
Herbicides	Aclonifen	74070-46-5
	Bentazone	25057-89-0
	Capric acid	334-48-5
	Clomazone	81777-89-1
	Diflufenican	83164-33-4
	Ethofumesate	26225-79-6
	Fenoxaprop-p-ethyl	71283-80-2
	Glyphosate	1071-83-6
	Halauxifen-methyl	943831-98-9
	Pelargonic acid	112-05-0
	Picloram	1918-02-1
	Propaquizafop	111479-05-1
	Pyridate	55512-33-9
Insecticides	Abamectin	71751-41-2
	Acetamiprid	135410-20-7
	Imidacloprid	138261-41-3
	Pirimicarb	23103-98-2
	Tau-fluvalinate	102851-06-9

The collected product samples were stored at the Laboratory for Chemistry and Microbiology, Danish Technological Institute (DTI) (Ref. 5), in their original packaging until the chemical analyses were initiated. The product samples were stored at ambient temperature and protected from light during the entire storage period.

1.2 Tolerance of active substance

The objective of the Danish EPA was to examine the content of active substances in the products. The results of the chemical analyses were subsequently compared to the specification of the product and the declared content on the label supplied by the authorisation holder.

The Danish Statutory Order on Pesticides of 815 of 18/06/2018 and Regulation 1107/2009 concerning Marketing of Plant Protection Products specify the general tolerance of deviation from the declared content of active substances. (Ref. 3, 4) These tolerances are listed in TABLE 2.

TABLE 2. The tolerance of deviation from the declared content of active substance, 2019.

Content of active substances in g/kg or g/L at 20°C	Tolerance of deviation
Up to 25	± 15% homogeneous formulation ± 25% non-homogeneous formulation
More than 25 up to 100	± 10%
More than 100 up to 250	± 6%
More than 250 up to 500	± 5%
More than 500	± 25 g/kg or ± 25 g/L

1.3 Analysis 2019

The analyses of the products for active substances were performed by Danish Technological Institute, Laboratory for Chemistry and Microbiology. DTI is a self-owned and not-for-profit Institute (Ref. 5).

The Laboratory for Chemistry and Microbiology is accredited by DANAK (Danish Accreditation and Metrology Fund), registration no. 90, according DS/EN ISO/IEC 17025:2005 (Ref. 6). The laboratory has a flexible scope for determination of active substances in pesticides. In addition, the method for determination of density of pesticides is accredited.

1.3.1 Analysing active substances

A total of 36 analyses for active substances were performed. The chemical analyses were as far as possible performed as at least five freshly prepared samples of each product. If the average result was outside the tolerance interval, then the analysis was repeated with a minimum of three new and freshly prepared samples.

The methods were validated with regard to linearity, specificity, accuracy and control tests at two levels. The chemical analyses for validation were performed as at least eight freshly prepared samples of the product. The analyses were distributed over at least two days for each product formulation. The mean value of the analyses and the SD (standard deviation) were calculated for each day and for all eight results. Recovery was determined by adding a known amount of the relevant active substance to a minimum of four samples of each product. The mean recovery and SD were calculated.

The expanded uncertainty UE (k=2) of each product was calculated on the basis of the spread of the analysis results, the recovery and on the purity of the reference standard. The expanded analysis uncertainty is used to determine a 95% confidence interval of the analysis result. The expanded uncertainty varies between 2-15% depending on the analytical method, the product formulation and the available reference standards.

1.3.2 Analysing impurities

One product was selected for analysis of the impurity 1,2-dichloroethane. The results were evaluated in accordance with the specified maximum concentration of the impurities in the products.

1.3.3 Physical-chemical testing

A total of 98 physical-chemical tests were performed. The density of all liquid products was measured, and the results were used to determine the content in g/L of the active substance in the product. Additionally, the 30 pesticide products were submitted to evaluation of appearance, and determination of persistent foam, suspensibility and emulsion stability. The tests performed vary with the product formulation. The results were compared to the values specified in connection with the authorisation of the product.

1.3.4 Screening by GC-MS

Screening of two parallel products and the associated original was carried out by gas chromatography with mass spectrometric detection (GC-MS) to compare the chemical profiles of the parallel products with the original products.

Additionally, three products were selected for screening to verify the presence of the solvent specified in the authorization of the product.

