



**Ministry of Environment  
of Denmark**  
Environmental  
Protection Agency

# Control of Pesticides 2021

May 2023

Publisher: The Danish Environmental Protection Agency

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ISBN: 978-87-7038-519-0

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# Preface

This report describes the analytical chemical control of pesticides on the Danish market, which was carried out in 2021 by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency. The control is part of the Danish National Strategy of Pesticides 2017-2021. Samples of selected types of pesticides on the Danish market were collected and analysed to verify whether 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 Strategy of Pesticides 2017-2021 is also engaged in acting 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 2021 (Ref. 1, 2).

Den planlagte kontrolkampagne dækkede 26 aktivstoffer i forskellige kombinationer i 32 plantebeskyttelsesprodukter (pesticider). Produkterne blev analyseret for at verificere, om indholdet af de respektive aktivstoffer var i overensstemmelse med produktspecifikationen og det deklarerede indhold.

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. 2281 af 29/12/2020 (gældende bekendtgørelse nr. 1569 af 19/12/2022) og i forordning 1107/2009 om markedsføring af plantebeskyttelsesmidler (Ref. 3, 4).

Følgende typer af produkter blev analyseret i den planlagte kontrolkampagne (se tabel på næste side):

- 10 fungicider indeholdende azoxystrobin, boscalid, cyazofamid, cyprodinil, fludioxonil, fluopyram, prothioconazol, pyraclostrobin og tebuconazol.
- 8 vækstreguleringsmidler indeholdende 6-benzyladenin, chlormequat-chlorid, daminozid, mepiquat-chlorid, paclobutrazol, prohexadion-calcium og trinexapac-ethyl.
- 4 herbicider indeholdende dicamba, dichlorprop-P, jern(II)sulfat, MCPA og propaquizafop.
- 7 insekticider indeholdende flupyradifuron, lambda-cyhalothrin, spinosad og tau-fluvalinat.
- 3 molluscicider indeholdende ferrifosfat.

Det målte indhold af aktivstoffer var i overensstemmelse med det deklarerede indhold i 31 produkter, idet resultaterne er indenfor tolerancen.

Der blev udført i alt 85 fysisk-kemiske test:

- Densitet blev målt på 19 produkter
- Udseende blev vurderet for 32 produkter
- Vedvarende skumdannelse blev bestemt for 20 produkter
- Emulsionsstabilitet blev vurderet for 5 produkter
- Suspensibilitet blev målt for 9 produkter.

To produkter, som blev testet for fysisk-kemiske parametre, var ikke i overensstemmelse med produkternes specifikationer. Uoverensstemmelsen gjaldt for henholdsvis udseende og vedvarende skumdannelse.

Oversigt over analyserede produkter og aktivstoffer i den planlagte kontrolkampagne

Aktivstof	Antal analyserede produkter	Antal indenfor tolerance	Antal udenfor tolerance
6-Benzyladenin	1	1	
Azoxystrobin	2	2	
Boscalid & Pyraclostrobin	1	1	
Chlormequat-chlorid	1		1
Cyazofamid	2	2	
Cyprodinil & Fludioxonil	1	1	
Daminozid	2	2	
Dicamba, Dichlorprop-P & MCPA	2	2	
Ferrifosfat	3	3	
Fluopyram & Prothioconazol	2	2	
Flupyradifuron	2	2	
Jern(II)sulfat	1	1	
Lambda-cyhalothrin	3	3	
Mepiquat-chlorid & Prohexadion-calcium	1	1	
Paclobutrazol	1	1	
Prohexadion-calcium	1	1	
Propaquizafop	1	1	
Spinosad	1	1	
Tau-fluvalinat	1	1	
Tebuconazol	1	1	
Tebuconazol & prothioconazol	1	1	
Trinexapac-ethyl	1	1	
Total	32	31	1

# 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), the Danish Chemical Inspection Service, in 2021 (Ref. 1, 2).

The planned control campaign covered 26 active substances in different combinations in 32 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.

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. 2281 of 29/12/2020 (applicable Danish Statutory Order 1569 of 19/12/2022) as well as in Regulation 1107/2009 concerning Marketing of Plant Protection Products (Ref. 3, 4).