1.3.5 Screening by FTIR

Screening of two parallel products and the associated original was carried out by Fourier-transform infrared spectroscopy (FRIT) to compare the profiles of the parallel products with the original products.

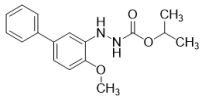
2. Analysis of active substances

In this report, pesticides are defined as plant protection products (PPP). In the Danish Pesticide Control Campaign 2019, 30 pesticide products were selected: acaricides, fungicides, herbicides and insecticides.

2.1 Acaricides

One acaricide containing bifenazate as active substance was selected for the 2019 campaign. TABLE 3 states the previous years the active substance was selected for control.

TABLE 3. Acaricide in the 2019 control campaign.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Bifenazate	149877-41-8	2014	

2.1.1 Analysis

Bifenazate was analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD) according to DTI's method OA-855. The method is accredited.

2.1.2 Results

The results from the performed measurements are listed in the following table. RSD % is the percentage relative reproducibility of the determinations of the product.

TABLE 4. Analysis results (g/kg) in acaricides.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
851963-29	Bifenazate	240	226-254	237	1.6	Comply

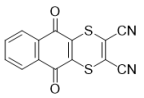
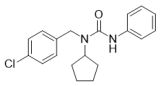
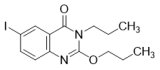
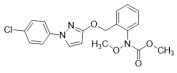
2.1.3 Conclusion

The measured content of bifenazate in the product complies with the declared content and with applicable Danish law.

2.2 Fungicides

Five fungicides containing dithianon, potassium phosphonate, pencycuron, proquinazid, and pyraclostrobin as active substances were selected for the 2019 campaign. TABLE 5 states the previous years the active substances were selected for control.

TABLE 5. Fungicides in the 2019 control campaign

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Dithianon	3347-22-6	2005	
Potassium phosphonate	13977-65-6	-	KH_2PO_3
Pencycuron	66063-05-6	2008, 2003	
Proquinazid	189278-12-4	-	
Pyraclostrobin	175013-18-0	2015, 2012, 2005	

'-' means not previously selected

2.2.1 Analysis

Dithianon, pencycuron, proquinazid, and pyraclostrobin were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Dithianon was analysed according to DTI's method OA-897. The method has been adapted from CIPAC method 153 Dithianon (Ref. 8).

Pencycuron and proquinazid were analysed according to DTI's method OA-880 and pyraclostrobin was analysed according to DTI's method OA-887.

Potassium phosphonate was analysed by titration according to the manufacturer's method for the product.

The methods for dithianon, pencycuron, proquinazid, and pyraclostrobin are accredited.

2.2.2 Results

The results of the performed measurements are listed in the following table. RSD % is the percentage relative reproducibility of the determinations of the product.

TABLE 6. Analysis results (g/L) in fungicides.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
851963-7	Dithianon	125	118-133	124	0.8	Comply
	Potassium Phosphonate	561	536-586	540	0.3	Comply
851963-8	Pyraclostrobin	200	188-212	202	3.2	Comply
851963-12	Pyraclostrobin	200	188-212	193	1.5	Comply
851963-13	Pencycuron	250	235-265	240	1.2	Comply
851963-26	Proquinazid	200	188-212	198	1.0	Comply

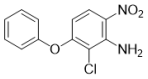
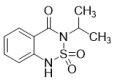
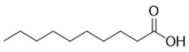
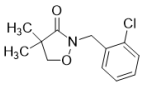
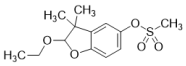
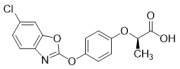
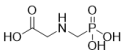
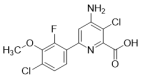
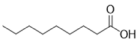
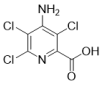
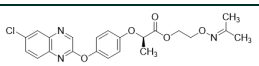
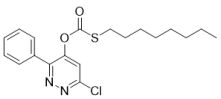
2.2.3 Conclusion

The measured content of dithianon, potassium phosphonate, pencycuron, proquinazid, and pyraclostrobin in the 5 products complies with the declared content and with applicable Danish law.

2.3 Herbicides

Nineteen herbicides containing the active substances aclonifen, bentazone, capric acid, clomazone, diflufenican, ethofumesate, fenoxaprop-p-ethyl, glyphosate, halauxifen-methyl, pelargonic acid, picloram, propaquizafop, and pyridate were selected for the 2019 campaign. TABLE 7 states the previous years the active substances were selected for control.

TABLE 7. Herbicides in the 2019 control campaign.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Aclonifen	74070-46-5	2016, 2008, 2000	
Bentazone	25057-89-0	2004	
Capric acid	334-48-5	-	
Clomazone	81777-89-1	2016, 2003	
Diflufenican	83164-33-4	2016, 2012, 2007	
Ethofumesate	26225-79-6	2011, 2002, 1997	
Fenoxaprop-p-ethyl	71283-80-2	2014, 2008, 1999	
Glyphosate	1071-83-6	2016, 2011, 2003	
Halauxifen-methyl	943831-98-9	-	
Pelargonic acid	112-05-0	-	
Picloram	1918-02-1	2014	
Propaquizafop	111479-05-1	2006, 1997	
Pyridate	55512-33-9	2002	

'-' means not previously selected

2.3.1 Analysis

Capric acid and pelargonic acid were analysed by gas chromatography with flame ionization detector (GC-FID) according to DTI's method OA-832.

Aclonifen, bentazone, clomazone, diflufenican, ethofumesate, glyphosate, halauxifen-methyl, picloram, propaquizafop, and pyridate were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Aclonifen was analysed according to DTI's method OA-870.
Clomazone was analysed according to DTI's method OA-870 and OA-900.
Bentazone, ethofumesate, propaquizafop, and pyridate were analysed according to DTI's method OA-880.
Diflufenican was analysed according to DTI's method OA-873.The method has been adapted from CIPAC method 462 diflufenican (Ref. 8).
Glyphosate was analysed according to DTI's method OA-811. The method was adapted from CIPAC method 284 Glyphosate (Ref. 8).
Halauxifen-methyl and picloram were analysed according to DTI's method OA-887.
Fenoxaprop-p-ethyl was analysed by normal phase HPLC-DAD according to DTI's method OA-852.The method has been adapted from CIPAC method 484 fenoxaprop-P-ethyl (Ref. 8).

The methods for analysis of aclonifen, bentazone, diflufenican, ethofumesate, fenoxaprop-p-ethyl, glyphosate, picloram, and propaquizafop are accredited.

2.3.2 Results

The results of the performed measurements are listed in tables 8 and 9. RSD % is the percentage relative reproducibility of the determinations of the product.

TABLE 8. Analysis results (g/kg) in herbicides.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
851963-24	Aclonifen	500	475-525	509	0.5	Comply
	Clomazone	30	27.0-33.0	30.9	3.3	Comply
851963-25	Pyridate	450	428-473	389	1.5	Non-comply

TABLE 9. Analysis results (g/L) in herbicides.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
851963-1	Glyphosate	7.2	6.12-8.28	7.37	0.2	Comply
	Pelargonic acid	20.4	17.3-23.5	20.9	5.6	Comply
851963-2	Pelargonic acid	16.9	14.4-19.4	15.0	5.0	Comply
	Capric acid	17.9	15.2-20.6	13.7	1.7	Non-comply
851963-3	Pelargonic acid	186.7	176-198	182	4.4	Comply
851963-4	Pelargonic acid	186.7	175-198	188	0.5	Comply
851963-5	Pelargonic acid	28	23.8-32.2	28.6	2.2	Comply
851963-11	Bentazone	480	456-504	500	0.8	Comply
851963-14	Pelargonic acid	187	175-198	184	0.6	Comply
851963-16	Diflufenican	40	36-44	40	0.4	Comply
	Glyphosate	250	235-265	244	0.9	Comply
851963-17	Fenoxaprop-p-ethyl	69	62-76	73	0.7	Comply
851963-18	Clomazone	360	342-378	377	2.2	Comply
851963-19	Fenoxaprop-p-ethyl	69	62-76	69	0.6	Comply
851963-20	Propaquizafop	100	90-110	104	0.4	Comply

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
851963-21	Ethofumesate	500	475-525	484	0.8	Comply
851963-22	Aclonifen	600	575-625	585	0.4	Comply
851963-23	Propaquizafop	100	90-110	100	1.4	Comply
851963-27	Ethofumesate	500	475-525	506	0.9	Comply
851963-30	Halauxifen-methyl	10	8.5-11.5	11	1.7	Comply
	Picloram	48	43.2-52.8	47	0.6	Comply