The following products were analysed in the planned control campaign (see table on next page):

- 10 fungicides containing azoxystrobin, boscalid, cyazofamid, cyprodinil, fludioxonil, fluopyram, , prothioconazole, pyraclostrobin, and/or tebuconazole.
- 8 growth regulators containing 6-benzyladenine, chlormequat chloride, daminozide, mepiquat chloride, paclobutrazol, prohexadione-calcium, and trinexapac-ethyl.
- 4 herbicides containing dicamba, dichlorprop-P, ferrous sulfate, MCPA, and propaquizafop.
- 7 insecticides containing flupyradifurone, lambda-cyhalothrin, spinosad and tau-fluvalinate.
- 3 molluscicides containing ferric phosphate.

The measured content of active substances complied with the declared content in 31 of the selected products as the results were within the range of tolerance.

In total, 85 physico-chemical tests were performed:

- Density was measured on 19 products.
- Appearance was assessed for 32 products.
- Persistent foaming was performed on 20 products.
- Emulsion stability was performed on 5 products.
- Suspensibility was performed on 9 products.

Two products that were tested for physico-chemical parameters did not comply with the specified values of the products regarding appearance or persistent foaming.

## Overview of analysed pesticides in the planned control campaign

Active substance	No. of analysed products	No. within tolerance	No. outside tolerance
6-Benzyladenine	1	1	
Azoxystrobin	2	2	
Boscalid & Pyraclostrobin	1	1	
Chlormequat chloride	1		1
Cyazofamid	2	2	
Cyprodinil & Fludioxonil	1	1	
Daminozide	2	2	
Dicamba, Dichlorprop-P & MCPA	2	2	
Ferric phosphate	3	3	
Fluopyram & Prothioconazole	2	2	
Flupyradifurone	2	2	
Ferrous sulfate	1	1	
Lambda-cyhalothrin	3	3	
Mepiquat chloride & Prohexadione-calcium	1	1	
Paclobutrazol	1	1	
Prohexadione-calcium	1	1	
Propaquizafop	1	1	
Spinosad	1	1	
Tau-fluvalinate	1	1	
Tebuconazole	1	1	
Tebuconazole & prothioconazole	1	1	
Trinexapac-ethyl	1	1	
Total	32	31	1



# Abbreviations

CIPAC: Collaborative International Pesticides Analytical Council  
DANAK: Danish Accreditation and Metrology Fund  
DTI: Danish Technological Institute  
FTIR: Fourier-transform infrared spectroscopy  
GC-FID: Gas chromatography - flame ionization detection  
GC-MS: Gas chromatography - mass spectrometry  
HPLC-DAD: High-performance liquid chromatography - diode array detection  
ICP-OES: Inductively coupled plasma - optical emission spectrometry  
LC-MS: Liquid chromatography-mass spectrometry  
MAM: Multi-active method  
PPP: Plant protection products  
RSD: Relative standard deviation  
SD: Standard deviation  
UE: expanded uncertainty

# 1. Control campaign 2021

## 1.1 Collecting products

The Danish planned control campaign conducted in 2021 covered 26 active substances in different combinations in 32 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 recently were included in the control campaign, and finally based on availability on the market. In addition, the control campaign focused on products produced by FMC (former Cheminova), the only Danish manufacturer of PPPs. All products were collected by the Danish Chemical Inspection Service of the Danish Environmental Protection Agency during the period from March to June 2021. 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.** Outline of selected active substances in the 2021 control campaign

Area of application	Active substance	CAS no.
Fungicide	Azoxystrobin	131860-33-8
	Boscalid	188425-85-6
	Cyazofamid	120116-88-3
	Cyprodinil	121552-61-2
	Fludioxonil	131341-86-1
	Fluopyram	658066-35-4
	Prothioconazole	178928-70-6
	Pyraclostrobin	175013-18-0
	Tebuconazole	107534-96-3
Growth regulator	6-Benzyladenine	1214-39-7
	Chlormequat chloride	999-81-5
	Daminozide	1596-84-5
	Mepiquat chloride	24307-26-4
	Paclobutrazol	76738-62-0
	Prohexadione-calcium	127277-53-6
	Trinexapac-ethyl	95266-40-3
Herbicide	Dicamba	1918-00-9
	Dichlorprop-P	15165-67-0
	Ferrous sulfate	7720-78-7
	MCPA	94-74-6
	Propaquizafop	111479-05-1
Insecticide	Flupyradifurone	951659-40-8
	Lambda-cyhalothrin	91465-08-6
	Spinosad	168316-95-8
	Tau-fluvalinate	102851-06-9
Molluscicide	Ferric phosphate	10045-86-0

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 No. 2281 of 29/12/2020 (applicable Danish Statutory Order 1569 of 19/12/2022) 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

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%

## 1.3 Analysis 2021

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 to DS/EN ISO/IEC 17025:2017 (Ref. 6). The laboratory has a flexible scope for determination of active substances in pesticides. In addition, the methods for determination of density of pesticides by densimeter and persistent foaming are accredited.

### 1.3.1 Analysing active substances

A total of 42 analyses for active substances were performed. Where relevant, methods were adapted from existing reference methods, e.g., CIPAC methods or methods from the manufacturer.

As far as possible, the chemical analyses were performed on 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 on 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 method 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 2-11% depending on the analytical method, the product formulation, and the available reference standards.

### **1.3.2 Physico-chemical testing**

A total of 85 physico-chemical tests were performed. The tests performed vary with the product formulation. The results were compared to the values specified in connection with the authorisation of the product.

The density of all liquid products (19 products) was measured, and the results were used to determine the content in g/L of the active substance in the product. Additionally, the pesticide products were submitted for evaluation of appearance (32 products), determination of persistent foam (20 products), suspensibility (9 products), and emulsion stability (5 products).

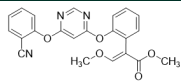

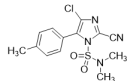
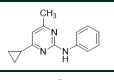
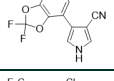
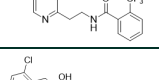
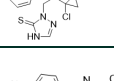
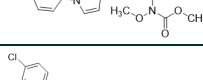
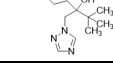
## 2. Analysis of active substances

In this report, pesticides are defined as plant protection products (PPP). In the planned Danish pesticide control campaign conducted in 2021, 32 pesticide products were selected: fungicides, growth regulators, herbicides, insecticides, and molluscicides.

### 2.1 Fungicides

Eleven fungicides containing the active substances azoxystrobin, boscalid, cyazofamid, cyprodinil, fludioxonil, fluopyram, , prothioconazole, pyraclostrobin and tebuconazole were selected for the 2021 campaign. TABLE 3 states the previous years the active substances were selected for control and outlines the analytical method applied for each active substance.

**TABLE 3.** Fungicides in the 2021 control campaign

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Azoxystrobin	131860-33-8	2018, 2017, 2006, 1999	GC-FID	OA-827	Yes	CIPAC 571 (Ref. 8)	
Boscalid	188425-85-6	2020, 2016, 2008	HPLC-DAD	OA-902	Yes		
Cyazofamid	120116-88-3	2020, 2008	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Cyprodinil	121552-61-2	2006, 2001	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Fludioxonil	131341-86-1	2013	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Fluopyram	658066-35-4	2020, 2018	HPLC-DAD	OA-889	Yes		
Prothioconazole	178928-70-6	2020, 2018, 2010, 2008	HPLC-DAD	OA-880/ OA-889*	Yes	CIPAC MAM (Ref. 9)	
Pyraclostrobin	175013-18-0	2020, 2019, 2015, 2012, 2005	HPLC-DAD	OA-902	Yes		
Tebuconazole	107534-96-3	2018, 2010, 2008, 2002	HPLC-DAD	OA-887	Yes	CIPAC MAM (Ref. 9)	

\*Method choice depend on product formulation

### 2.1.1 Results and conclusion

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

The concentration of active substances complies with the declared content and with applicable Danish law in 10 out of 10 products.