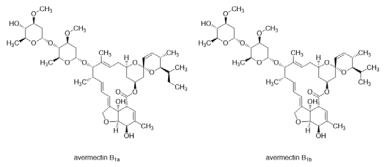
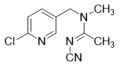
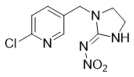
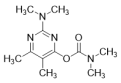
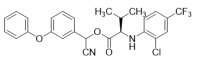
2.3.3 Conclusion

In 17 of the 19 products, the measured content of dithianon, pencycuron, proquinazid, and pyraclostrobin complies with the declared content and with applicable Danish law.
For one product, the measured concentration of the active substance pyridate did not comply with the declared content.
For one product, only the measured concentration of the active substance capric acid did not comply with the declared content, whereas the other active substance pelargonic acid did comply.

2.4 Insecticides

Five insecticides containing abamectin, acetamiprid, imidacloprid, pirimicarb, and tau-fluvalinate as active substances were selected for the 2019 campaign. TABLE 10 states the previous years the active substances were selected for control.

TABLE 10. Insecticides in the 2019 control campaign.

Name	CAS no.	Year selected for control	Molecular structure (Ref. 7)
Abamectin	71751-41-2	-	
Acetamiprid	135410-20-7	2015	
Imidacloprid	138261-41-3	2012, 2004	
Pirimicarb	23103-98-2	2006, 1999	
Tau-fluvalinate	102851-06-9	2016, 1998	

'-' means not previously selected

2.4.1 Analysis

Abamectin, acetamiprid, imidacloprid, pirimicarb, and tau-fluvalinate were analysed by reversed phase high-performance liquid chromatography combined with diode array detection (HPLC-DAD).

Abamectin was analysed according to DTI's method OA-899. Acetamiprid was analysed according to DTI's method OA-863.
Imidacloprid was analysed according to DTI's method OA-812. The method was adapted from CIPAC method 582 imidacloprid.
Pirimicarb was analysed according to DTI's method OA-880, and tau-fluvalinate was analysed according to DTI's method OA-872.

All the methods are accredited.

2.4.2 Results

The results of the performed measurements are listed in the tables 11 and 12. RSD % is the percentage relative reproducibility of the determinations of the product.

TABLE 11. Analysis results (g/kg) in insecticides.

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
851963-6	Imidacloprid	700	675-725	687	1.0	Comply
851963-9	Acetamiprid	200	188-212	204	0.2	Comply
851963-10	Pirimicarb	500	475-525	503	1.1	Comply

TABLE 12. Analysis results (g/L) in insecticides.

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
851963-15	Tau-fluvalinat	240	226-254	153	0.5	Non-comply
851963-28	Abamectin	18	15.3-20.7	19.7	1.4	Comply

2.4.3 Conclusion

The measured content of imidacloprid, acetamiprid, pirimicarb, and abamectin in 4 of the 5 products complies with the declared content and with applicable Danish law. For one product, the active substance tau-fluvalinate did not comply with the declared content.

3. Analysis of impurities

3.1 1,2-dichloroethane

One product containing bentazone as active substance was analysed for the content of 1,2-dichloroethane.

3.1.1 Analysis

The analysis was performed by headspace GC-MS according to the United States Pharmacopeia (USP) 467 method for residual solvents (Ref. 9).

3.1.2 Results

The results of the performed measurements are listed in TABLE 13.

TABLE 13. Analysis results for 1,2-dichloroethane.

DTI sample no.	Active substance	Max. content mg/kg active substance	Analysis result mg/kg active substance
851963-11	Bentazone	3.0	42.7

3.1.3 Conclusion

The measured concentration was above the allowed maximum concentration.

4. Physical-chemical testing

The density of all liquid products was measured. Additionally, the 30 pesticide products were submitted to a test programme depending on the formulation type. The tests include evaluation of appearance, determination of persistent foam, emulsion stability and suspensibility. The results were subsequently compared to the values specified in connection with the authorisation of the product. In total, 98 physical-chemical tests were performed.

As the physical-chemical parameters are subject to confidentiality; only the general conclusions have been included in this report.

4.1 Physical-chemical testing of selected pesticides

Details concerning performed physical-chemical test are provided below.

4.1.1 Appearance

The colour and physical state of the formulation was described after homogenization of the product.