**TABLE 4.** Analysis results (g/kg) in fungicides

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
969743-6	Cyprodinil	375	356-394	362	2.4	Comply
	Fludioxonil	250	235-265	249	1.1	Comply
969743-26	Boscalid	267	254-280	266	0.6	Comply
	Pyraclostrobin	67	60.3-73.7	65.9	0.9	Comply

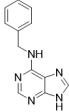

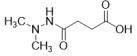

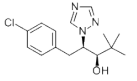
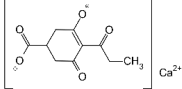
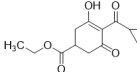
**TABLE 5.** Analysis results (g/L) in fungicides

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
969743-8	Fluopyram	125	118-133	127	1.0	Comply
	Prothioconazole	125	118-133	124	0.2	Comply
969743-9	Cyazofamid	160	150-170	161	0.9	Comply
969743-16	Tebuconazole	160	150-170	160	1.4	Comply
	Prothioconazole	80	72.0-88.0	80.9	0.5	Comply
969743-17	Azoxystrobin	250	235-265	248	0.2	Comply
969743-21	Tebuconazole	200	188-212	206	0.7	Comply
969743-22	Fluopyram	125	118-133	127	1.6	Comply
	Prothioconazole	125	118-133	124	1.0	Comply
969743-25	Cyazofamid	160	150-170	155	0.7	Comply
969743-30	Azoxystrobin	250	235-265	235	0.6	Comply

## 2.2 Growth regulators

Eight growth regulators containing the active substances 6-benzyladenine, chlormequat chloride, daminozide, mepiquat chloride, paclobutrazol, prohexadione-calcium, and trinexapac-ethyl were selected for the 2021 campaign. TABLE 6 states the previous years the active substances were selected for control and outlines the analytical method applied for each active substance.

**TABLE 6.** Growth regulators in the 2021 control campaign

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
6-Benzyladenine	1214-39-7	-	HPLC-DAD	OA-906	Yes		
Chlormequat chloride	999-81-5	2016, 2006	LC-MS	OA-1200	No		
Daminozide	1596-84-5	2009, 2008	HPLC-DAD	OA-905	Yes	Method of manufacturer	
Mepiquat chloride	24307-26-4	2018, 2017, 2006	LC-MS	OA-1200	Yes		
Paclobutrazol	76738-62-0	2018, 2008	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	
Prohexadione-calcium	127277-53-6	2018, 2017, 2013	HPLC-DAD	OA-882	Yes	Method of manufacturer	
Trinexapac-ethyl	95266-40-3	2017, 2009, 1999	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	

"-" means not previously selected for control



## 2.2.1 Results and conclusion

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

The concentration of active substances complies with the declared content and with applicable Danish law in 7 out of 8 products. Due to the analytical uncertainties of the analysis of active substance in the last product is it not possible to definitive state that the product does not comply with Danish law.

**TABLE 7.** Analysis results (g/kg) in growth regulators

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
969743-20	Daminozide	850	825-875	853	0.9	Comply
969743-23	Prohexadione-Ca	100	90.0-110	97.7	0.9	Comply
969743-33	Daminozide	850	825-875	838	0.6	Comply

**TABLE 8.** Analysis results (g/L) in growth regulators

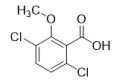
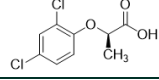
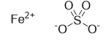
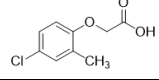
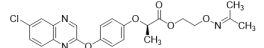
DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
969743-7	Trinexapac-ethyl	250	238-263	250	0.2	Comply
969743-24	Mepiquat chloride	300	285-315	287	1.1	Comply
	Prohexadione-Ca	50	45.0-55.0	48.4	2.0	Comply
969743-27	Paclobutrazol	4.0	3.4-4.6	4.1	0.4	Comply
969743-28	6-Benzyladenine	20.0	17.0-23.0	20.8	0.4	Comply
969743-29	Chlormequat Cl	460	437-483	487	0.3	*(Non-comply)

\* Due to the measurement uncertainty of the analysis result it cannot be definitively stated that the product dose not comply with Danish law.

## 2.3 Herbicides

Four herbicides containing the active substances dicamba, dichlorprop-P, ferrous sulfate, MCPA or propaquizafop were selected for the 2021 campaign. TABLE 9 states the previous years the active substances were selected for control and outlines the analytical method applied for each active substance.