4.1.2 Density

The density of the formulations was determined according to DTI's analysis method UA-312. The method is based on CIPAC MT 3 (Ref. 8). The density of the product is determined as the average of a triple determination carried out by measuring with a Densito 30 PX densimeter.

4.1.3 Persistent foaming

The test for persistent foaming was performed with DTI's method PCA 100 according to the CIPAC method MT 47.2 (Ref. 8). The concentration tested was the maximum concentration prescribed for the product. Standard CIPAC water D pre-pared according to CIPAC MT 18.1.4 was used unless otherwise specified for the product (Ref. 8). The amount of foam was reported at the times prescribed for the product. The test was performed in duplicate for each pesticide product.

4.1.4 Emulsion stability

The test for emulsion stability was performed according to DTI's method PCA 106 corresponding to the CIPAC method MT 36.3 (Ref. 8). Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water A and D, prepared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product (Ref. 8). The test was performed in duplicate for each pesticide product.

4.1.5 Suspensibility

The test for suspensibility was performed according to DTI's method PCA 102 corresponding to the CIPAC method MT 184 (Ref. 8). Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water D, pre-pared according to CIPAC MT 18.1.4, was used unless otherwise specified for the product (Ref. 8).

4.1.6 Results

The tests performed on selected pesticides are summarized in TABLE 14.

TABLE 14. Physical-chemical tests performed on selected pesticide products. An 'X' signifies that the test was performed.

DTI sample no.	Appearance	Density	Persistent foam	Emulsion stability	Suspensibility
851963-1	X	X			
851963-2	X	X			
851963-3	X	X	X	X	
851963-4	X	X	X	X	
851963-5	X	X			
851963-6	X		X		X
851963-7	X	X	X		X
851963-8	X	X	X	X	
851963-9	X				
851963-10	X				
851963-11	X	X			
851963-12	X	X	X	X	
851963-13	X	X	X		
851963-14	X	X	X	X	
851963-15	X	X	X	X	
851963-16	X	X	X		X
851963-17	X	X	X	X	
851963-18	X	X	X		X
851963-19	X	X	X	X	
851963-20	X	X	X	X	
851963-21	X	X	X		X
851963-22	X	X	X		X
851963-23	X	X	X	X	
851963-24	X				X
851963-25	X				
851963-26	X	X	X	X	
851963-27	X	X	X		X
851963-28	X	X	X		
851963-29	X	X	X		X
851963-30	X	X	X	X	

4.1.7 Conclusion

In most cases, the test results are comparable with specified values of the product or are within the legal requirements and tolerances. For three products, the results of persistent foam, emulsion stability and appearance were not comparable with the specified values, and the products do not comply with the legal requirements.

5. Solvent screening

5.1 Screening of formulation solvents in selected products

Screenings were carried out of selected products by gas chromatography with mass spectrometric detection (GC-MS) to identify the solvent used and compare it to the specified solvent.

The formulation of the product is subject to confidentiality, and only the general conclusions have been included in this report.

5.2 GC-MS analysis

A subsample of the product was diluted with dichloromethane and analysed by gas chromatography with mass spectrometric detection (GC-MS), scan m/z 35 - 350. The resulting mass spectral data was compared to the NIST17 library to identify the formulation solvents. The selected products are listed in TABLE 15.

TABLE 15. Selected products for screening of formulation solvents.

DTI sample no.	Active substance
851963-8	Pyraclostrobin
851963-12	Pyraclostrobin
851963-20	Propaquizafop
851963-23	Propaquizafop
851963-26	Proquinazid
851963-28	Abamectin
851963-30	Halauxifen-methyl & picloram

5.2.1 Results and conclusion

The specified solvents were identified in all the selected products. In one product, an additional solvent (not specified in the authorisation) was identified.

6. Parallel products

Two products under a parallel trade permit were compared to the respective original product by gas chromatography with mass spectrometric detection (GC-MS) and fourier-transform infrared spectroscopy (FTIR) to investigate if it contains the same solvents and additives as the original product. Furthermore, active substance concentration and physical-chemical properties were compared.

6.1 Regulation in Denmark

The requirements for parallel trade permits are described in detail in Article 52 of Regulation No. 1107/2009 (Ref. 10).

6.1.1 Parallel trade permits

A parallel trade permit is an authorisation for the import of a plant protection product that is identical with a product already authorised in Denmark. A parallel trade permit is valid only for Denmark. It is not valid in the rest of the North zone. For each country, an application must be made to obtain the permit.

A plant protection product under a parallel trade permit may only be placed on the market and used in accordance with the authorisation of the original product. The parallel trade permit will expire at the same time as the authorisation of the original product. If the authorisation of the original product is withdrawn for reasons other than safety, the parallel trade permit will be similarly affected.

6.1.2 Identical products

A plant protection product is identical with a product already authorised in Denmark only if:

A. It is produced by the same company or an associated company or under licence according to the same method of manufacture as that of the authorised product.
B. It has the same specification, that is, contains the same active substance, safeners and synergists. The plant protection product is of the same formulation type; and the contents of the co-formulants and the packaging are the same or equivalent.

The packaging and co-formulants must not have more negative effects on health or the environment than the original product.

6.2 Analysed products

The analysed products are listed in TABLE 16.

TABLE 16. Parallel and original products analysed in the 2019 campaign.

DTI sample no.	Permit	Active substances
851963-8	Original	Pyraclostrobin
851963-12	Parallel	
851963-20	Original	Propaquizafop
851963-23	Parallel	

6.3 GC-MS analysis

Subsamples of the parallel product and the original product were dissolved in dichloro-methane. The extracts were analysed by gas chromatography with mass spectrometric detection (GC-MS) in scan mode, and the resulting chromatograms were compared.

6.4 FTIR analysis

Subsamples of the parallel products and the original products were analysed using Perkin Elmer Spectrum TWO FTIR with ATR. Infrared radiation was sent through a crystal, where the sample was placed. The samples were measured directly with no preparation or cleaning. Resolution 4 cm^{-1}, 4 scan per sample, and the resulting spectra were compared.

6.5 Results and conclusion

The results of the comparison of the parallel product and the original product are listed in TABLE 17. For sample 851963-12, there was no difference between the parallel product and the original products based on the applied parameters. For sample 851963-23, a discrepancy was found between the chemical profile of the parallel product when compared to the original when comparing the GC-MS chromatogram and the FTIR spectrum.

TABLE 17. Comparison of the parallel products with the original product.

Parallel DTI sample no	Parameter	Parallel vs. original product
851963-12	a.s. concentration	Equivalent
	Apperance	Equivalent
	Density	Equivalent
	GC-MS-screening	Equivalent
	FTIR-screening	Equivalent
851963-23	a.s. concentration	Equivalent
	Apperance	Equivalent
	Density	Equivalent
	GC-MS-screening	Not equivalent
	FTIR-screening	Not equivalent

References

1. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; http://eng.mst.dk/chemicals/ and http://mst.dk/kemi/pesticider/

2. Danish EPA, 2018, approved Pesticides 2018 http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/ (Danish)

3. Statutory Order on Pesticides. Statutory Order from the Ministry of the Environment, No. 815 of 18/06/2018, Statutory Order is in Danish.

4. The regulation of the European Commission (EU) No. 546/2011 of 10 June 2011 concerning the implementation of the regulation of the European Parliament and the European Council (EF) No. 1107/2009 concerning uniform principles for evaluation and approval of crop protection agents

5. Danish Technological Institute, Kongsvang Allé 29, DK-8000 Aarhus C, Denmark, http://www.dti.dk/

6. The Danish Accreditation and Metrology Fund – DANAK, http://english.danak.dk/

7. The e-Pesticide Manual, seventeenth Edition, online version, 2016. British Crop Protection Council, United Kingdom

8. CIPAC method no.153, 284, 462, 484, 582, MT 3, MT 18.1.4, MT 36.3, MT 47.2 and MT 184, http://www.cipac.org/

9. United States Pharmacopeia (USP) 467 method for residual solvents

10. REGULATION (EC) No. 1107/2009 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC

Control of Pesticides 2019

English

The analytical chemical authority control of pesticide products on the Danish market that was carried out in 2019 by the Danish Environmental Protection Agency (Danish EPA), Danish Chemical Inspection Service, is described in this report. Samples of selected types of pesticides were collected on the Danish market and analysed to verify whether the content of the active substances in the products in question complies with the product specification and the labelled content. 30 different pesticide products were analysed.

Danish

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der er udført i 2019 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. I alt 30 bekæmpelsesmidler blev undersøgt.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
5000 Odense C

www.mst.dk