**TABLE 9.** Herbicides in the 2021 control campaign

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Dicamba	1918-00-9	2004, 2000	HPLC-DAD	OA-904	Yes		
Dichlorprop-P	15165-67-0	2004	HPLC-DAD	OA-904	Yes		
Ferrous sulfate	7720-78-7	-	ICP-OES	UA-266	No	EPA Method 3050 (Ref. 10)	
MCPA	94-74-6	2020, 2016, 2012, 2004	HPLC-DAD	OA-904	Yes		
Propaquizafop	111479-05-1	2019, 2006, 1997	HPLC-DAD	OA-880	Yes	CIPAC MAM (Ref. 9)	

"-" means not previously selected for control

### 2.3.1 Results and conclusion

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

The concentration of active substances complies with the declared content and with applicable Danish law in all of the 4 products.

**TABLE 10.** 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
969743-15	Ferrous sulfate	98.4	88.6-108.2	92.9	0.4	Comply

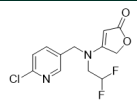
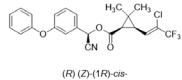
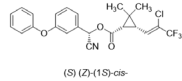
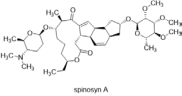
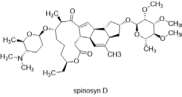
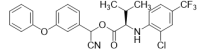
**TABLE 11.** Analysis results (g/L) in herbicides

DTI sample no.	Active substance	Label claim g/L	Tolerance interval g/L	Analysis result g/L	RSD %	Comply/ Non-comply
969743-2	Dichlorprop-P	1.5	1.28-1.73	1.56	1.4	Comply
	Dicamba	0.32	0.27-0.37	0.30	0.7	Comply
	MCPA	5.2	4.42-5.98	5.15	5.2	Comply
969743-3	Propaquizafop	100	90.0-110	102	0.3	Comply
969743-19	Dichlorprop-P	1.5	1.28-1.73	1.60	1.0	Comply
	Dicamba	0.32	0.27-0.37	0.31	0.6	Comply
	MCPA	5.2	4.42-5.98	5.17	1.1	Comply

## 2.4 Insecticides

Seven insecticides containing the active substances flupyradifurone, lambda-cyhalothrin, spinosad or tau-fluvalinate were selected for the 2021 campaign. TABLE 12 states the previous years the active substances were selected for control and outlines the analytical method applied for each active substance.

**TABLE 12.** Insecticides in the 2021 control campaign

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Flupyradifurone	951659-40-8	-	HPLC-DAD	OA-880/OA-907*	No	CIPAC MAM (Ref. 9)	
Lambda-cyhalothrin	91465-08-6	2016, 2003	GC-FID	OA-839	Yes		 (R)- (Z)- (1R)- cis-  (S)- (Z)- (1S)- cis-
Spinosad	168316-95-8	2020, 2015, 2011	HPLC-DAD	OA-805	Yes	CIPAC 636 (Ref. 11)	 spinosyn A  spinosyn D
Tau-fluvalinate	102851-06-9	2019, 2016, 1998	HPLC-DAD	OA-872	Yes	Method of manufacturer	

"-" means not previously selected for control.

\*Method depends on product formulation.

### 2.4.1 Results and conclusion

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

The concentration of active substances complies with the declared content and with applicable Danish law in all of the 7 products.

**TABLE 13.** 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
969743-4	Lambda-cyhalothrin	50.0	45.0-55.0	50.5	1.5	Comply
969743-5	Lambda-cyhalothrin	25.0	18.8-31.3	24.9	2.2	Comply
969743-10	Flupyradifurone	18.8	14.1-23.5	19.9	1.8	Comply
969743-11	Lambda-cyhalothrin	25	18.8-31.3	24.9	1.4	Comply

**TABLE 14.** 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
969743-1	Flupyradifurone	0.08	0.068-0.092	0.08	0.3	Comply
969743-13	Tau-fluvalinate	240	226-254	240	0.9	Comply
969743-32	Spinosad	120	113-127	116	1.5	Comply

## 2.5 Molluscicides

Three molluscicides containing the active substance ferric phosphate were selected for the 2021 campaign. TABLE 15 states the previous years the active substance was selected for control and outlines the analytical method applied for the active substance.

**TABLE 15.** Molluscicides in the 2021 control campaign

Name	CAS no.	Year selected for control	Analytical method				Molecular structure (Ref. 7)
			Principle	DTI method	Accreditation	Adapted from reference method	
Ferric phosphate	10045-86-0	2014	ICP-OES	UA-266	No	EPA Method 3050 (Ref. 10)	$\text{Fe}^{3+} \quad \begin{array}{c} \text{O} \\ \parallel \\ \text{O}^--\text{P}-\text{O}^- \\ \mid \\ \text{O} \end{array}$

### 2.5.1 Results and conclusion

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

The concentration of active substances complies with the declared content and with applicable Danish law in all of the 3 products.

**TABLE 16.** Analysis results (g/kg) in molluscicides

DTI sample no.	Active substance	Label claim g/kg	Tolerance interval g/kg	Analysis result g/kg	RSD %	Comply/ Non-comply
969743-12	Ferric phosphate	24.2	18.2-30.3	23.4	0.2	Comply
969743-14	Ferric phosphate	8.1	6.1-10.1	6.9	0.2	Comply
969743-18	Ferric phosphate	25.0	18.8-31.3	20.1	1.2	Comply

## 3. Physico-chemical testing

The collected pesticide products were submitted to a test program depending on the formulation type. The tests include evaluation of appearance, determination of density, 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, 85 physico-chemical tests were performed.

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

### 3.1 Physico-chemical testing of selected pesticides

Details concerning the performed physico-chemical tests are provided below.

#### 3.1.1 Appearance

The colour and physical state of the formulation were described after homogenization of the product according to DTI's method UA-407.

#### 3.1.2 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. 12), and the density of the product is determined as the average of a triple determination carried out by measuring with a Densito 30 PX densitometer.

#### 3.1.3 Persistent foaming

The test for persistent foaming was performed with DTI's method UA-400 according to the CIPAC method MT 47 (Ref. 13). The concentration tested was the highest in-use concentration prescribed for the product. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 14). The amount of foam present after 1 minute was reported. The test was performed in duplicate for each pesticide product.

#### 3.1.4 Emulsion stability

The test for emulsion stability was performed according to DTI's method UA-406 corresponding to the CIPAC method MT 36 (Ref. 15). Highest and lowest in-use concentrations prescribed for the product were tested. Standard CIPAC water D, prepared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 14). The test was performed in duplicate for each pesticide product.

#### 3.1.5 Suspensibility

The test for suspensibility was performed according to DTI's method UA-402 corresponding to the CIPAC method MT 184 (Ref. 16). The suspensibility was tested at a single in-use concentration prescribed for the product. Standard CIPAC water D, pre-pared according to CIPAC MT 18, was used unless otherwise specified for the product (Ref. 14).

#### 3.1.6 Results

The tests performed on selected pesticides are summarized in TABLE 17.



**TABLE 17.** Physico-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
969743-1	X	X			
969743-2	X	X			
969743-3	X	X	X	X	
969743-4	X		X		
969743-5	X				
969743-6	X		X		X
969743-7	X	X	X	X	
969743-8	X	X	X		
969743-9	X	X	X		X
969743-10	X				
969743-11	X				
969743-12	X				
969743-13	X	X	X	X	
969743-14	X				
969743-15	X				
969743-16	X	X	X	X	
969743-17	X	X	X		X
969743-18	X				
969743-19	X	X			
969743-20	X		X		
969743-21	X	X	X	X	
969743-22	X	X	X		
969743-23	X		X		X
969743-24	X	X	X		X
969743-25	X	X	X		X
969743-26	X				
969743-27	X	X	X		X
969743-28	X	X	X		X
969743-29	X	X	X		
969743-30	X	X			
969743-32	X	X	X		X
969743-33	X		X		

### 3.1.7 Conclusion

In most cases, the test results are comparable with specified values of the product or are within the legal requirements and tolerances. For one product, the result of persistent foam was not comparable with the specified values, and the products do not comply with the legal requirements.

## 4. 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 physico-chemical properties were compared.

### 4.1 Regulation in Denmark

The requirements for parallel trade permits are described in detail in Article 52 of Regulation No. 1107/2009 (Ref. 17).

#### 4.1.1 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, then the parallel trade permit will be similarly affected.

#### 4.1.2 Identical products

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

- A. It is produced by the same company or an associated company or under license 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 substances, safeners, and synergists.
- C. 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.

### 4.2 Analysed products

The analysed products are listed in TABLE 18.

**TABLE 18.** Parallel and original products analysed in the 2021 campaign

DTI no.	Permit	Active substances
969743-9	Original	Cyazofamid
969743-25	Parallel	
969743-8	Original	Fluopyram & Prothioconazole
969743-22	Parallel	

### 4.3 GC-MS analysis

A sub-sample of each product was analysed according to DTI's method OA-840:

The sub-sample was diluted by water and acetone and analysed by gas chromatography coupled with mass spectrometry (GC-MS) in scan mode, and the resulting chromatograms were compared.

Discrepancies between the chromatograms of the original and parallel product were identified by comparison to the NIST 20 library (Ref. 18). The identity of suspected compounds was subsequently verified, and the concentration was quantified by using an external reference standard.

### 4.4 FTIR analysis

A sub-sample was analysed by fourier-transform infrared spectroscopy (FTIR) according to DTI's method UA-234: The sample was analyzed using Perkin Elmer Spectrum Two™ FTIR with ATR (Attenuated total reflection). 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<sup>-1</sup>, 4 scan per sample.

### 4.5 Results and conclusion

The results of the comparison of the parallel product and the original product are listed in TABLE 19. For the parallel product numbered 969743-25, there was no significant difference from the original product based on the applied parameters. For the parallel product numbered 969743-22, an additional compound was identified by GC-MS which was not present in the original product.

**TABLE 19.** Comparison of the parallel products with the original product

Parallel product no.	Parameter	Parallel vs. original product
969743-25	Active substance concentration	Equivalent
	Appearance	Equivalent
	Density	Equivalent
	Persistent foaming	Equivalent
	Suspensibility	Equivalent
	GC-MS-screening	Equivalent
	FTIR-screening	Equivalent
969743-22	Active substance concentration	Equivalent
	Appearance	Equivalent
	Density	Equivalent
	Persistent foaming	Equivalent
	GC-MS-screening	Not equivalent
	FTIR-screening	Equivalent

## 5. References

1. Ministry of Environment and Food of Denmark, Environmental Protection Agency (Danish EPA) site; <http://eng.mst.dk/chemicals/pesticides/> and <http://mst.dk/kemi/pesticider/>
2. Danish EPA, 2021, approved Pesticides 2021 <http://mst.dk/kemi/database-for-bekaempelsesmidler/bmd/> (Danish)
3. Statutory Order on Pesticides No. 2281 of 29/12/2020 (applicable Danish Statutory Order 1569 of 19/12/2022)
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, Eighteenth Edition, online version, 2021. British Crop Protection Council, United Kingdom
8. CIPAC method Azoxystrobin 571, <http://www.cipac.org/>
9. CIPAC Multi-active method for the analysis of active substances in formulated products to support quality control, <http://www.cipac.org/>
10. EPA method 3050 ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS
11. CIPAC method 636 Spinosad. <http://www.cipac.org/>
12. CIPAC MT 3 Specific gravity, density and weight per millilitre. <http://www.cipac.org/>
13. CIPAC MT 47 Persistent foaming. <http://www.cipac.org/>
14. CIPAC MT 18 Standard waters. <http://www.cipac.org/>
15. CIPAC MT 36 Emulsion characteristics of emulsifiable concentrates. <http://www.cipac.org/>
16. CIPAC MT 184 Suspensibility of formulations forming suspensions on dilution with water. <http://www.cipac.org/>
17. 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
18. NIST20 Mass spectral library, NIST 2020 release.

# Appendix 1: Pesticide products collected for the planned control campaign 2021

**TABLE 20.** Fungicide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
969743-6	Cyprodinil & Fludioxonil	1-201	Switch 62.5 WG	Syngenta Nordics A/S
969743-8	Prothioconazole & Fluopyram	18-597	Propulse SE 250	Bayer A/S
969743-9	Cyazofamid	352-8	Ranman Top	ISK Biosciences Europe N.V.
969743-16	Prothioconazole & Tebuconazole	18-575	Folicur Xpert	Bayer A/S
969743-17	Azoxystrobin	1-172	Amistar	Syngenta Nordics A/S
969743-21	Tebuconazole	347-39	Orius Max 200 EW	Nufarm Deutschland GmbH
969743-22	Prothioconazole & Fluopyram	623-7	PRO-Tector	Vestjydsk Agro
969743-25	Cyazofamid	623-5	Potato Top	Vestjydsk Agro
969743-26	Boscalid & Pyraclostrobin	19-151	Signum	BASF A/S
969743-30	Azoxystrobin	396-41	Mirador 250 SC	ADAMA Registrations B.V.

**TABLE 21.** Growth regulator products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
969743-7	Trinexapac-ethyl	11-59	Cuadro NT	Cheminova A/S
969743-23	Prohexadione-calcium	544-7	Kudos	Fine Agrochemicals Ltd.
969743-24	Mepiquat chloride & Prohexadione-calcium	19-201	Medax Top	BASF A/S
969743-27	Paclobutrazol	544-3	Pirouette	Fine Agrochemicals Ltd.
969743-28	6-Benzyladenine	544-5	Configure	Fine Agrochemicals Ltd.
969743-29	Chlormequat chloride	49-94	Kompakt 5C	Klarsø A/S
969743-33	Daminozide	544-6	Dazide Enhance	Fine Agrochemicals Ltd.

**TABLE 22.** Herbicide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
969743-2	Dichlorprop-P, Dicamba & MCPA	49-38	Toxan Plænerens klar-til-brug	Klarsø A/S
969743-3	Propaquizafop	396-12	Agil 100 EC	ADAMA Registrations B.V.
969743-15	Ferrous sulfate	49-121	Trim mod mos xtra	Klarsø A/S
969743-19	Dichlorprop-P, Dicamba & MCPA	49-116	Trim Easyspray Plænerens	Klarsø A/S

**TABLE 23.** Insecticide products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
969743-1	Flupyradifurone	579-9	Provanto Spray	SBM Développement SAS
969743-4	Lambda-cyhalothrin	347-25	Kaiso Sorbie	Nufarm Deutschland GmbH
969743-5	Lambda-cyhalothrin	396-77	Lamdex	ADAMA Registrations B.V.
969743-10	Flupyradifurone	579-8	Provanto Insektpinde	SBM Développement SAS
969743-11	Lambda-cyhalothrin	1-252	Axiendo 2.5 WG	Syngenta Nordics A/S
969743-13	Tau-fluvalinate	396-82	Mavrik	ADAMA Registrations B.V.
969743-32	Spinosad	64-51	Conserve	Corteva Agriscience Denmark A/S

**TABLE 24.** Growth regulator products

DTI sample no.	Active substance(s)	Reg. no.	Name of product	Authorization holder
969743-12	Ferric phosphate	364-59	Sluxx HP	W. Neudorff GmbH KG
969743-14	Ferric phosphate	364-15	Ferramol N	W. Neudorff GmbH KG
969743-18	Ferric phosphate	774-3	Ferrex garden	Frunol Delicia GmbH

## Control of Pesticides 2021

### English

The analytical chemical authority control of pesticide products on the Danish market that was carried out in 2021 by the Danish Environmental Protection Agency (Danish EPA), the Danish Chemical Inspection Service, is described in this report. Samples of selected types of plant protection products (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. 32 different pesticide products were analysed as part of the planned control program.

### Danish

Den analytisk kemiske kontrol af pesticidprodukter på det danske marked, der er udført i 2021 af den danske Miljøstyrelses Kemikalieinspektion, er beskrevet i denne rapport. Prøver fra udvalgte typer af bekæmpelsesmidler (pesticider) er blevet indsamlet og analyseret for at verificere, om indholdet af de respektive aktivstoffer er i overensstemmelse med det deklarerede indhold. I alt 32 bekæmpelsesmidler (pesticider) blev undersøgt som en del af den planlagte kontrolkampagne.



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